

Chemical Speciation Network (CSN)

Annual Quality Report

Samples Collected January 1, 2021 through December 31, 2021

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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, 2021 through December 31, 2021 (batches 75-86, where each batch 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 93.5% for PTFE filters, 93.7% for nylon filters, and 91.7% for quartz filters. Data from sites with non-standard sampler configurations are not included in the completeness calculations.

The EPA did not conduct a Technical Systems Audit (TSA) of the UC Davis laboratory during the 2021 data reporting period.

2. Summary of Laboratory Operation Issues

2.1 RTI Ion Analysis Laboratory

There were no operational issues reported during this period.

2.2 UC Davis X-ray Fluorescence Laboratory

2.2.1 Instrument Repair Delays

During this reporting period, the XRF systems experienced longer than usual delays in some repairs requiring parts from the manufacturer. These were in-part due to global production and shipping delays, poor quality assurance review of high voltage generator units, and waning support for the Panalytical Epsilon 5 EDXRF instrument which is no longer in production. Specific instruments impacted and details of the delays are discussed in section 3.2.1.

2.2.2 Purchase of New Bruker S2-Puma EDXRF Instruments

During this reporting period the AQRC purchased three new Bruker S2-Puma EDXRF instruments to replace the aging Panalytical Epsilon 5 instruments that are nearing the end of their service support from the manufacturer. The new instruments were purchased in November 2021 and were not delivered to AQRC in this reporting period. Once delivered they will undergo extensive testing and qualification to ensure they are fit for use before starting any network sample analysis.

2.3 UC Davis Thermal Optical Analysis Laboratory

2.3.1 OC4 Fraction Update

UCD Sunset analyzers measure lower OC4 fraction than DRI instruments. Two variables may contribute to this discrepancy: 1) the baseline threshold for advancing to the next step on the Sunset instrument is set too high, and/or 2) the oven temperature is slightly lower in the Sunset instruments than the DRI instruments. The Sunset software does not wait for the laser reflectance to return to zero before advancing to the next step, but to a system defined, baseline value, and the user is not allowed to adjust the baseline value. To overcome this obstacle, the analysis protocol was adjusted for the Sunset instruments in November 2020 to fix the OC4 fraction time to 580 seconds. This results in longer analysis times and more comparable OC4 results between the different analyzers. More details can be found in the Data Advisory, https://aqrc.ucdavis.edu/sites/g/files/dgvnsk1671/files/files/page/CSN_DataAdvisory_carbon.pdf
:

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 (Section 3.2.4.5). 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, 2021 through December 31, 2021. 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	13,486	13,186	12,612	574	95.6	93.5
Nylon	13,486	13,186	12,630	556	95.8	93.7
Quartz	13,486	13,077	12,369	708	94.6	91.7

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, 2021 through December 31, 2021.

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, 2021 through December 31, 2021. 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
28-049-0020-5	Jackson Ncore, MS	95.9%	96.7%	54.9%	AO (40%) Other (60%)	AO (50%) AH (25%) AM (25%)	AH (93%) AO (4%) Other (3%)
32-003-0540-5	Jerome Mack Middle School, NV	95.9%	95.1%	62.3%	BI (80%) AB (20%)	BI (67%) AB (17%) BJ (16%)	AH (89%) BI (9%) AB (2%)
37-067-0022-5	Winston-Salem – Hattie Ave., NC	62.3%	63.9%	57.4%	BA (65%) AH (9%) Other (26%)	BA (68%) AH (9%) Other (23%)	AH (81%) BA (8%) Other (11%)
39-035-0076-5	Southerly WTP, OH	98.0%	100%	66.0%	AJ (100%)	---	AH (100%)
46-099-0008-5	Sioux Falls School of Deaf, SD	51.5%	51.5%	51.5%	BA (100%)	BA (100%)	BA (100%)
46-099-0009-5	SF-USD, SD	56.9%	56.9%	80.0%	AN (89%) BB (11%)	AN (89%) BB (11%)	AN (46%) Other (54%)

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, 2021 through December 31, 2021. Codes are ordered by frequency of occurrence.

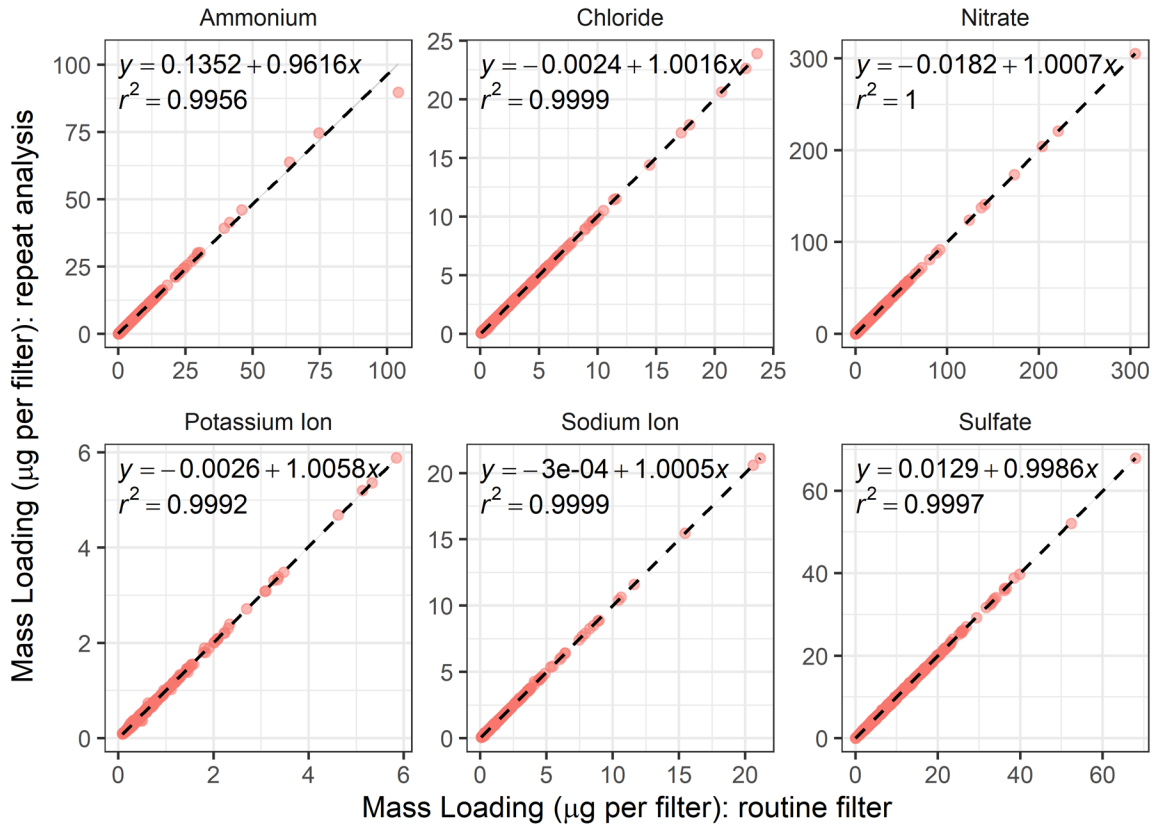
Null Code	SASS PTFE	SASS Nylon	URG Quartz	Total	Null Code Description
AN	109	106	103	318	Machine Malfunction
AH	99	94	243	436	Sample Flow Rate or CV out of Limits
AV	61	61	62	184	Power Failure
AF	56	56	51	163	Scheduled but not Collected
BJ	50	50	33	133	Operator Error
BA	35	35	24	94	Maintenance/Routine Repairs
AB	30	30	30	90	Technician Unavailable
AO	27	27	28	82	Bad Weather
AQ	22	24	12	58	Collection Error
AJ	16	5	5	26	Filter Damage
BB	14	14	14	42	Unable to Reach Site
AG	12	12	30	54	Sample Time out of Limits
BI	11	11	14	36	Lost or damaged in transit
AL	10	11	14	35	Voided by Operator
AD	5	5	0	10	Shelter Storm Damage
BE	4	4	4	12	Building/Site Repair
AR	4	2	9	15	Lab Error
SV	2	3	19	24	Sample Volume Out of Limits
AM	2	2	1	5	Miscellaneous Void
AI	2	2	0	4	Insufficient Data (cannot calculate)
SA	1	1	1	3	Storm Approaching
AZ	1	1	10	12	Q C Audit
AW	1	0	0	1	Wildlife Damage
AK	0	0	1	1	Filter Leak

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.

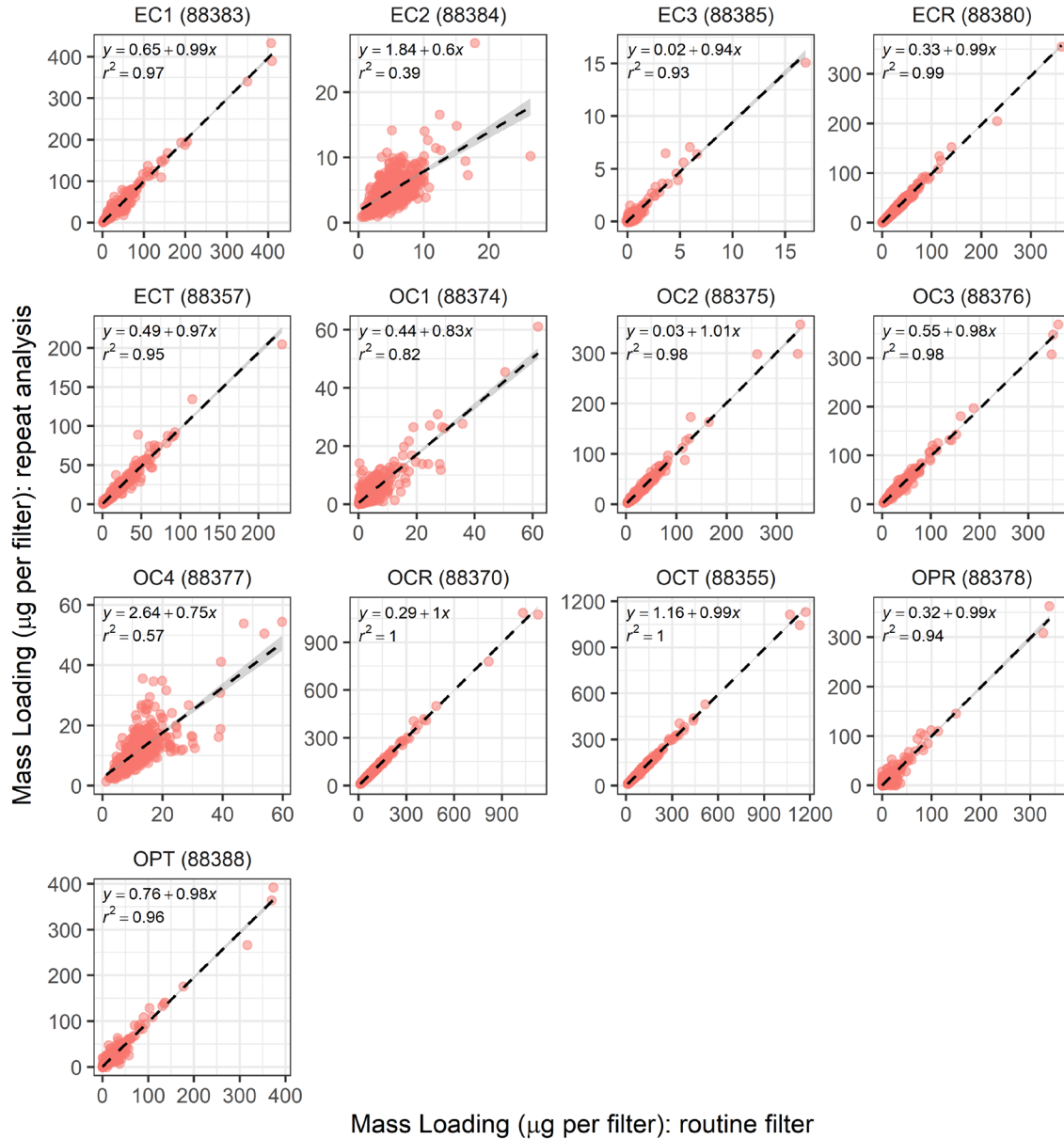
Comparisons of ion mass loadings from repeat analyses (replicates and/or duplicates) on nylon filters analyzed by IC show agreement (Figure 3.1-1). Eight different IC instruments were used for routine and repeat analyses where both replicate and duplicate analyses are performed using the same extract.

Figure 3.1-1: Ion repeat analysis (replicates and/or duplicates) results; data from valid samples collected January 1, 2021 through December 31, 2021.



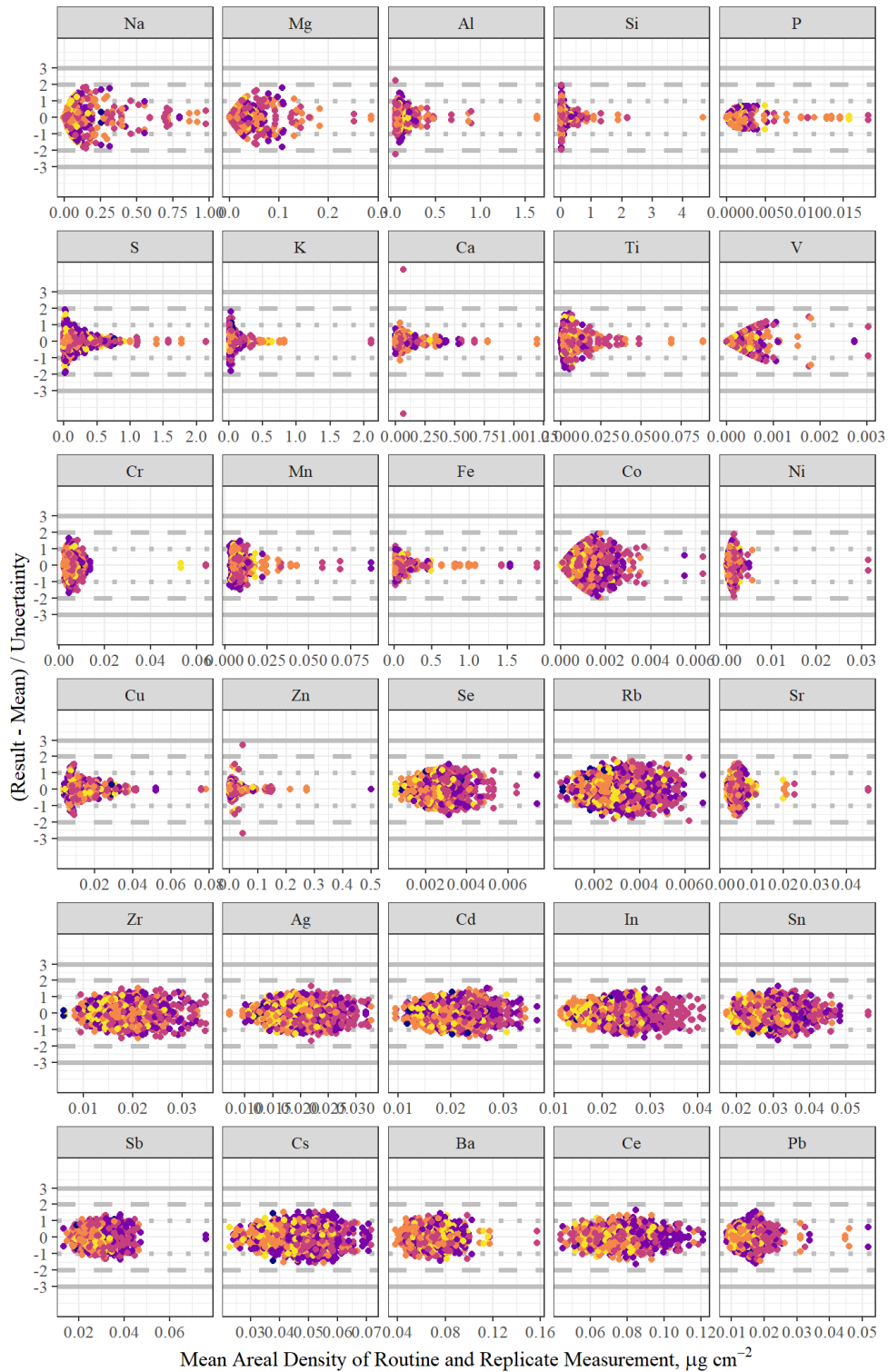
Comparison of carbon mass loadings from repeat analyses (replicates and/or duplicates) on valid quartz filters analyzed by TOA generally show agreement (Figure 3.1-2), with agreement deteriorating for carbon fractions with lower mass loadings (e.g. EC2, OC1, OC4). Repeat analyses are performed on the 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, 2021 through December 31, 2021. 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). AQS parameter codes indicated in parentheses.



Replicate EDXRF analyses of routine CSN samples were started on December 20, 2020. The data for 2021 has been collected and criteria are being evaluated. Analytical precision will be evaluated in the next report. Preliminary results are shown in Figure 3.1-4 below. 4.2% of network filters were put through replicate analysis. Each color represents a different analyzer. A minimum of 2x analytical MDL is required for replicate analysis to be plotted as valid. Cl and Br are not included since they are volatile elements that are lost under vacuum. Dashed horizontal lines (2 standard deviations) are warnings and solid lines (3 standard deviations) are limits. Using the statistical data for sample year 2021, we set limits for each measured element. There was one Ca failure as shown. This was an instance where the routine and replicate were off by an order of magnitude due to a contamination or other isolated incident. Arsenic is also not plotted because there were no measurements above the 2x analytical MDL requirement. The method developed using 2021 data will be applied in future samples, however, we need a large data set to generate the statistics first. This is noted because if the analyzer equipment changes, a new data set of replicates must be collected specific to the analyzer.

Figure 3.1-3: Preliminary Replicate Analysis Results by Element and Instrument. Sample year 2021.



XRF replicates were previously not performed by EDXRF on 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. For this reporting period, EDXRF precision was evaluated by analyzing the same set of 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 3.1-4 through Figure 3.1-18 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 3.1-5 through 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 RTI (see Section 2.1.1 of the CSN 2019 Annual Quality Report) 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. This trend has continued through 2020. 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. Both of these are also observed to be gradually increasing since 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. Median nitrate mass loadings of field blanks from June 2020 through December 2020 are more comparable to those measured prior to the laboratory transition.

Figure 3.1-4: Time series of ammonium measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no nylon filter field blanks were collected. The colored 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. Outlier points that are off scale are plotted at the 1 μg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

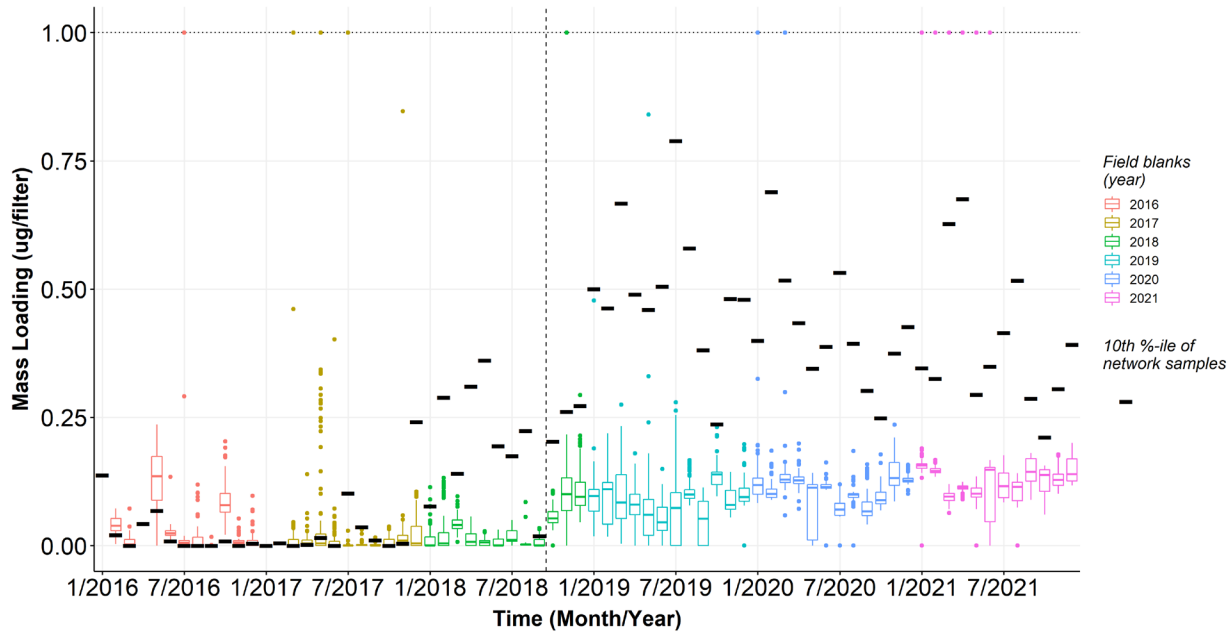


Figure 3.1-5: Time series of chloride measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no nylon filter field blanks were collected. The colored horizontal lines indicate median, and the upper and 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. Outlier points that are off scale are plotted at the 5 μg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

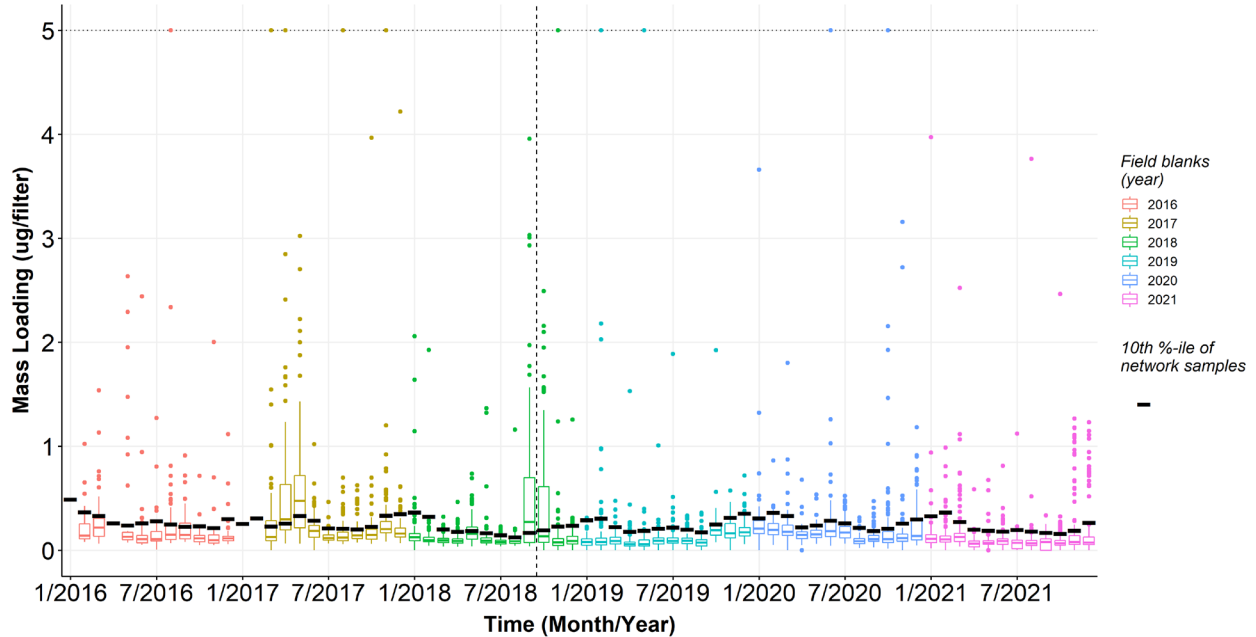


Figure 3.1-6: Time series of nitrate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no nylon filter field blanks were collected. The horizontal lines indicate median, and the upper and lower 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. Outlier points that are off scale are plotted at the 5 μg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

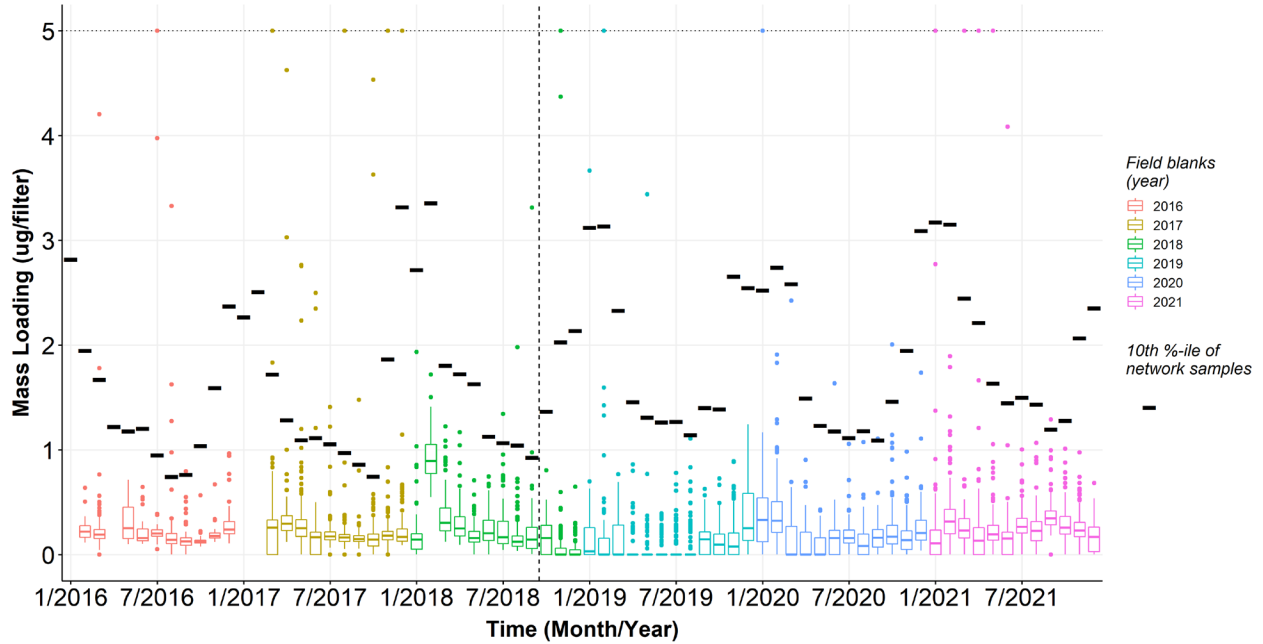


Figure 3.1-7: Time series of potassium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no nylon filter field blanks were collected. The colored horizontal lines indicate median, and the upper 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. Outlier points that are off scale are plotted at the 0.5 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

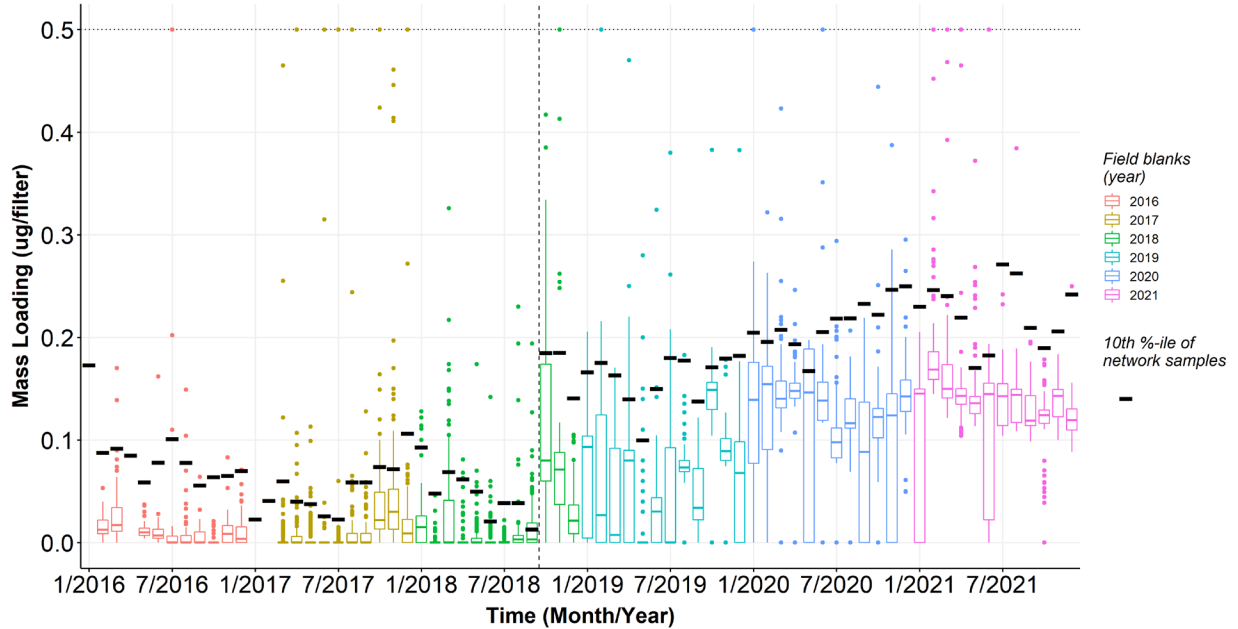


Figure 3.1-8: Time series of sodium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no nylon filter field blanks were collected. The colored horizontal lines indicate median, and the upper 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. Outlier points that are off scale are plotted at the 2 μg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

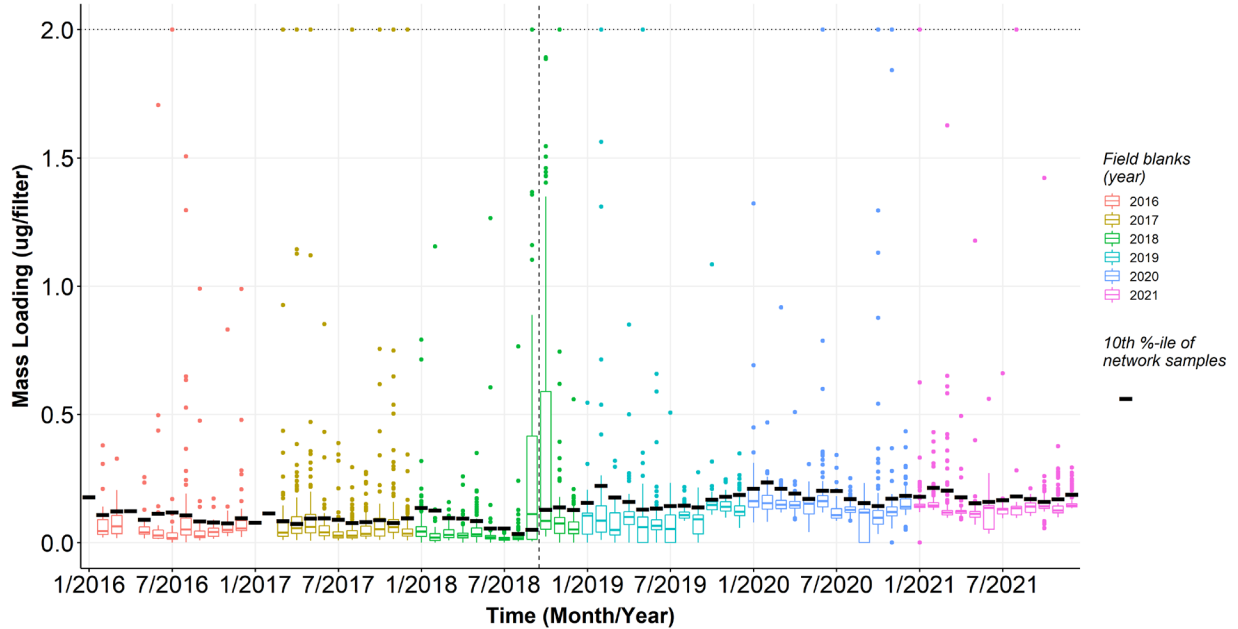
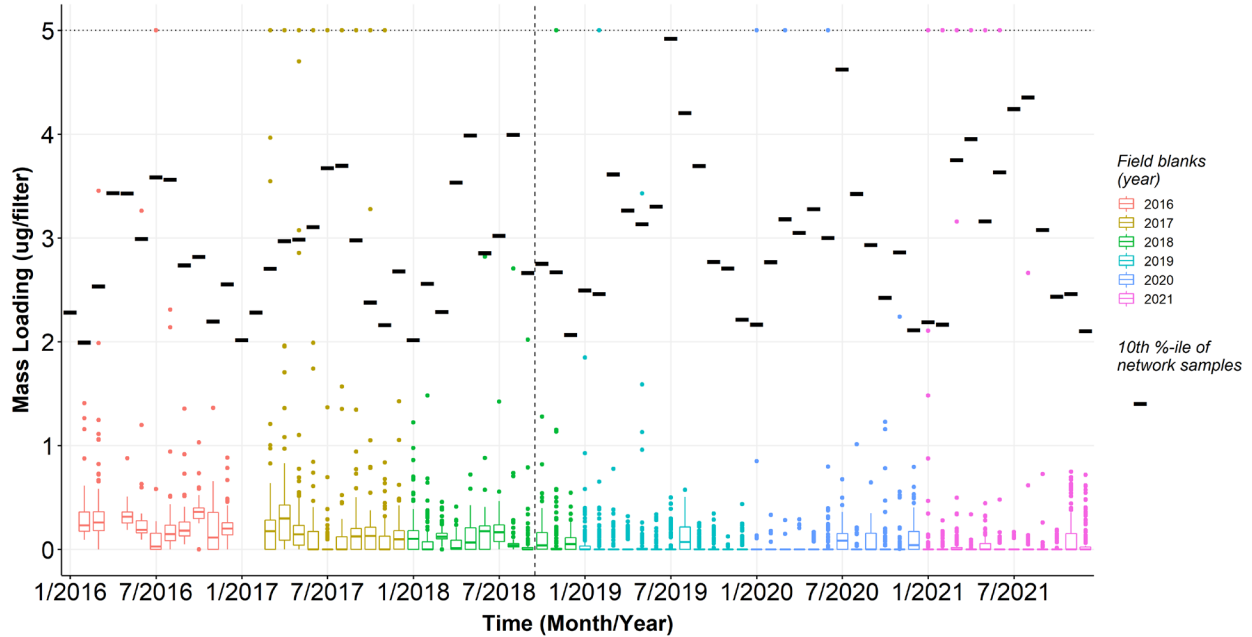


Figure 3.1-9: Time series of sulfate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no nylon filter field blanks were collected. The colored horizontal lines indicate median, and the upper and 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. Outlier points that are off scale are plotted at the 5 μg/filter boundary shown by the horizontal dotted line. 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 (Figure 3.1-10) and elemental carbon (Figure 3.1-11) 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 of the CSN 2019 Annual Quality Report and the Carbon Analyzer Change Data Advisory available at <https://www.epa.gov/amtic/chemical-speciation-network-data-reporting-and-validation>) 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, 2021. As discussed in the CSN 2019 Annual Quality Report, 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 the change in the signal integration threshold and other small differences between instrumentation and laboratory methods associated with the transition. 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 are likely caused by differences in the organic and elemental carbon split point associated with the transition.

Figure 3.1-10: 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, 2021. Gaps in time series are present when no quartz filter field blanks were collected. The colored 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. Outlier points that are off scale are plotted at the 75 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates laboratory transition from DRI to UC Davis. The black horizontal dashes indicate the 10th percentile of network samples.

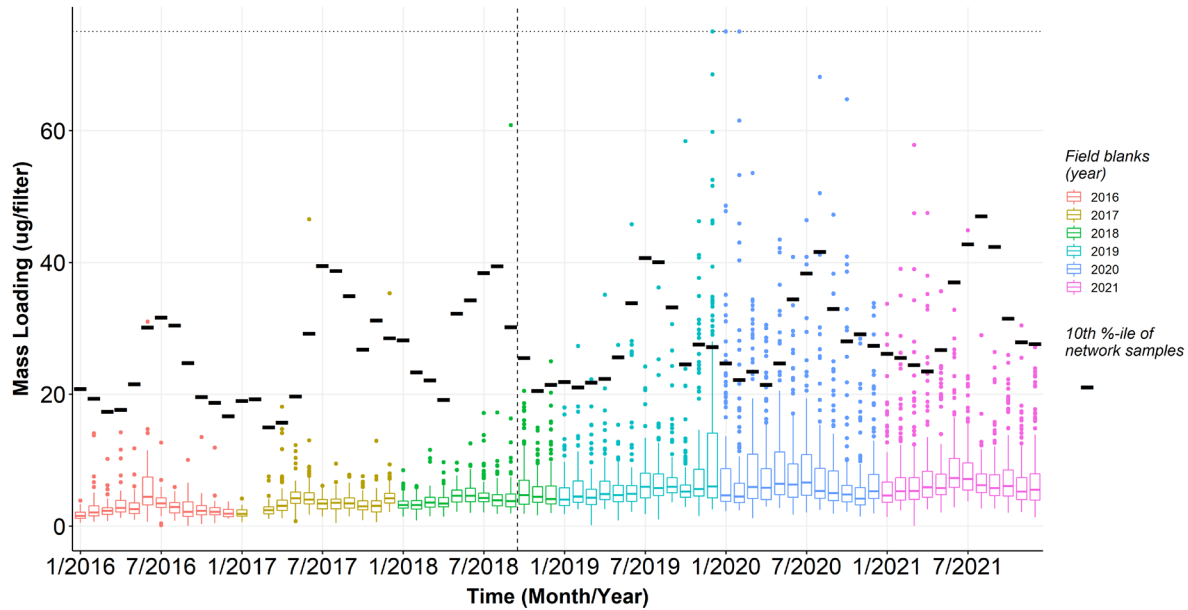
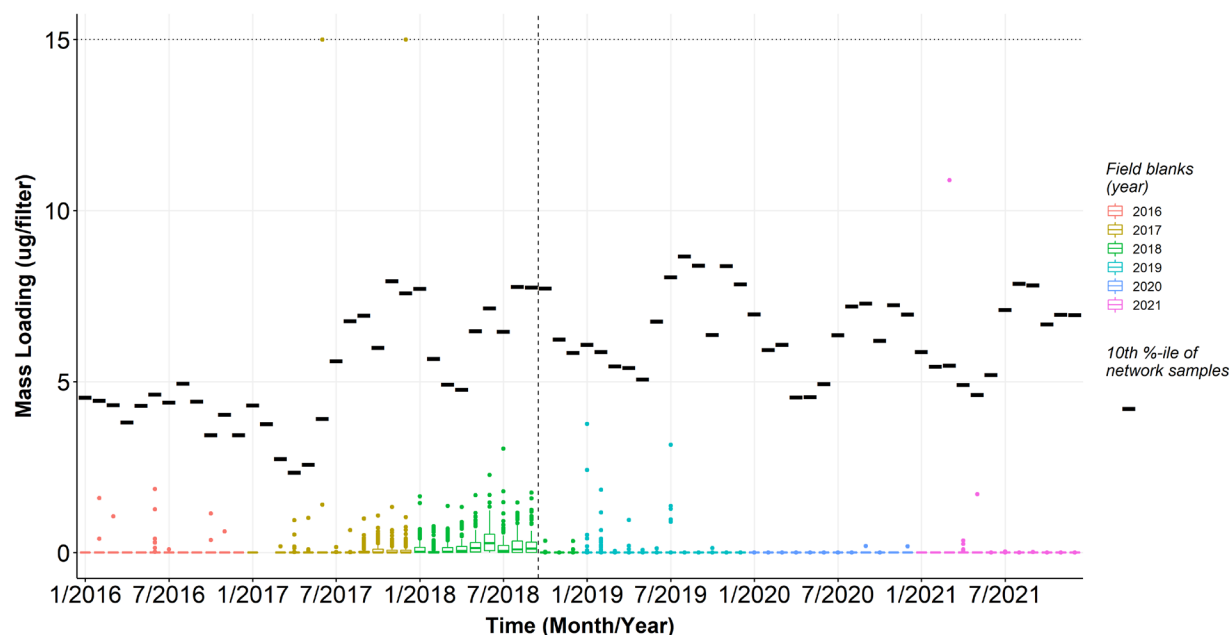


Figure 3.1-11: Time series of elemental carbon by reflectance (ECR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no quartz filter field blanks were collected. The colored horizontal lines 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. Outlier points that are off scale are plotted at the 15 µg/filter boundary shown by the horizontal dotted line. 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 in Figures 3.1-12 through 3.1-17 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, and were implemented beginning with analysis of samples and field blanks collected October 2018. For further details see the XRF Protocol Change Data Advisory (available at <https://www.epa.gov/amtic/chemical-speciation-network-csn-data-reporting-and-validation-files>). 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 sulfur (S; Figure 3.1-13), potassium (K; Figure 3.1-14), calcium (Ca; Figure 3.1-15), titanium (Ti; Figure 3.1-16), iron (Fe; Figure 3.1-17), or zinc (Zn; Figure 3.1-18). However, silicon (Si; Figure 3.1-12) monthly median field blank mass loadings continue to show increased variability. The XRF application did not change for silicon, or any elements below Mn. The increased variability may instead be related to the change from analyzing filters on three instruments to five instruments beginning with February 2019 filters (analysis beginning May 2019; see Table 4.2-1 in the CSN 2019 Annual Quality Report).

Figure 3.1-12: Time series of silicon (Si) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no PTFE filter field blanks were collected. The colored 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. Outlier points that are off scale are plotted at the 2.5 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

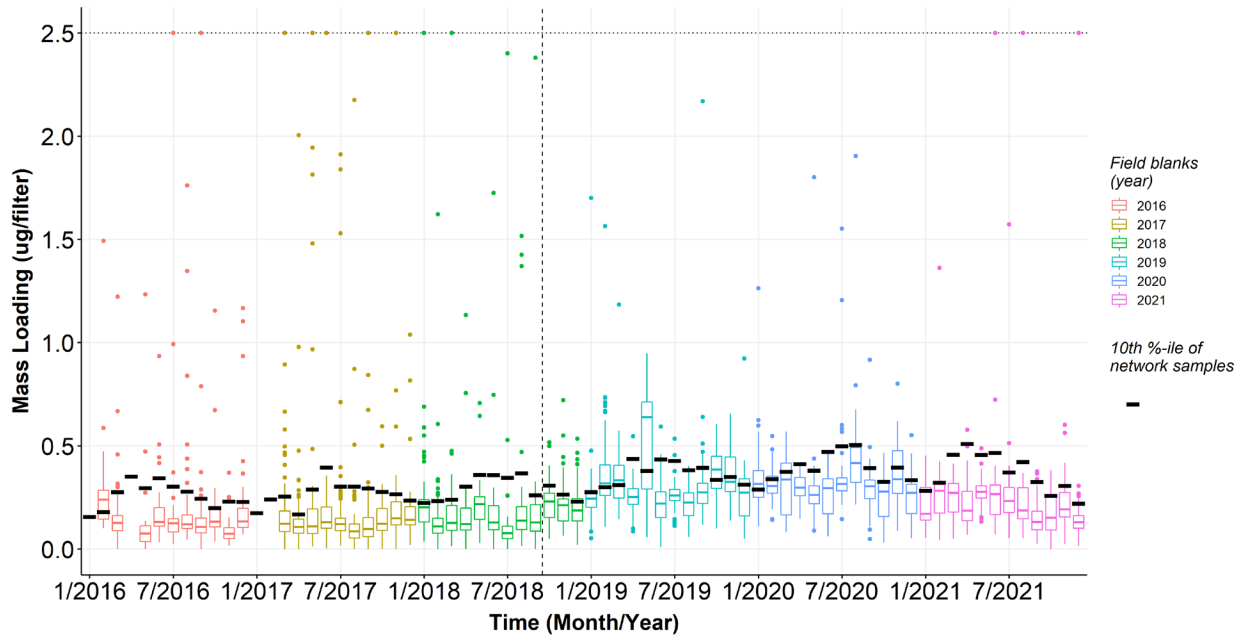


Figure 3.1-13: Time series of sulfur (S) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper 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. Outlier points that are off scale are plotted at the 2.5 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

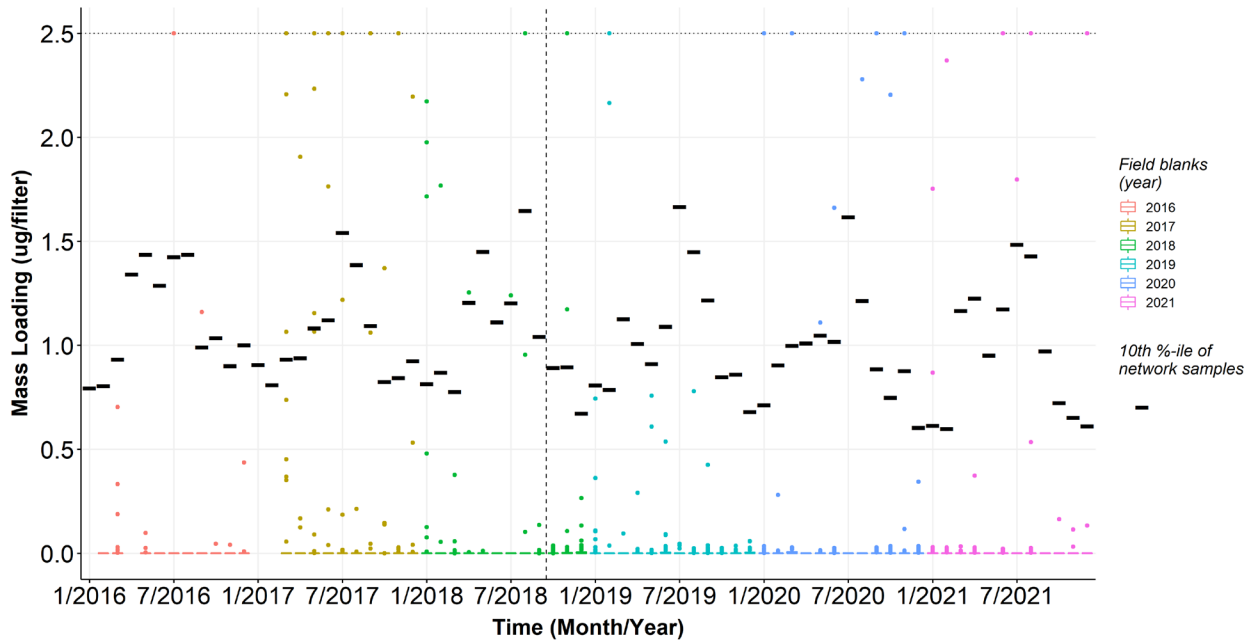


Figure 3.1-14: Time series of potassium (K) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper 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. Outlier points that are off scale are plotted at the 2.5 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

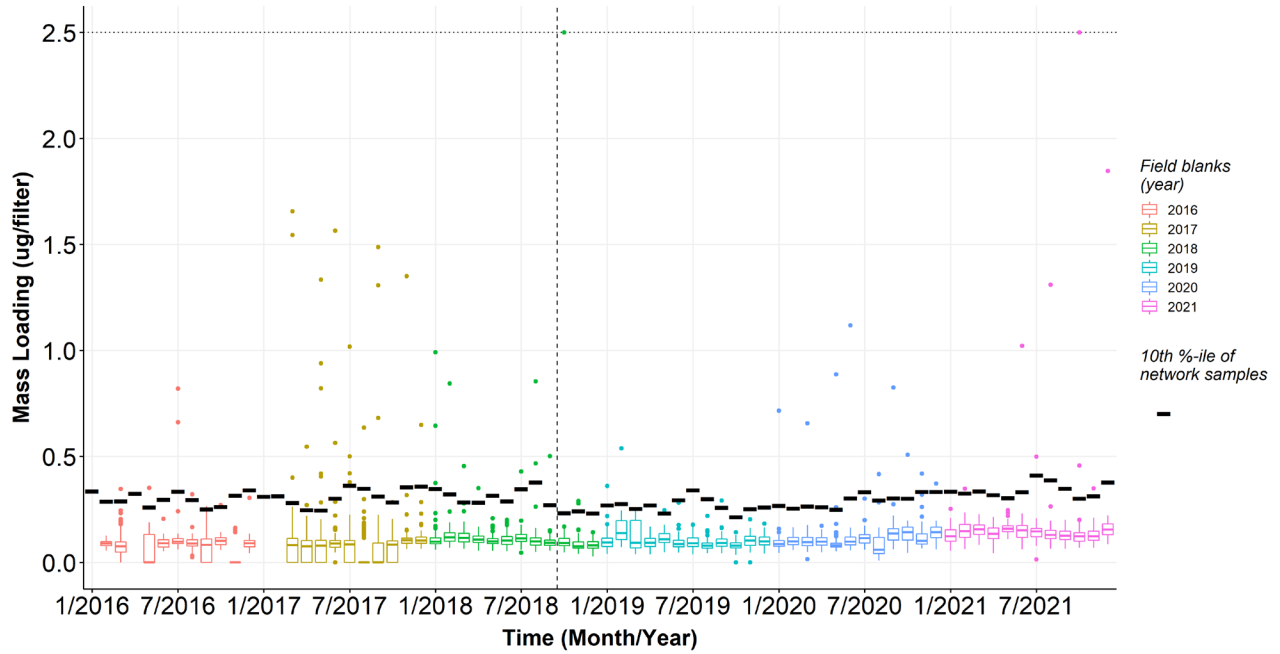


Figure 3.1-15: Time series of calcium (Ca) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper 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. Outlier points that are off scale are plotted at the 2.5 μg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

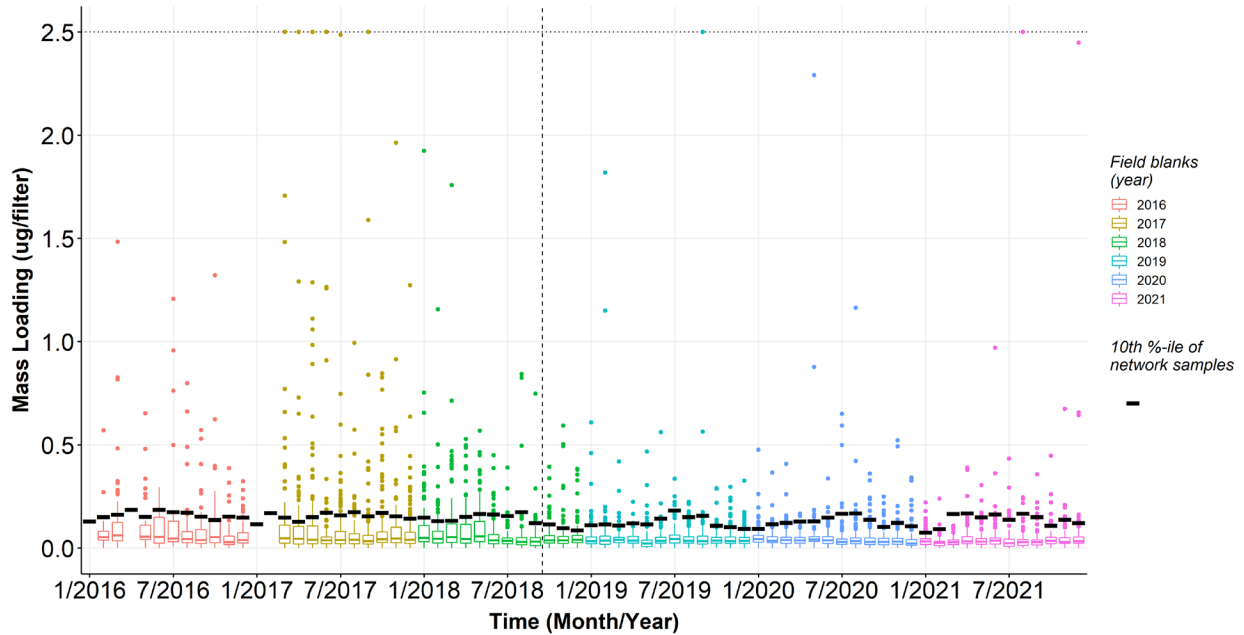


Figure 3.1-16: Time series of titanium (Ti) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper 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. Outlier points that are off scale are plotted at the 0.15 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

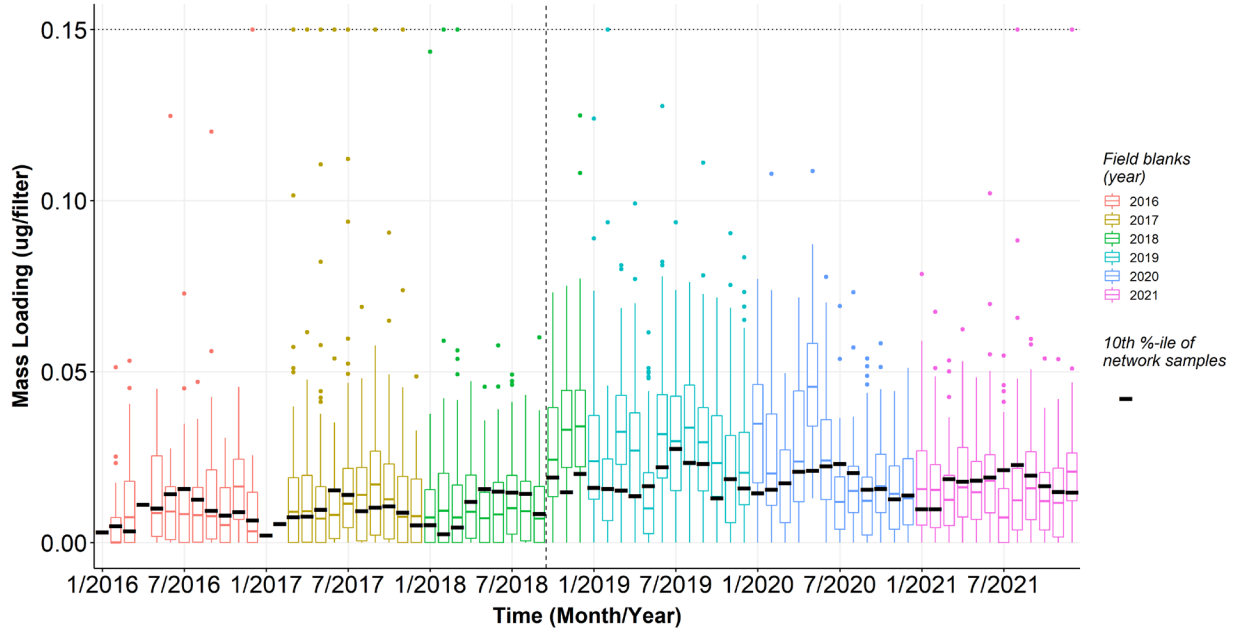


Figure 3.1-17: Time series of iron (Fe) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper and 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. Outlier points that are off scale are plotted at the 2.5 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

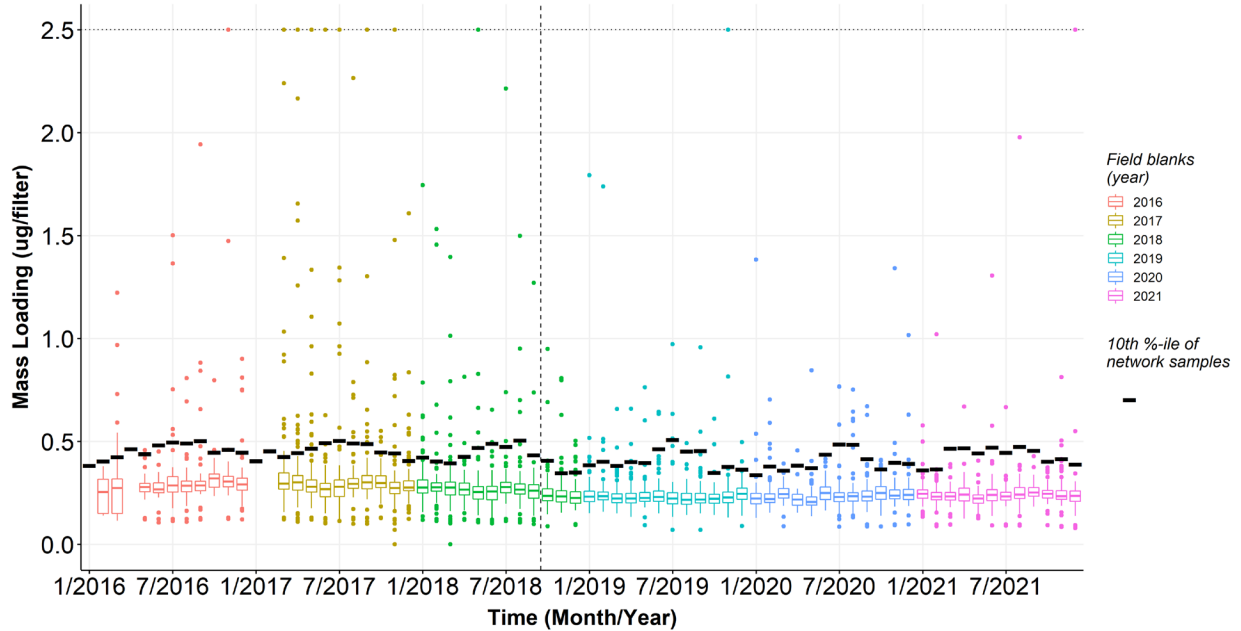
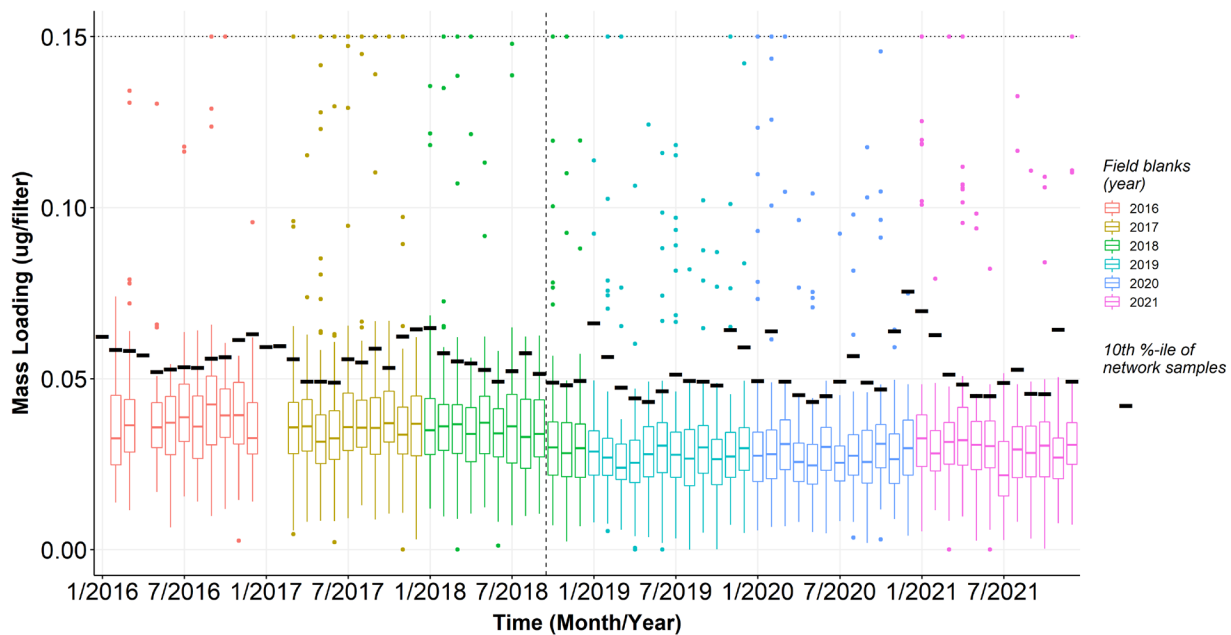


Figure 3.1-18: Time series of zinc (Zn) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2021. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper and 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. Outlier points that are off scale are plotted at the 0.15 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.



Beginning with the shipment to UCD of filters collected in July 2020, the Sample Handling Laboratory, Wood PLC, included five laboratory blanks for each filter type (PTFE, nylon, and quartz) as part of the routine shipment. A total of 60 laboratory blanks of each filter type were analyzed during the current reporting period. Summaries of the analyses are in Section 4.1.6 (nylon), Section 4.2.6 (PTFE), and Section 4.3.6 (carbon).

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, daily blank QC filters, or the lowest standard or spiked solution), the analytical MDL is assigned as a floor value.

The average MDLs calculated for this reporting period (samples collected January 1, 2021 through December 31, 2021) are compared to those calculated using the same method from the previous reporting period (samples collected January 1, 2020 through December 31, 2020) (Table 3.1-4). MDLs calculated during this reporting period were within the range of 50% to 200% of values from the previous reporting period for all species except elemental carbon species (ECR) MDLs are lower relative to their 2020 MDLs.

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, 2020 through December 31, 2020 (previous reporting period) and January 1, 2021 through December 31, 2021 (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 (2020) and the current reporting period (2021). Typical MDLs are from the CSN laboratory analysis contract’s statement of work.

Species	EPA Attachment D	2020 (previous reporting period)		2021 (current reporting period)	
	Typical MDL, ng/m ³	Average MDL, ng/m ³	% Above MDL	Average MDL, ng/m ³	% Above MDL
Ag	38	13	9.3	13	5.3
Al	25	23	48	24	58
As	2.7	0.10	6.5	0.10	3.3
Ba	59	28	13	33	8.9
Br	2.3	0.13	31	0.10	31
Ca	7.6	9.9	88	8.3	93
Cd	23	14	7.8	14	5.1
Ce	88	36	8.2	38	6.1
Cl	11	4.0	45	3.8	45
Co	2.0	1.6	6.8	1.7	3.9
Cr	2.6	2.3	25	2.2	22
Cs	46	27	9.4	29	4.0
Cu	2.5	4.3	23	4.6	21
Fe	3.3	8.5	97	7.6	97
In	33	15	11	16	5.2
K	11	5.4	99	5.1	99
Mg	19	45	17	45	16
Mn	2.9	3.0	28	3.1	25
Na	55	81	31	91	28
Ni	1.9	1.2	23	1.3	18
P	16	1.9	9.0	1.5	12
Pb	6.4	6.7	23	7.1	15
Rb	2.6	3.2	8.8	3.2	5.5
S	9.9	1.1	100	0.79	100

Species	EPA Attachment D	2020 (previous reporting period)		2021 (current reporting period)	
	Typical MDL, ng/m ³	Average MDL, ng/m ³	% Above MDL	Average MDL, ng/m ³	% Above MDL
Sb	52	16	8.6	17	7.4
Se	2.6	2.5	11	2.6	7.7
Si	19	14	79	13	90
Sn	36	16	9.4	17	7.1
Sr	3.5	2.9	14	3.1	12
Ti	5.3	2.9	51	2.5	61
V	3.9	0.72	9.2	0.7	8.6
Zn	3.5	1.7	93	2.2	89
Zr	23	14	7.8	15	5.8
Ammonium	25	13	95	13	93
Chloride	27	25	76	30	77
Nitrate	22	39	99	38	99
Potassium Ion	24	13	79	13	80
Sodium Ion	30	14	65	14	61
Sulfate	35	29	100	33	100
Elemental Carbon (EC1)	95	34	100	23	100
Elemental Carbon (EC2)	63	31	99	19	99
Elemental Carbon (EC3)	63	5.7	72	4.8	82
Elemental Carbon (ECR)	63	2.8	100	0.039	100
Elemental Carbon (ECT)	63	0.32	100	0.52	100
Organic Carbon (OC1)	63	15	69	11	73
Organic Carbon (OC2)	63	38	100	34	99
Organic Carbon (OC3)	95	490	56	300	76
Organic Carbon (OC4)	95	96	87	79	98
Organic Carbon (OCR)	63	640	90	410	97
Organic Carbon (OCT)	63	640	91	410	97
Organic Pyrolyzed (OPR)	95	66	90	44	88
Organic Pyrolyzed (OPT)	63	66	95	43	94

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 2021.

3.2.1 Elemental Analysis

3.2.1.1 XRF-5 X-ray Intensity Loss

On 2/4/2021 a drop in X-ray intensity on XRF-5 was noticed and all sample analysis was stopped. The manufacturer's investigation linked this to the high voltage generator. This was reported in last year's Annual Quality Report. However, it is being reported again here because

due to a quality issue with the supplier of the generators, multiple replacements also failed and XRF-5 remained unusable well into this report's analysis period. XRF-5 was operational again on June 17, 2021 and began analyzing CSN samples again on August 6, 2021. No CSN sample analyses from this reporting period were affected by the intensity drop on XRF-5 as it occurred prior to this analysis period.

3.2.1.2 XRF-3 X-ray Intensity Loss

XRF-3 showed decreased X-ray intensity and a resulting drop in QC concentrations after the weekly detector calibration performed on 3/31/2021. All analysis was stopped on the instrument and no samples were analyzed after the intensity drop. A manufacturer technician came out on 4/7/2021 and determined the detector sleeve had shifted and broken. The sleeve was replaced, but low intensity continued, so the detector was moved closer to the sample. This repair necessitated a new calibration which was done, QC tests passed and XRF-3 started analyzing samples again on 4/23/2021.

Another drop in intensity occurred on 5/20/2021 and sample analysis was stopped on 5/21/2021. This did not affect CSN samples as the instrument was analyzing IMPROVE network samples at the time. All IMPROVE samples analyzed since the last QC before the intensity drop were reanalyzed on another instrument and the reanalysis results were reported. After prolonged troubleshooting by the manufacturer, it was determined a new X-ray tube and high voltage generator were required. Out of stock parts delayed the repair which finished on 7/12/2021. A new calibration was completed, all QC tests passed, and the instrument resumed IMPROVE sample analysis on 7/23/2021 with CSN sample analysis resuming on 11/17/2021.

3.2.1.3 XRF-5 Contamination Issue

This incident is being reported for completeness, but no CSN samples were analyzed on XRF-5 during the period of observed contamination. On June 22, 2021 and July 9, 2021 zinc levels on the daily QC blank increased over the acceptance limit. Additionally, the daily QC multi-element (QC-ME) sample showed higher than usual zinc and copper. However, during this time period the server that stores the XRF data was moved and the QC tools were not available. These high values were not discovered until July 15, 2021 when manganese failed acceptance on the daily blank QC. All analysis was then stopped and an investigation determined that powder coating was rubbing off of a cover piece when the sample chamber cap opened and closed when loading samples for analysis. This was due to bad placement of the cover piece when the manufacturer reinstalled it during a repair completed in June. The cover was repositioned so it did not interfere with the cap opening and closing and the analysis chamber was cleaned to remove any powder coating debris.

The investigation also determined that no samples analyzed since the manufacturer's repair had any indication of contamination. Only the daily QC samples showed any sign of contamination due to their multiple analyses. The QC samples were cleaned which returned them to acceptable levels for the contaminant elements. So, there was no contamination of the instrument itself only of the daily QC samples. No network samples were reanalyzed and as stated previously, no CSN samples were analyzed on this instrument during the period when contaminants were observed on the QC samples.

3.2.1.4 Failed Quality Control for Silicon Issue

UCD reanalyzed 348 CSN samples from October 2019 originally run on an XRF instrument that failed QC for silicon. A Corrective Actions Report (CAR) was accepted by the EPA on August 16, 2021. UCD updated the data in AQS on September 9, 2021; a total of 331 silicon measurements, 331 Soil results, and 331 Reconstructed Mass results were updated. No updates were made for 17 filters as these were reported as invalid throughout the CSN data pathway. Data were updated having taken into consideration SLT edits on impacted filters during review in DART as well as any changes made in AQS since UCD originally submitted the data.

3.2.2 Ion Analysis

During this reporting period there were no issues with Ion Analysis.

UCD identified the incorrect analytical MDL had been applied to data between 10/01/2018 and 12/31/2019; the analytical MDL originally applied during this time was from DRI instead of from RTI, who began performing IC analysis on CSN samples beginning October 2018. As described in Section 3.1.3.2, the MDL is the higher of the analytical MDL and field blank-based MDL. Potassium ion is the primary ion where the analytical MDL is the overall MDL. Though impacts are primarily on potassium ion MDLs, UCD suggested the MDLs, uncertainties, and 'MD' qualifier flag in AQS be updated for all ions for the time period 10/01/2018 to 12/31/2019. Per instruction from the EPA, UCD updated and redelivered the ions data for October 2018 through December 2019 on March 16, 2022. UCD detailed these changes in MDLs over time in a document emailed to the EPA on May 4, 2022. In addition, UCD updated the Contract Transition Data Advisory to include details on analytical MDLs and delivered to the EPA for review on May 4, 2022.

3.2.3 Carbon Analysis

The TOA protocol was updated for samples analyzed during this report period. UCD Sunset analyzers measure lower OC4 than DRI carbon analyzers. In an attempt to minimize the differences between the analyzers, the OC4 step duration was fixed at 580s to allow more time for the organic carbon to evolve. Five of the UCD analyzers implemented the fixed OC4 duration on Nov 6, 2020, during analysis of August 2020 samples. The sixth instrument was installed after this date and was mistakenly setup with a non-fixed OC4 duration. Its protocol was updated to a fixed 580 seconds on February 3, 2021. The SOP will be revised with the fixed OC4 time and detailed explanations at the next revision. The correct time is posted on a deviation in the lab and staff have been re-trained.

A total of 3,220 filters were analyzed by the sixth instrument, including both sample and field blank filters, covering Intended Use Dates between 10/30/2020 and 11/9/2021, from the analysis time period 1/19/2021 and 2/3/2022. The OC4, OP, EC1, EC, and OC parameters, including both transmittance and reflectance parameters and corrected and raw data, have been flagged with the '2 – Operational Deviation' and '4 – Lab Issue' qualifiers for the impacted filters. Relevant Reconstructed Mass parameters have also been updated where parent species were flagged. Data for filters through October 2021, a total of 2,855 filters, were updated in AQS accordingly on April 22, 2022. The impacted filters from November 2021 were flagged and delivered to AQS on May 18, 2022.

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 Bromine and Chlorine Reanalysis

Beginning with filters from September 2021, the bromine (Br) and chlorine (Cl) are marked invalid with the 'AL – Voided by Operator' null code for any filters reanalyzed at XRF. Please see Section 7.1 of the UC Davis QAPP for Analysis of Samples (available at <https://www.epa.gov/amtic/quality-assurance-project-plan-qapp-analysis-chemical-speciation-network-csn-samples>) for further details on the reason for invalidation.

3.2.5 Technical System Audit

The EPA did not conduct an audit during the time when 2021 samples were analyzed.

The EPA last 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 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). The EPA sent a close-out letter to UC Davis on May 7, 2021.

3.2.6 System Audits

UCD performed an internal audit on December 17, 2020. A third-party auditor, T&B Systems, was contracted to perform the audit. The auditors were provided with a tour of the data processing and validation tools. No issues were noted for correction. The next internal audit will take place in late 2022 or early 2023.

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 75 through 86, covering the sampling period January 1, 2021 through December 31, 2021. Routine analysis of these samples was performed March 16, 2021 through March 7, 2022. Both routine analysis and reanalysis was performed May 18, 2021 through April 11, 2022. 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; three cation systems: C9,

C10, and C3) and reported the results of those analyses to UC Davis. Table 4.1-1 details the analysis dates for each batch of data, including both routine analysis and reanalysis.

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 (2021)	Analysis Batch #	IC Analysis Dates
January	75	3/16/2021- 5/18/2021
February	76	4/13/2021- 6/08/2021
March	77	5/10/2021 – 7/09/2021
April	78	6/14/2021– 8/21/2021
May	79	7/19/2021 – 9/16/2021
June	80	8/13/2021 – 09/16/2021
July	81	9/13/2021 – 11/08/2021
August	82	10/12/2021 – 12/15/2021
September	83	11/12/2021 – 1/13/2022
October	84	12/17/2021 – 2/21/2022
November	85	1/18/2022 – 3/24/2022
December	86	2/17/2022 – 4/11/2022

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*. 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 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2021).

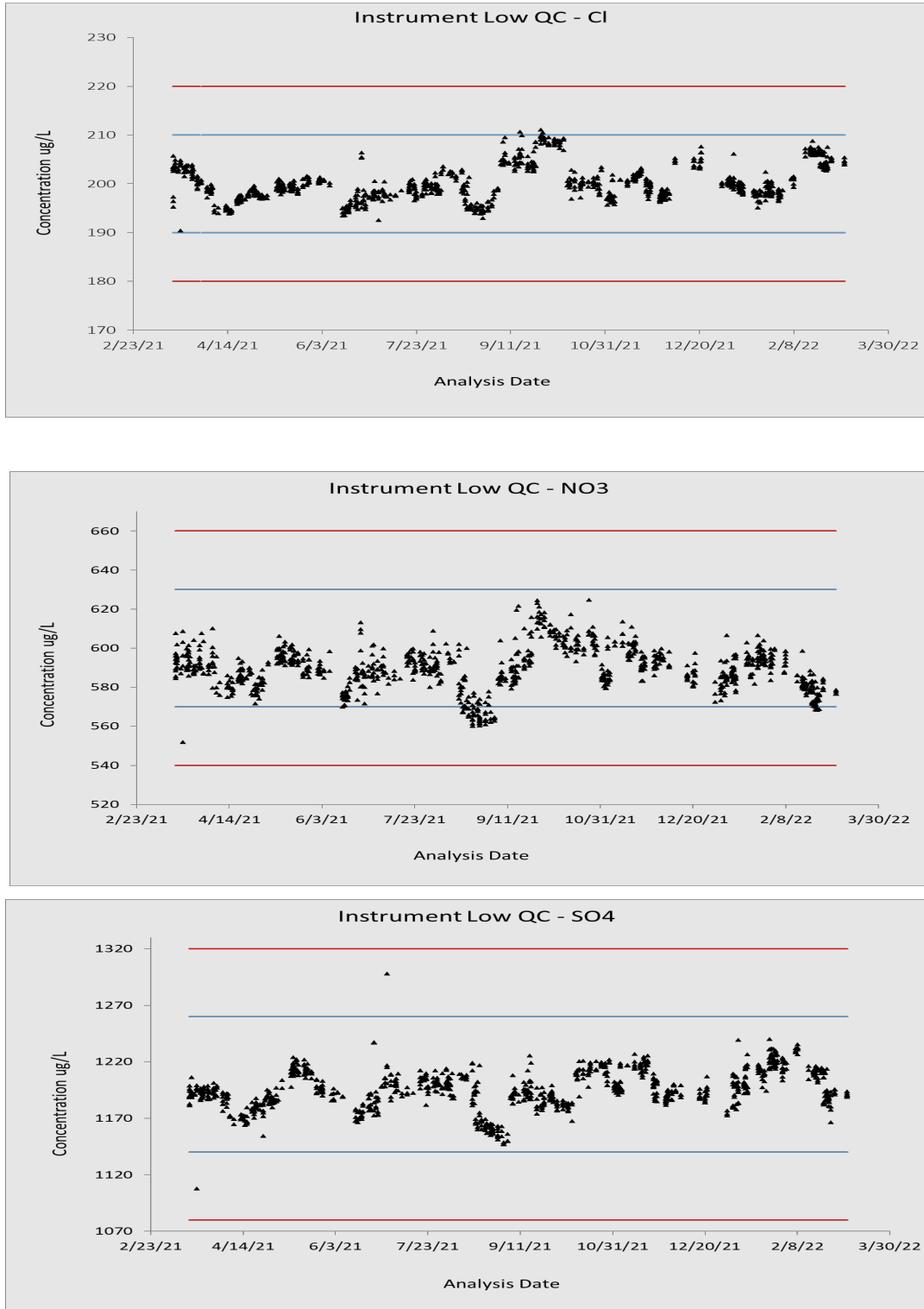
QC Sample	Cl ⁻ (ppb)	NO ₃ ⁻ (ppb)	SO ₄ ²⁻ (ppb)
Instrument Low QC	200	600	1200
Instrument Medium QC	500	1500	3000
Instrument Medium-High QC	1000	3000	6000
Instrument High QC	2000	6000	12000

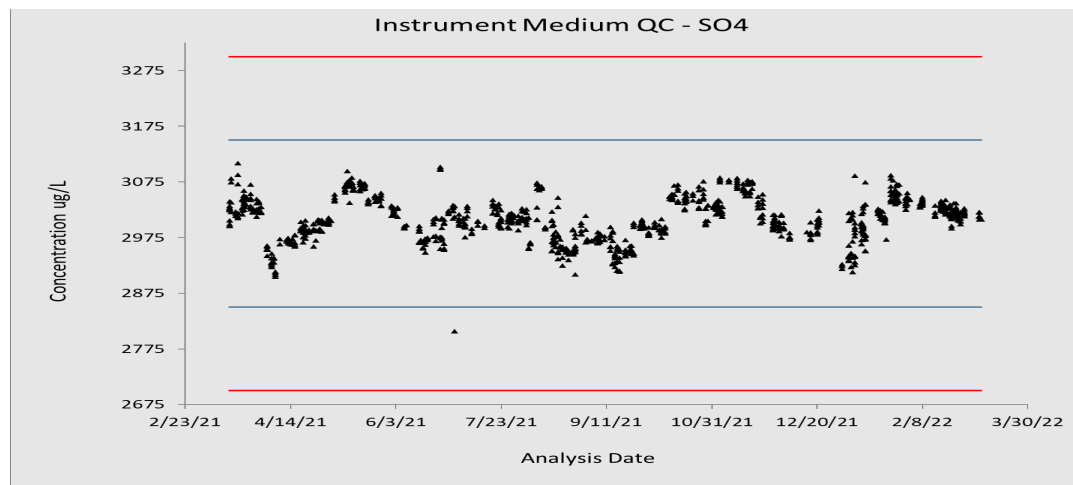
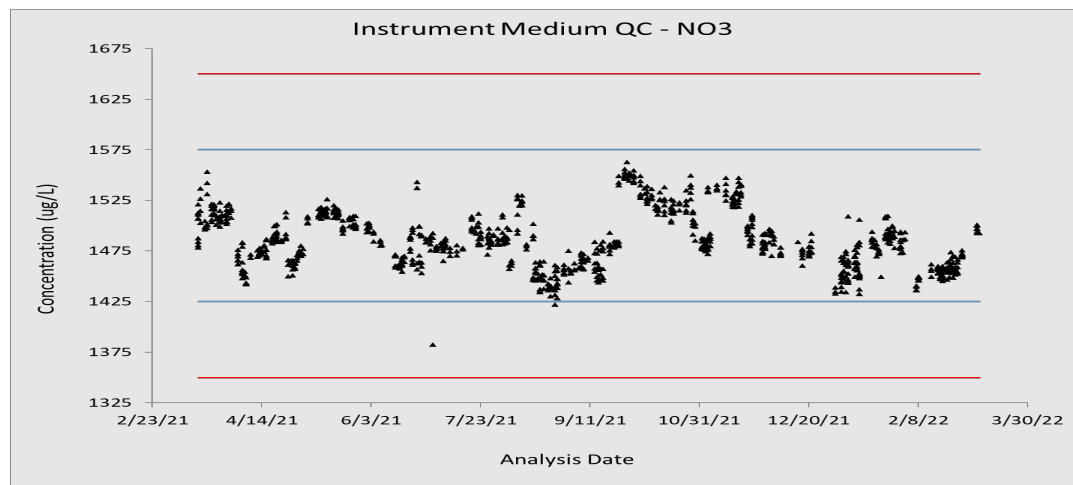
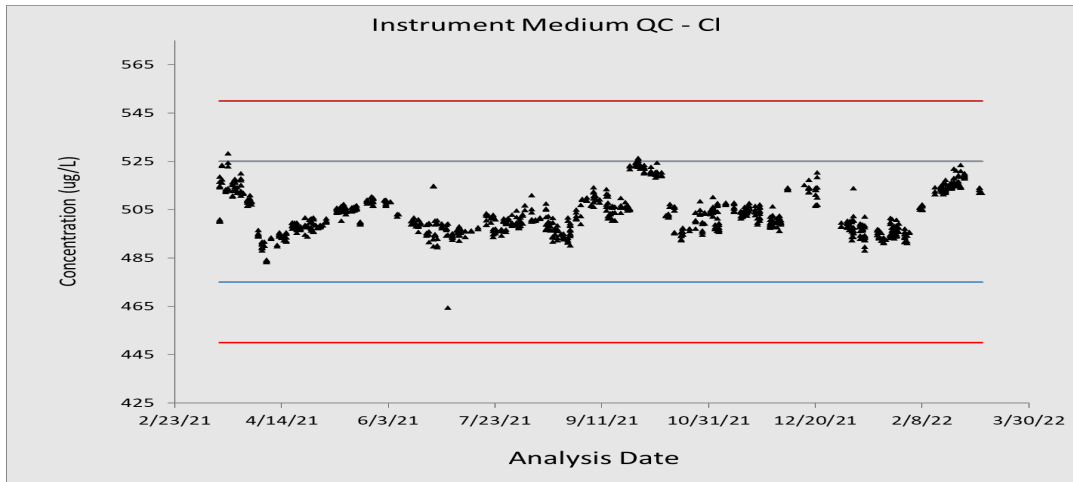
Table 4.1-4: Target concentrations of cation CCV check standards for the analysis period 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2021).

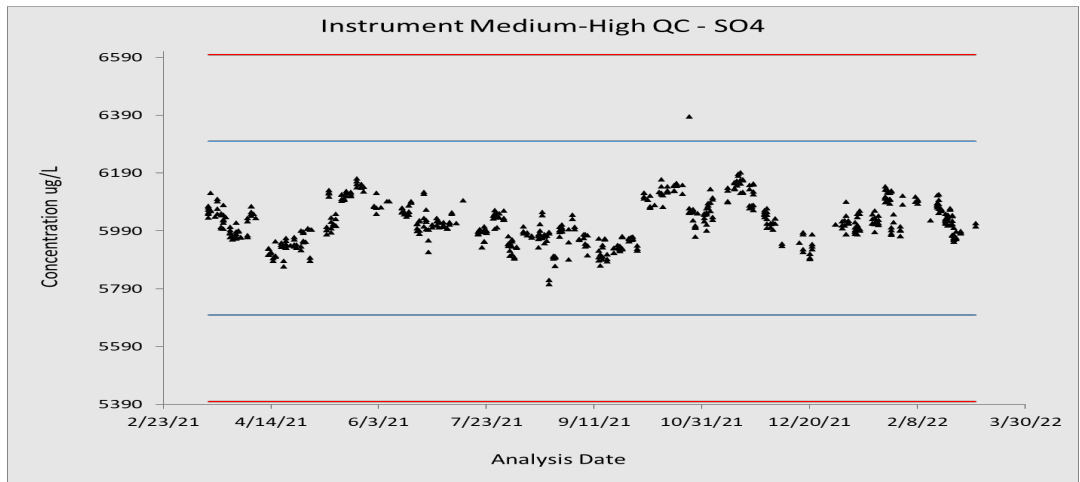
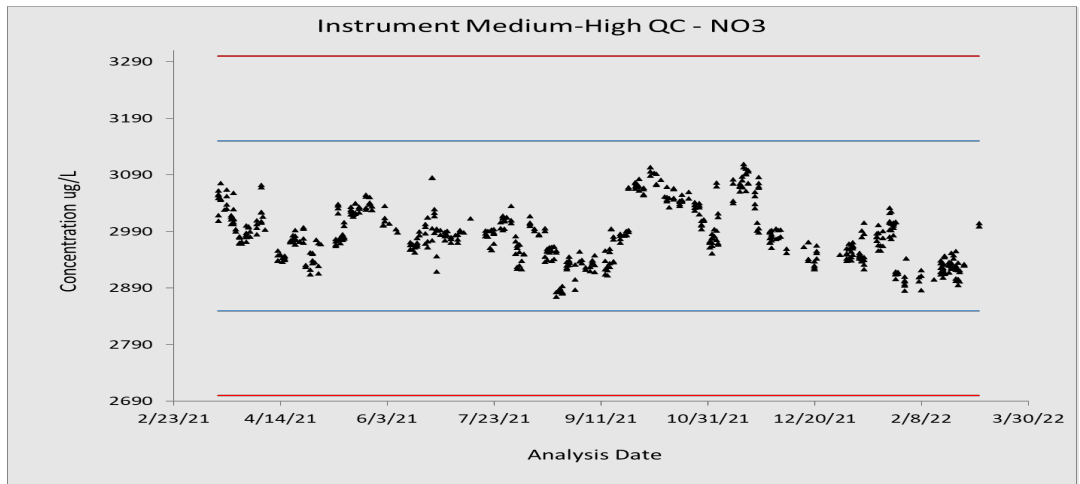
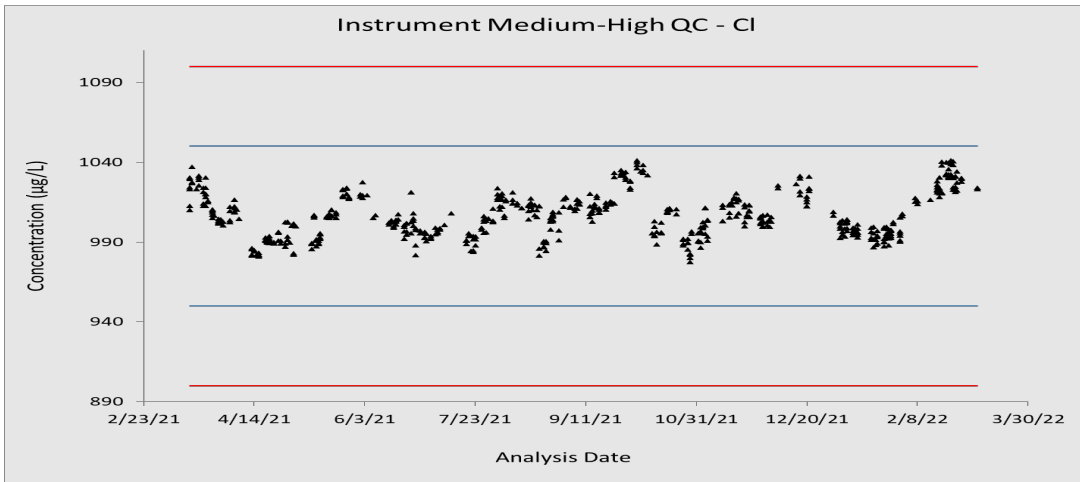
QC Sample	Na ⁺ (ppb)	NH ₄ ⁺ (ppb)	K ⁺ (ppb)
Instrument Low QC	20	20	20
Instrument Medium QC	250	250	250
Instrument Medium-High QC	750	750	750
Instrument High QC	2000	2000	2000

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. Failures occurred at a rate less than 1% for all check standards and data obtained during failures were not reported. Only data with check standards within limits were reported.

Figure 4.1-1: Control charts for anion CCV check standards at low, medium, medium-high, and high concentrations measured in units of $\mu\text{g/L}$ (see Table 4.1-3) for the analysis period 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2021). 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.







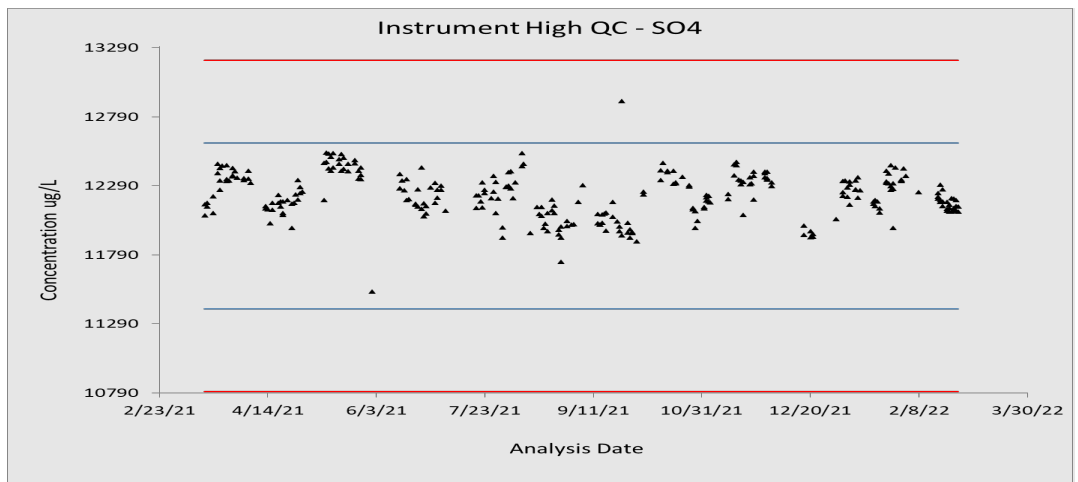
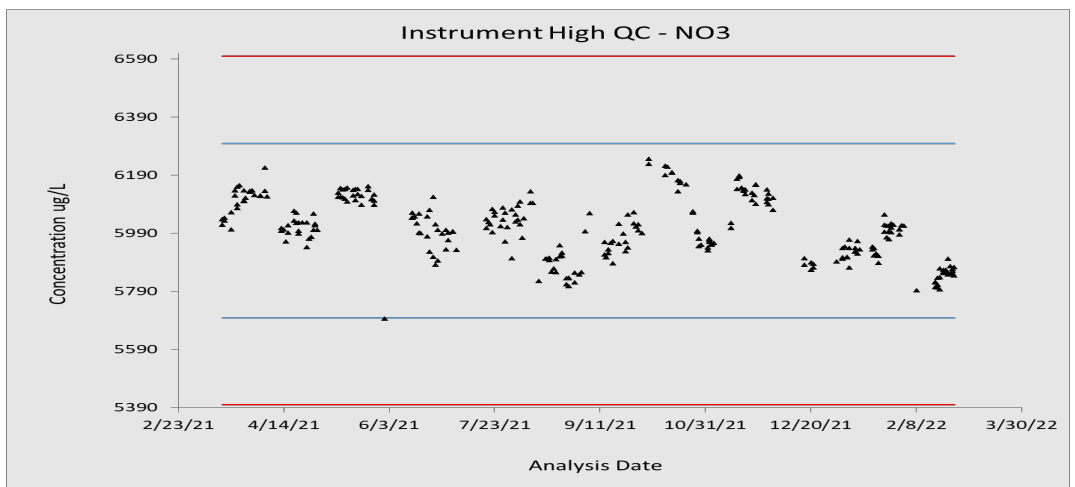
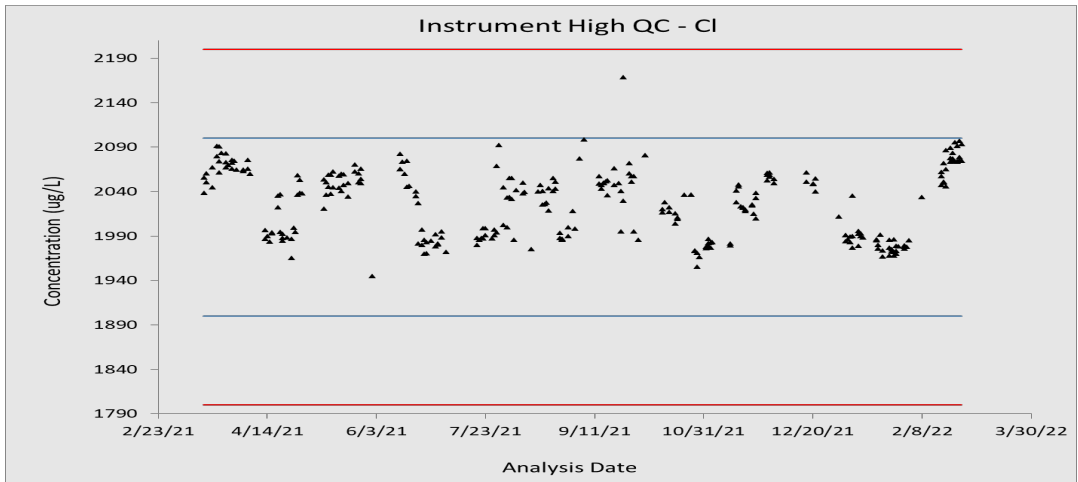
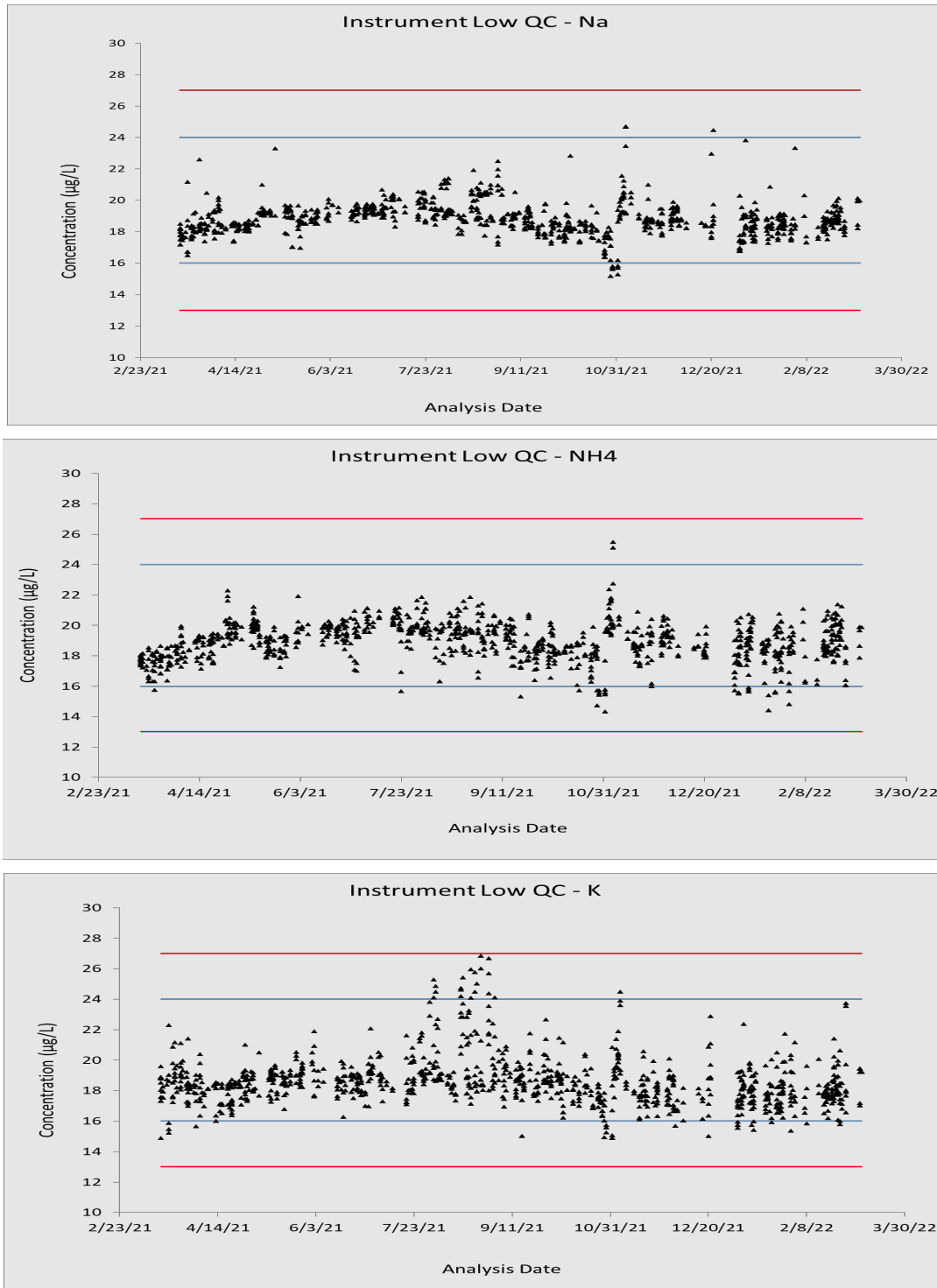
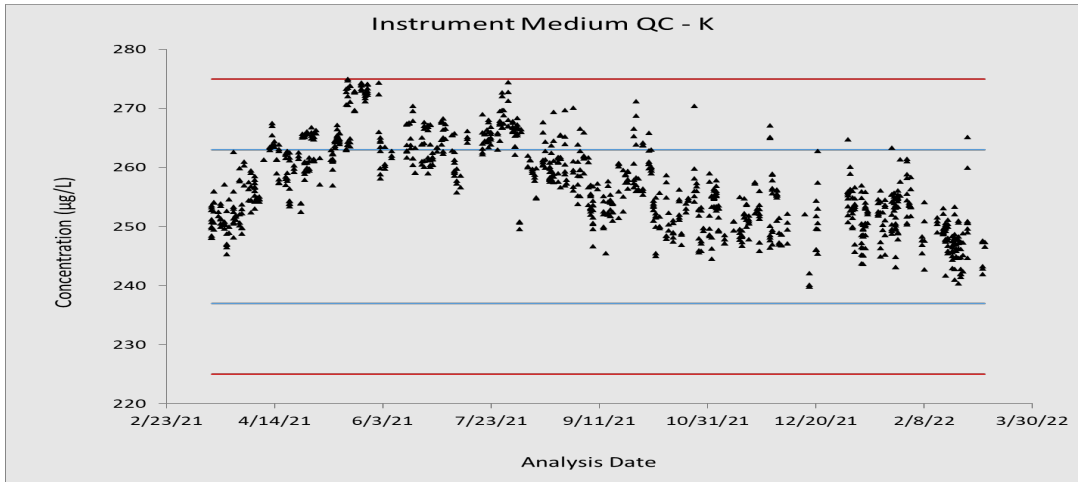
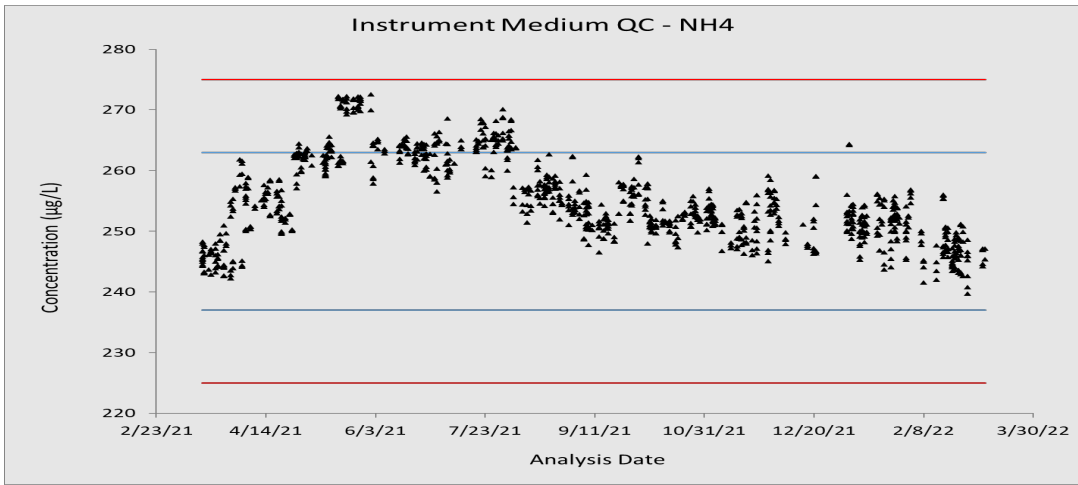
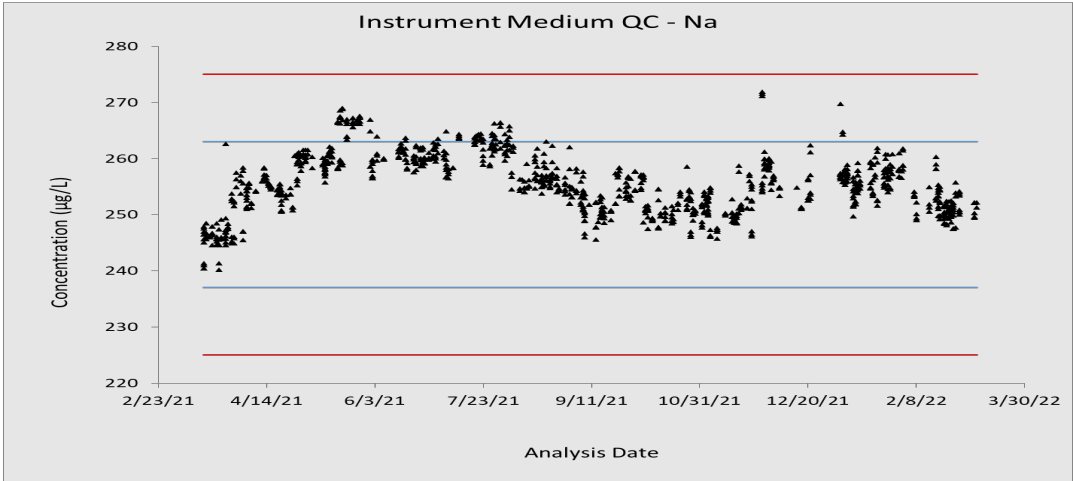
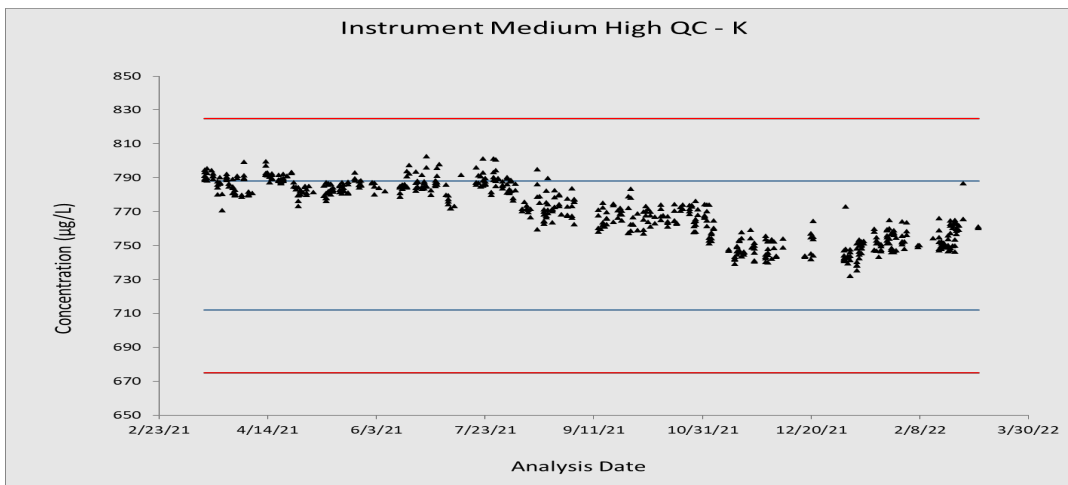
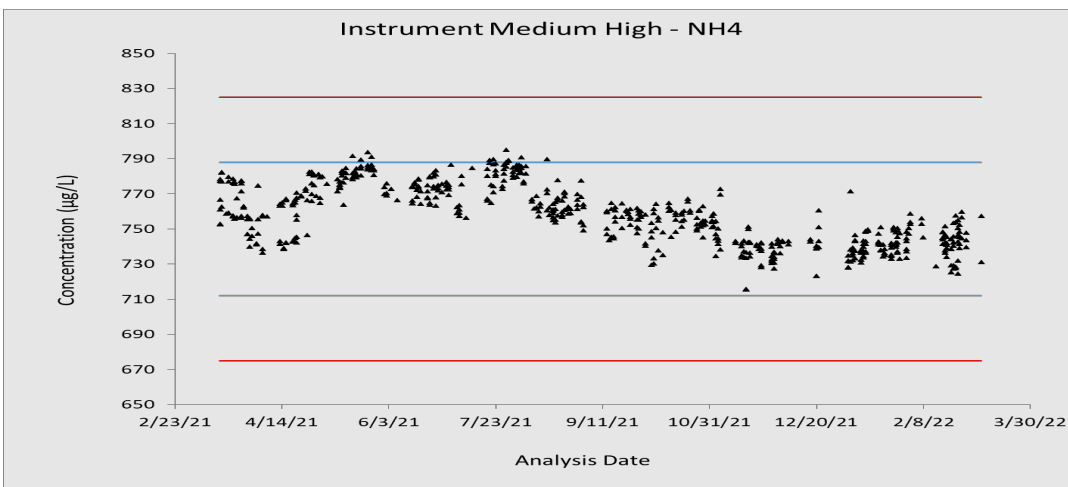
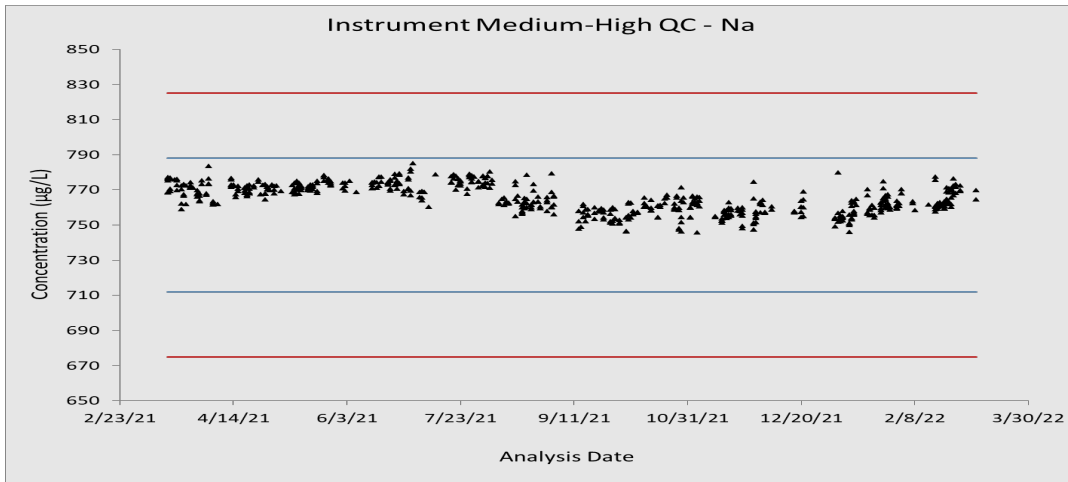
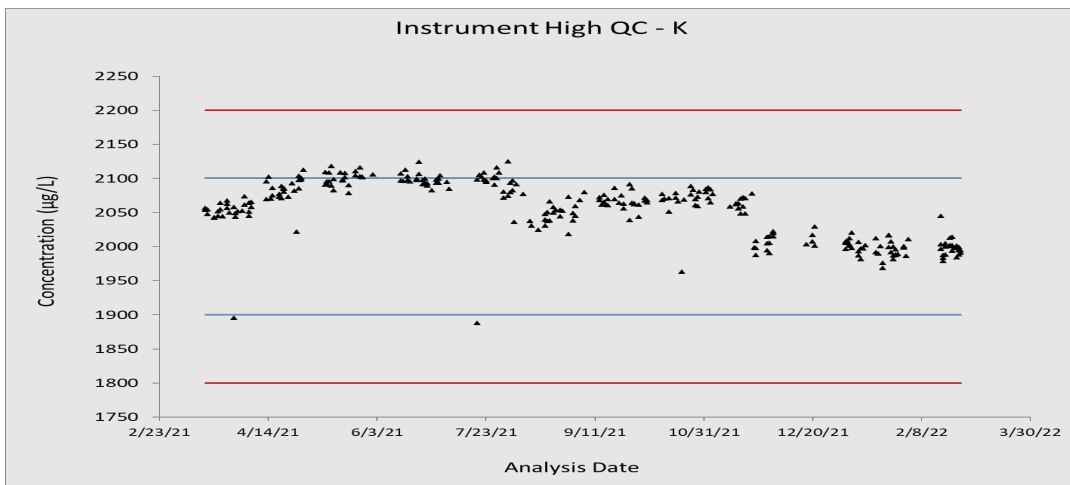
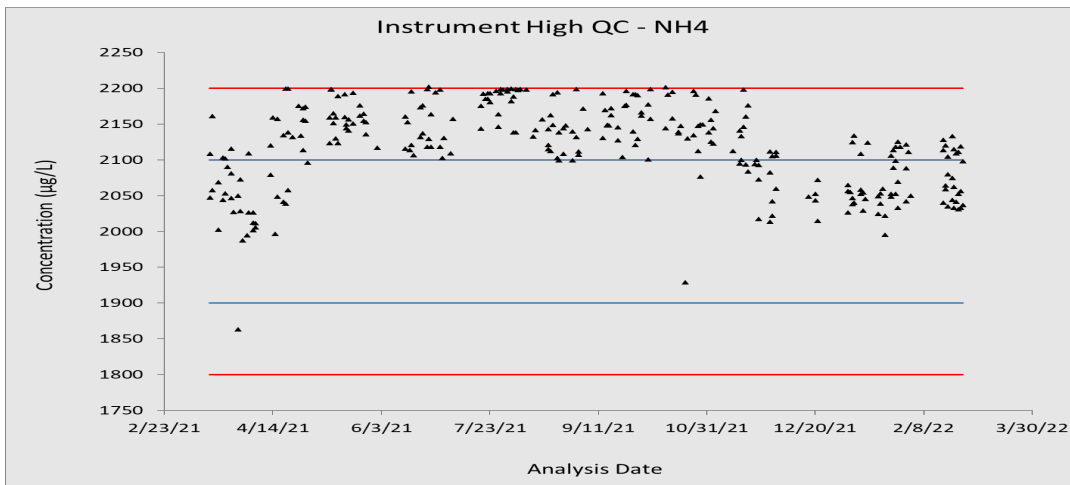
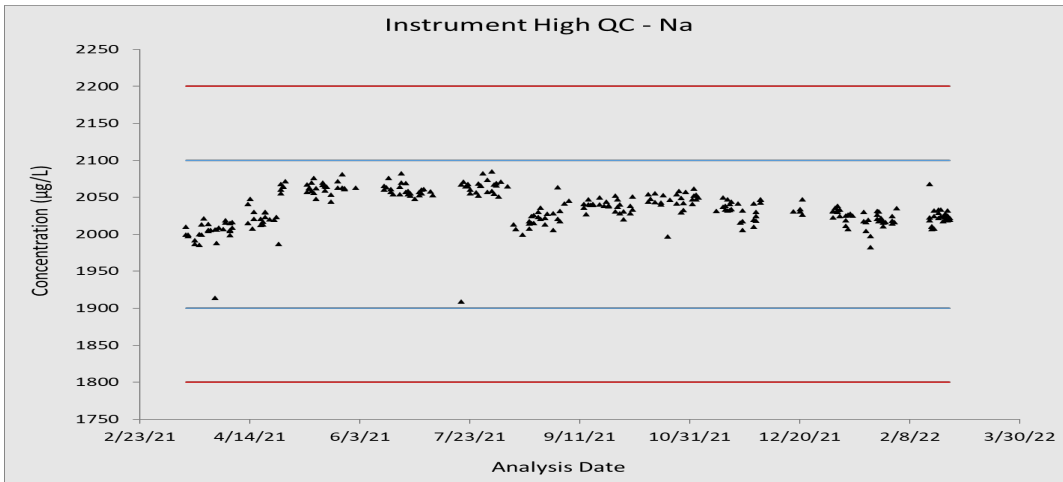


Figure 4.1-2: Control charts for cation CCV check standards at low, medium, medium-high, and high concentrations measured in units of $\mu\text{g/L}$ (see Table 4.1-4) for the analysis period 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2021). Red lines show upper and lower control 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.



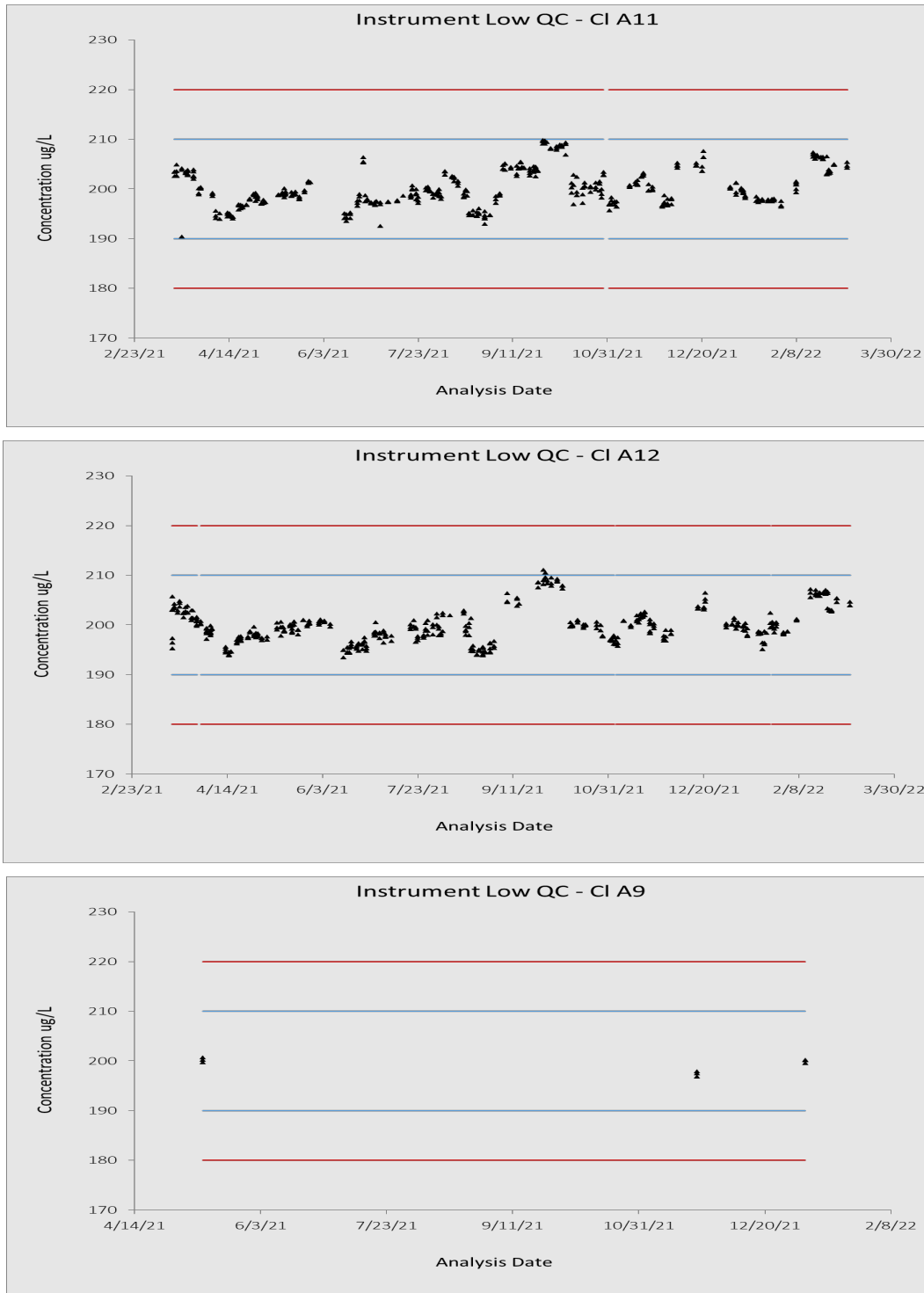


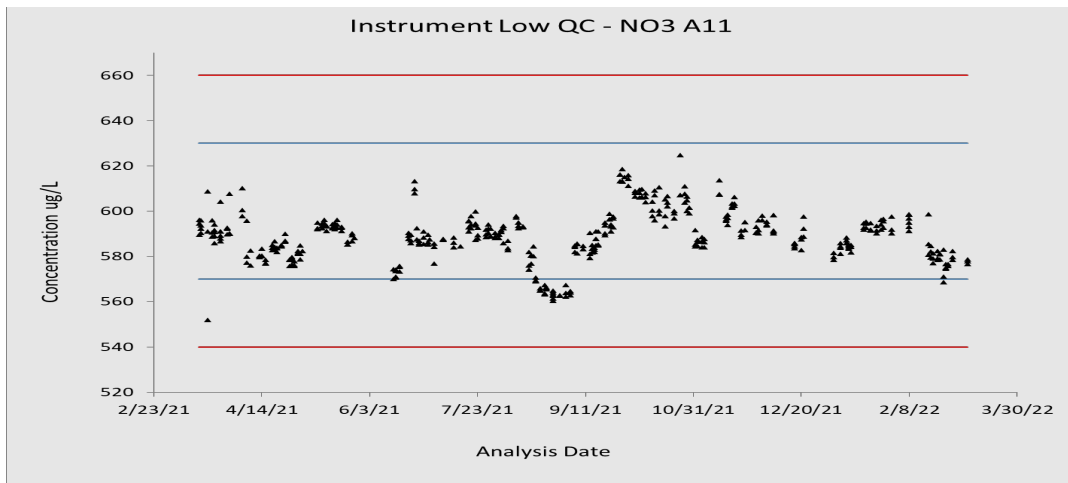
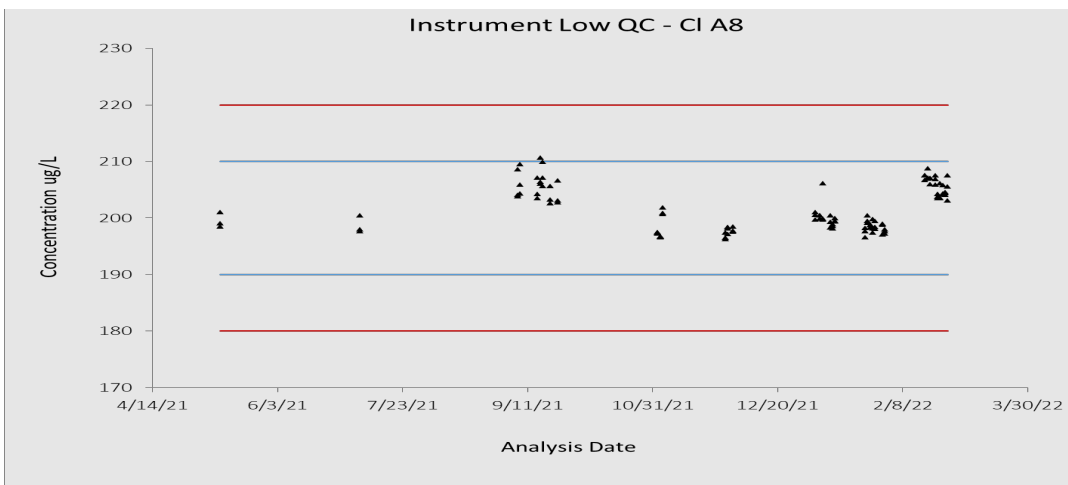
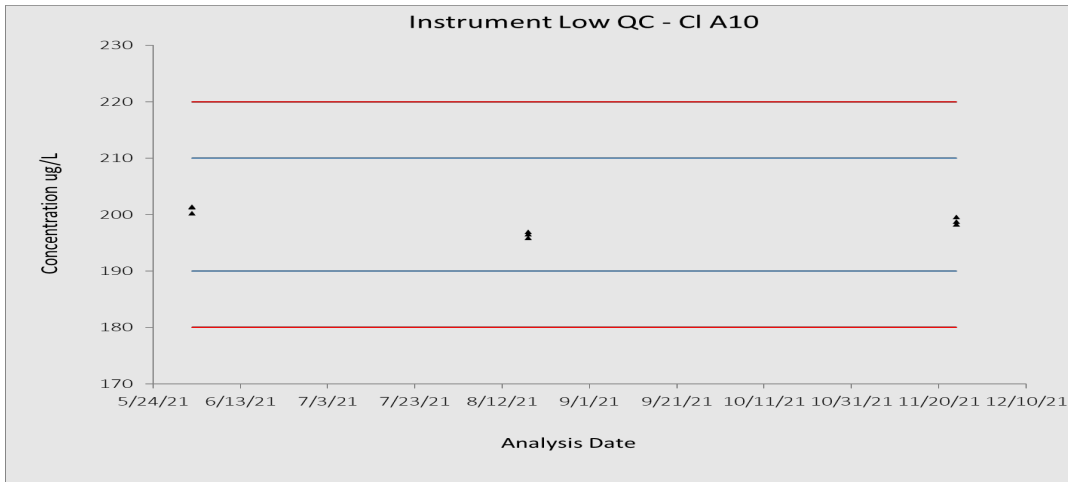


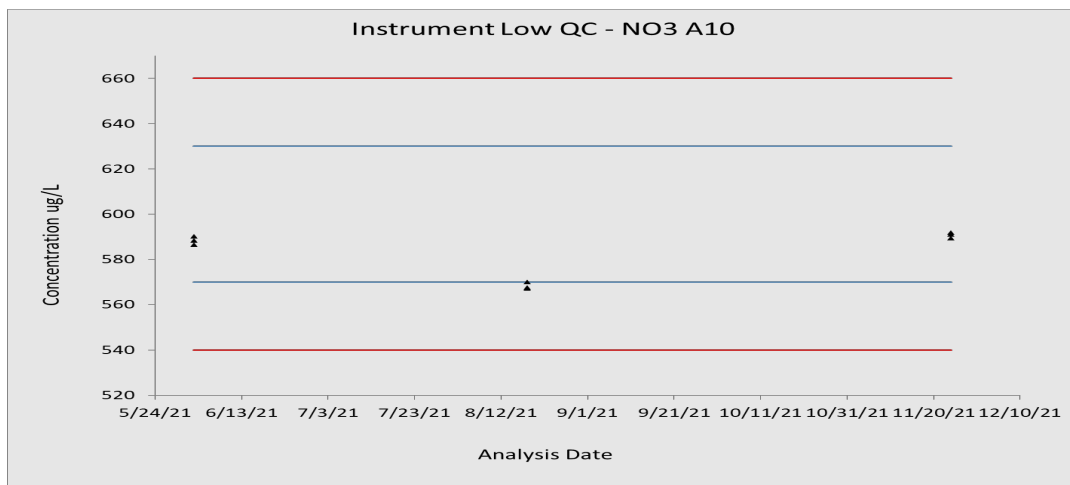
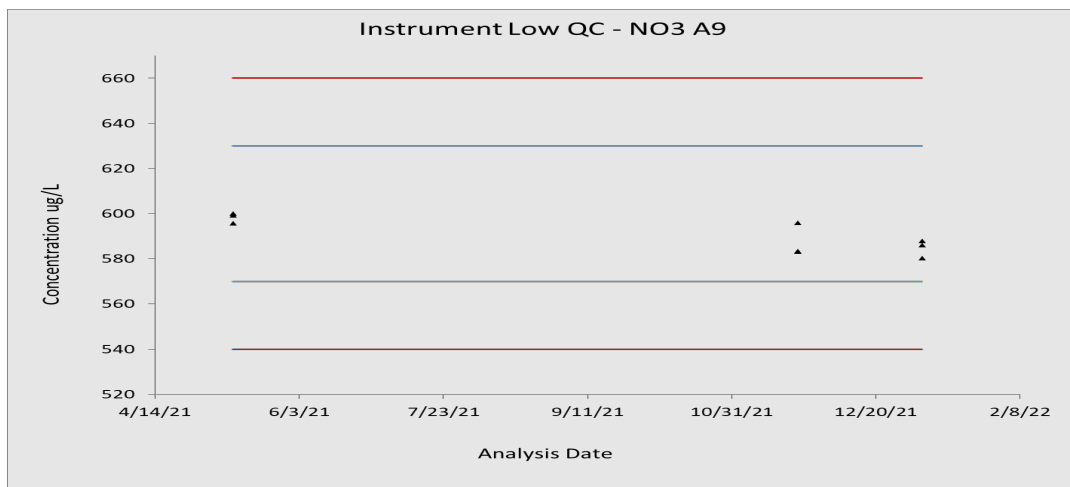
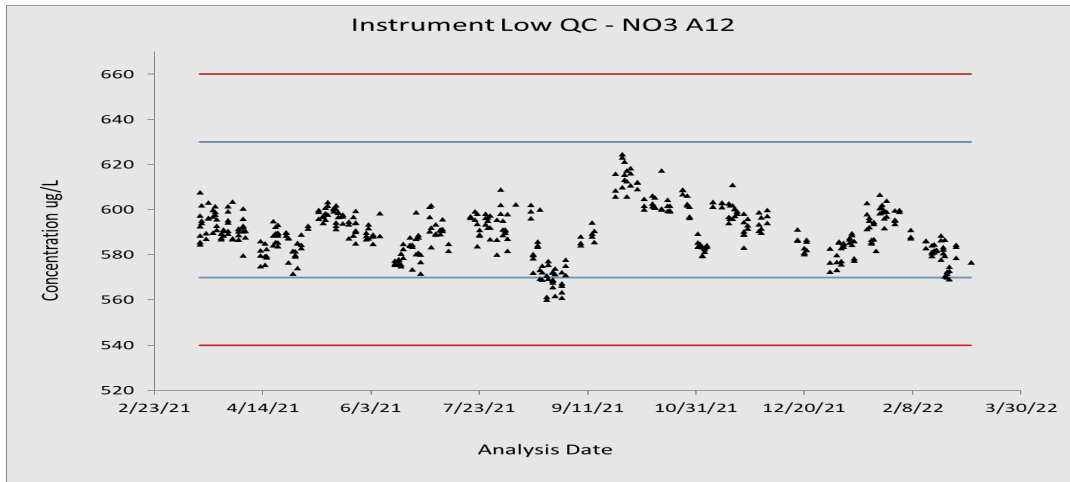


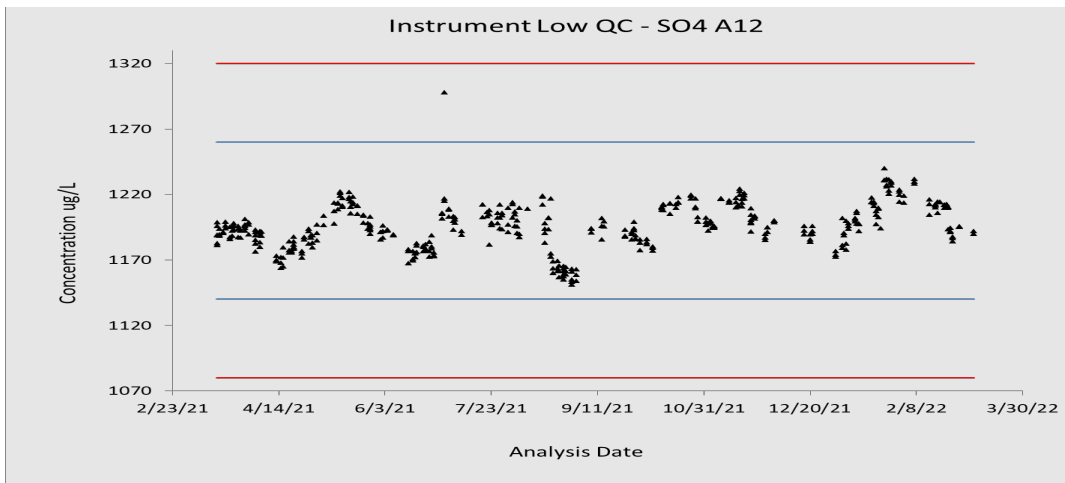
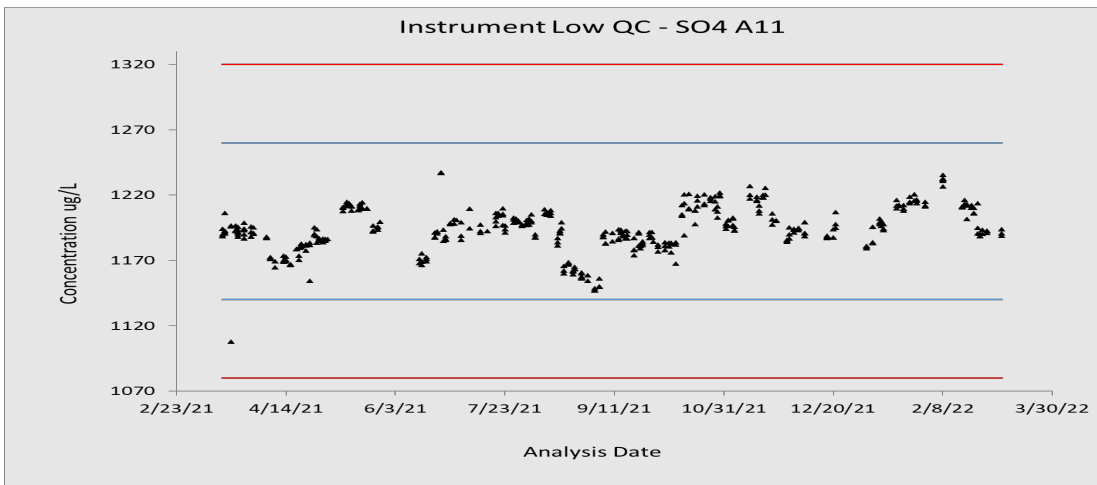
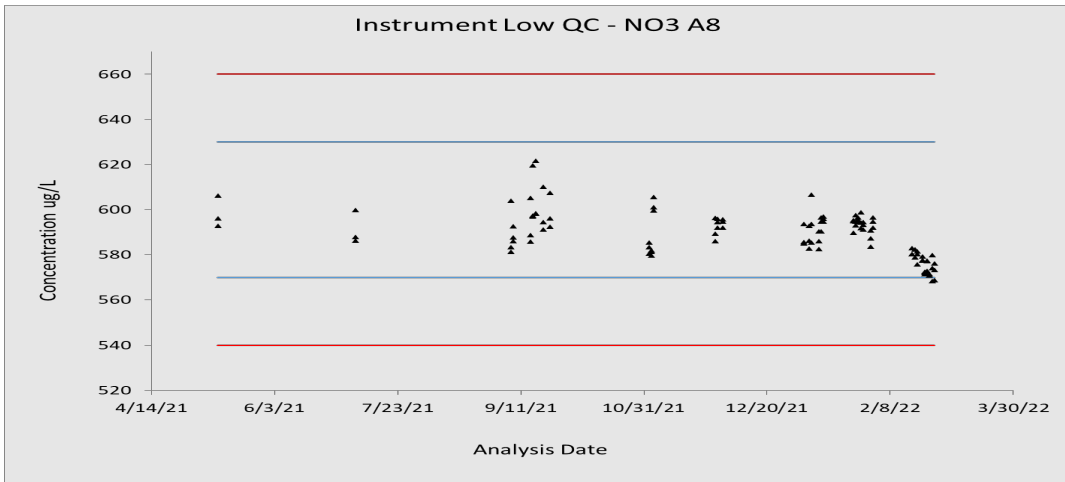
For the purpose of demonstrating instrument-to-instrument performance, control charts for the lowest CCV check standards were generated, where instruments A11, A12, A9, A10, and A8 are compared for anions (Figure 4.1-3) and instruments C9, C10, and C3 are compared for cations (Figure 4.1-4). The control 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 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2021). Red lines show upper and lower control limits set at $\pm 10\%$ of the nominal concentrations. Blue lines show upper and lower warning limits.









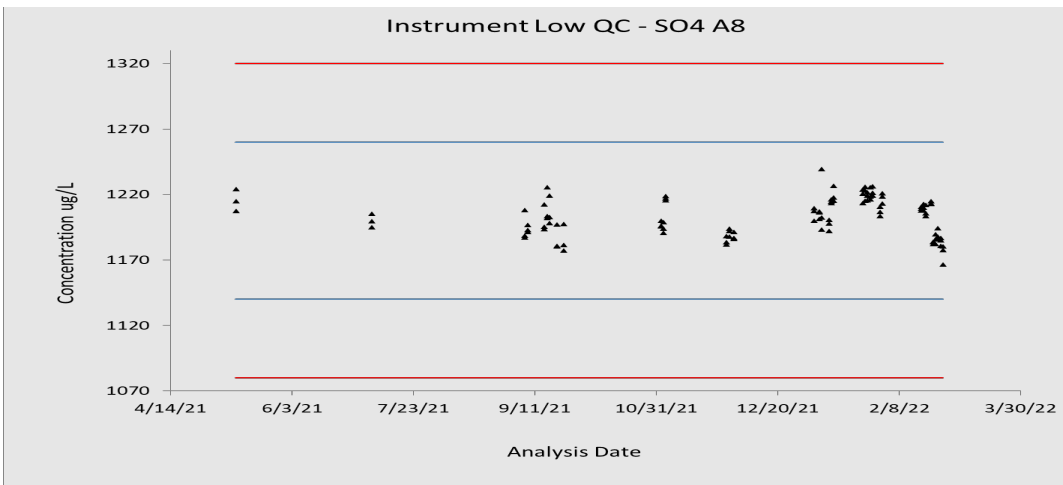
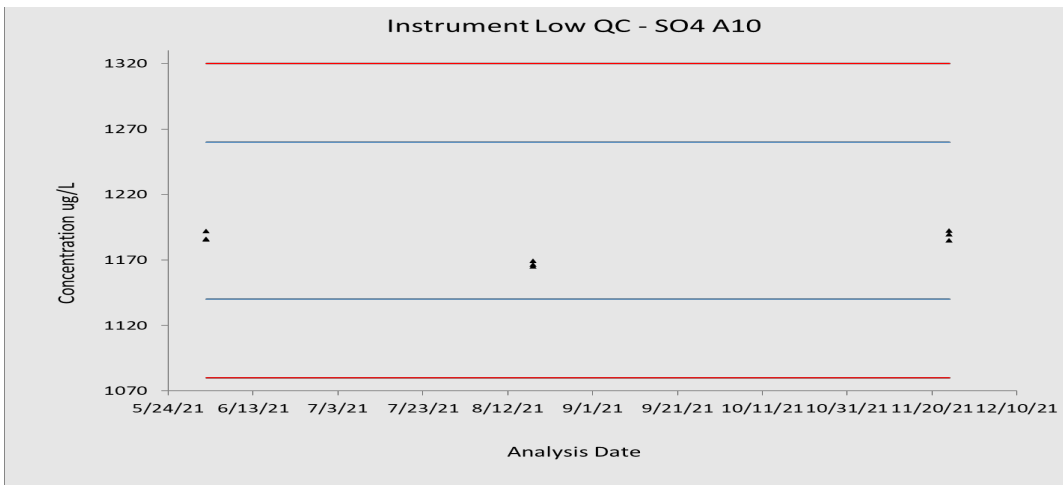
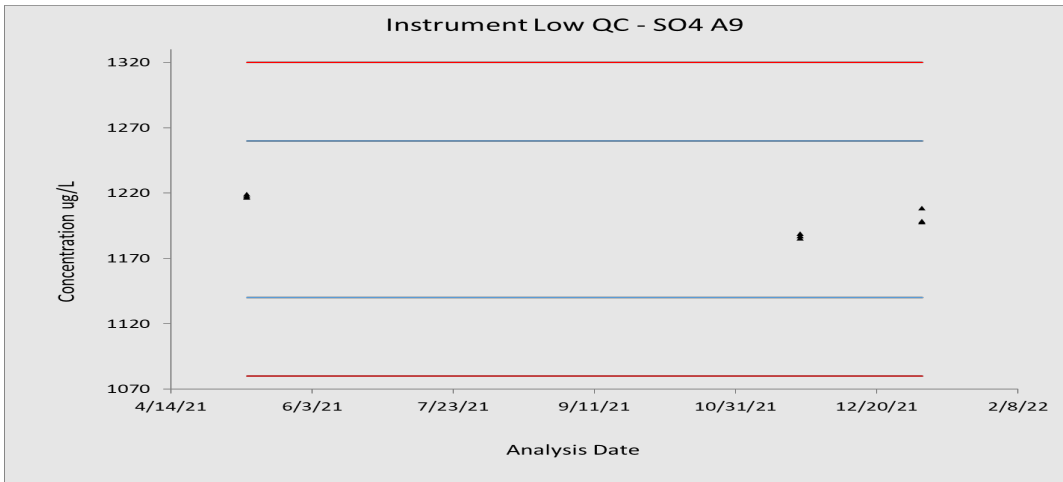
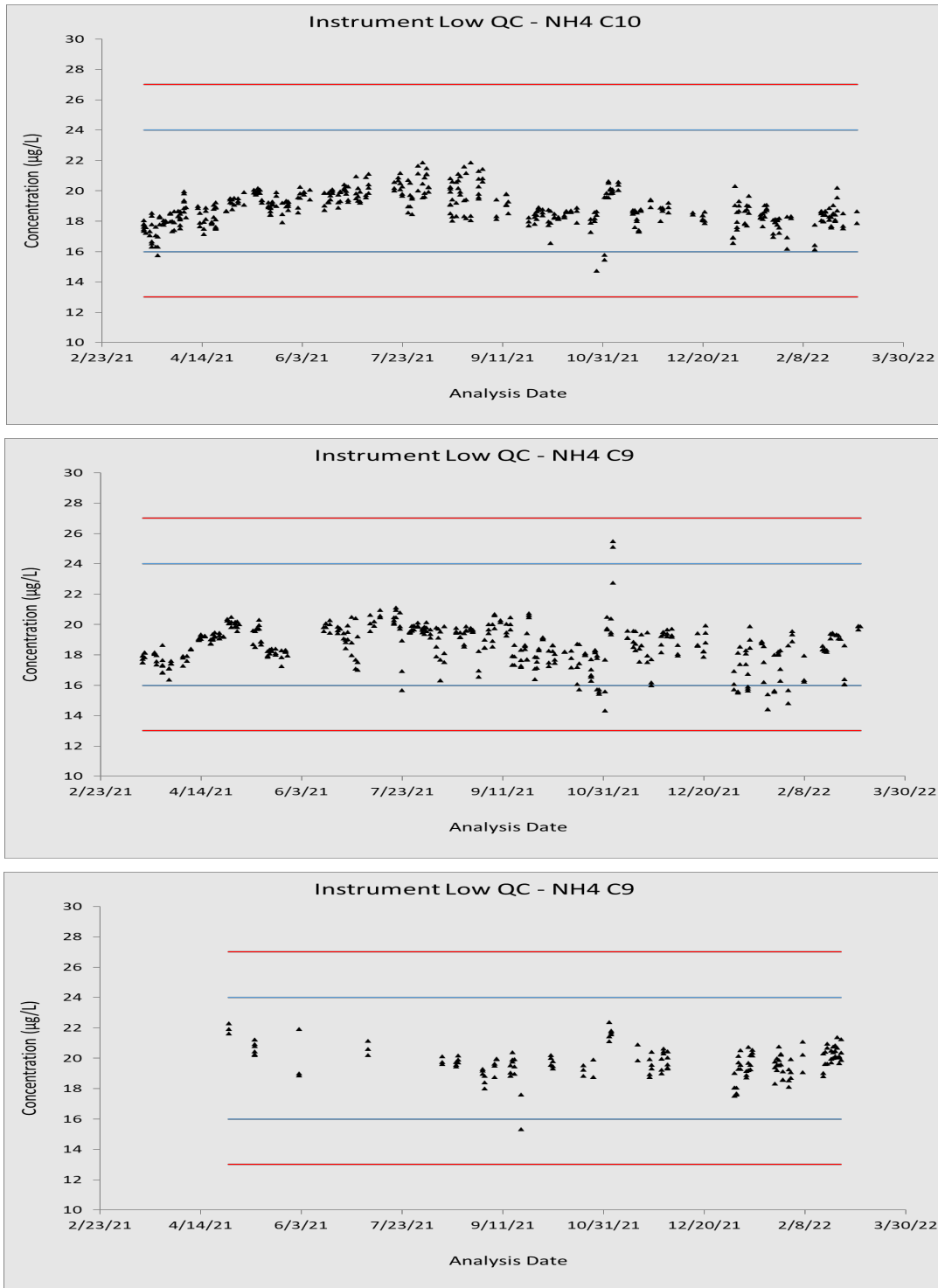
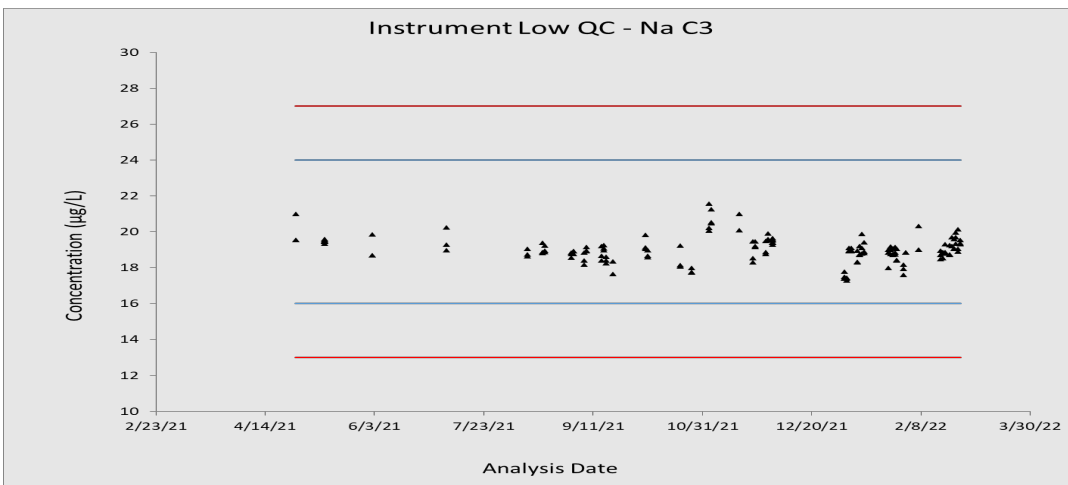
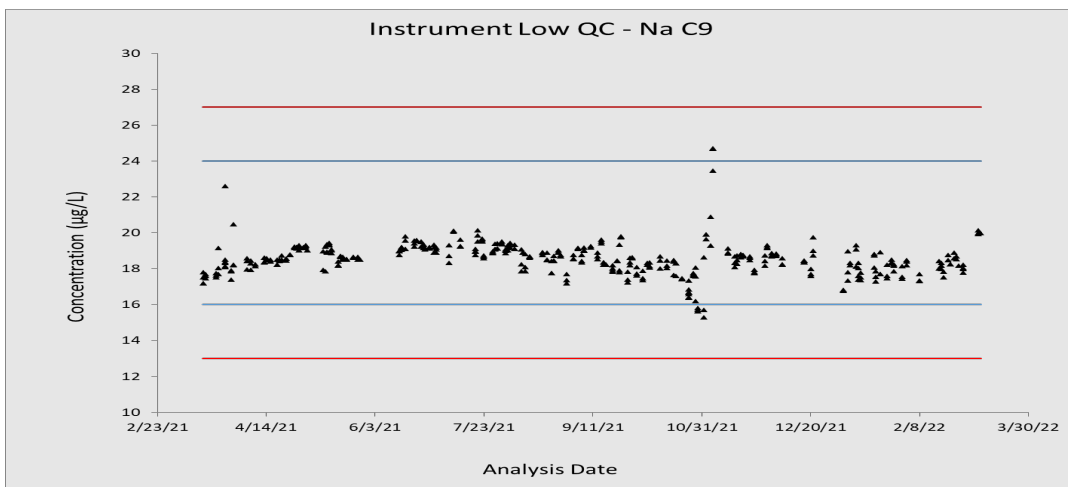
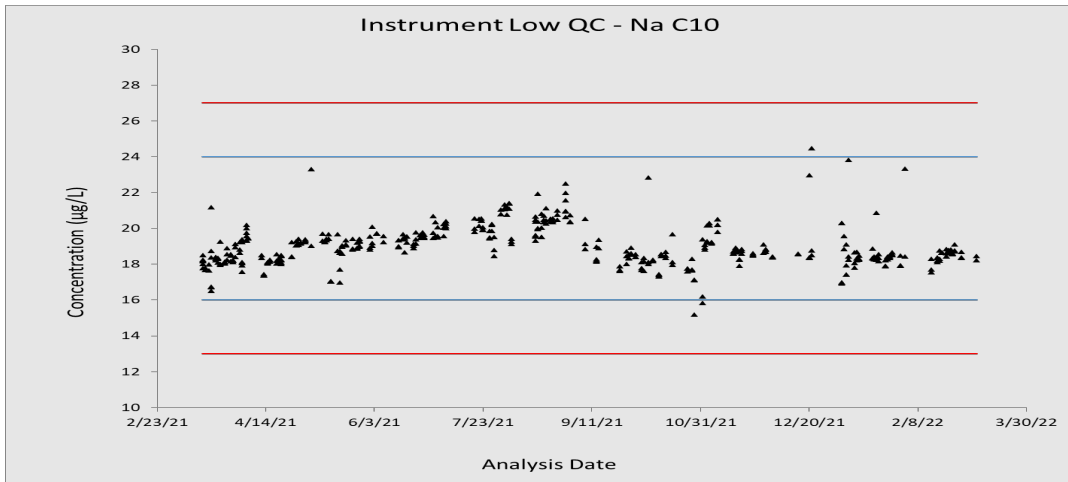
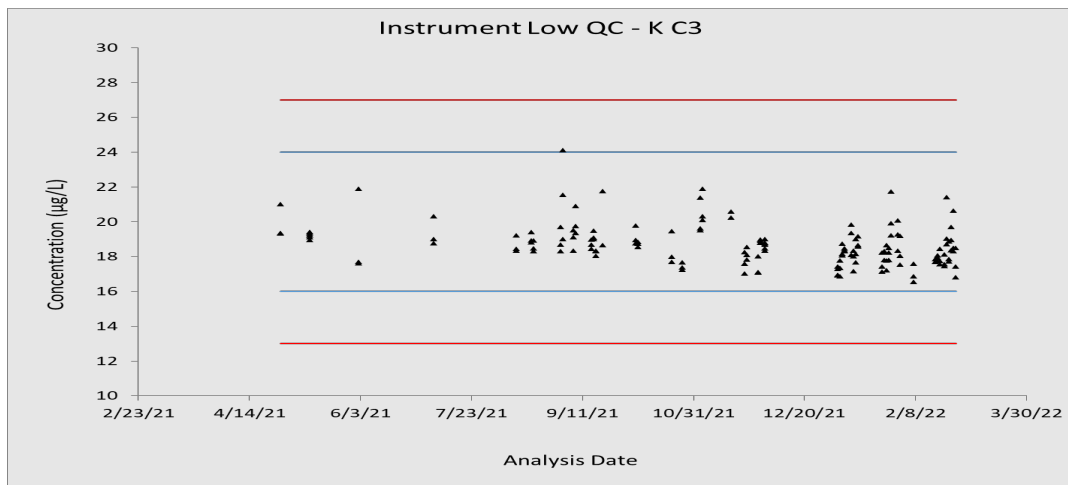
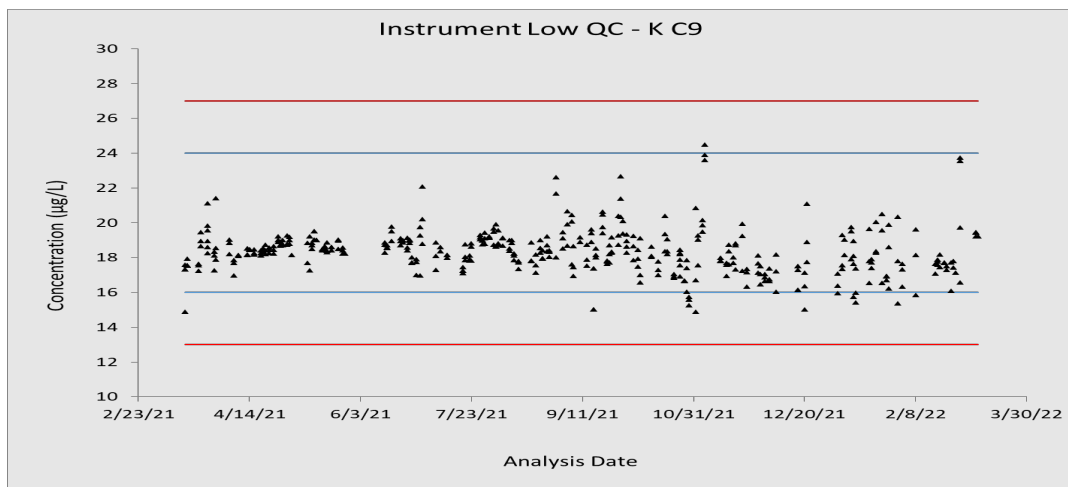
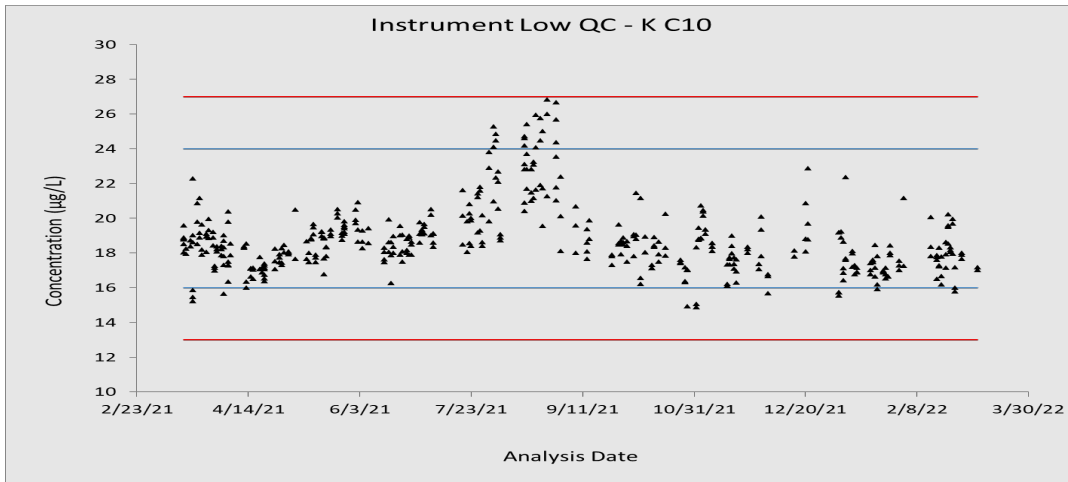


Figure 4.1-4: Control charts for cation CCV check standards showing comparability between instruments (C9 and C10, Thermo Dionex Aquion systems; C3 Thermo Dionex ICS-2000 systems) at low concentrations (see Table 4.1-4) for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2021). Red lines show upper and lower control limits set at $\pm 35\%$ of the nominal concentrations. Blue lines show upper and lower warning limits.





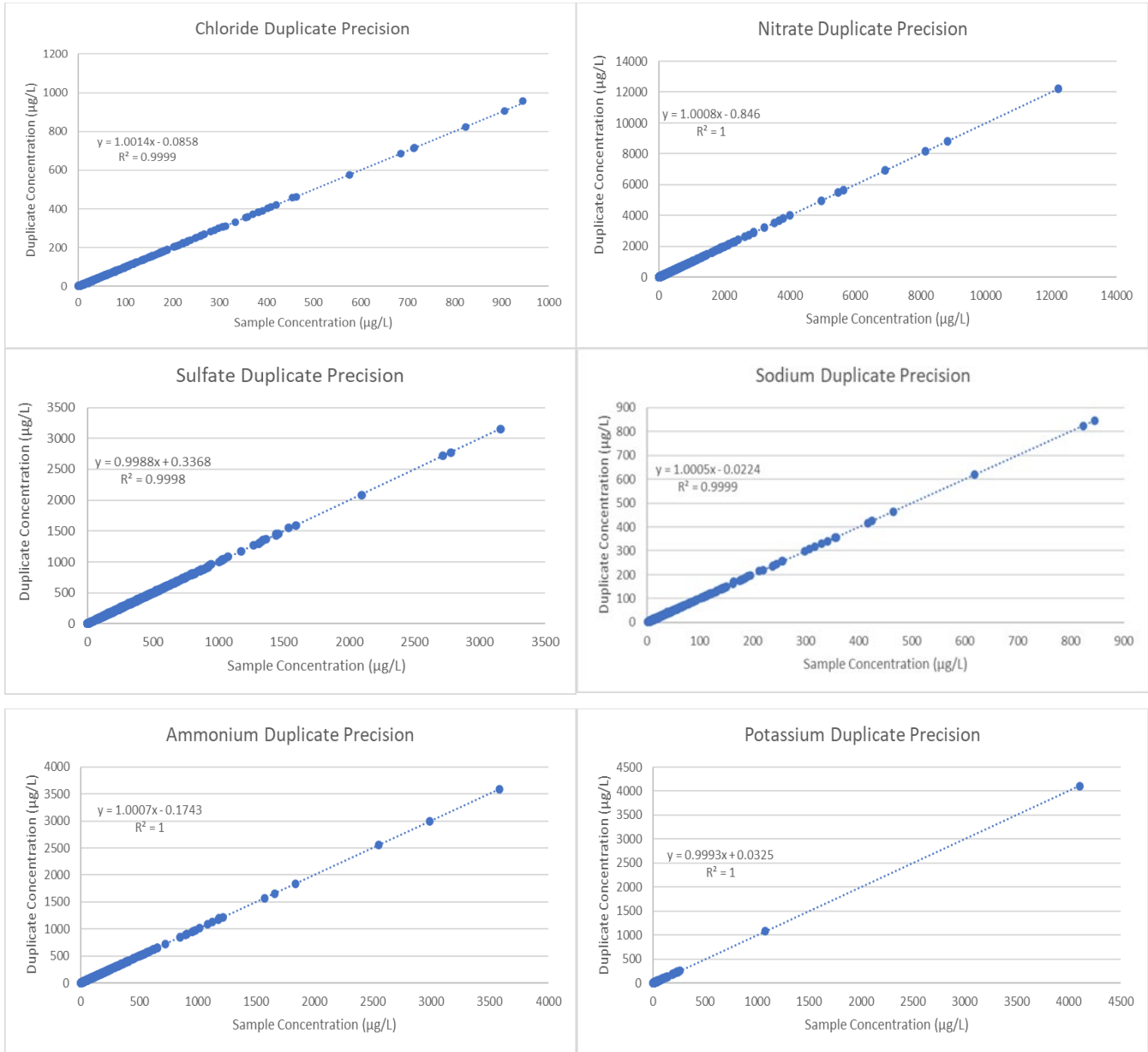


4.1.2.3 Duplicate Samples

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 2021 were analyzed (March 16, 2021 through March 7, 2022), there were a total of 886 duplicate samples analyzed for anions (Figure 4.1-5), there were no cases where the RPD did not meet the acceptance criteria. Additionally during this analysis period, there were a total of 883 duplicate samples analyzed for cations (Figure 4.1-5), with one case each where the RPD did not meet the acceptance criteria for potassium. In all cases when duplicate precision failed to meet the acceptance criteria, five samples were reanalyzed (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 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2022). Cases that did not meet the acceptance criteria, as described in Section 4.1.2.3, are included in these figures.

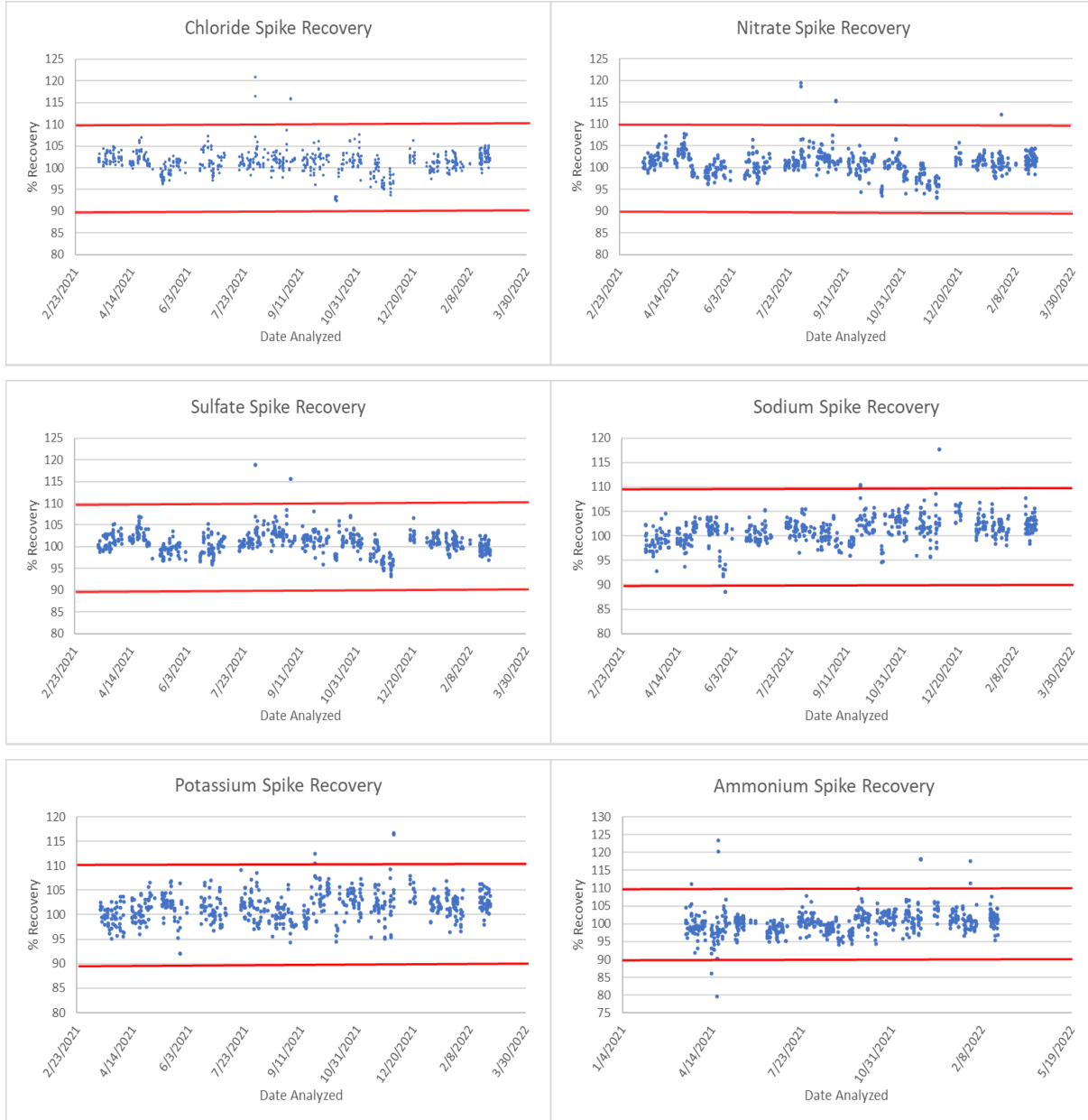


4.1.2.3 Spiked Sample Extracts

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 572 matrix spikes were analyzed for anions. There were nine cases where either chloride, nitrate, or sulfate failed spike recovery criteria (Figure 4.1-6); samples were reanalyzed for all cases. A total of 605 matrix spikes were analyzed for cations. There were fourteen cases where spiked samples failed to meet

recovery criteria of 90-100% for either sodium, ammonium, or potassium spiked samples (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 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2021). The red lines are drawn to indicate the acceptable recovery limits of 90% to 110%.



4.1.2.4 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 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2021). Black line indicates the analytical method detection limit.

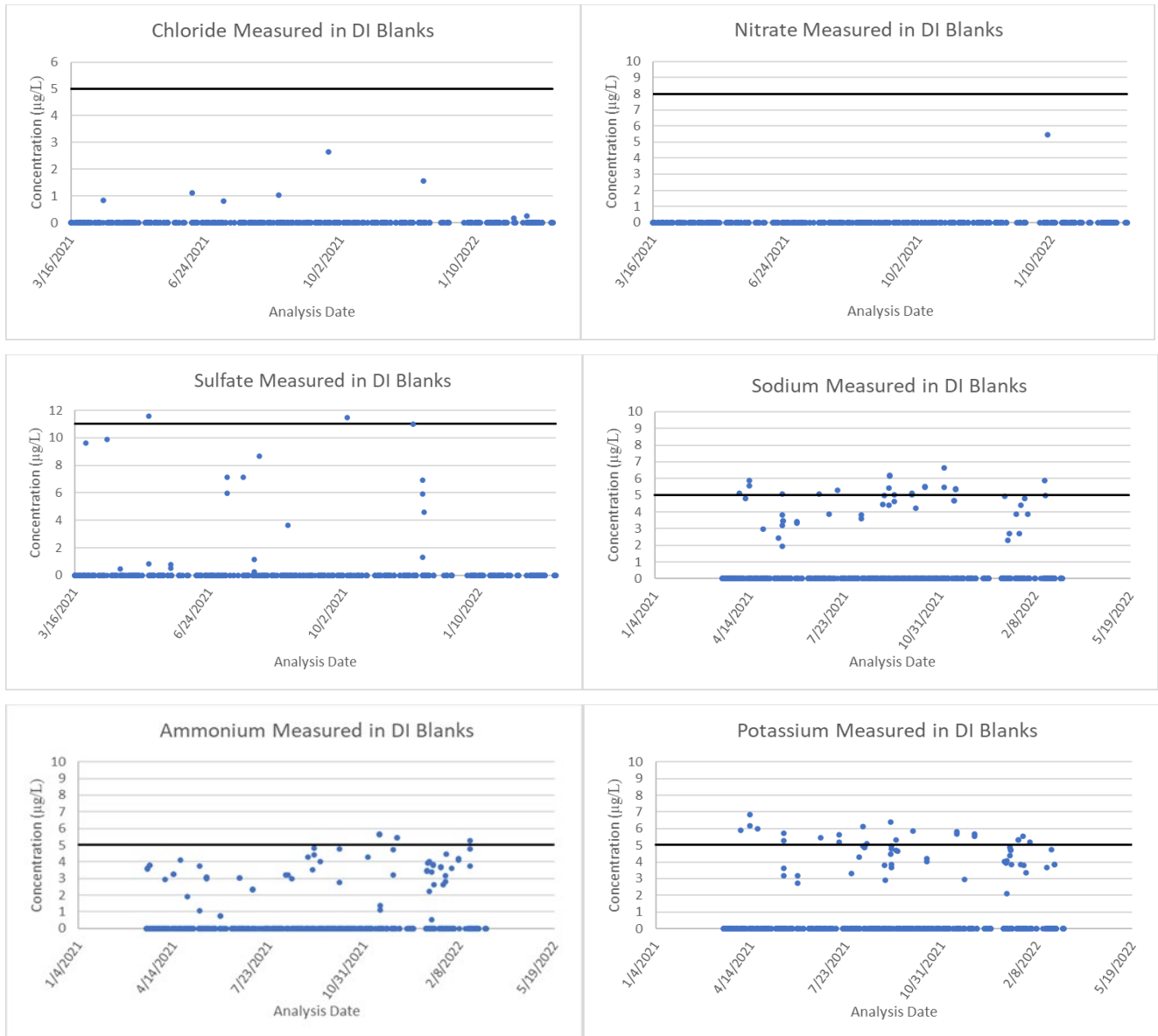
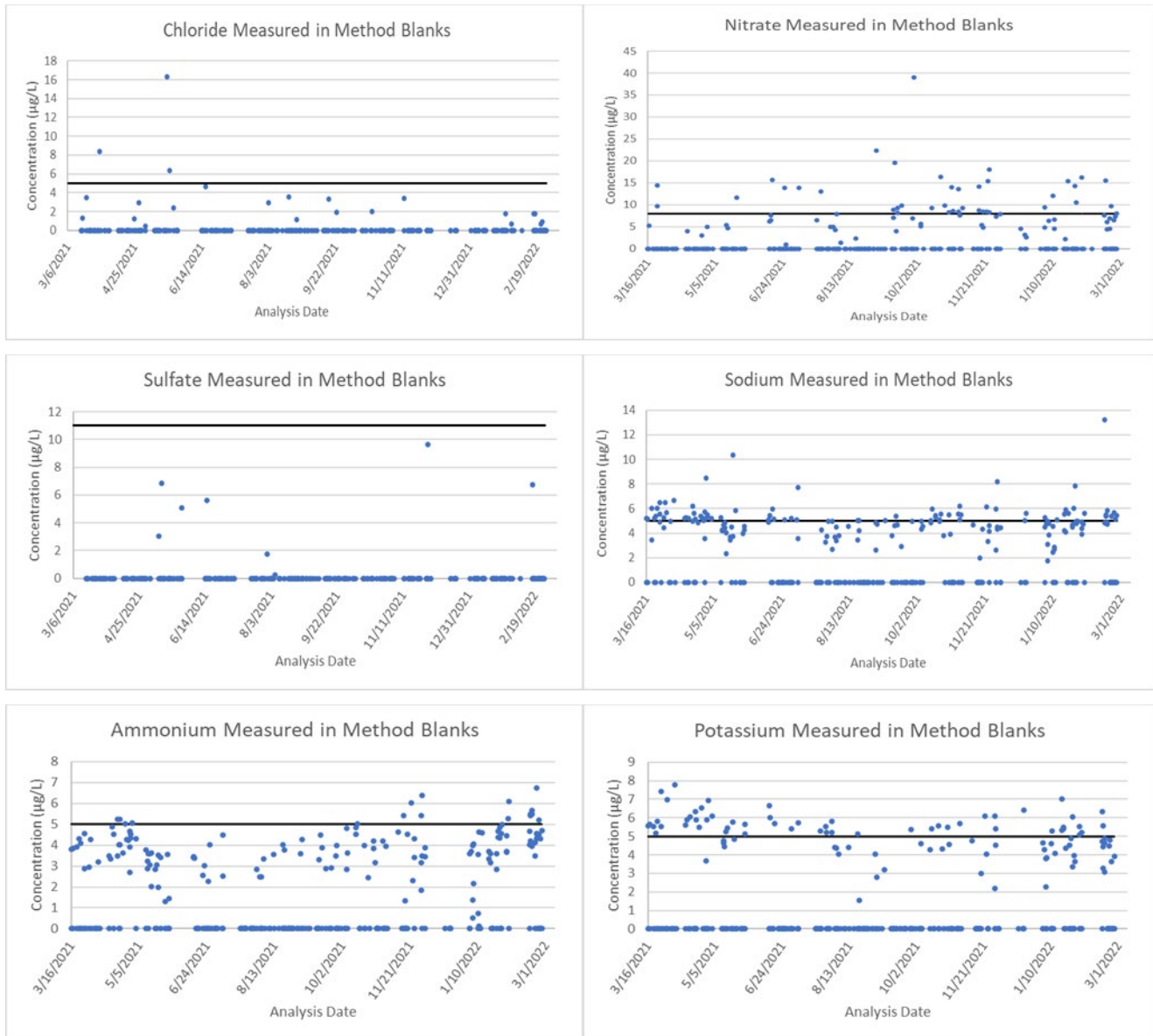


Figure 4.1-8: Concentrations of anions and cations in method blanks for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2021). Black line indicates the analytical method detection limit.



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.

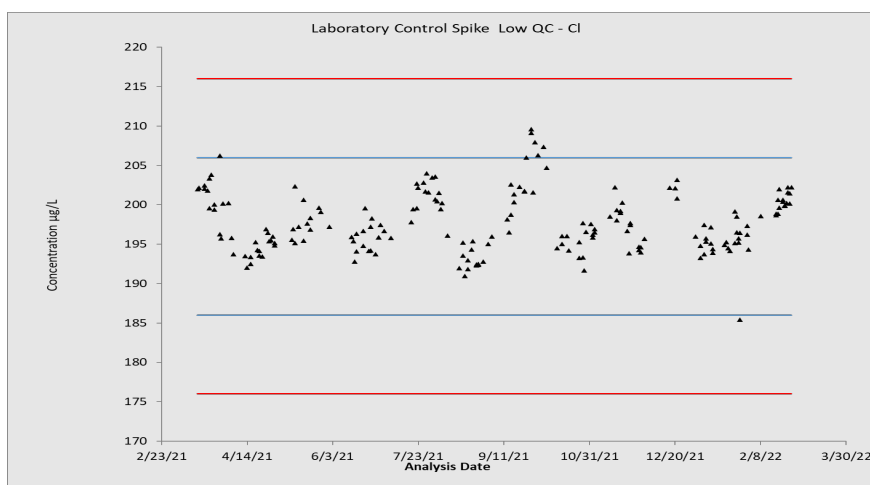
Table 4.1-5: Target concentrations for anion LCS for the analysis period 03/16/2021 through 03/7/2022 (samples collected 1/1/2021 through 12/31/2021).

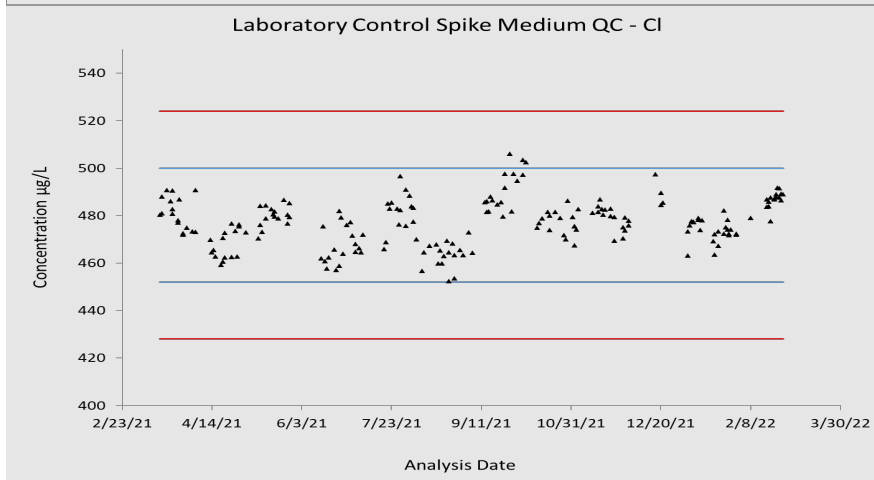
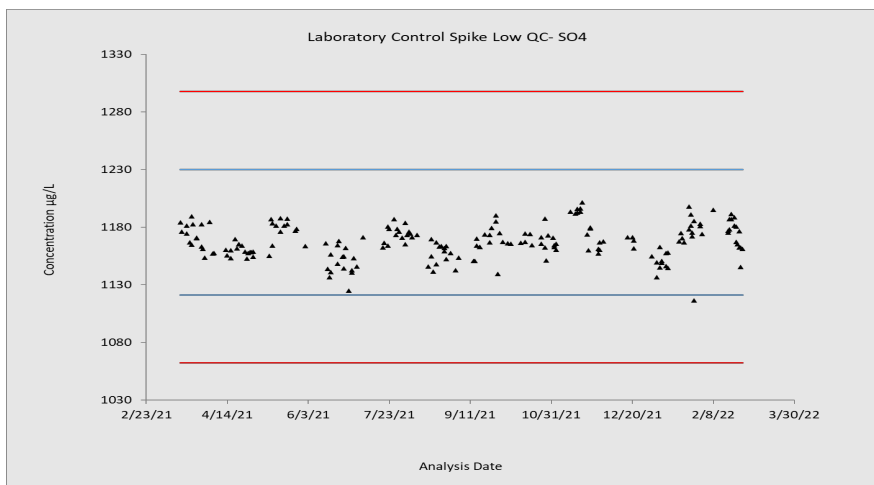
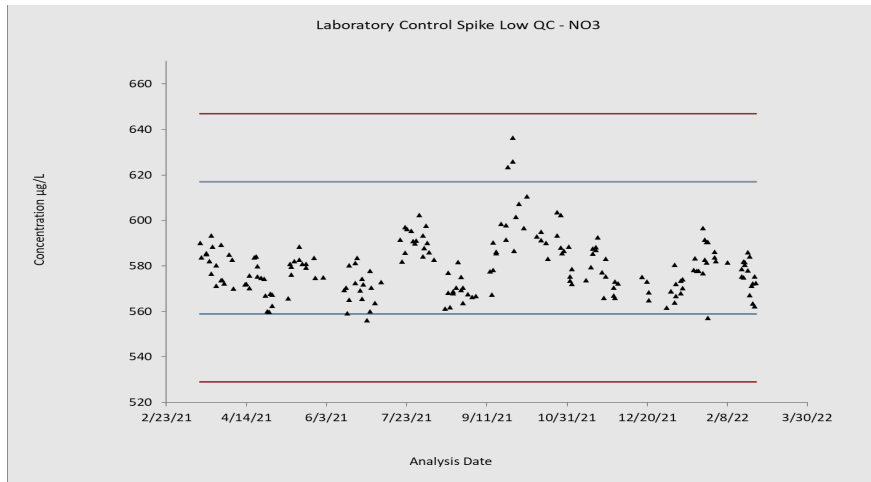
QC Sample	Cl ⁻ (ppb)	NO ₃ ⁻ (ppb)	SO ₄ ²⁻ (ppb)
LCS Low	196	588	1180
LCS Medium	476	1430	2860
LCS High	2000	6000	12000

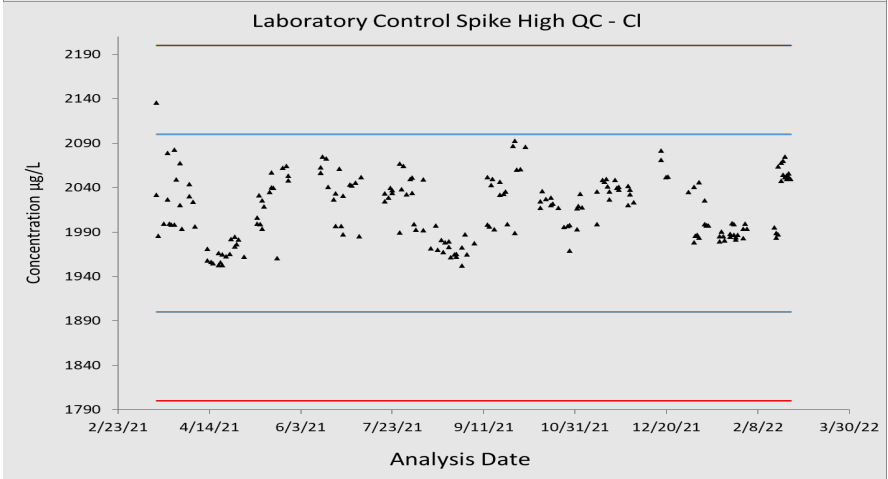
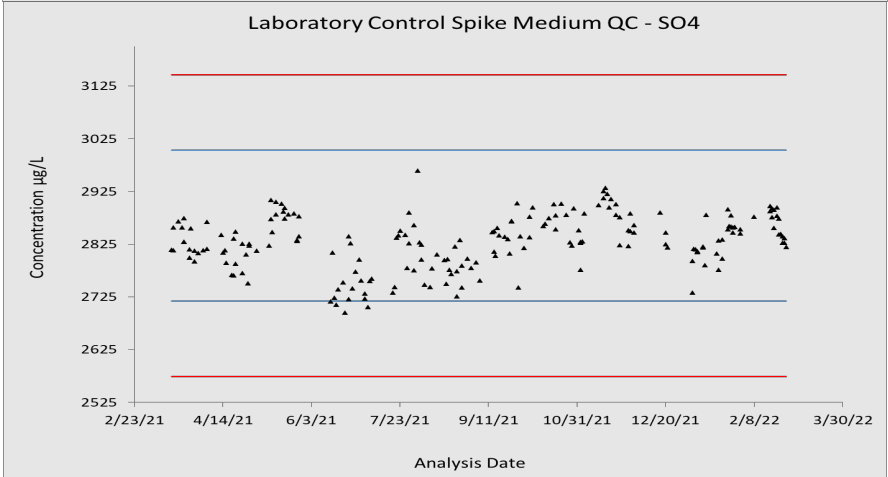
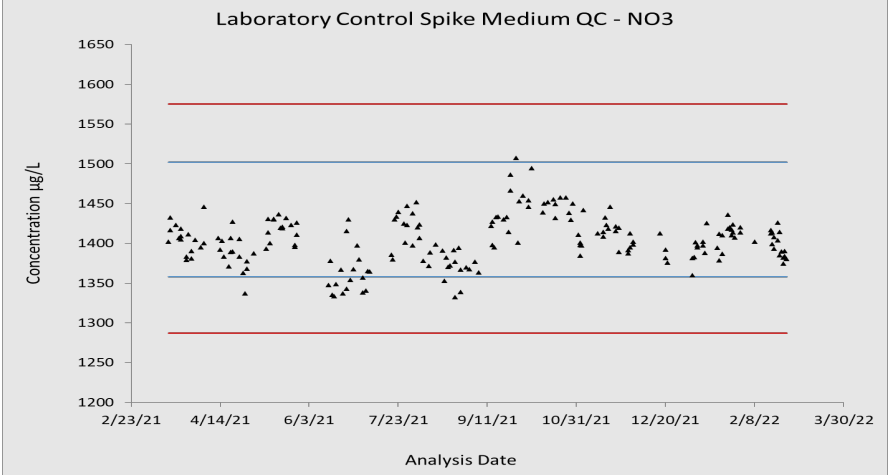
Table 4.1-6: Target concentrations for cation LCS for the analysis period 3/16/2021 through 03/7/2021 (samples collected 1/1/2021 through 12/31/2021).

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 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2022). Red lines show upper and lower control limits per the CCV check standard acceptance criteria. Blue lines show upper and lower warning limits.







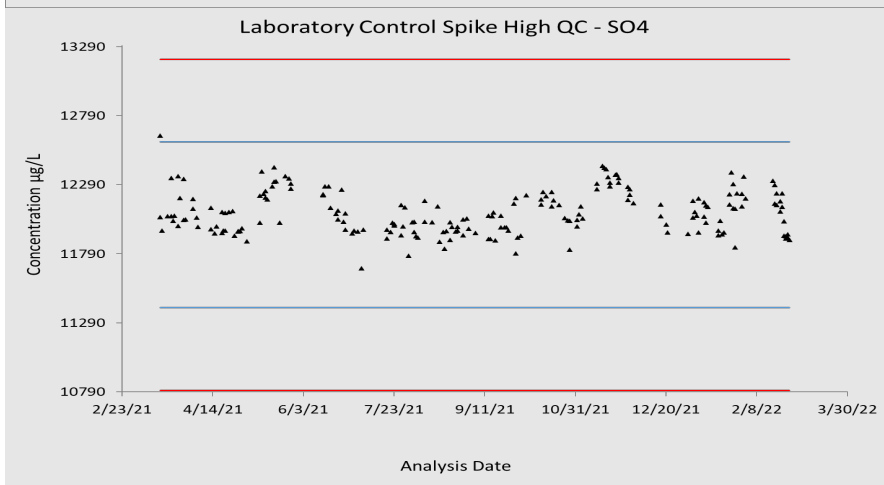
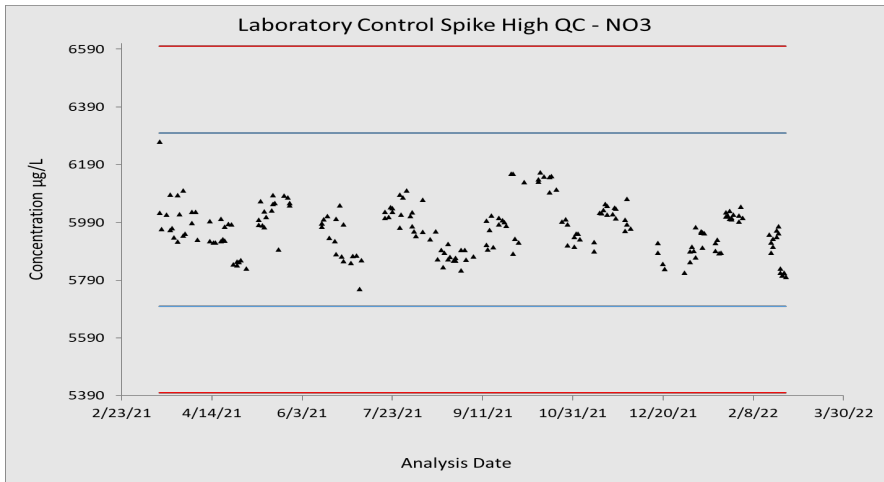
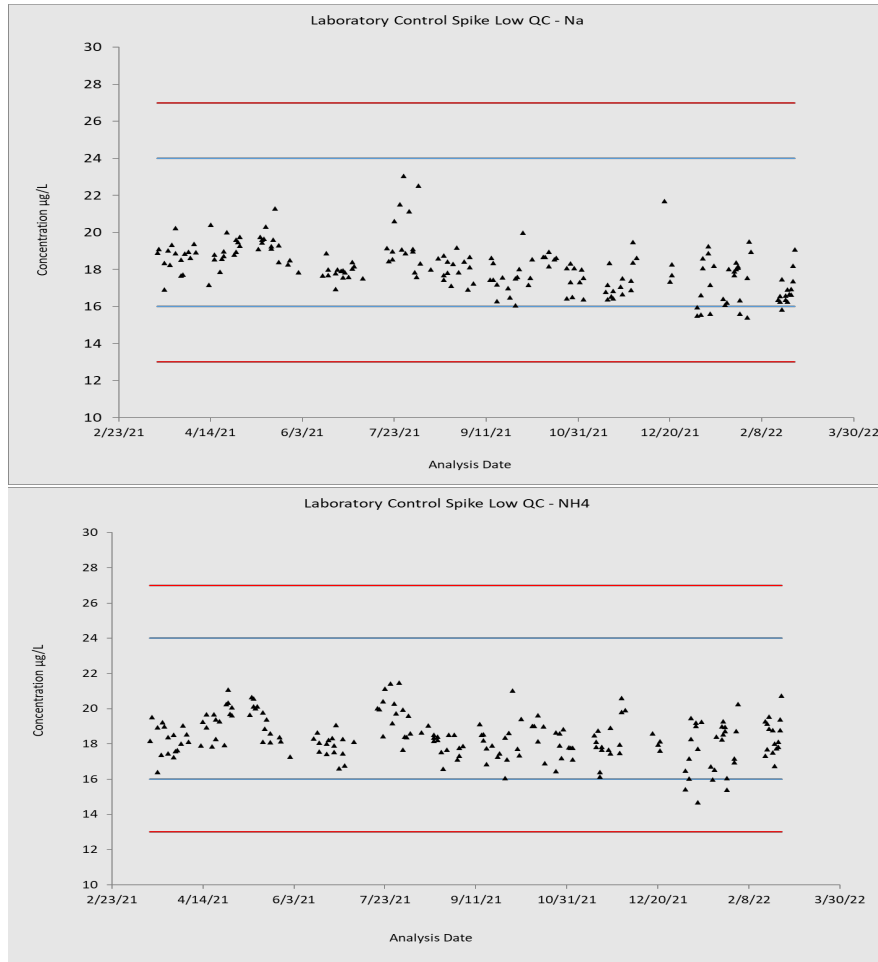
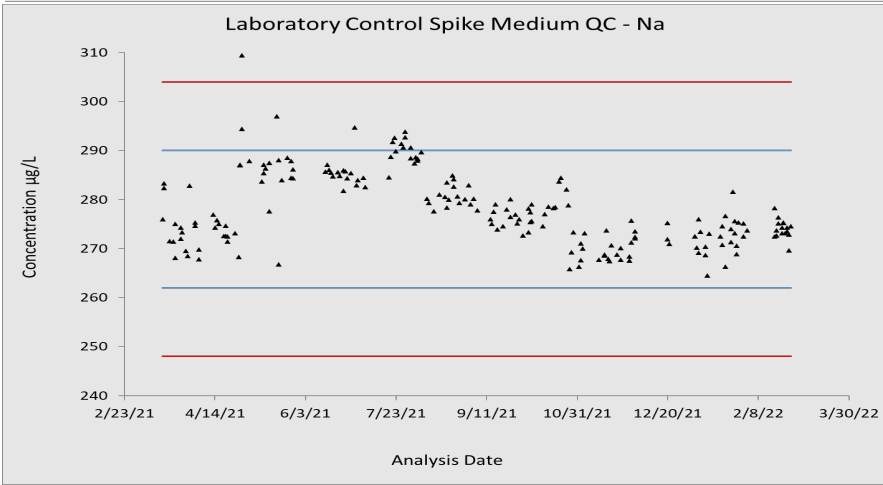
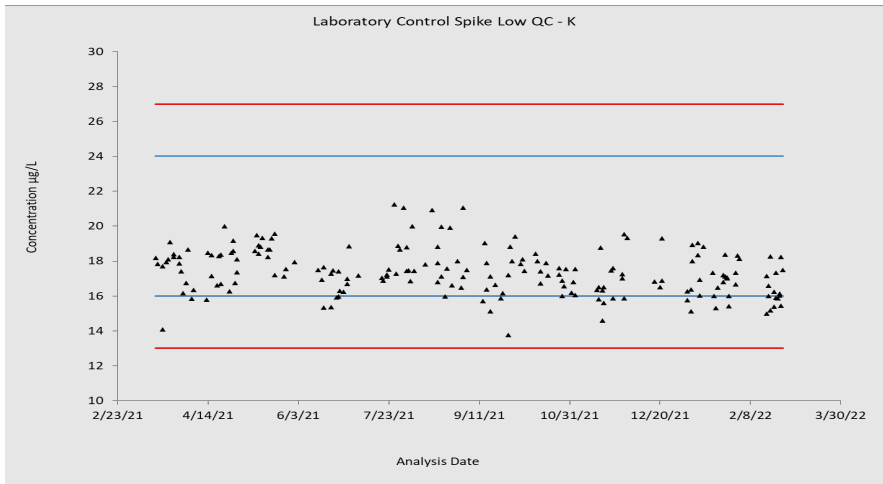
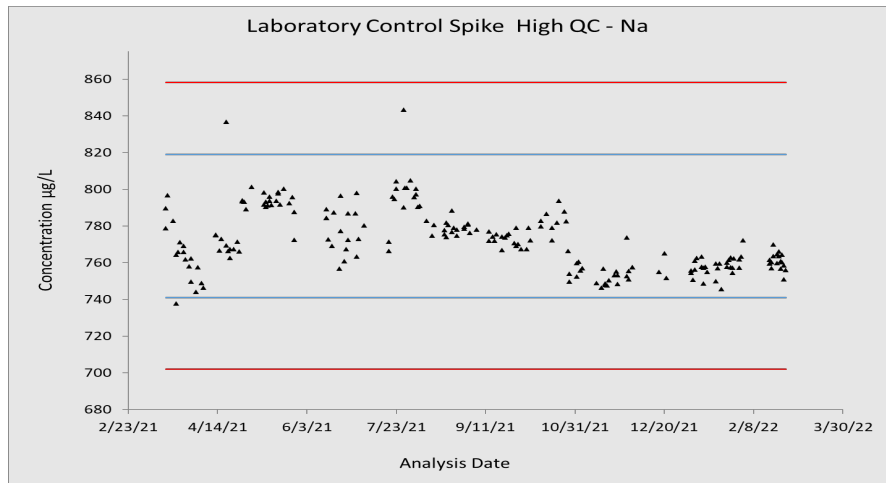
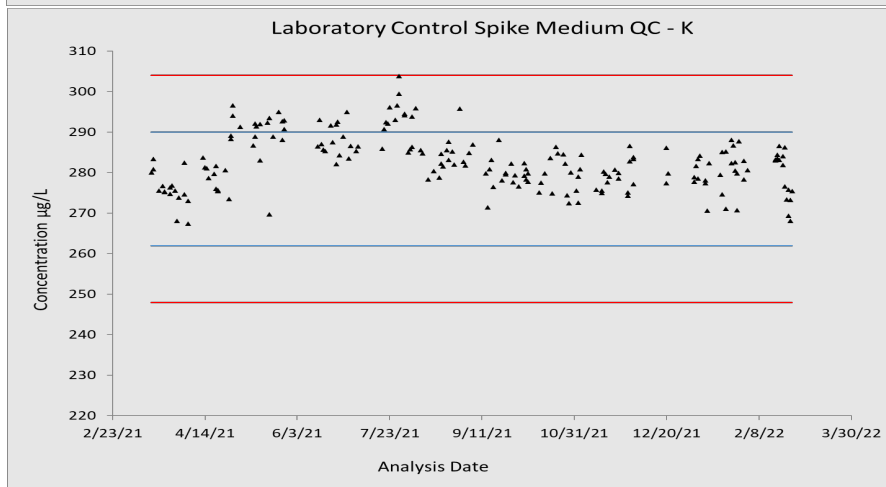
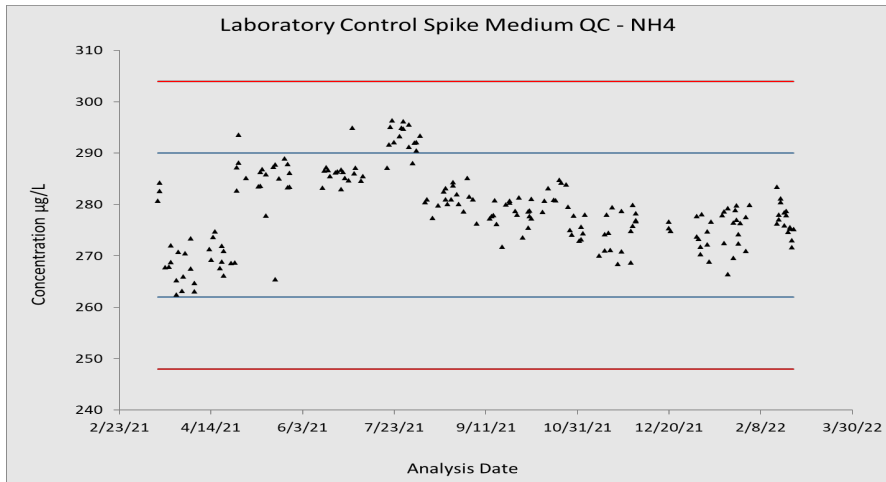
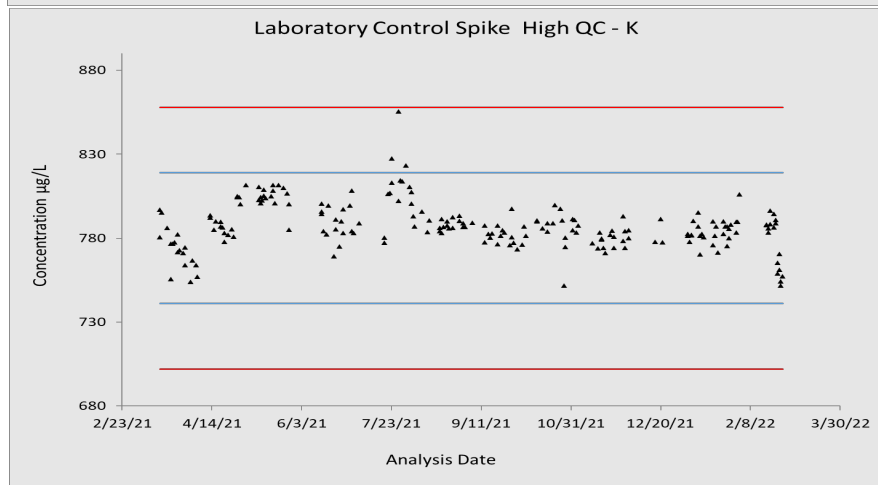
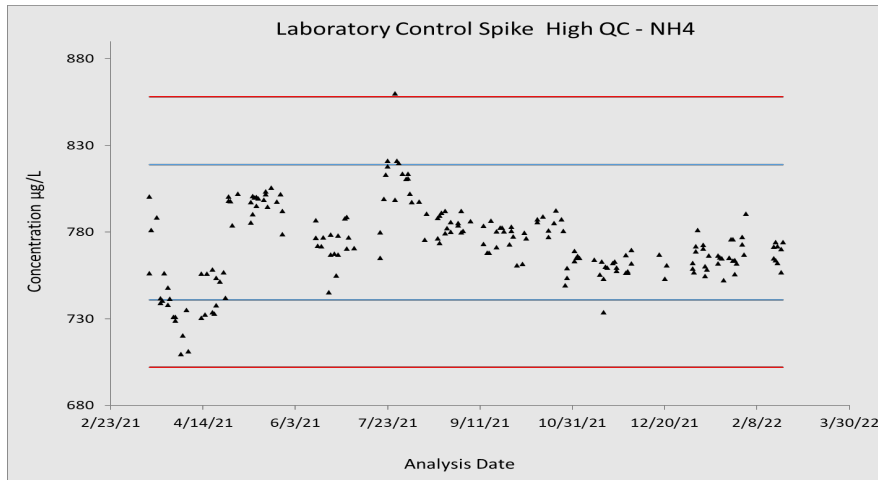


Figure 4.1-10: Control charts for cation LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2021). Red lines show upper and lower control limits per the CCV check standard acceptance criteria. Blue lines show upper and lower warning limits.









4.1.2.5 *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.

Results as well as previous years' data may be viewed using this URL:

https://bqs.usgs.gov/PCQA/Interlaboratory_Comparison/graphOutput.php?page=start.

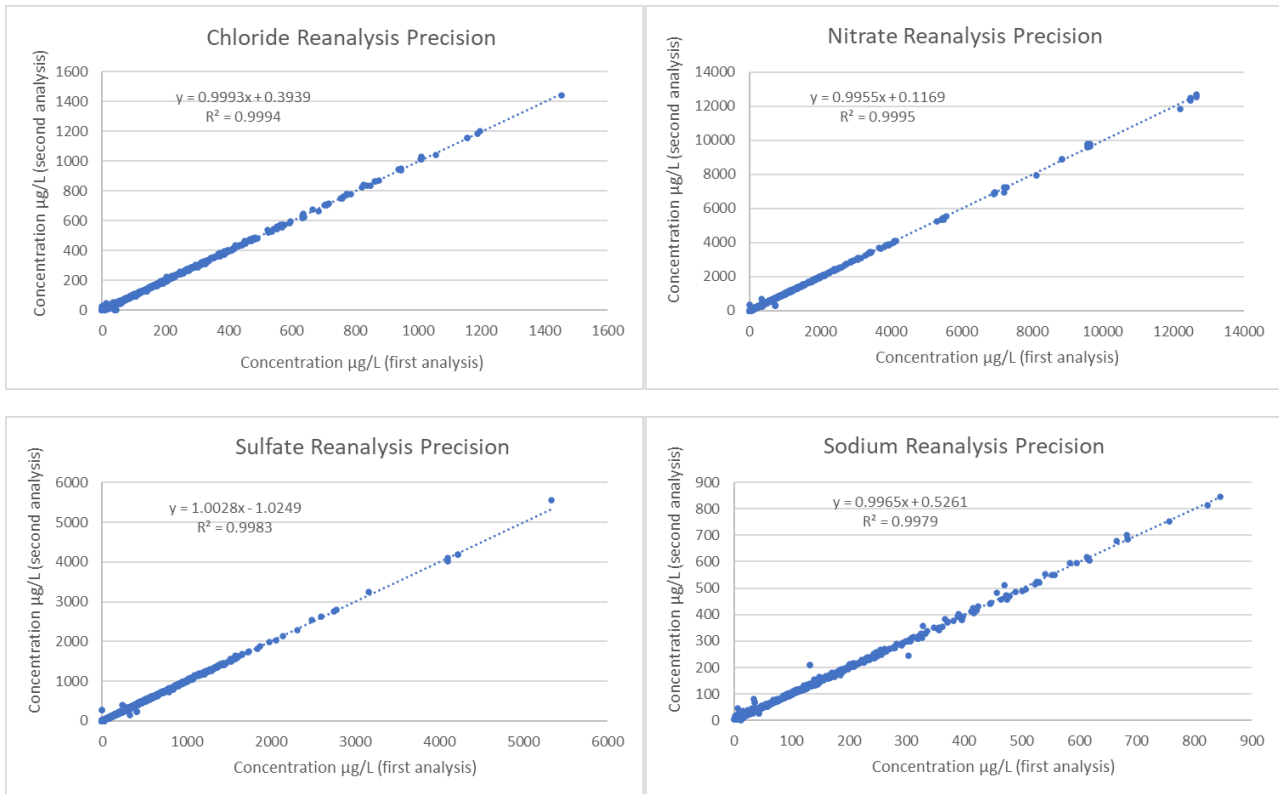
4.1.2.6 *Reanalysis*

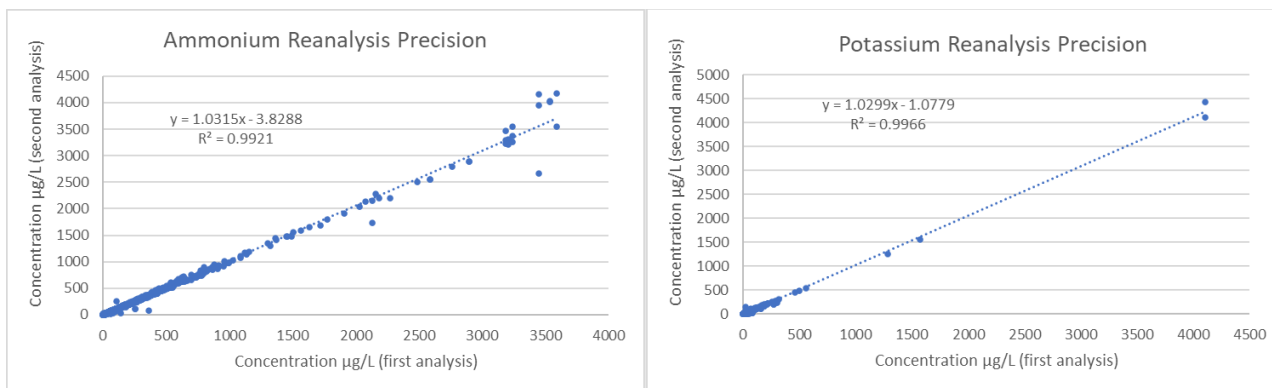
Replicate analyses are reanalyses where two analyses are performed on the same sample extract using different instruments. Five percent of all samples are randomly selected for reanalysis and are reanalyzed using different instruments and different calibration curves (these reanalyses are specific to 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). Sample will also be reanalyzed that are flagged 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. Most reviewed-flagged 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 2,168 samples reanalyzed for anions and 2,150 samples reanalyzed for cations (Figure 4.1-11). Less than 0.6% and 1.6% 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 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 3/16/2021 through 3/7/2022 (samples collected 1/1/2021 through 12/31/2021).





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.

4.1.3 Audits, Performance Evaluations, Training, and Accreditations

4.1.3.1 System Audits

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

4.1.3.2 Performance Evaluations

No performance evaluations were conducted during this reporting period.

4.1.3.3 Training

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

4.1.3.4 Accreditations

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

4.1.4 Summary of Filter Blanks

4.1.4.1 Field Blanks

Over the sampling period (January 1, 2021 through December 31, 2021) there were 1,658 valid nylon filter field blanks. Table 4.1-7a and Table 4.1-7b summarize the field blank statistics.

Table 4.1-7: Nylon filter field blank statistics in $\mu\text{g/mL}$ for the analysis period 3/24/2021 through 2/25/2022 (samples collected 1/1/2021 through 12/31/2021).

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^-	1,658	0.003	0.005	0.000	0.159	0.009
NO_3^-	1,658	0.009	0.011	0.000	0.549	0.022
SO_4^{2-}	1,658	0.000	0.003	0.000	0.772	0.027
Na^+	1,658	0.005	0.006	0.000	0.097	0.004
NH_4^+	1,658	0.005	0.005	0.000	0.273	0.009
K^+	1,658	0.006	0.005	0.000	0.122	0.004

Table 4.1-8: Nylon filter field blank statistics in $\mu\text{g/filter}$ (extraction volume 25 mL) for the analysis period 3/24/2021 through 2/25/2022 (samples collected 1/1/2021 through 12/31/2021).

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^-	1,658	0.082	0.121	0.000	3.974	0.216
NO_3^-	1,658	0.222	0.280	0.000	13.714	0.555
SO_4^{2-}	1,658	0.000	0.071	0.000	19.294	0.669
Na^+	1,658	0.134	0.140	0.000	2.416	0.106
NH_4^+	1,658	0.123	0.135	0.000	6.828	0.231
K^+	1,658	0.141	0.136	0.000	3.047	0.091

4.1.4.2 Laboratory Blanks

As described in Section 3.1.3, beginning with filters from the sampling period July 1, 2020, five nylon laboratory blanks are shipped with each batch of routine filters to the analysis laboratory and analyzed. A total of 60 nylon laboratory blanks were analyzed during the current reporting period, where each set of laboratory blanks were analyzed either before or straight after the routine analysis of the associated batch. Table 4.1-8a and Table 4.1-8b summarize the laboratory blank statistics.

Table 4.1-9: Nylon filter laboratory blank statistics in µg/mL for the analysis period 4/7/2021 through 2/27/2022 (samples collected 1/1/2021 through 12/31/2021).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl ⁻	60	0.001	0.002	0.000	0.014	0.003
NO ₃ ⁻	60	0.011	0.014	0.000	0.049	0.011
SO ₄ ²⁻	60	0.000	0.000	0.000	0.005	0.001
Na ⁺	60	0.005	0.005	0.000	0.011	0.002
NH ₄ ⁺	60	0.006	0.006	0.000	0.016	0.003
K ⁺	60	0.006	0.006	0.000	0.016	0.003

Table 4.1-10: Nylon filter laboratory blank statistics in µg/filter (extraction volume 25 mL) for the analysis period 4/7/2021 through 2/27/2021 (samples collected 1/1/2021 through 12/31/2021).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl ⁻	60	0.032	0.060	0.000	0.356	0.083
NO ₃ ⁻	60	0.266	0.343	0.000	1.217	0.283
SO ₄ ²⁻	60	0.000	0.007	0.000	0.136	0.025
Na ⁺	60	0.131	0.128	0.000	0.265	0.041
NH ₄ ⁺	60	0.113	0.114	0.000	0.179	0.046
K ⁺	60	0.148	0.149	0.000	0.410	0.065

4.2 UC Davis X-ray Fluorescence Laboratory

The UC Davis X-ray Fluorescence Laboratory received and analyzed PTFE filters from samples collected January 1, 2021 through December 31, 2021. UC Davis performed analysis for 33 elements using energy dispersive X-ray fluorescence (EDXRF) instruments. These analyses were performed during an analysis period from February 19, 2021 through April, 22, 2022, including both routine analysis and reanalysis. 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 2021 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	75	2021-02-19 - 2021-05-19	2021-03-23 - 2021-04-12	2021-03-19 - 2021-03-31	2021-03-20 - 2021-04-12	NA
February	76	2021-04-21 - 2021-05-27	2021-04-21 - 2021-05-14	2021-04-23 - 2021-05-08	2021-04-21 - 2021-05-07	NA
March	77	2021-05-14 - 2021-07-08	2021-05-15 - 2021-07-24	NA	2021-05-14 - 2021-06-08	NA
April	78	2021-06-19 - 2021-08-13	2021-06-19 - 2021-07-12	NA	2021-06-19 - 2021-07-12	NA
May	79	2021-07-23 - 2021-09-21	2021-07-23 - 2021-08-19	NA	2021-07-23 - 2021-08-05	2021-08-06 - 2021-08-14
June	80	2021-08-20 - 2021-10-13	2021-08-19 - 2021-09-14	NA	2021-08-28 - 2021-09-13	NA
July	81	2021-09-17 - 2021-10-10	2021-09-19 - 2021-10-09	2021-11-17 - 2021-11-17	2021-09-21 - 2021-11-15	NA
August	82	2021-10-19 - 2021-12-17	2021-10-22 - 2021-11-07	NA	2021-10-18 - 2021-11-07	2021-10-22 - 2021-11-05
September	83	2021-11-24 - 2022-01-18	2021-11-27 - 2021-12-14	2021-12-03 - 2021-12-15	2021-11-25 - 2021-12-15	NA
October	84	2022-01-01 - 2022-01-20	2021-12-31 - 2022-02-17	2021-12-31 - 2022-01-20	2022-01-01 - 2022-01-20	NA
November	85	2022-01-20 - 2022-03-22	2022-01-21 - 2022-03-23	2022-01-20 - 2022-02-05	2022-01-20 - 2022-02-07	NA
December	86	2022-02-22 - 2022-04-22	2022-03-23 - 2022-03-24	NA	2022-02-23 - 2022-03-26	NA
All Months	75-86	2021-02-19 - 2022-04-22	2021-03-23 - 2022-03-24	2021-03-19 - 2022-02-05	2021-03-20 - 2022-03-26	2021-08-06 - 2021-11-05

4.2.1 Summary of QC Checks and Statistics

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

Table 4.2-2: UC Davis quality control measures for element analysis by EDXRF.

Analysis	Frequency	Criterion	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	<ul style="list-style-type: none"> • XRF software automatically adjusts the energy channels
Laboratory Blank	Daily	≤ acceptance limits with exceedance of any elements 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 • Reanalyze network samples since last pass QC as needed.
UCD Multi-element sample	Daily	Larger of ± 10% or 3 standard deviations of reference mass loadings for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb with exceedance of any 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 QC sample if necessary • Reanalyze network samples since last passing QC as needed.
Precision of UCD Multi-element sample	Daily	Relative standard deviation of last 5 measurements less than 10 % for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn and less than 20% for Pb	
UCD Multi-element sample	Weekly	Larger of ± 10% or 3 standard deviations of reference mass loadings for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb with exceedance of any element not to occur in two consecutive measurements	
Sample Replicate Measures	Weekly	For elements with mass loadings between 5*MDL and 3*uncertainty the relative percent difference (RPD) must be, $-50\% \leq RPD \leq 50\%$, and for mass loadings greater than 3*uncertainty, $-20\% \leq RPD \leq 20\%$. Elements checked = Al, Si, S, K, Ca, Cr, Fe, and Pb	
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 within acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	

Daily QC checks include a laboratory blank (PTFE blank) and a multi-elemental reference material (ME-RM) to monitor contamination and stability/performance of the instruments. A UC Davis-made ME-RM is also analyzed weekly to check the instrument performance as well as replicate sample measurements. Inter-instrumental comparability is monitored by analyzing the bias and precision between instruments of the weekly UC Davis ME-RM. Long-term inter-instrumental comparability is monitored using a set of reanalysis filters which are reanalyzed monthly on each instrument. Long-term reproducibility is monitored using the reanalysis filters

and by analyzing a NIST SRM 2783 standard monthly and comparing the EDXRF error from the certified/reference mass loadings to acceptance limits.

4.2.2 Summary of QC Results

QC tests conducted over the course of the analysis period showed good overall control of the instruments and process. There were occasional acceptance criteria failures, which were investigated promptly and corrected with no impact on sample results. 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.

QC failures and issues and the corrective actions taken are reported in section 3.2.1. All QC issues during this reporting period were found and acted upon quickly. In all cases sample results were not impacted because the samples were either reanalyzed or no CSN samples were being analyzed during the observed QC issue. A summary of the QC performance of the instruments is presented below.

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 contamination on the blank and instrument contamination. Some occasional exceedances of the acceptance criteria are 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, copper) 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 nineteen samples from 2021 were reanalyzed for suspected zinc contamination. Of those, thirteen were found to have zinc contamination and the reanalysis result was reported. For the rest the original valid result was reported.

All XRF instruments had intermittent elevated measurements of zinc on the daily PTFE blank throughout the analysis period. 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-2 had single elevated values for sulfur and calcium on 6/15/2021. This was the first measure of a new QC blank after replacing the old blank. The levels returned to baseline values for both elements at the next day's measurement, so this was not a QC failure. The elevated signals were confined to the specific blank sample and no network samples were affected by this spike.

XRF-5 had failures for Cu and Zn from late June 2021 through mid-July 2021. These are related to contamination from the powder coating rubbing off the instrument's cap cover. No CSN samples were analyzed during this time. More details can be found in section 3.2.1.3.

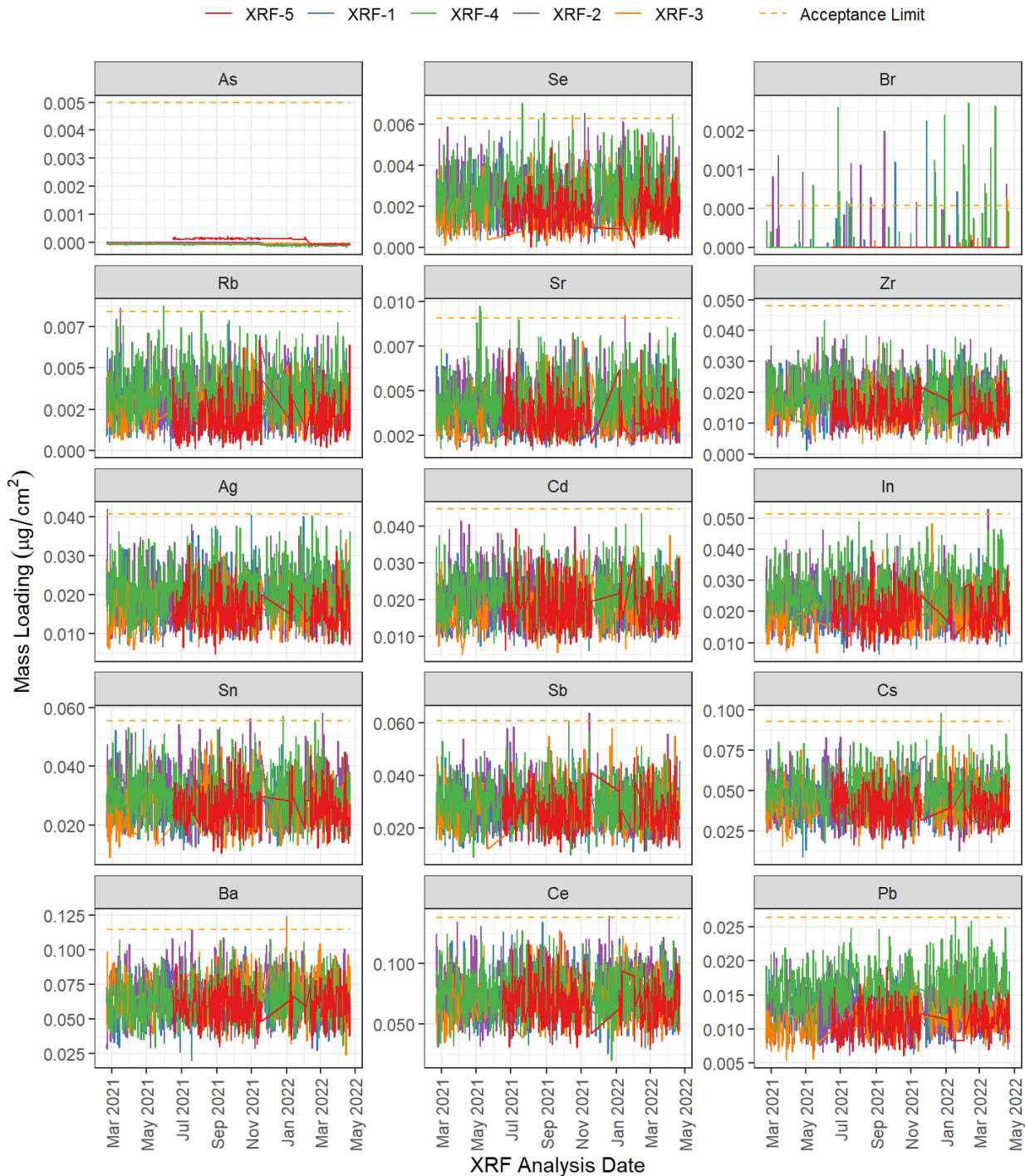
XRF-1 had an elevated iron value above the acceptance limit on 9/25/2021. The blank QC filter was cleaned and reanalyzed the next day, 9/26/2021, but still had an elevated iron response. So, the blank filter was replaced with a new one which measured on 9/27/2021 and had an acceptable iron response. So, the elevated signal was confined to the specific blank filter and no network samples were affected.

XRF-4 had a very elevated zinc signal above the acceptance limit on 1/4/2022. The blank QC filter was cleaned and the following day's analysis showed the zinc had returned to normal acceptable levels. This high zinc signal was confined to the specific blank QC filter and no network samples were affected.

Figure 4.2-1: Analysis results from daily PTFE blanks for the analysis period 2/19/2021 through 4/22/2022 (see Table 4.2-1 for corresponding sampling dates). Elements Na through Zn shown.



Figure 4.2-2: Analysis results from daily PTFE blanks for the analysis period 2/19/2021 through 4/22/2022 (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 criterion is the larger of +/- 10% or +/- three standard deviations 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. Also, note that the Lower Limit and Upper Limit do not represent exact QC criteria as they are averaged over the reporting period and may include more than one QC-ME sample which would have different reference and limit values. These values are merely representative. The QC result is considered unacceptable if it fails the QC criteria as outlined in Table 4.2-2.

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 2/19/2021 through 4/22/2022 (see Table 4.2-1 for corresponding sampling dates), N = 586.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	2.020	1.709	2.438	0	0	1.9
Si	0.895	0.751	1.159	0	0	2.1
S	17.253	15.746	19.245	0	0	0.6
K	2.415	2.204	2.694	0	0	0.7
Ca	2.399	2.143	2.619	0	0	0.7
Cr	0.996	0.895	1.094	0	0	0.7
Fe	2.829	2.501	3.057	0	0	1.0
Zn	0.348	0.305	0.373	0	0	1.2
As	0.681	0.609	0.745	0	0	0.9
Se	0.472	0.439	0.536	0	0	1.5
Rb	0.234	0.210	0.256	0	0	1.5
Sr	0.226	0.203	0.248	0	0	1.6
Cd	0.300	0.271	0.331	0.5	0	3.7
Sn	0.351	0.315	0.396	0	0	3.7
Pb	0.088	0.063	0.105	0	0	7.6

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 2/20/2021 through 4/22/2022 (see Table 4.2-1 for corresponding sampling dates), N = 634.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.784	1.469	2.047	0	0	1.8
Si	0.832	0.637	1.017	0	0	2.4
S	15.010	13.349	16.315	0	0	0.6
K	2.100	1.900	2.322	0	0	0.7
Ca	2.044	1.830	2.237	0	0	1.0
Cr	0.850	0.764	0.934	0	0	0.8
Fe	2.391	2.142	2.618	0	0	0.8
Zn	0.260	0.223	0.273	0.7	0	2.1
As	0.584	0.529	0.647	0	0	1.2
Se	0.420	0.378	0.462	0	0	1.2
Rb	0.203	0.182	0.223	0	0	1.9
Sr	0.199	0.177	0.216	0	0	1.9
Cd	0.265	0.220	0.311	0	0	4.8
Sn	0.314	0.263	0.349	0.9	0	4.6
Pb	0.095	0.076	0.115	1.3	0	8.2

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 2/20/2021 through 4/22/2022 (see Table 4.2-1 for corresponding sampling dates), N = 576.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.816	1.381	2.012	0	0	2.2
Si	0.797	0.602	0.946	0	0	1.5
S	14.676	13.089	15.998	0	0	1.0
K	2.130	1.871	2.286	0	0	1.0
Ca	1.995	1.795	2.193	0	0	1.5
Cr	0.854	0.761	0.930	0	0	1.1
Fe	2.386	2.122	2.594	0.781	0	2.8
Zn	0.277	0.242	0.296	1.563	0	3.8
As	0.585	0.522	0.638	0.781	0	4.1
Se	0.417	0.376	0.459	0.781	0	4.1
Rb	0.199	0.180	0.220	0	0	1.8
Sr	0.194	0.175	0.214	0	0	1.6
Cd	0.260	0.228	0.295	1.563	0	3.9
Sn	0.303	0.260	0.355	0	0	4.2
Pb	0.090	0.063	0.110	0.781	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 2/20/2021 through 4/22/2022 (see Table 4.2-1 for corresponding sampling dates), N = 635.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.844	1.656	2.393	0	0	2.0
Si	1.018	0.672	1.137	0	0	3.5
S	16.230	14.853	18.154	0	0	0.6
K	2.337	2.146	2.623	0	0	0.6
Ca	2.458	2.190	2.677	0	0	0.8
Cr	0.996	0.897	1.096	0	0	1.1
Fe	2.758	2.478	3.029	0	0	0.6
Zn	0.386	0.340	0.416	0	0	2.1
As	0.685	0.617	0.754	0	0	1.1
Se	0.485	0.443	0.542	0	0	1.1
Rb	0.237	0.213	0.260	0	0	1.8
Sr	0.228	0.205	0.250	0	0	1.8
Cd	0.301	0.267	0.347	0.2	0	4.4
Sn	0.351	0.321	0.398	1.7	0	4.0
Pb	0.082	0.067	0.101	2.9	0	9.4

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 3/19/2021 through 4/22/2022 (see Table 4.2-1 for corresponding sampling dates), N = 437.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.897	1.438	2.083	0	0	1.3
Si	0.701	0.565	0.932	0	0	1.4
S	15.364	13.643	16.674	0	0	0.5
K	2.179	1.941	2.373	0	0	0.3
Ca	2.070	1.872	2.288	0	0	0.7
Cr	0.892	0.792	0.968	0	0	0.6
Fe	2.463	2.220	2.713	0	0	0.4
Zn	0.308	0.272	0.332	0	0	1.3
As	0.616	0.547	0.669	0	0	0.7
Se	0.449	0.397	0.485	0	0	0.8
Rb	0.211	0.187	0.228	0	0	1.6
Sr	0.204	0.182	0.223	0	0	1.6
Cd	0.278	0.231	0.309	0	0	3.5
Sn	0.326	0.273	0.370	0	0	4.2
Pb	0.079	0.061	0.103	0	0	7.6

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. Also, note that the Lower Limit and Upper Limit columns do not represent exact acceptance limits. They are averaged over the reporting period and may include more than one QC-ME sample which would have different reference and limit values. These values are merely representative. The QC result is considered unacceptable if it fails the QC criteria as outlined in Table 4.2-2.

Tables 4.2-8 through 4.2-12 show the EDXRF statistics of the weekly UC Davis ME-RM through 4/22/2022.

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 2/25/2021 through 4/13/2022 (see Table 4.2-1 for corresponding sampling dates), N = 58.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.088	0.862	1.360	0	0	2.6
Si	1.152	1.094	1.360	0	0	2.1
S	8.596	8.063	9.855	0	0	1.8
K	1.269	1.174	1.434	0	0	0.8
Ca	1.213	1.062	1.297	0	0	1.7
Cr	0.459	0.418	0.511	0	0	0.9
Fe	1.339	1.201	1.468	0	0	1.4
Zn	0.378	0.327	0.400	0	0	1.6
As	0.319	0.288	0.352	0	0	1.4
Se	0.229	0.208	0.254	0	0	1.3
Rb	0.112	0.100	0.123	0	0	2.7
Sr	0.115	0.103	0.126	0	0	2.4
Cd	0.157	0.127	0.184	0	0	6.8
Pb	0.235	0.210	0.256	0	0	3.1

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 2/24/2021 through 4/20/2022 (see Table 4.2-1 for corresponding sampling dates), N = 63.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.077	0.862	1.360	0	0	3.0
Si	1.197	1.094	1.360	0	0	3.1
S	8.681	8.063	9.855	0	0	2.4
K	1.265	1.174	1.434	0	0	1.5
Ca	1.214	1.062	1.297	0	0	1.4
Cr	0.459	0.418	0.511	0	0	0.9
Fe	1.328	1.201	1.468	0	0	0.9
Zn	0.376	0.327	0.400	0	0	1.6
As	0.315	0.288	0.352	0	0	1.7
Se	0.230	0.208	0.254	0	0	1.9
Rb	0.111	0.100	0.123	0	0	3.2
Sr	0.116	0.103	0.126	0	0	2.8
Cd	0.157	0.127	0.184	0	0	6.7
Pb	0.233	0.210	0.256	0	0	3.8

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 2/23/2021 through 4/18/2022 (see Table 4.2-1 for corresponding sampling dates), N = 50.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.178	0.862	1.360	0	0	4.5
Si	1.232	1.094	1.360	0	0	4.0
S	8.595	8.063	9.855	0	0	2.2
K	1.298	1.174	1.434	0	0	1.9
Ca	1.216	1.062	1.297	0	0	2.1
Cr	0.463	0.418	0.511	0	0	1.4
Fe	1.327	1.201	1.468	0	0	1.3
Zn	0.379	0.327	0.400	0	0	2.4
As	0.320	0.288	0.352	0	0	2.4
Se	0.230	0.208	0.254	0	0	2.2
Rb	0.110	0.100	0.123	0	0	2.6
Sr	0.113	0.103	0.126	0	0	2.6
Cd	0.155	0.127	0.184	0	0	6.4
Pb	0.238	0.210	0.256	2.0	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 2/24/2021 through 4/21/2022 (see Table 4.2-1 for corresponding sampling dates), N = 62.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	0.965	0.862	1.360	0	0	3.4
Si	1.215	1.094	1.360	1.6	0	3.4
S	8.645	8.063	9.855	1.6	0	2.0
K	1.285	1.174	1.434	0	0	1.4
Ca	1.221	1.062	1.297	0	0	1.4
Cr	0.463	0.418	0.511	0	0	1.2
Fe	1.342	1.201	1.468	0	0	0.8
Zn	0.377	0.327	0.400	0	0	1.8
As	0.320	0.288	0.352	0	0	1.7
Se	0.229	0.208	0.254	0	0	1.9
Rb	0.112	0.100	0.123	0	0	3.0
Sr	0.115	0.103	0.126	0	0	2.9
Cd	0.156	0.127	0.184	0	0	6.7
Pb	0.234	0.210	0.256	0	0	3.9

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 6/17/2021 through 4/19/2022 (see Table 4.2-1 for corresponding sampling dates), N = 34.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.125	0.862	1.360	0	0	4.1
Si	1.147	1.094	1.360	0	0	2.5
S	8.655	8.063	9.855	0	0	2.1
K	1.279	1.174	1.434	0	0	1.4
Ca	1.203	1.062	1.297	0	0	1.1
Cr	0.464	0.418	0.511	0	0	0.9
Fe	1.325	1.201	1.468	0	0	0.9
Zn	0.378	0.327	0.400	0	0	1.1
As	0.321	0.288	0.352	0	0	2.0
Se	0.231	0.208	0.254	0	0	1.5
Rb	0.111	0.100	0.123	0	0	2.3
Sr	0.114	0.103	0.126	0	0	2.4
Cd	0.159	0.127	0.184	0	0	5.4
Pb	0.233	0.210	0.256	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 as 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,

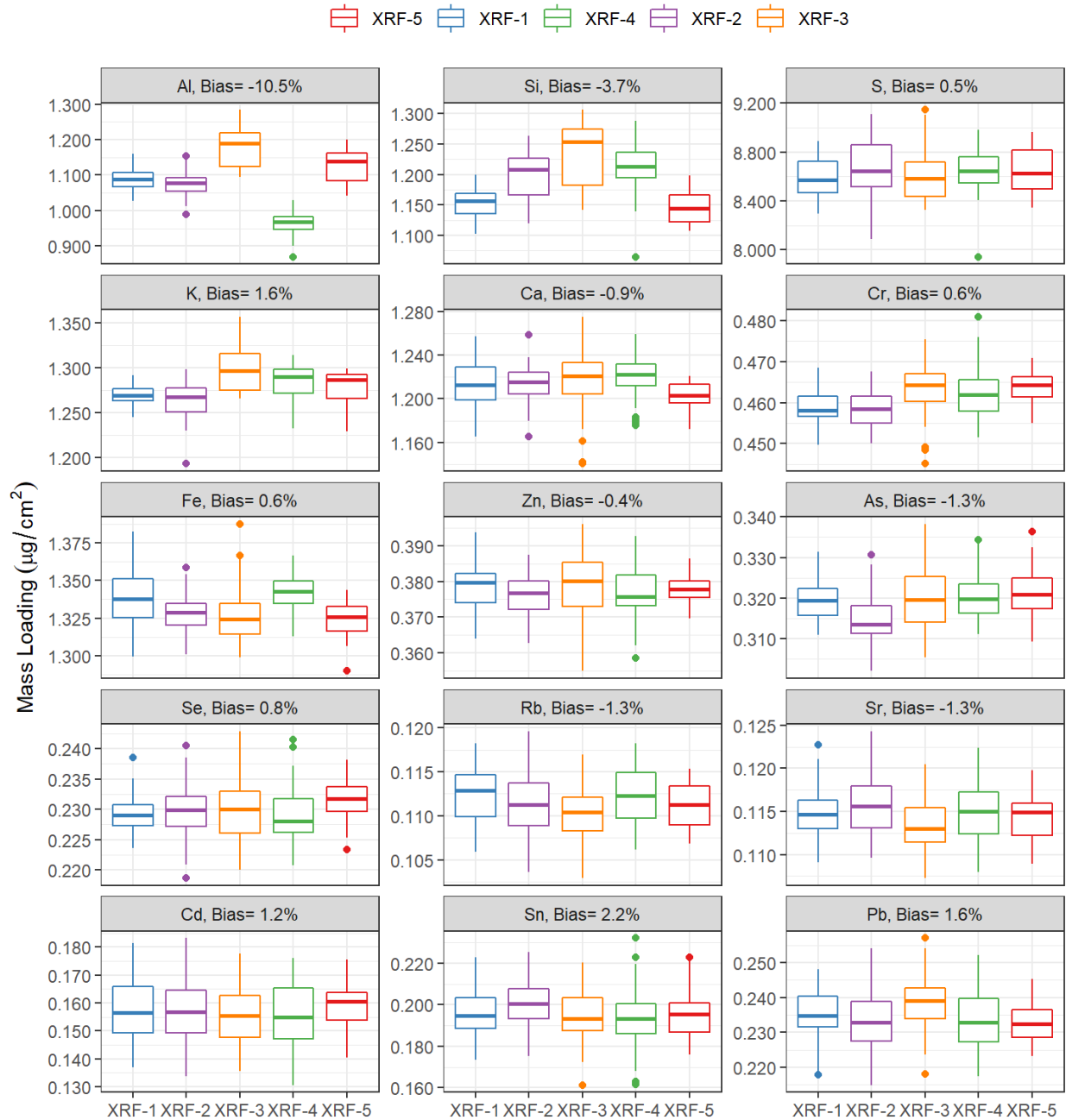
$$Precision_i = \sqrt{\frac{n \sum_{j=1}^n d_{i,j}^2 - (\sum_{j=1}^n d_{i,j})^2}{n(n-1)}}$$

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 2/19/2021 through 4/22/2022 (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	0.9	-0.1	9.2	-10.5	4.3	2.6	3.0	4.9	3.0	4.3
Si	-3.3	0.4	3.4	2.0	-3.7	2.0	3.1	4.1	3.5	2.4
S	-0.5	0.5	-0.5	0.1	0.2	1.8	2.4	2.2	2.0	2.1
K	-0.8	-1.1	1.6	0.5	0.0	0.8	1.5	1.9	1.4	1.4
Ca	-0.1	-0.1	0.2	0.6	-0.9	1.7	1.4	2.1	1.4	1.0
Cr	-0.5	-0.5	0.5	0.3	0.6	0.9	0.9	1.4	1.2	0.9
Fe	0.5	-0.3	-0.5	0.6	-0.6	1.4	0.9	1.3	0.8	0.9
Zn	0.2	-0.4	0.4	-0.2	0.1	1.6	1.6	2.4	1.8	1.1
As	0.2	-1.3	0.3	0.5	0.8	1.4	1.7	2.4	1.7	2.1
Se	-0.2	0.0	0.1	-0.3	0.8	1.3	1.9	2.2	1.9	1.5
Rb	0.7	-0.1	-1.3	0.6	-0.3	2.7	3.2	2.6	3.0	2.3
Sr	0.0	0.9	-1.3	0.2	-0.3	2.4	2.9	2.5	2.9	2.4
Cd	0.4	0.1	-0.8	-0.5	1.2	6.9	6.7	6.4	6.7	5.4
Sn	-0.1	2.2	-0.8	-1.3	-0.3	5.9	5.8	6.6	7.1	5.7
Pb	0.3	-0.7	1.6	-0.4	-0.8	3.1	3.8	3.3	3.9	2.5

Figure 4.2-3: 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

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

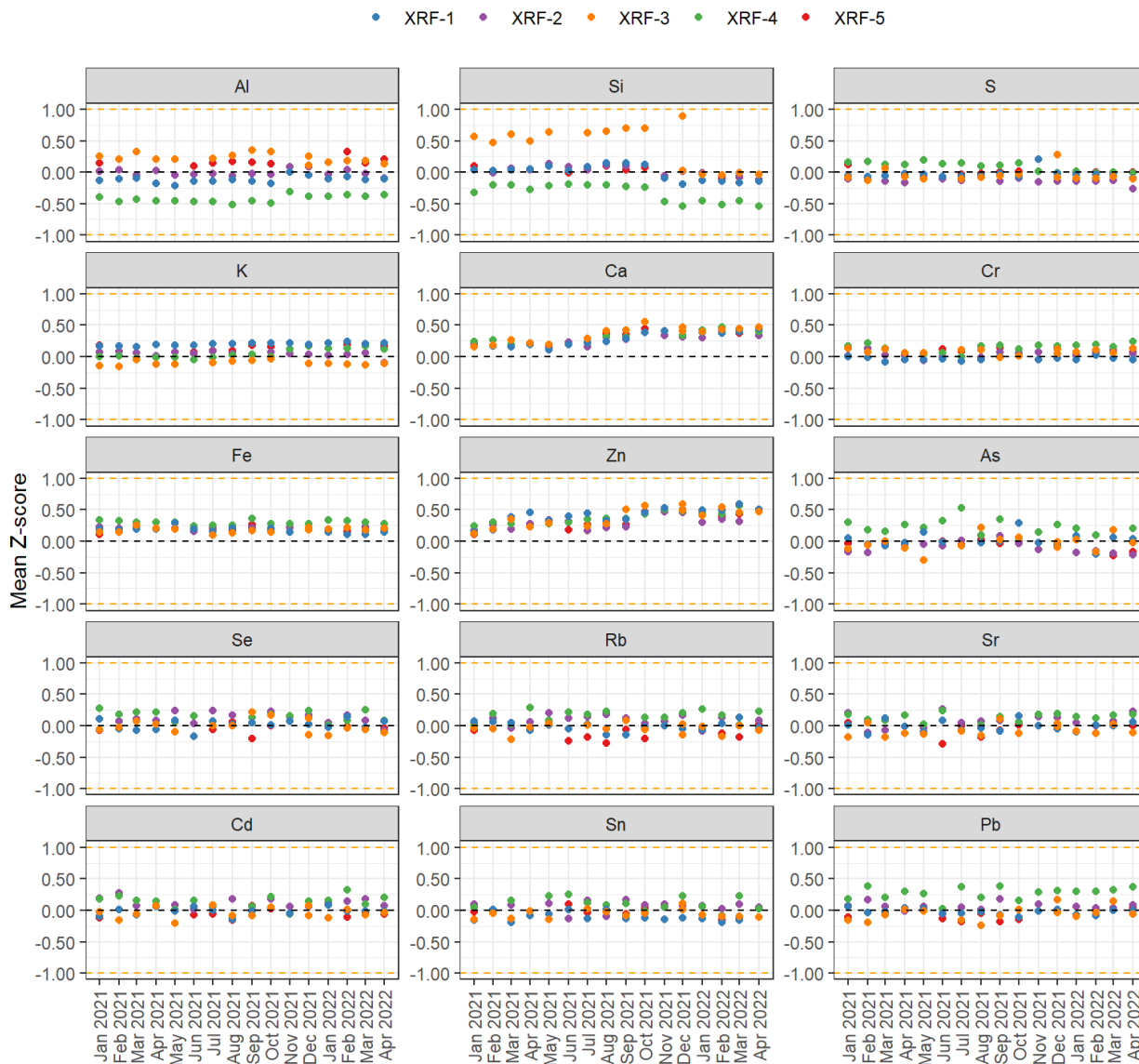
where x_{ij} is that month's result, \widehat{x}_{ij} is the reference value for element i in filter j , and $U(x_{ij})$ and $U(\widehat{x}_{ij})$ are the uncertainty of that month's result and the reference uncertainty respectively. The instrument-specific reference values for the samples of the reanalysis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

$$\text{Bias}_i = \frac{1}{N} \sum_j z_{ij} \quad \text{and} \quad \text{RMS}_i = \sqrt{\frac{1}{N} \sum_j z_{ij}^2}$$

Every month, z-scores are plotted and checked to be within -1 to 1 for elements which have mass loadings 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 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-3 were near the upper limit through December 2021. These higher z-scores are due to a higher bias for silicon for that calibration. When the instrument was recalibrated in December 2021 the silicon z-score dropped to near zero indicating the new calibration has far less bias for silicon. Additionally, XRF-3 does not have a z-score result in June 2021 because the instrument was not operational that month due to maintenance issues. See section 3.2.1.2 for further details.

Figure 4.2-4: 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. It should be noted that the NIST certification of elemental concentrations expired 9/1/2021. NIST SRM 2783 is out of stock and NIST has not indicated they will recertify the SRM. No other air particulate on filter media SRM exists, therefore, UC Davis continues to analyze SRM 2783. 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 (2/19/2021 through 4/22/2022) 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 November/December 2020 and 2021. Calibrations required after maintenance repairs are listed. The results from the monthly NIST SRM 2783 analyses indicate that calibrations for all instruments were stable over the calibration periods.

Figure 4.2-5: Error of each EDXRF instrument from the NIST SRM 2783 standard run monthly for the analysis period 2/19/2021 through 4/22/2022.

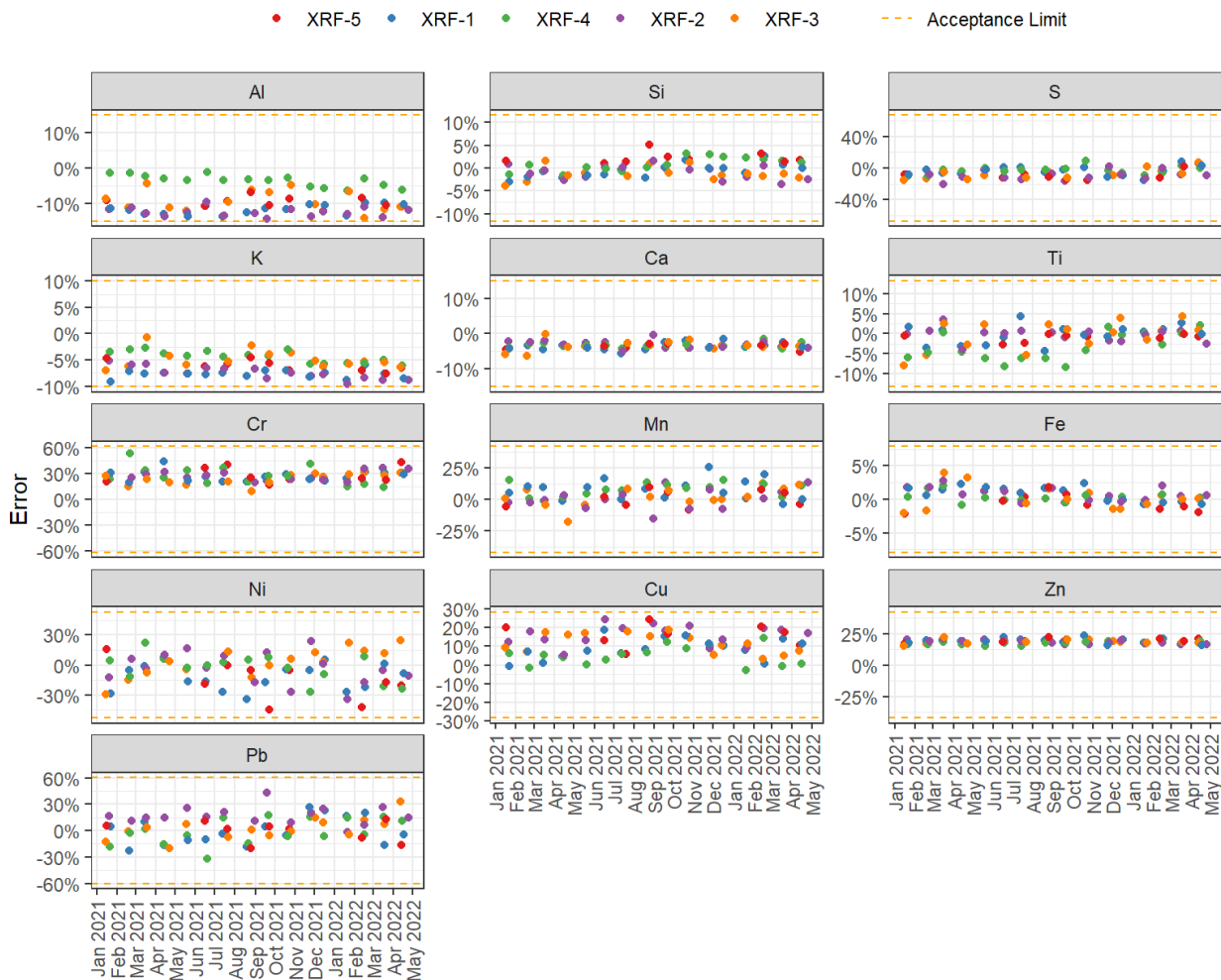


Table 4.2-14: Dates for calibrations performed on each EDXRF instrument during this analysis period (February 19, 2021 through April, 22, 2022).

EDXRF Instrument	Calibration Date	Reason for Calibration	Range of Sample Dates Analyzed
XRF-1	11/25/2020	Annual Calibration	1/1/2021 – 8/26/2021
XRF-3	12/22/2020	Annual Calibration	1/1/2021 – 1/25/2021
XRF-4	11/25/2020	Annual Calibration	1/4/2021 – 8/29/2021
XRF-2	11/04/2020	Annual Calibration	1/13/2021 – 8/14/2021
XRF-3	4/22/2021	Detector moved	2/15/2021 – 2/21/2021
XRF-5	6/15/2021	X-ray tube replaced	5/10/2021 – 8/26/2021
XRF-3	7/21/2021	X-ray tube replaced	7/9/2021 – 7/9/2021
XRF-1	11/24/2021	Annual Calibration	8/8/2021 – 11/30/2021
XRF-4	11/24/2021	Annual Calibration	9/4/2021 – 12/24/2021
XRF-2	11/26/2021	Annual Calibration	9/10/2021 – 12/30/2021
XRF-3	12/02/2021	Annual Calibration	9/19/2021 – 11/30/2021
XRF-1	2/17/2022	X-ray tube replaced	11/09/2021 – 12/30/2021
XRF-5	2/11/2022	Secondary X-ray target repositioned	N/A

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

No system audits were performed during this analysis period.

4.2.4.2 Performance Evaluations

No performance evaluations were conducted during this reporting period.

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, and Cryogen Safety.

Only personnel listed in *UC Davis CSN Quality Assurance Project Plan (QAPP)*, trained on the appropriate SOPs and Technical Information materials (*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 Blanks

4.2.5.1 Field Blanks

Over the sampling period (January 1, 2021 through December 31, 2021) there were 1,650 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 2021 sampling analysis period 2/19/2021 through 4/22/2022 (samples collected 1/1/2021 through 12/31/2021).

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	1650	0.020	0.020	0.007	0.050	0.006
Al	1650	0.070	0.071	0.023	0.176	0.013
As	1650	0.000	0.000	0.000	0.000	0.000
Ba	1650	0.064	0.064	0.026	0.118	0.015
Br	1650	0.000	0.000	0.000	0.002	0.000
Ca	1650	0.002	0.004	0.000	0.378	0.011
Cd	1650	0.020	0.021	0.006	0.044	0.006
Ce	1650	0.075	0.076	0.034	0.151	0.018
Cl	1650	0.002	0.003	0.000	0.181	0.006
Co	1650	0.001	0.001	0.000	0.004	0.001
Cr	1650	0.004	0.004	0.002	0.019	0.001
Cs	1650	0.046	0.047	0.013	0.105	0.013
Cu	1650	0.009	0.008	0.003	0.021	0.003
Fe	1650	0.020	0.021	0.007	0.388	0.011
In	1650	0.023	0.024	0.008	0.048	0.007
K	1650	0.012	0.012	0.001	0.720	0.018
Mg	1650	0.009	0.015	0.000	0.110	0.017
Mn	1650	0.006	0.006	0.000	0.025	0.002
Na	1650	0.000	0.017	0.000	0.156	0.027
Ni	1650	0.001	0.001	0.000	0.005	0.001
P	1650	0.000	0.000	0.000	0.027	0.001
Pb	1650	0.014	0.014	0.006	0.028	0.003
Rb	1650	0.003	0.003	0.000	0.012	0.001
S	1650	0.000	0.001	0.000	0.523	0.019
Sb	1650	0.028	0.029	0.008	0.063	0.008
Se	1650	0.002	0.002	0.000	0.007	0.001
Si	1650	0.017	0.019	0.000	0.308	0.014
Sn	1650	0.029	0.029	0.010	0.062	0.008
Sr	1650	0.004	0.004	0.002	0.011	0.001
Ti	1650	0.001	0.001	0.000	0.021	0.001
V	1650	0.000	0.000	0.000	0.002	0.000
Zn	1650	0.002	0.003	0.000	0.025	0.001
Zr	1650	0.018	0.019	0.002	0.049	0.007

4.2.5.2 Laboratory Blanks

Five PTFE laboratory blanks are shipped with each batch of routine filters to the analysis laboratory and analyzed. A total of 60 PTFE laboratory blanks were analyzed during the current reporting period. Table 4.1-16 summarizes the laboratory blank statistics.

Table 4.2-16: PTFE filter laboratory blank statistics for the 2021 sampling analysis period 2/19/2021 through 4/22/2022 (samples collected 1/1/2021 through 12/31/2021).

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	60	0.020	0.020	0.009	0.034	0.006
Al	60	0.064	0.065	0.053	0.092	0.008
As	60	0.000	0.000	0.000	0.000	0.000
Ba	60	0.066	0.066	0.038	0.113	0.015
Br	60	0.000	0.000	0.000	0.001	0.000
Ca	60	0.002	0.002	0.000	0.005	0.001
Cd	60	0.019	0.019	0.008	0.035	0.005
Ce	60	0.078	0.078	0.048	0.113	0.017
Cl	60	0.002	0.002	0.000	0.006	0.001
Co	60	0.001	0.001	0.000	0.003	0.001
Cr	60	0.004	0.004	0.002	0.006	0.001
Cs	60	0.042	0.044	0.024	0.080	0.013
Cu	60	0.010	0.009	0.004	0.014	0.003
Fe	60	0.019	0.019	0.011	0.030	0.003
In	60	0.024	0.024	0.009	0.041	0.007
K	60	0.013	0.012	0.005	0.018	0.003
Mg	60	0.007	0.011	0.000	0.061	0.014
Mn	60	0.006	0.006	0.003	0.013	0.001
Na	60	0.000	0.020	0.000	0.108	0.030
Ni	60	0.001	0.001	0.000	0.002	0.000
P	60	0.000	0.000	0.000	0.002	0.000
Pb	60	0.013	0.014	0.009	0.024	0.003
Rb	60	0.003	0.003	0.001	0.008	0.001
S	60	0.000	0.000	0.000	0.001	0.000
Sb	60	0.026	0.028	0.014	0.050	0.007
Se	60	0.003	0.003	0.001	0.005	0.001
Si	60	0.013	0.015	0.004	0.030	0.006
Sn	60	0.028	0.029	0.017	0.045	0.007
Sr	60	0.004	0.004	0.002	0.007	0.001
Ti	60	0.001	0.002	0.000	0.005	0.001
V	60	0.000	0.000	0.000	0.001	0.000
Zn	60	0.003	0.003	0.001	0.009	0.001
Zr	60	0.019	0.019	0.007	0.042	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 75 through 86, covering the field sampling period beginning from January 1, 2021 through December 31, 2021. Analyses of these samples were performed March 11, 2021 through April 1st, 2022. Six existing Thermal Optical Carbon Analyzers (Sunset Laboratory Model 5L; designated as Alpha, Beta, Delta, Gamma, Zeta, and Theta) were used for analysis during the whole period using the IMPROVE_A temperature protocol.

Table 4.3-1: Sampling months in 2021 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 (2021)	Analysis Batch #	TOA Analysis Dates
January	75	3/11/2021 – 4/7/2021
February	76	4/7/2021 – 4/27/2021
March	77	5/6/2021 – 6/10/2021
April	78	6/10/2021 – 8/20/2021
May	79	7/15/2021 – 8/13/2021
June	80	8/17/2021 – 9/16/2021
July	81	9/22/2021 – 10/22/2021
August	82	10/25/2021 – 11/18/2021
September	83	11/18/2021 – 12/20/2021
October	84	1/3/2022 – 2/3/2022
November	85	1/25/2022 – 2/28/2021
December	86	3/7/2022 – 4/1/2022
All month	75-86	3/11/2021 – 4/1/2022

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 or a consistent one-side bias is observed with the daily single-point sucrose standard check, whichever comes first). 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	$\leq 1.0 \mu\text{g C/cm}^2$	Repeat analysis. If same result, check filter lot 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 multi-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	Within $\pm 10\%$ RPD when $\text{TC} > 10 \mu\text{g C/cm}^2$ within $\pm 20\%$ RPD when $\text{ECR} > 2.5 \mu\text{g C/cm}^2$ or Within $\pm 1 \mu\text{g/cm}^2$ when $\text{TC} \leq 10 \mu\text{g C/cm}^2$ Within $\pm 0.5 \mu\text{g/cm}^2$ when $\text{ECR} \leq 2.5 \mu\text{g C/cm}^2$.	Investigate instrument and sample anomalies. Analyze the third punch on a different analyzer
Inter-instrument Comparison Check	Weekly	Within $\pm 10\%$ RPD* when $\text{TC} > 10 \mu\text{g C/cm}^2$ Within $\pm 20\%$ RPD when $\text{EC} > 2.5 \mu\text{g C/cm}^2$ or Within $\pm 1 \mu\text{g/cm}^2$ when $\text{TC} \leq 10 \mu\text{g C/cm}^2$ Within $\pm 0.5 \mu\text{g/cm}^2$ when $\text{EC} \leq 2.5 \mu\text{g C/cm}^2$ *RPD for each analyzer is calculated against the average measurement from all analyzers	Analyze a second punch from the same sample on the failed analyzer. If same result, analyzer taken offline and investigated for the root cause of the failure
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. These blanks are purchased by UC Davis and are not necessarily the same as the quartz filters used for sampling. The filters are pre-fired by UC Davis to remove contaminant carbon according to SOP #402. 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.

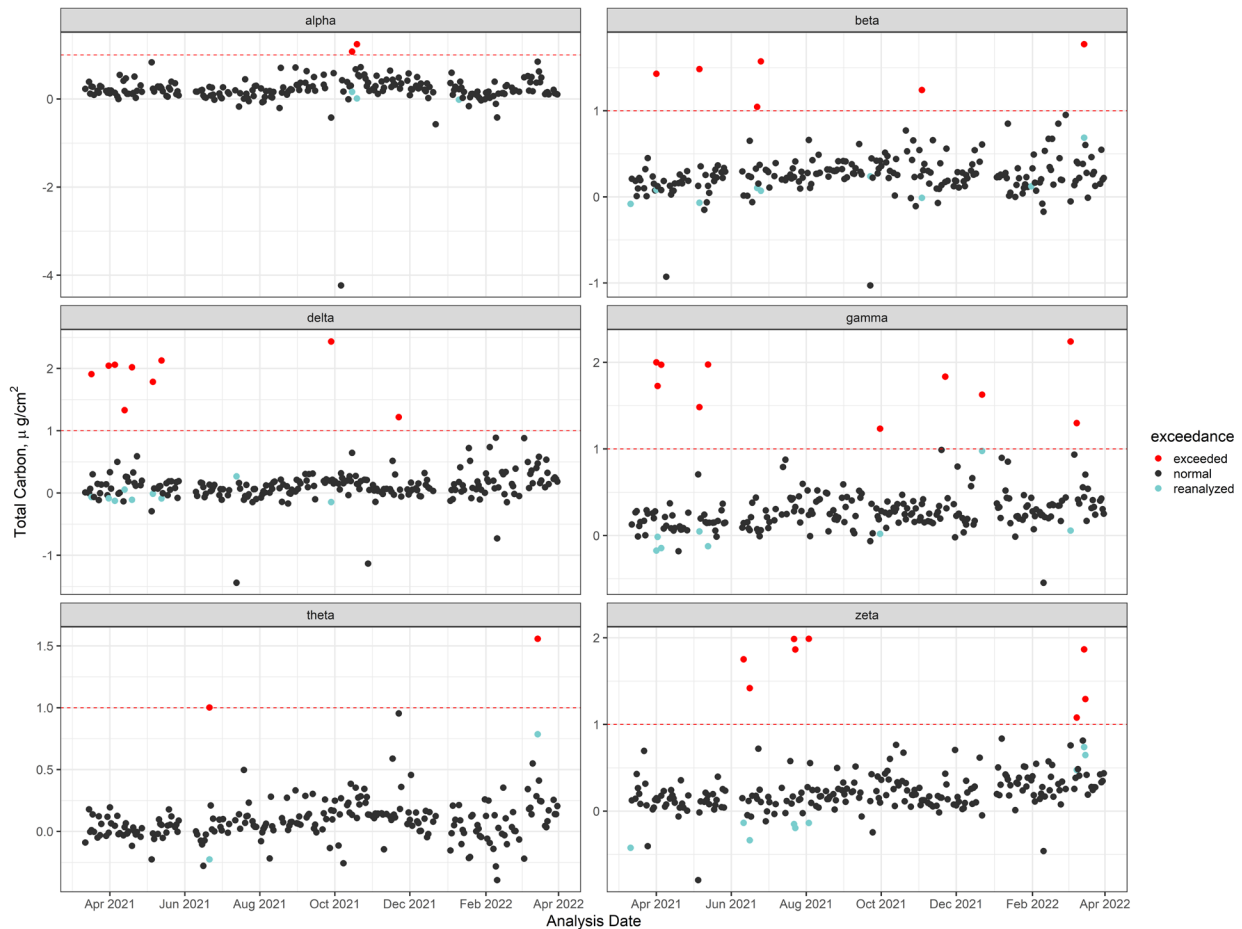
Table 4.3-3: Statistics of daily quartz filter laboratory blank and instrument blank total carbon (TC) analyses on all carbon analyzers for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021).

Blank Type	Count	Median (µg/cm ²)	Average (µg/cm ²)	Min (µg/cm ²)	Max (µg/cm ²)	St.Dev. (µg/cm ²)	# Exceedance
Laboratory Blank	1354	0.18	0.23	-4.23	2.44	0.34	37
Laboratory Blank – R*	40	-0.01	0.07	-0.42	0.98	0.31	1
Instrument Blank	1358	-0.09	-0.09	-1.78	1.03	0.13	42
Instrument Blank – R*	57	-0.18	-0.23	-1.76	0.29	0.33	13

*Laboratory/Instrument Blank - R: Repeated laboratory/instrument blank when original analysis fails the acceptance criteria.

For laboratory blanks, if the TC areal density exceeds 1.0 µg C/cm², a second punch taken from the same blank filter lot is analyzed (Laboratory Blank-R). Usually, the exceedances can result from contamination on the filter blanks, on the punching device, or in the system. 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 (one case during the report period), a new lot of quartz blank filters is used to determine the source of contamination. Occasionally, exceedances result from unstable FID baseline, which is distinguishable from contamination. On April 28, 2020, the carbon analyzers were brought back online after being down for over a month due to COVID-19. The laboratory blanks were repeated 5 times on each analyzer to achieve an operable and stable baseline. Figure 4.3-1 and Figure 4.3-2 show the results of daily laboratory and instrument blanks, respectively, analyzed by each instrument during this reporting period.

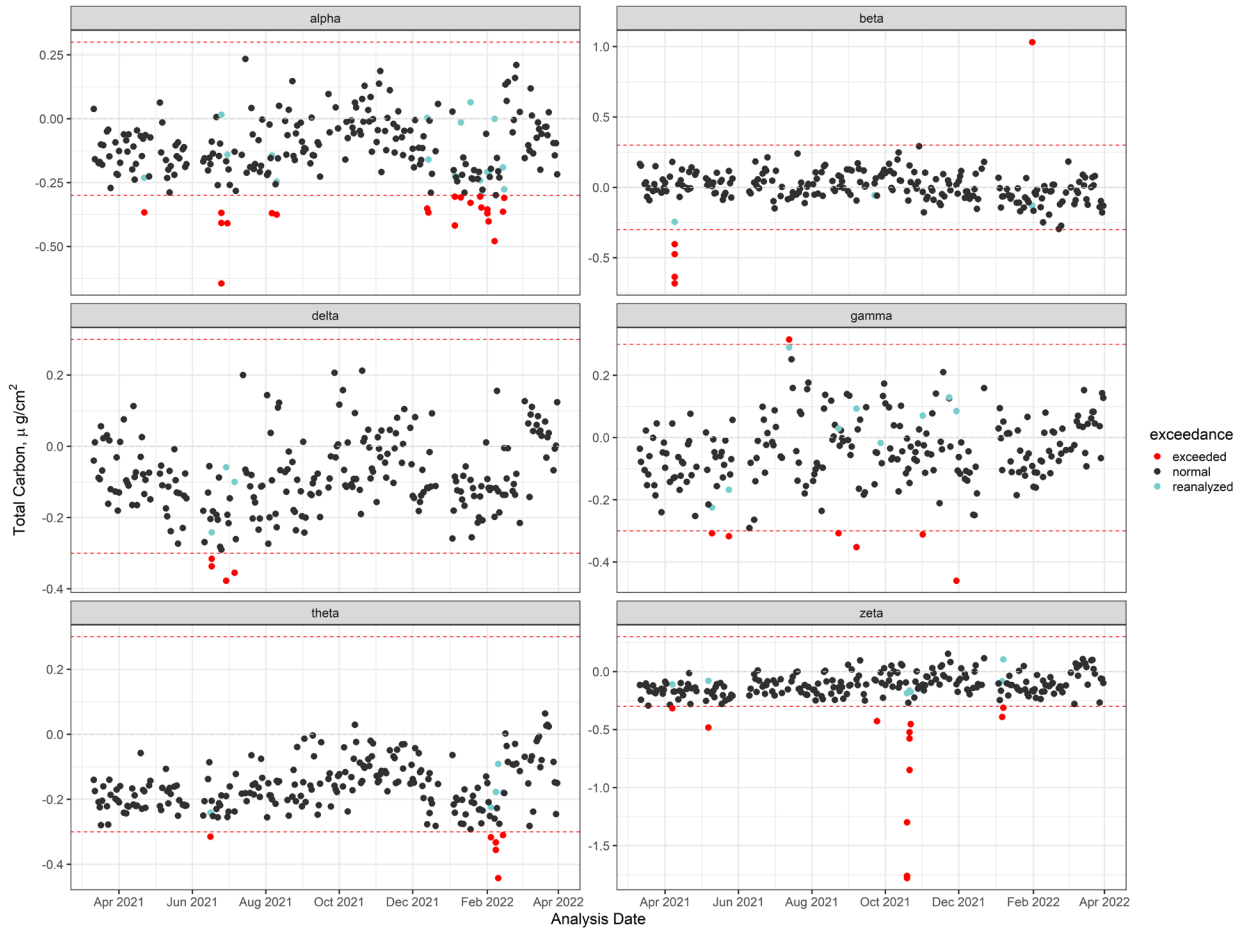
Figure 4.3-1: Total carbon results of daily quartz filter laboratory blanks from each analyzer for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021). Red dashed horizontal line indicates the acceptance criteria of $1.0 \mu\text{g C}/\text{cm}^2$ for total carbon areal density. For cases when the acceptance criteria were exceeded (red points), a repeat analysis (blue points) was performed.



Instrument blank (IB) analysis is performed following the laboratory blank analysis by reusing the sample punch. The instrument blank acceptance criteria is TC (total carbon) within $\pm 0.3 \mu\text{g}/\text{cm}^2$. When the instrument blank fails to meet the QC criteria (red points in Figure 4.3-2), analysis is repeated (blue points in Figure 4.3-2). If the Instrument Blank-R analysis still exceeds the acceptance limit (seven cases during the report period; Table 4.3-3), the operator checks the instrument and gas line for possible contamination and examines the stability of the FID baseline from thermograms. The analysis results from instrument (and laboratory) blanks must be acceptable before continuing with analysis of the sucrose standard.

Figure 4.3-2 shows the results of daily analyses of instrument blanks by each instrument. In most cases the repeated IB analysis is satisfactory.

Figure 4.3-1: Results of daily instrument blanks from each analyzer for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021). Horizontal dash lines in red color indicate the acceptance criteria of $\pm 0.3 \mu\text{g C/cm}^2$ for total carbon areal density. For cases when the acceptance criteria was exceeded (red points), a repeated analysis was performed until the instrument pass QC criteria. The blue points show the reanalyzed IB passed the QC criteria.



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 its 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 (or as needed). Sucrose calibration standards cover a wide range of the TC levels from $2.11 \mu\text{g C/cm}^2$ through $210.5 \mu\text{g C/cm}^2$, 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 µgC/cm².

Sucrose ID	Concentration (µg C/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
Sucrose 17*	36.38

*A secondary source standard acquired from the manufacturer, i.e., Sunset laboratory Inc.

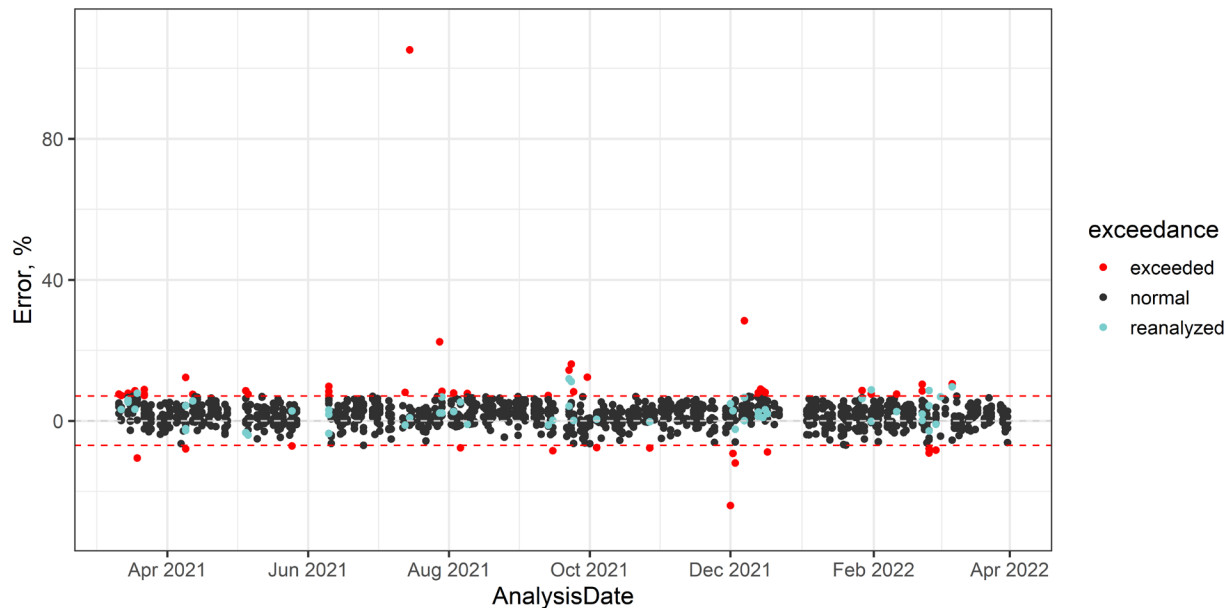
Upon completion of the sucrose analysis, the measured TC is compared against the true value (i.e. calculated TC) provided in Table 4.3-4. The % error between the measured and calculated TC is derived using Equation 4.3-1. If the error exceeds the ± 7% acceptance criteria, a second analysis is performed 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 ± 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 60 exceedances out of the 1,416 sucrose analyses during the report period. All repeat-analyses of the sucrose solution showed acceptable results (Figure 4.3-3).

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

Table 4.3-5: Statistics of daily single-point sucrose standard total carbon analyses on all carbon analyzers for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021).

Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
1,416	1.84	1.81	-24.02	105.24	4.31	60

Figure 4.3-2: Results of daily single-point sucrose calibration standard check for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021) for all instruments. 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 (CH₄) from a cylinder containing 5% CH₄ in helium is injected into the system as an internal gaseous standard. The CH₄ 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 analyzed on the original analyzer (or on a different analyzer if the original analyzer is not available). Table 4.3-6 summarizes the statistics of the calibration peak area checks. There were 12 exceedances during this reporting period. Two of the 12 exceedances occurred because the FID ignition turned off during analysis. All repeat analyses of the affected samples had acceptable results. One exceedance occurred because the front oven cap was opened and the sample was removed before the analysis had finished. Two of the 12 exceedances occurred when the clamp that connects the oven ball joint was not sufficiently tightened, resulting in a leak and gradual pressure drop in the system. Two exceedances occurred due to FID ignition being off during the analysis. Seven calibration peak area exceedances due to the FID error were performed by the carbon analyzer. On 10/18/2021 the methanator oven was replaced due to a decrease in calibration area readings on Zeta. On 6/24/2021, the methanator oven was replaced on Alpha due to a decrease in calibration area reading.

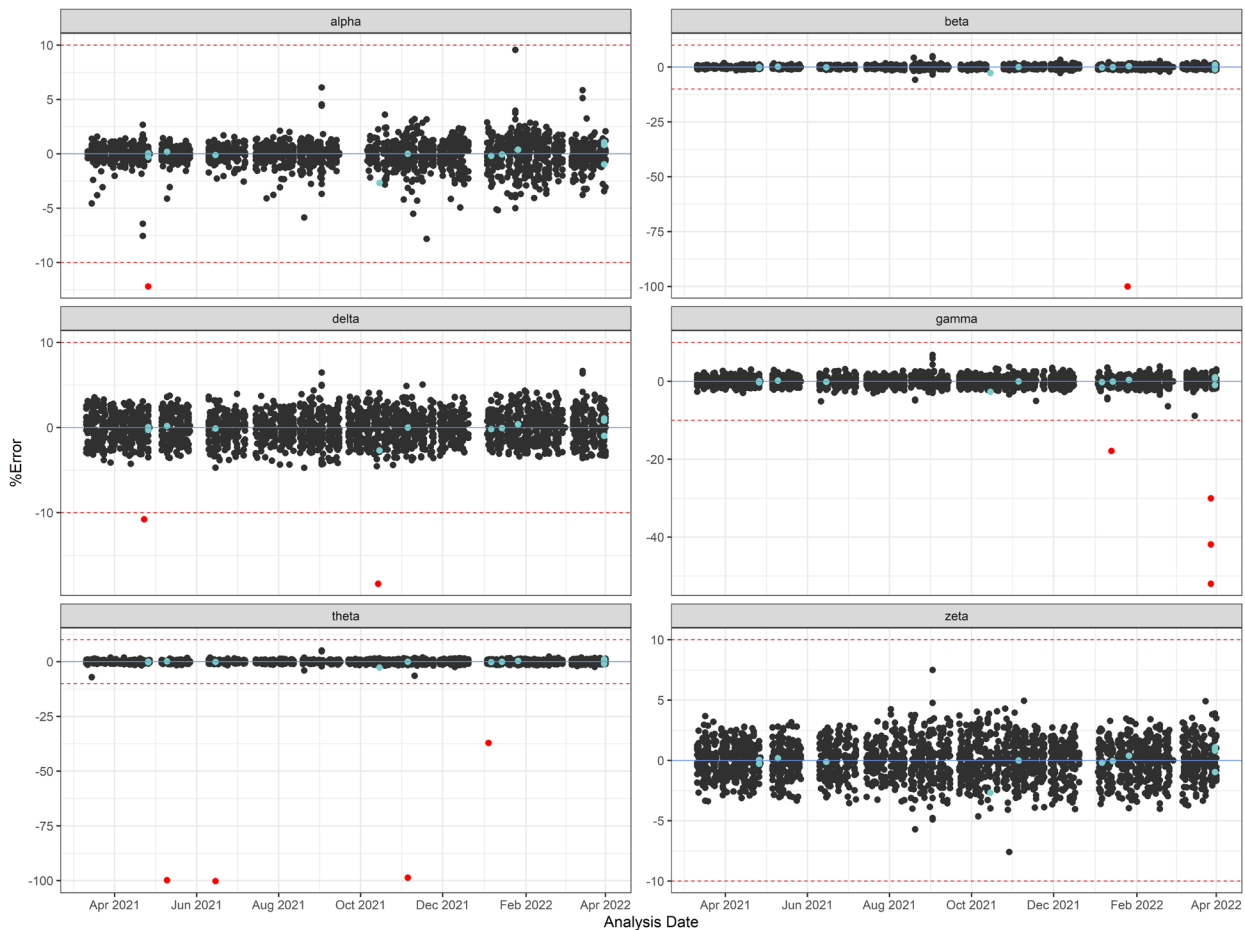
$$Error (\%) = \left(\frac{Cal. Peak - Average Cal. Peak}{Average Cal. Peak} \right) \times 100\%$$

(Eq. 4.3-2)

Table 4.3-6: Statistics of internal calibration peak area check on all carbon analyzers for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021).

Analyzer	Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
Alpha	2367	0.08	-0.01	-12.20	9.57	1.16	1
Beta	2339	-0.02	-0.04	-100.00	4.95	2.18	1
Delta	2514	0.04	-0.02	-18.35	6.65	1.77	2
Gamma	2396	-0.01	-0.06	-52.00	6.80	1.92	4
Zeta	2483	0.03	0.00	-7.58	7.50	1.54	0
Theta	3053	0.01	-0.11	-100.21	5.11	3.26	4

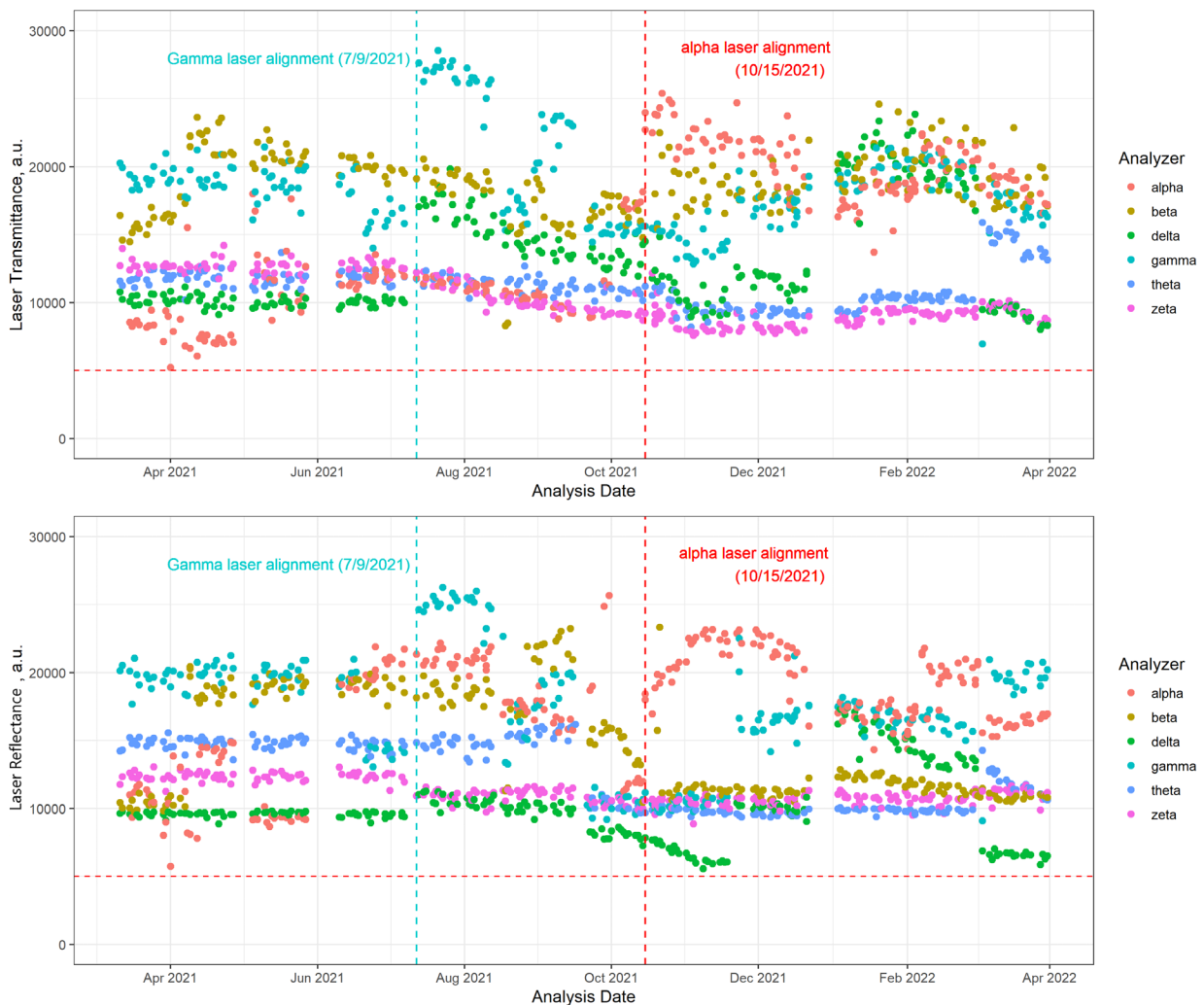
Figure 4.3-3: Results of internal calibration area check for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021). Red dashed lines indicate the acceptance criteria of $\pm 10\%$ error from the mean value. For cases when calibration area exceeded the acceptance criteria, a repeated analysis (blue points) was performed and the original analysis was voided (red points).



4.3.2.4 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. Gamma had a laser source alignment on 7/9/2021. Alpha had back oven heating coil replaced, which resulted in laser fine-tuning and signal optimization performed on 10/15/2021. During this report period, there were no exceedances of laser reflectance signal.

Figure 4.3-4: Laser initial readings (top: Transmittance; bottom: Reflectance) of the instrumental blank analysis for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021). Red dashed line indicates the acceptance criteria of 5000 a.u. of the laser signal. Other vertical lines indicate dates of related maintenance on the instrument optical components. Different analyzers are indicated by data point color.



4.3.2.5 Network Sample Replicates

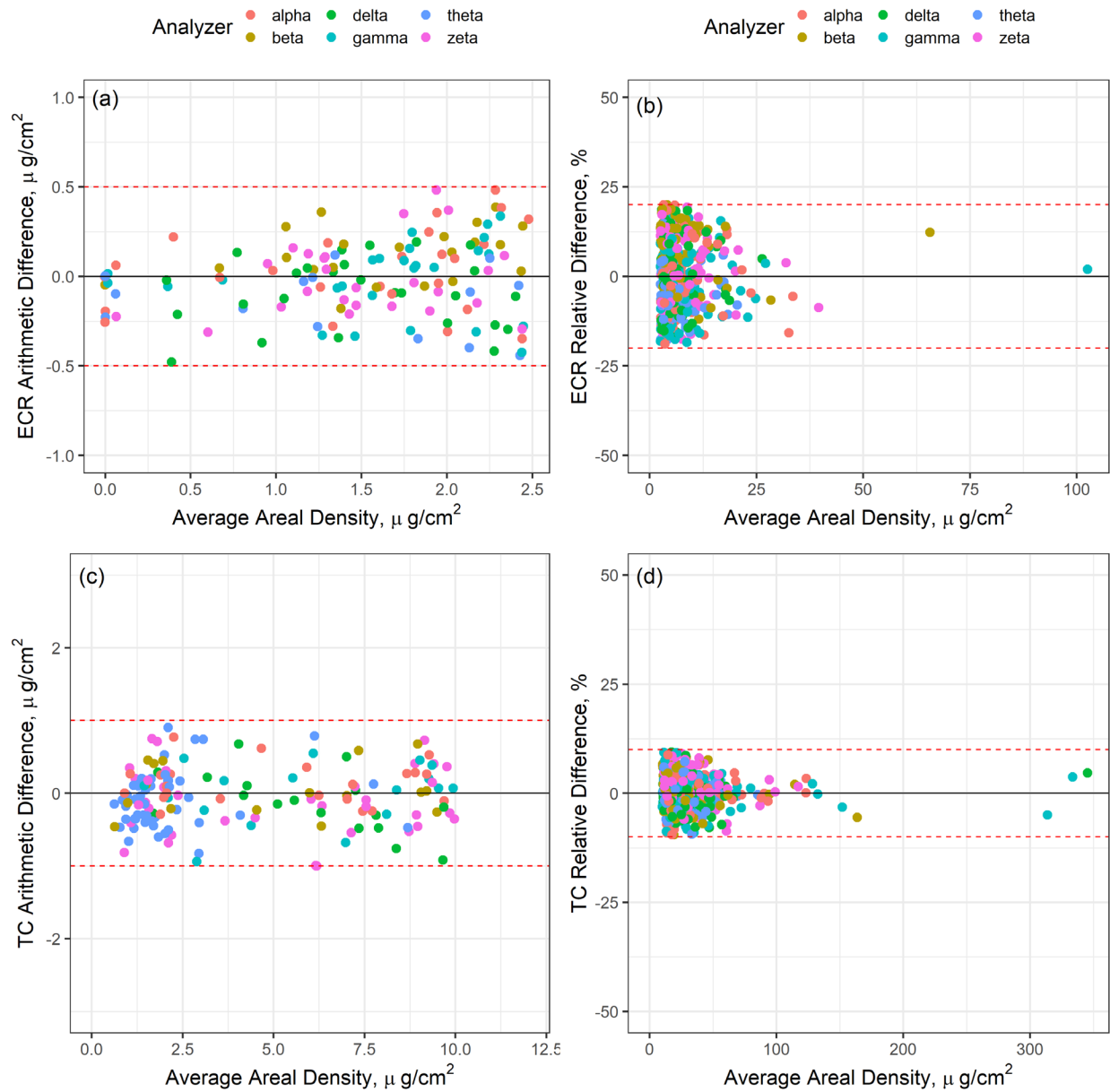
Replicate analyses are performed on every 20th CSN filter (samples and field blanks), where replicate analysis results are obtained from a second punch from the same filter analyzed on a randomly selected analyzer. Table 4.3-7 lists the acceptance criteria for replicate analysis and the summary statistics from this reporting period. A total of 708 replicate analyses were performed out of the 15002 samples and field blanks. For cases that exceeded the acceptance criteria, a third punch (if available) was analyzed on a different analyzer, and 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 4.3-7 shows the results of the replicate analyses. There was a total of 42 TC exceedances and 69 ECR exceedances during this reporting period. Samples with exceedances were reanalyzed on a third analyzer. Only the passing re-analysis result is plotted in Figure 4.3-7 and the failing test is overwritten in the data creating the figure. This is noted in Table 4.3-7 where all reanalysis of exceedances passed. All other reanalyses had satisfactory results.

Table 4.3-7: Acceptance criteria and the summary statistics of the replicate analyses for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021).

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	42	42
ECR	*RPD < ±20% when EC > 2.5 µg /cm ² or Absolute difference <±0.5 µg/cm ² when EC ≤2.5 µg/cm ²	708	69	69

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

Figure 4.3-5: Results of CSN replicate analysis for ECR (Panel a and b) and TC (Panel c and d) for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021). The red dashed lines in each panel represents the acceptance criteria. These plots include passing retests of exceedances, the original failures are not plotted.

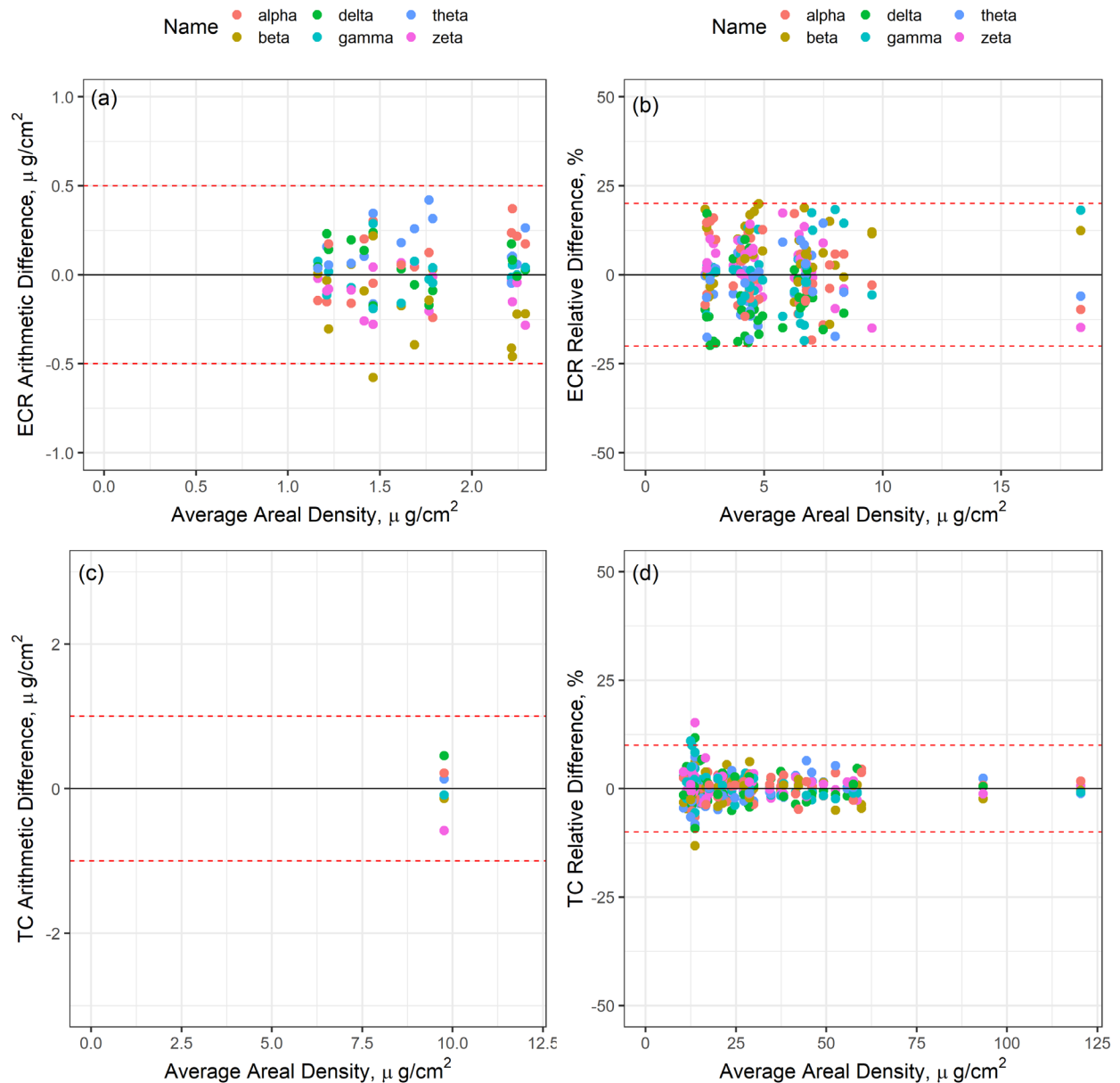


4.3.2.6 Inter-instrument Comparison Check

Instrument inter-comparison is evaluated weekly by analyzing performance check (PC) samples collected at UC Davis. Pre-fired quartz filters with 37 mm diameter are used to provide enough deposit area for at least seven 0.6 cm^2 punches. A total of 65 weekly PC samples were analyzed during this reporting period. Six 0.6 cm^2 punches were taken from the same PC sample, one was

analyzed by each instrument. Figure 4.3-6 shows the results of the weekly PC samples for each analyzer.

Figure 4.3-6: Results of the weekly performance check samples by each analyzer for ECR (Panel a and b) and TC (Panel c and d) for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021). The red dashed lines in each panel represent the acceptance criteria. Note the difference in limits and method between figures (a) and (b), low ECR and normal ECR respectively. Note the difference in limits and method between figures (c) and (d), low TC and normal TC respectively.



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. Acceptance criteria at higher filter loadings (TC > 10 $\mu\text{g C}/\text{cm}^2$ and ECR > 2.5 μg

C/cm²) are based on the relative difference (%) by dividing the difference between the measurement of a given analyzer (*i*) and the average value for the same PC sample obtained from all analyzers used in comparison by the average value using the equation as follows:

$$Relative\ difference_i\ (\%) = \frac{(Measured_i - Average) \times 100}{Average} \quad (Eq. 4.3-3)$$

The acceptance criteria for inter-instrument comparison at low filter loadings (TC ≤ 10 µg C/cm² and ECR ≤ 2.5 µg C/cm²) are based on the arithmetic difference between the measurement from a given analyzer and the average value for the same PC sample obtained from all analyzers used in each comparison. The acceptance criteria for inter-instrumental check is the same as that for the network sample replicates (See Table 4.3-2 for details). Exceeding the acceptance criteria results in further investigation of the instrument, and reanalysis of the performance check sample. Table 4.3-8 summarizes the statistics of the instrument bias for ECR and TC. There were nine exceedances during this reporting period.

Table 4.3-8: Statistics (median, mean, and standard deviation) of the relative (%) and arithmetic difference values from the weekly inter-instrument comparison analysis of high and low PC filter loadings, respectively. Analysis period covers the dates starting from 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021).

Relative difference (%) for high filter loadings (Acceptance limit: ±10% for TC and ±20% for ECR)								
ECR > 2.5 µg/cm ²					TC > 10 µg/cm ²			
Analyzer	Count	Median	Mean	St. Dev.	Count	Median	Mean	St. Dev.
Alpha	39	-1.55	0.37	9.32	55	0.19	-0.04	2.52
Beta	49	5.04	6	8.27	61	0	-0.42	2.93
Delta	30	-7.59	-6.28	8.76	50	-1.05	-0.26	3.54
Gamma	38	-0.69	0.11	9.12	54	-0.3	0.5	3.14
Zeta	34	-0.54	-1.41	7.9	52	-0.79	-0.29	3.12
Theta	40	3.5	3.14	7.14	54	0.17	0.64	3.11
Arithmetic difference for low filter loadings (Acceptance limit: ±1 µg/cm ² for TC and ±0.5 µg/cm ² for ECR)								
ECR: 0 - 2.5 µg/cm ²					TC: 0 - 10 µg/cm ²			
Analyzer	Count	Median	Mean	St. Dev.	Count	Median	Mean	St. Dev.
Alpha	17	-0.14	-0.09	0.18	1	-0.22	-0.22	NA
Beta	13	0.09	0.12	0.21	1	0.14	0.14	NA
Delta	21	-0.14	-0.16	0.22	1	-0.45	-0.45	NA
Gamma	17	0	-0.01	0.13	1	0.09	0.09	NA
Zeta	19	-0.1	-0.15	0.16	1	-0.14	-0.14	NA
Theta	14	0.06	0.08	0.11	NA	NA	NA	NA

NA: Not available.

4.3.2.7 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 with at least 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 new calibration constant for each analyzer is calculated by taking the ratio of the current constant and the calibration slope. The calibration constant is automatically updated in the database after the calibration is completed. 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 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021).

Analyzer	Calibration Date	Slope	r^2	Calibration Constant
Alpha ³	3/22/2021	0.9734	1.0000	21.2923
Alpha ²	3/7/2022	1.0161	0.9999	20.9787
Alpha ²	7/12/2021	1.0267	1.0000	20.7386
Alpha ³	1/3/2022	0.9863	1.0000	21.3165
Beta ³	3/22/2021	1.0211	1.0000	20.9335
Beta ²	7/12/2021	0.9897	1.0000	21.1514
Beta ²	3/7/2022	1.0075	1.0000	21.1078
Beta ³	1/3/2022	0.9973	1.0000	21.2661
Delta ³	3/22/2021	0.9927	0.9998	21.3599
Delta ²	3/7/2022	0.9951	1.0000	20.9608
Delta ²	7/14/2021	1.0323	0.9997	20.6916
Delta ¹	8/13/2021	1.0061	0.9997	20.5661
Delta ³	1/3/2022	0.9860	0.9999	20.8581
Gamma ³	3/22/2021	1.0055	1.0000	20.3554
Gamma ²	7/14/2021	0.9946	1.0000	20.4659
Gamma ²	3/7/2022	1.0009	1.0000	20.8224
Gamma ³	1/3/2022	0.9819	0.9999	20.8432
Theta ³	3/22/2021	0.9807	0.9995	21.2723
Theta ²	7/12/2021	1.0394	1.0000	20.4659
Theta ²	3/7/2022	1.0304	1.0000	20.7275
Theta ³	1/3/2022	0.9789	0.9999	21.3576
Zeta ³	3/22/2021	1.0273	0.9999	20.5692
Zeta ¹	8/13/2021	1.0444	1.0000	20.7882
Zeta ²	7/12/2021	0.9474	0.9999	21.7112
Zeta ²	3/7/2022	0.9970	1.0000	22.0037
Zeta ³	1/3/2022	0.9476	0.9992	21.9377

¹ Sucrose result is high

² Calibration gas cylinder was replaced on 7/13/2021 and 3/4/2022

³ Semi-annual sucrose calibration

4.3.2.8 *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 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 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 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 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021). 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
Alpha ¹	3/10/2021	No	11	20	21	18	-9	-22
Alpha ²	4/28/2021	Yes	6	9	6	5	-7	-16
Alpha ¹	9/20/2021	No	3	4	-1	-3	-9	-19
Alpha ³	10/06/2021	Yes	-23	-53	-79	-92	-52	-58
Alpha ¹	12/21/2021	No	-27	-52	-61	-66	-21	-31
Beta ¹	3/10/2021	No	14	24	14	11	-16	-32
Beta ³	4/8/2021	Yes	-7	-23	-63	-84	-26	-28
Beta ¹	9/22/2021	No	-23	-49	-72	-88	-38	-34
Beta ²	10/22/2021	Yes	2	14	28	31	7	-4
Beta ¹	12/21/2021	No	-8	-10	-1	4	-3	-16
Gamma ¹	3/10/2021	No	12	24	26	26	-4	-13
Gamma ⁴	6/18/2021	Yes	-16	-36	-61	-82	-26	-26
Gamma ⁵	7/09/2021	Yes	2	-12	-41	-52	-48	-45
Gamma ³	7/12/2021	Yes	11	20	21	18	-9	-22
Gamma ¹	9/20/2021	No	-27	-48	-61	-73	-43	-43
Gamma ³	12/21/2021	Yes	-48	-93	-121	-138	-64	-69
Gamma ⁵	03/08/2022	Yes	-3	-6	5	4	4	-3
Delta ¹	3/10/2021	No	5	11	17	15	6	5
Delta ³	7/12/2021	Yes	-25	-49	-69	-90	-27	-26
Delta ¹	9/21/2021	No	-3	-7	-8	-5	-7	-8
Delta ³	12/22/2021	Yes	8	5	-19	-30	-23	-31
Delta ⁶	03/04/2022	No	26	39	22	8	-8	-18
Zeta ¹	3/10/2021	No	-19	-32	-25	-21	6	-6
Zeta ¹	9/20/2021	No	-12	-21	-10	-10	8	-3
Zeta ¹	12/22/2021	No	-17	-27	-20	-21	11	-2
Theta ¹	03/10/2021	No	30	45	42	37	5	0
Theta ¹	9/20/2021	No	29	38	36	29	3	-1
Theta ¹	12/21/2021	No	29	41	40	35	3	-2
Theta ³	03/03/2022	Yes	8	13	25	23	9	0

¹ Semi-annual temperature calibration

² Alpha's main oven was repositioned on 4/27/2021. Beta main oven was repositioned on 10/21/2021

³ Beta's main oven was replaced on 4/7/2021. Delta's main oven was replaced on 7/9/2021. Gamma's main oven was replaced on 7/12/2021. Alpha's main oven was replaced on 10/4/2021. Gamma changed main oven on 12/20/2021. Delta changed main oven on 12/21/2021. Theta main oven was changed on 3/3/2022

⁴ Gamma's main oven heating coils was replaced on 6/18/2021

⁵ Gamma main oven was repositioned and rewrapped on 7/9/2021. Gamma's main oven was rewrapped on 3/8/2022

⁶ Pushed heating coil on delta

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

4.3.4.2 Performance Evaluations

The UC Davis Thermal Optical Analysis Laboratory did not participate in an inter-laboratory comparison study during this reporting period.

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 Information materials.

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

4.3.5.1 Field Blanks

Over the sampling period (January 1, 2021 through December 31, 2021) there were 1678 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 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021). 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	1,678	0.04	0.07	-0.06	4.00	0.14
EC2	1,678	0.06	0.08	-0.02	0.71	0.09
EC3	1,678	0.00	0.00	-0.06	0.99	0.03
ECR	1,678	0.00	0.00	-0.03	3.09	0.08
ECT	1,678	0.00	0.00	-0.03	2.25	0.06
OC1	1,678	0.16	0.16	-0.01	0.57	0.07
OC2	1,678	0.44	0.47	0.01	4.64	0.21
OC3	1,678	0.66	1.05	0.03	12.64	1.19
OC4	1,678	0.20	0.31	-0.07	4.21	0.32
OCR	1,678	1.65	2.14	-0.03	16.37	1.57
OCT	1,678	1.65	2.14	-0.03	16.37	1.57
OPR	1,678	0.11	0.15	-0.13	1.66	0.19
OPT	1,678	0.11	0.15	-0.13	2.49	0.19

4.3.5.2 Laboratory Blanks Supplied by Wood PLC

Five quartz laboratory blanks are shipped from the Sample Handling Laboratory (Wood PLC) with each batch of routine filters to the analysis laboratory and analyzed. These filters are different than those used for daily QC as described in section 4.3.2.1. These filters are from the same filter lots as the sample filters and are pre-fired by Desert Research Institute (Reno, NV) and delivered to Wood PLC along with the quartz filters to be used for sampling. There are no QC criteria for these laboratory blanks. A total of 60 quartz laboratory blanks were analyzed during the current reporting period, with four runs of analysis per filter using different analyzers for each run. Table 4.1-12 summarizes the laboratory blank statistics.

Table 4.3-12: Quartz filter laboratory blank statistics for the analysis period 3/11/2021 through 4/1/2022 (samples collected 1/1/2021 through 12/31/2021). 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	60	-0.01	-0.01	-0.08	0.25	0.04
EC2	60	0.00	0.01	-0.06	0.34	0.04
EC3	60	0.01	0.01	-0.06	0.31	0.03
ECR	60	0.00	0.00	-0.05	0.31	0.02
ECT	60	0.00	0.01	-0.05	0.54	0.04
OC1	60	0.05	0.05	0.01	0.13	0.02
OC2	60	0.05	0.05	0.00	0.30	0.03
OC3	60	0.07	0.13	0.00	1.31	0.17
OC4	60	-0.01	-0.01	-0.29	0.67	0.09
OCR	60	0.18	0.23	-0.41	2.76	0.34
OCT	60	0.17	0.23	-0.41	2.76	0.34
OPR	60	0.00	0.01	-0.20	0.54	0.09
OPT	60	0.00	0.01	-0.20	0.50	0.08

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, 2021 through December 31, 2021. 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, 2021 through December 31, 2021.

Sampling Month (2021)	Analysis Batch #	Filter Receipt Date	AQS Delivery Date	Days
January	75	March 10, 2021	July 2, 2021	114
February	76	April 7, 2021	August 5, 2021	120
March	77	May 5, 2021	September 2, 2021	120
April	78	June 9, 2021	October 7, 2021	120
May	79	July 14, 2021	November 10, 2021	119
June	80	August 11, 2021	December 9, 2021	120
July	81	September 9, 2021	January 7, 2022	120
August	82	October 6, 2021	February 2, 2022	119
September	83	November 10, 2021	March 10, 2022	120
October	84	December 15, 2021	April 13, 2022	119
November	85	January 12, 2022	May 12, 2022	120
December	86	February 9, 2022	June 9, 2022	120

6. Quality Assurance and Data Validation

6.1 QAPP Revisions

The UC Davis Quality Assurance Project Plan (QAPP) for Laboratory Analysis and Data Processing/Validation for Chemical Speciation of PM_{2.5} Filter Samples is reviewed and updated annually; The last QAPP revision (1.4) was delivered to the EPA for review on July 30, 2021, titled the UC Davis 2021 QAPP, revised again on August 31, 2021, and accepted by the EPA on September 15, 2021. The next draft is currently under revision.

6.2 SOP Revisions

The UC Davis 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 are reviewed and updated annually. The 2022 revisions are currently in process.

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 801E, 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>.

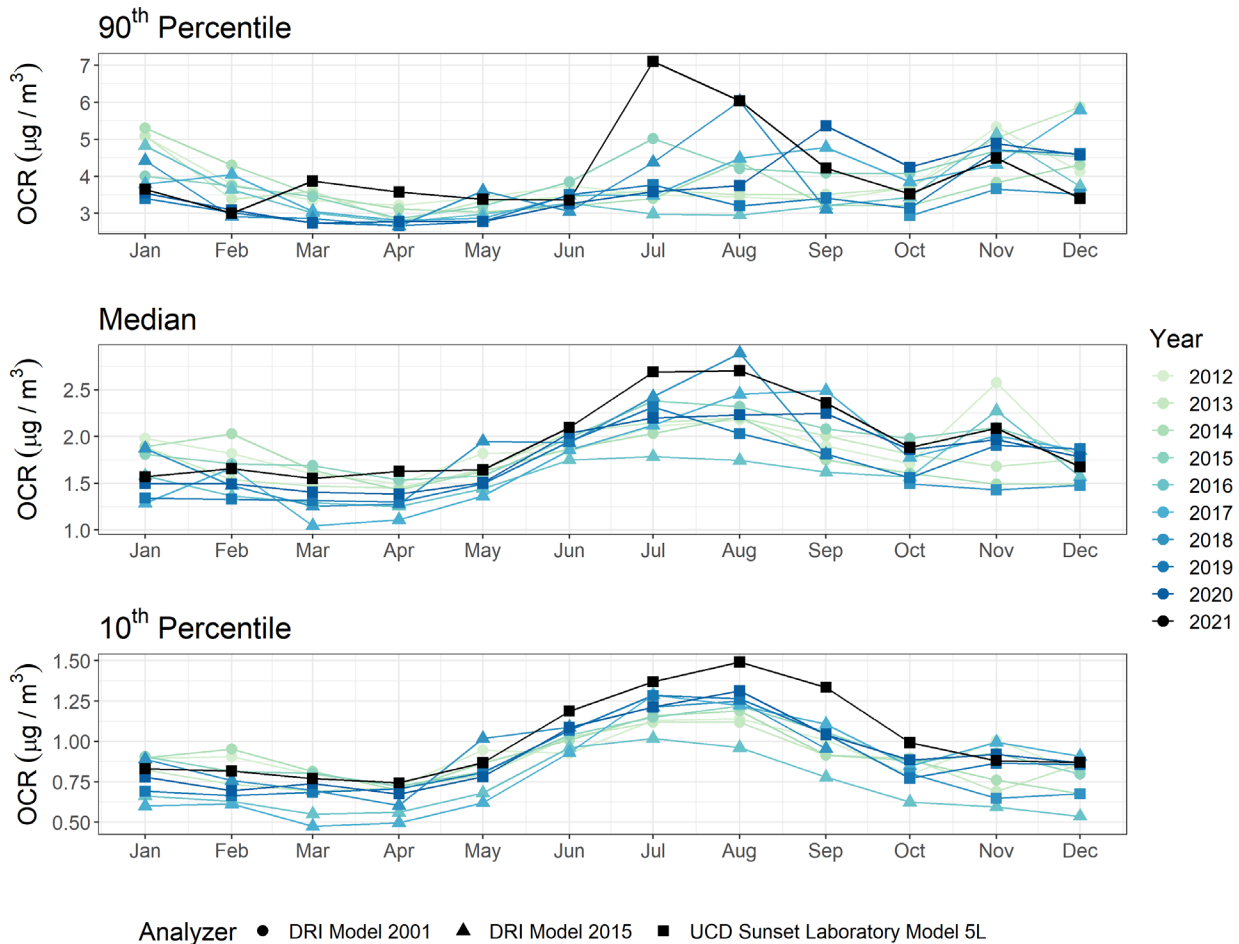
6.4.1 Summary of Monthly Data Validation Review Results

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.

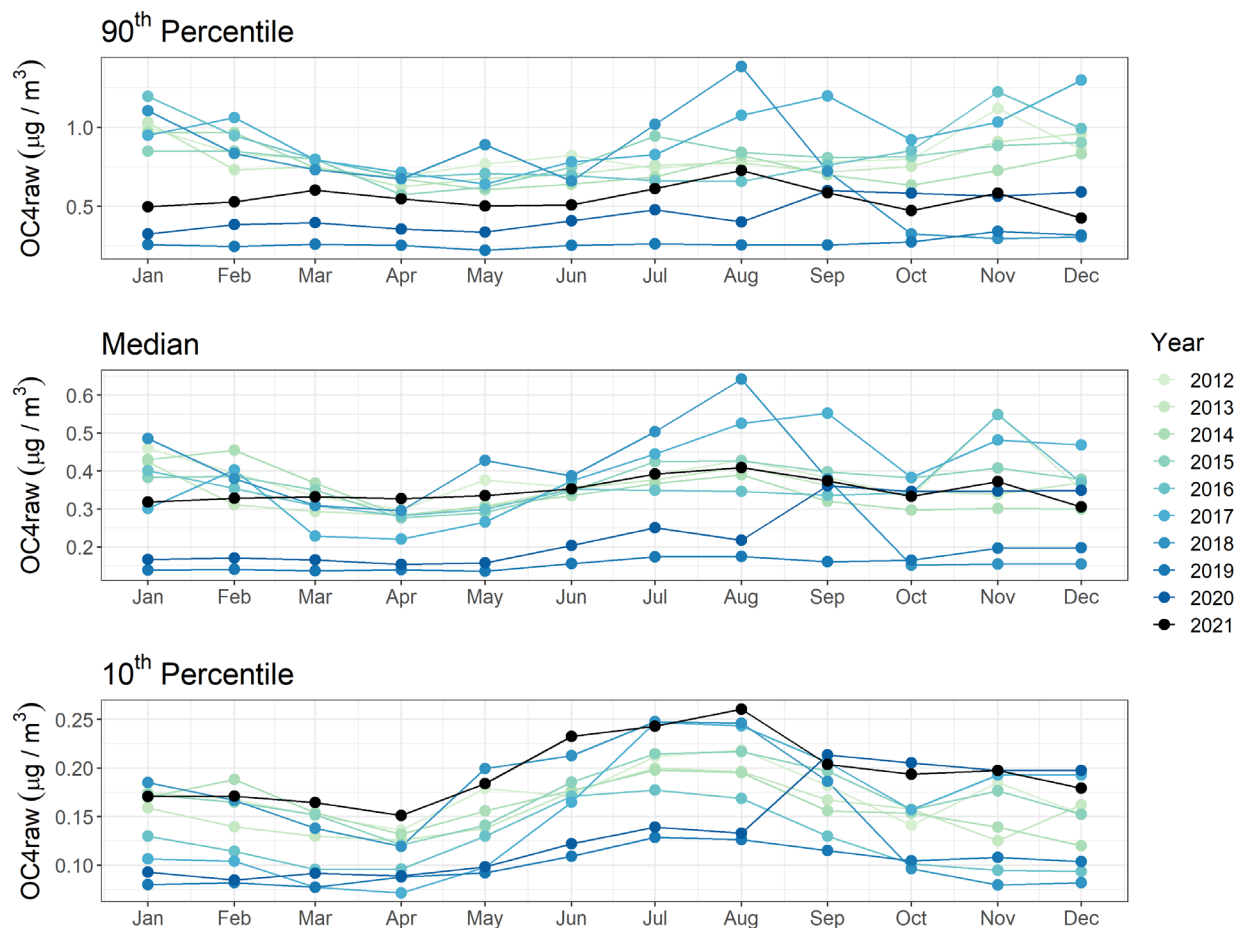
Figure 6.4-1 shows time series for the network-wide 90th percentile, median (50th percentile), and 10th percentile concentrations of organic carbon by reflectance (OCR). This figure shows concentration data without blank correction to enable comparison across a wider timeframe. The carbon fraction OCR is 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).



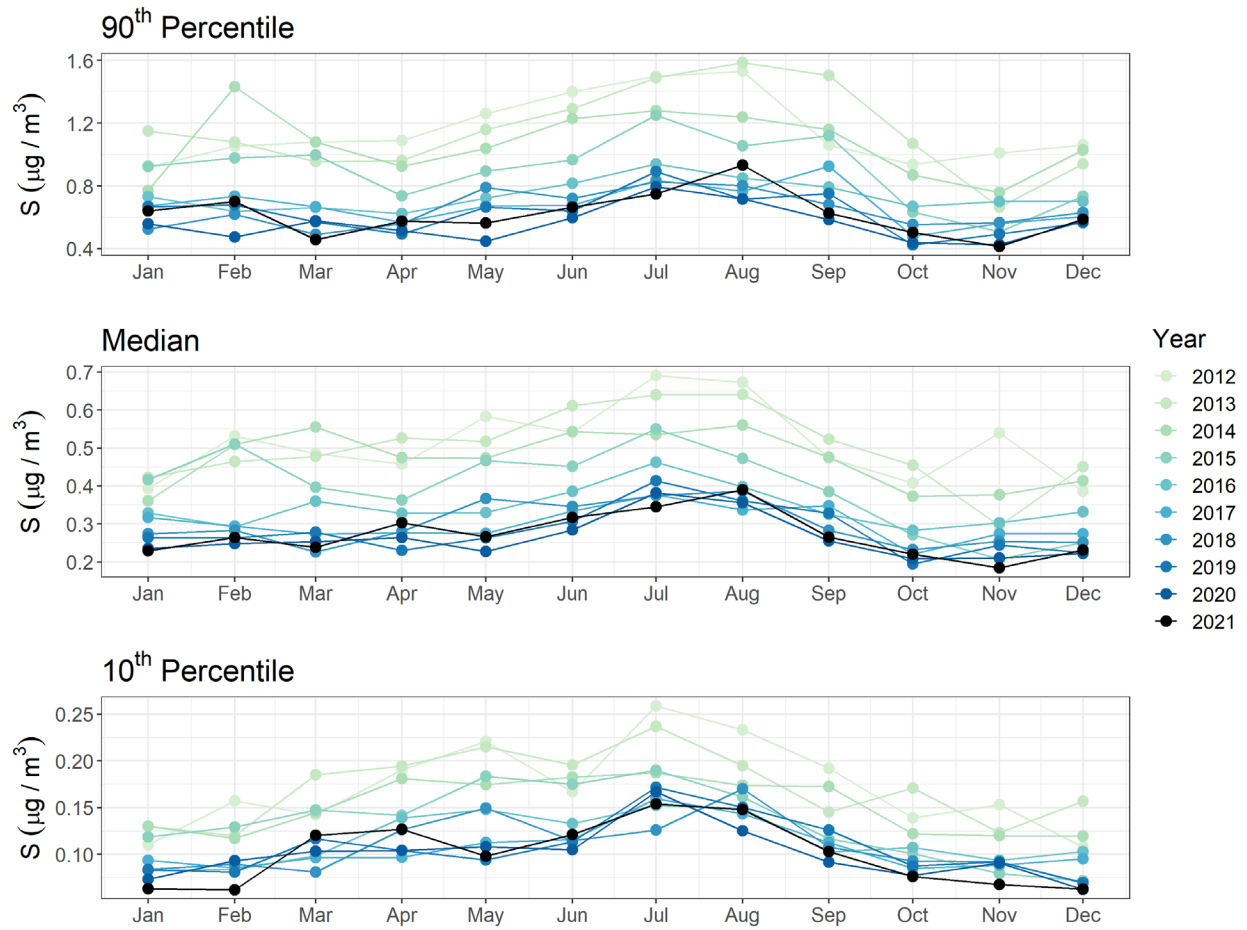
The OC4 plot in Figure 6.4-2 indicates when AQRC changed the OC4 time setting to be 580s for every analysis. This is seen in the 10th percentile plot as a jump in Sept 2020 when the change was implemented. This change allowed analyzers to collect all the OC4 without cutting the analysis short. The change was not as visible in other Carbon fractions.

Figure 6.4-2: Multi-year time series of network-wide OC4 fraction (OC4; raw data without blank correction).



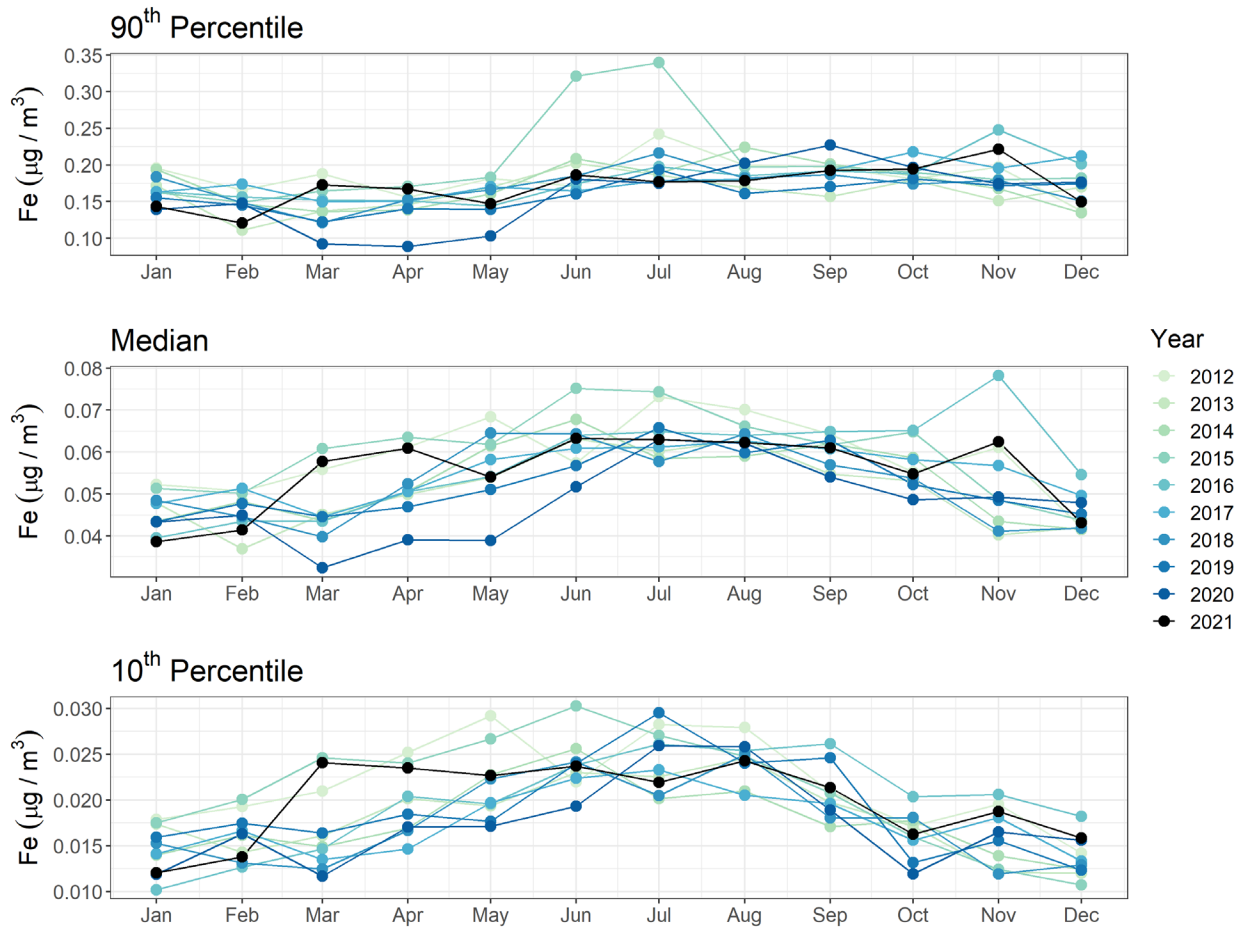
Similar to recent years, the 2021 sulfur concentrations generally continue to be low (Figure 6.4-4), with reduced seasonal variability.

Figure 6.4-3: Multi-year time series of network-wide sulfur (S) concentrations.



The 2020 iron concentrations are similar to previous years with the median peaking in the summer months (Figure 6.4-5). 2020 data showed lower Fe concentrations in the median and 90th percentiles, perhaps as a result of Covid-19 shutdowns. The 2021 data returned to normal and sometimes higher levels could be from lockdowns lifted and levels rose across all 3 plots.

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



Copper 10th, median, and 90th percentile values show a see-saw pattern from June through December 2021 (Figure 6.4-5). This erratic pattern was caused by the blank correction. The median field blank concentration is subtracted from each ambient sample concentration to account for any background contamination inherent in the blank filters themselves or picked up during handling. Figure 6.4-6 shows that the Cu field blank concentrations are not normally distributed and instead show a bifurcated distribution; unfortunately, the medians fall on alternating sides of the distribution in the latter half of 2021, resulting in significantly different blank corrections each month. The ambient concentrations are close to zero (MDL=0.005 $\mu\text{g}/\text{m}^3$), so these changes in blank correction are obvious in the ambient concentrations. This is an artifact in the measurements produced by the blank correction technique.

Figure 6.4-5: Multi-year time series of network-wide copper (Cu) concentrations.

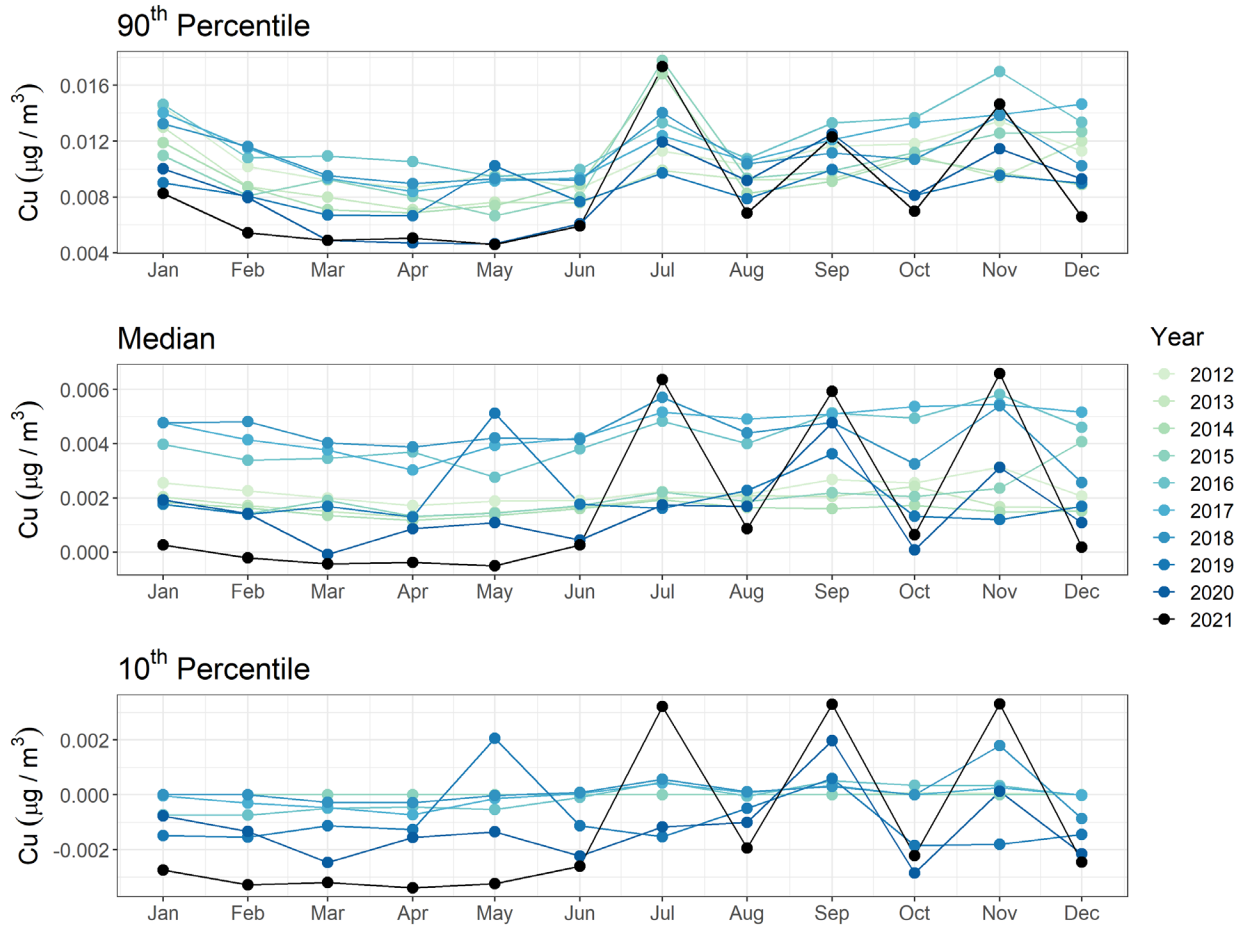
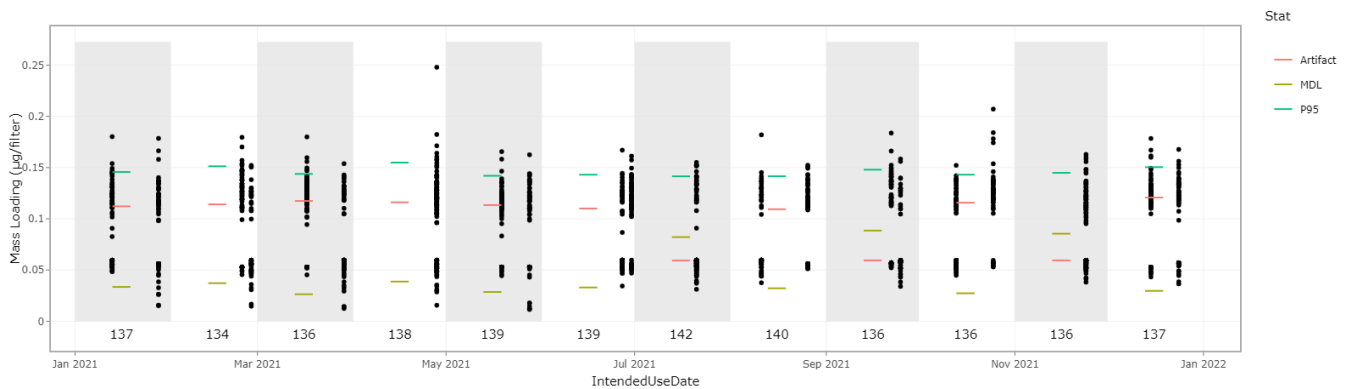
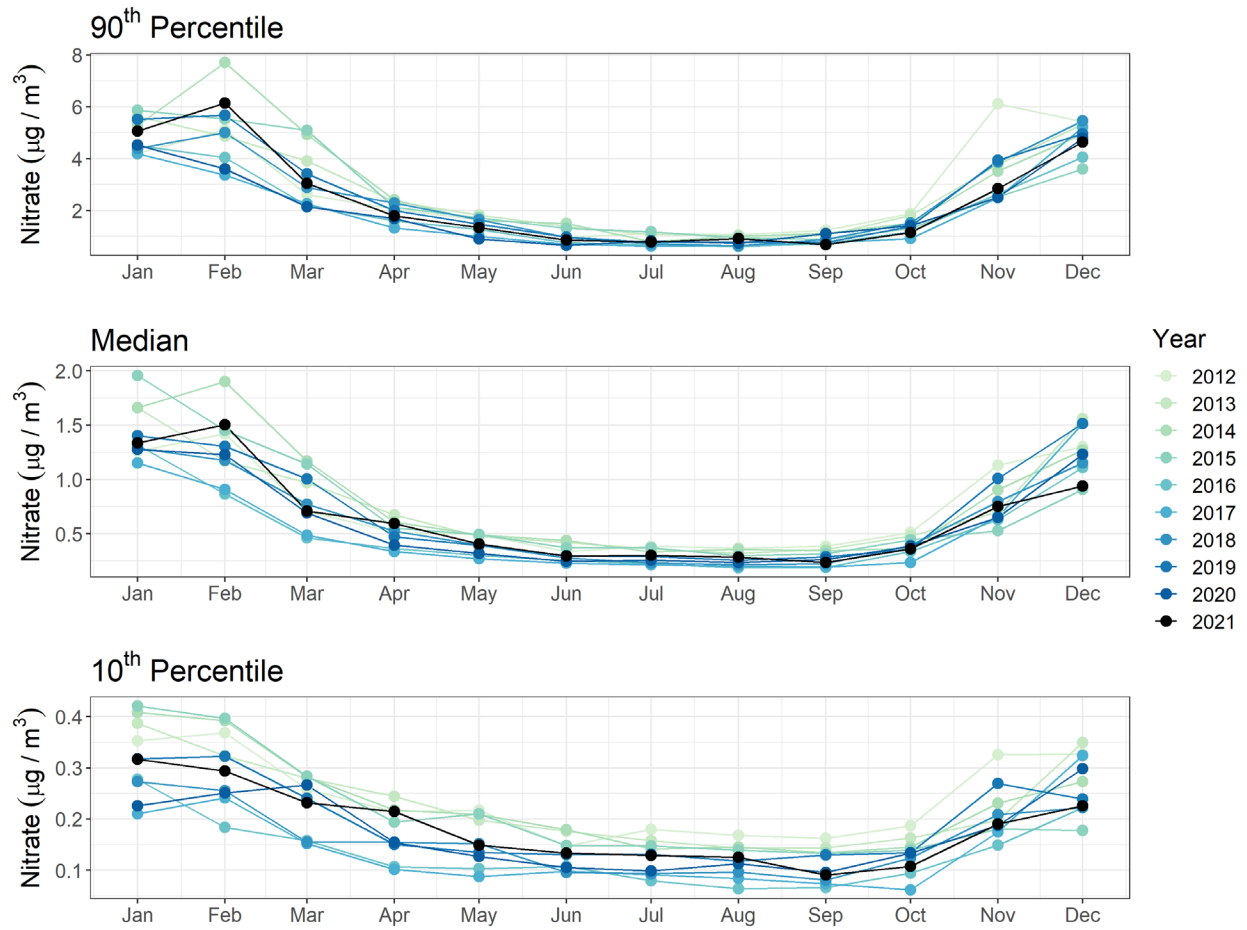


Figure 6.4-6: 2021 Cu Field Blanks.



The 2021 nitrate concentrations continue to show strong seasonality with elevated winter concentrations (Figure 6.4-8).

Figure 6.4-7: Multi-year time series of network-wide nitrate concentrations.



As discussed in Section 3.2.1.4, 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 through 2021 RCM and soil results are shown in Figure 6.4-8 and 6.4-9, respectively.

Figure 6.4-8: Multi-year time series of network-wide composite variable reconstructed mass (RCM) concentrations.

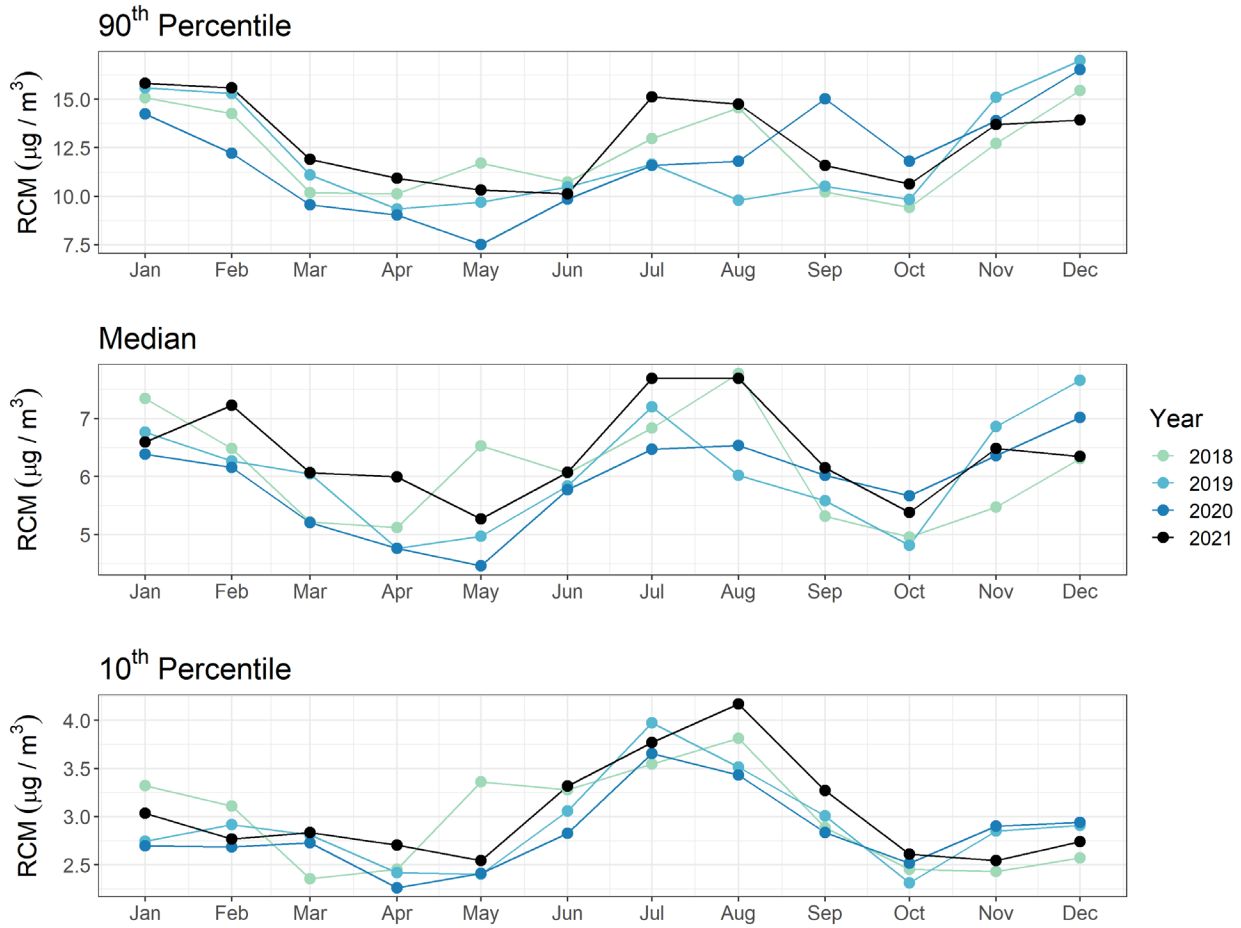
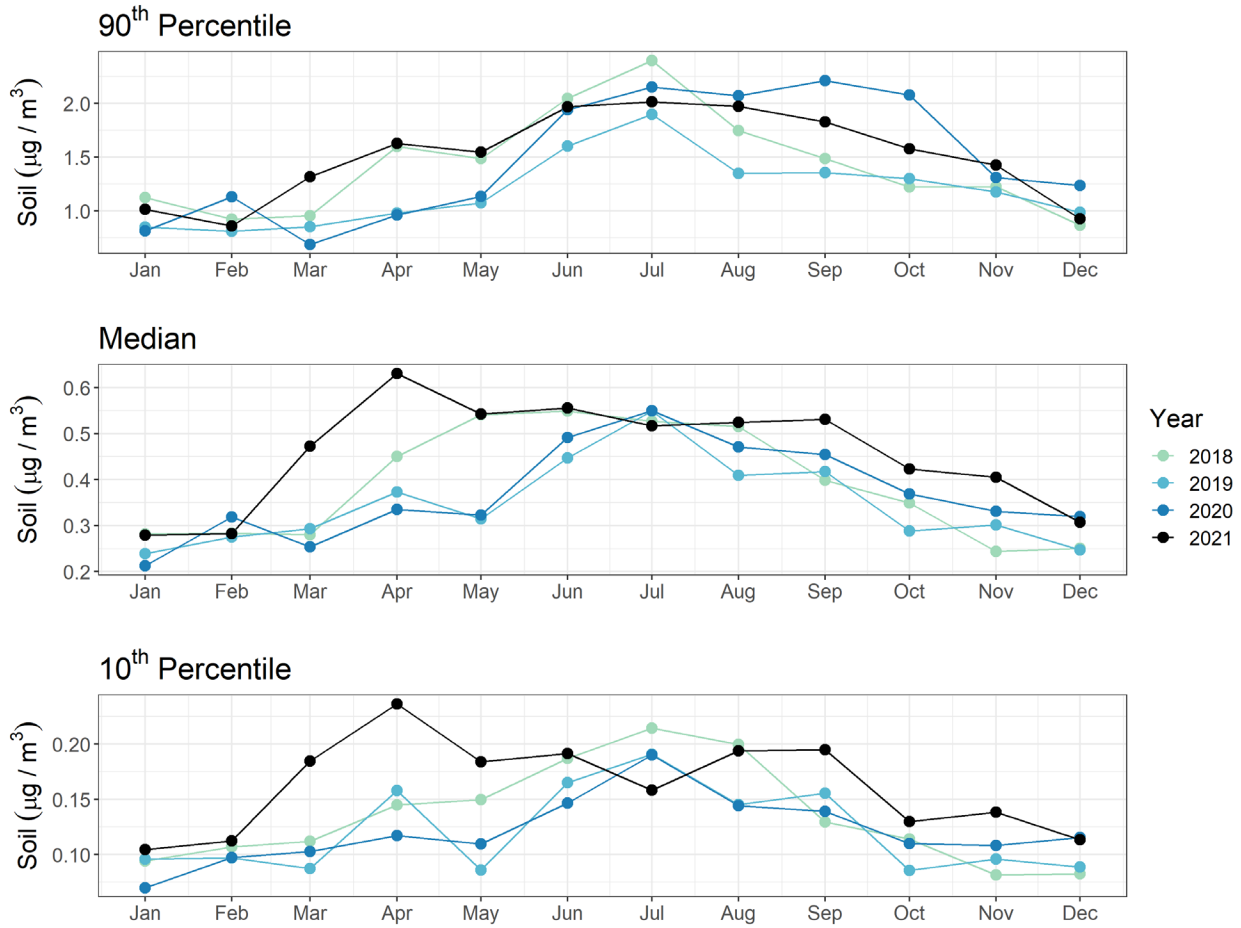


Figure 6.4-9: Multi-year time series of network-wide composite variable soil concentrations.



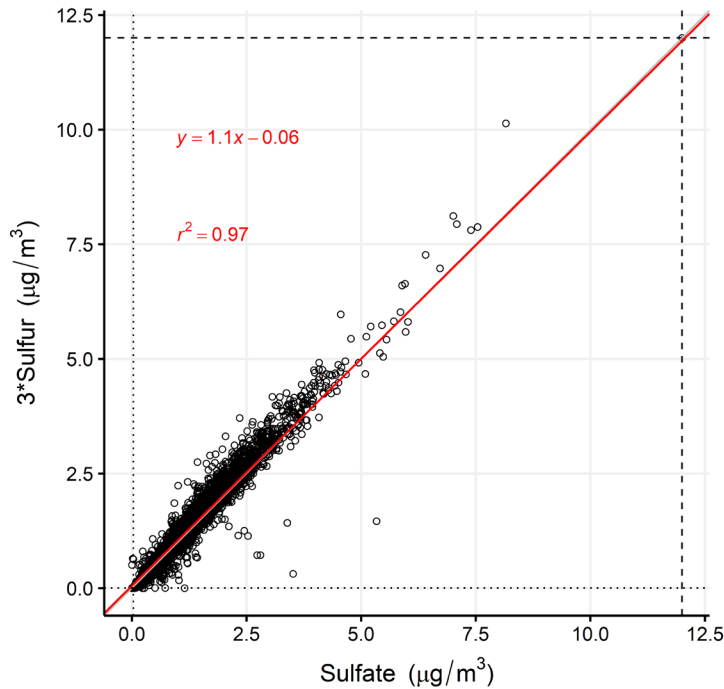
6.4.1.2 Comparisons Between Modules

The following graphs compare two independent measures of aerosol properties that are expected to correlate. These graphs are used to identify cases where the two measurements do not correlate well, which can result from real atmospheric and anthropogenic events or analytical and sampling issues.

6.4.1.3 Sulfur versus Sulfate

PTFE filters are analyzed for elemental sulfur using EDXRF, and nylon filters are analyzed for sulfate (SO_4) using IC. The molecular weight of SO_4 (96 g/mol) is three times the atomic weight of S (32 g/mol), so the concentration ratio $(3 \times \text{S})/\text{SO}_4$ should be one if all particulate sulfur is present as water-soluble sulfate. In practice, real measurements routinely yield a ratio greater than one, as was the case in 2018 and 2019 and is again the case in 2021 (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.

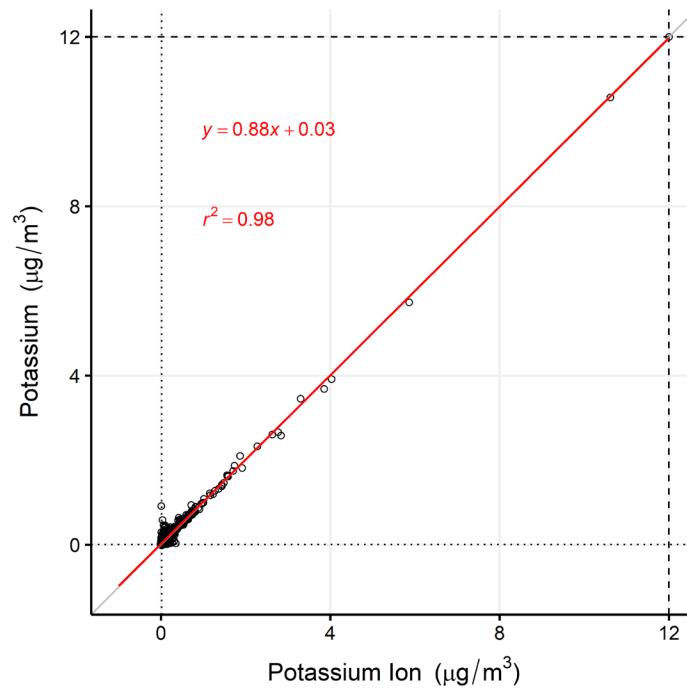
Figure 6.4-8: Scatter plot of $(3 \times \text{S})$ versus SO_4 , samples collected January 1, 2021 through December 31, 2021. Number of observations (complete pairs) is 12,565. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression. Outlier points that are off scale are plotted at the $12 \mu\text{g}/\text{m}^3$ boundaries shown by the dashed lines.



6.4.1.4 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).

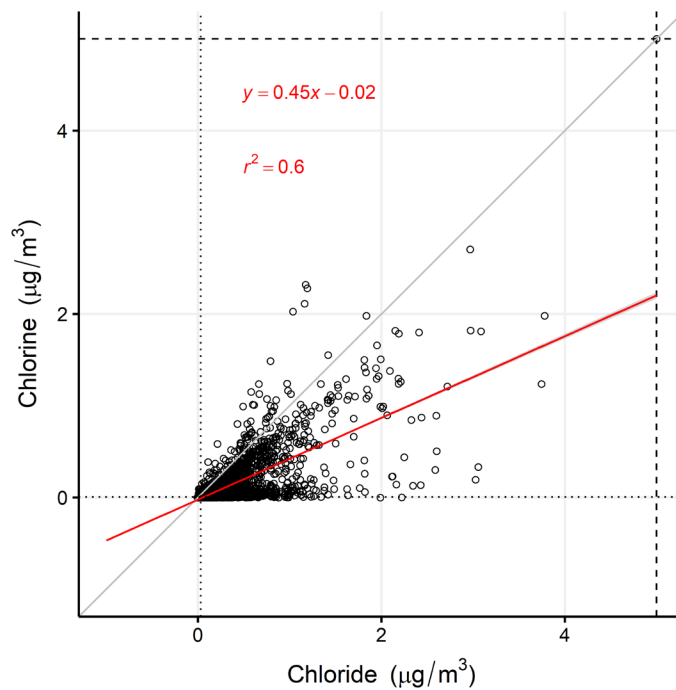
Figure 6.4-10: Scatter plot of potassium versus potassium ion, samples collected January 1, 2021 through December 31, 2021. Number of observations (complete pairs) is 12,566. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression. Outlier points that are off scale are plotted at the 12 µg/m³ boundaries shown by the dashed lines.



6.4.1.5 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 6.4-11: Scatter plot of chlorine versus chloride ion, samples collected January 1, 2021 through December 31, 2021. Number of observations (complete pairs) is 12,551. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression. Outlier points that are off scale are plotted at the 5 $\mu\text{g}/\text{m}^3$ boundaries shown by the dashed lines.



6.4.1.6 *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:

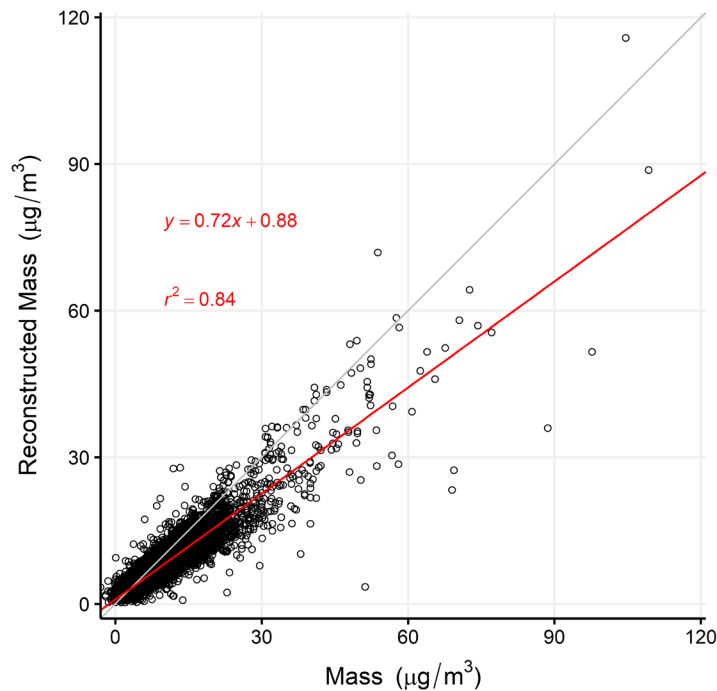
$$\text{RCM} = (4.125 \times \text{S}) + (1.29 \times \text{NO}_3^-) + (1.4 \times \text{OC}) + (\text{EC}) + \\ (2.2 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} + 2.42 \times \text{Fe} + 1.94 \times \text{Ti}) + (1.8 \times \text{chloride})$$

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 $\text{PM}_{2.5}$ 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 6.4-12: Scatter plot of reconstructed mass (RCM) versus AirNow Tech $\text{PM}_{2.5}$ mass data (Mass), samples collected January 1, 2021 through December 31, 2021. Number of observations (complete pairs) is 9,220. Solid gray line indicates 1:1. Solid red line indicates regression.



6.5 Uncertainty Estimates and Collocated Precision Summary Statistics

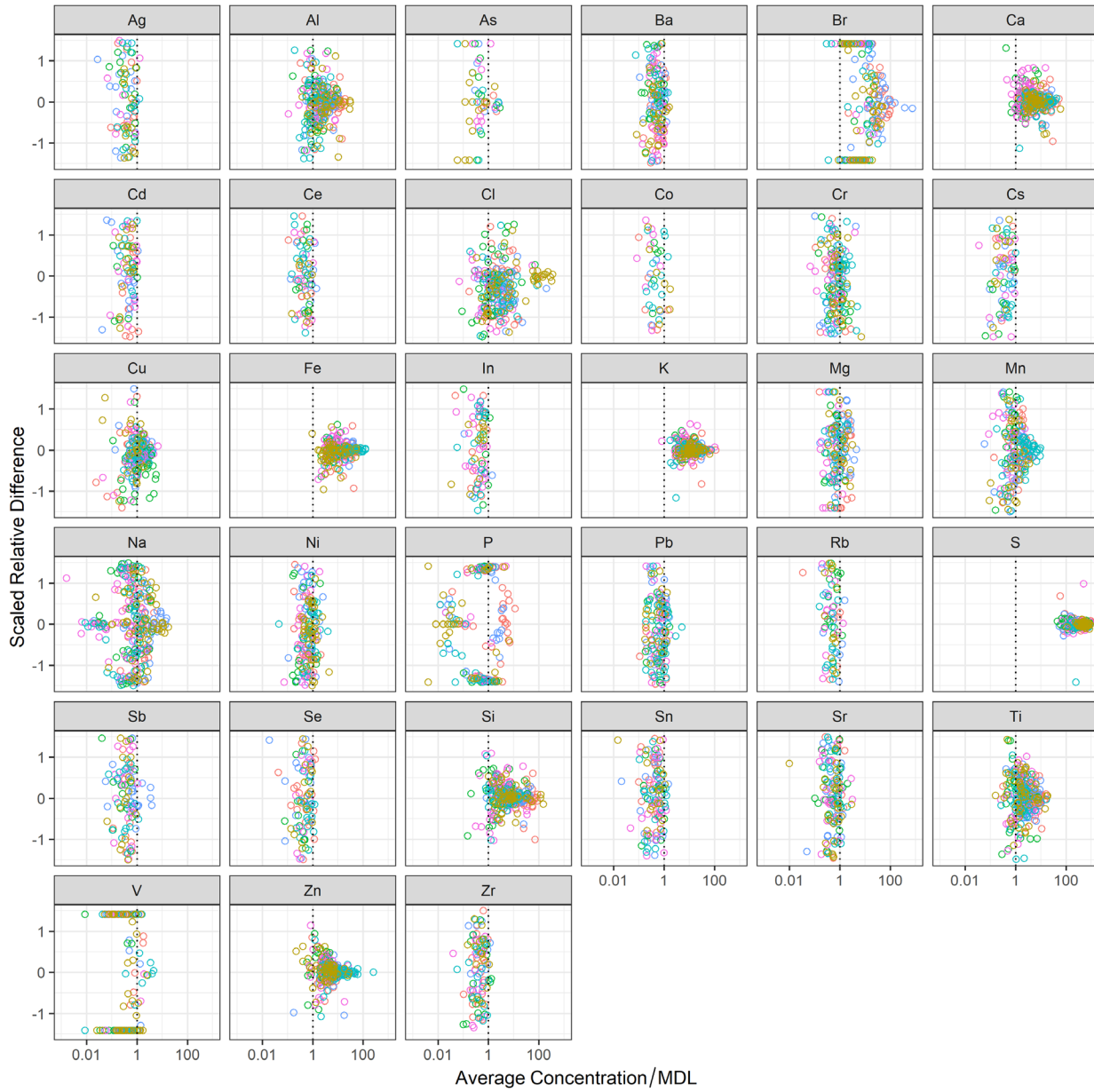
Several network sites are equipped with collocated samplers, where simultaneous samples are collected on independent samplers and analyzed using the same analytical protocols. Differences between the resulting data provide a measure of the total uncertainty associated with filter substrates, sampling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

Figure 6.5-1: Scaled relative differences for element measurements at sites with collocated samplers across the network (January 1, 2020 through December 31, 2021). Dotted vertical lines indicate MDL.



- | | |
|--|--------------------------------------|
| ○ Bakersfield - California Ave. (06-029-0014) | ○ G.T. Craig (39-035-0060) |
| ○ Deer Park (48-201-1039) | ○ Riverside - Rubidoux (06-065-8001) |
| ○ Dudley Square - Roxbury (Boston) (25-025-0042) | ○ Rutgers (34-023-0011) |

Figure 6.5-2: Scaled relative differences for ion measurements at sites with collocated samplers across the network (January 1, 2020 through December 31, 2021). Dotted vertical lines indicate MDL.

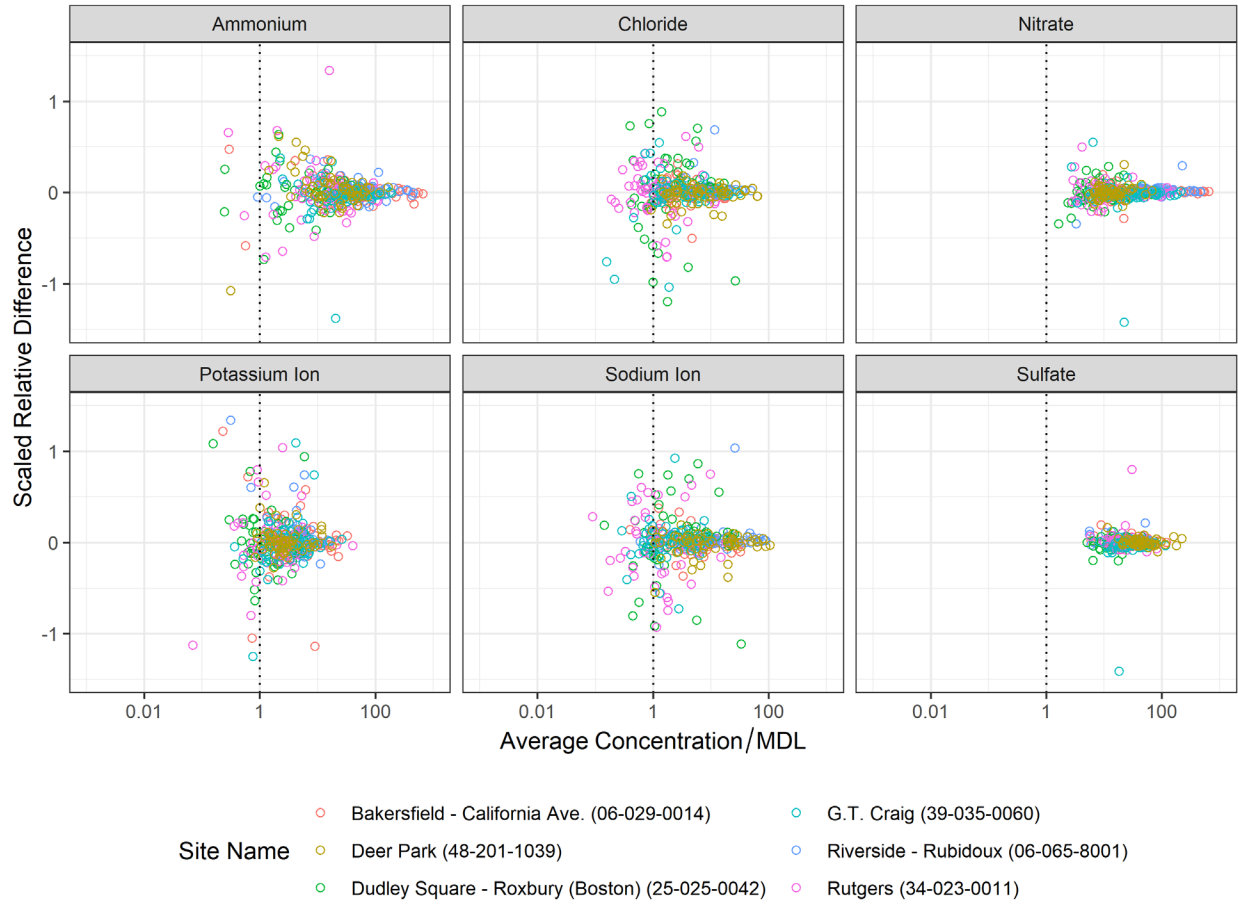
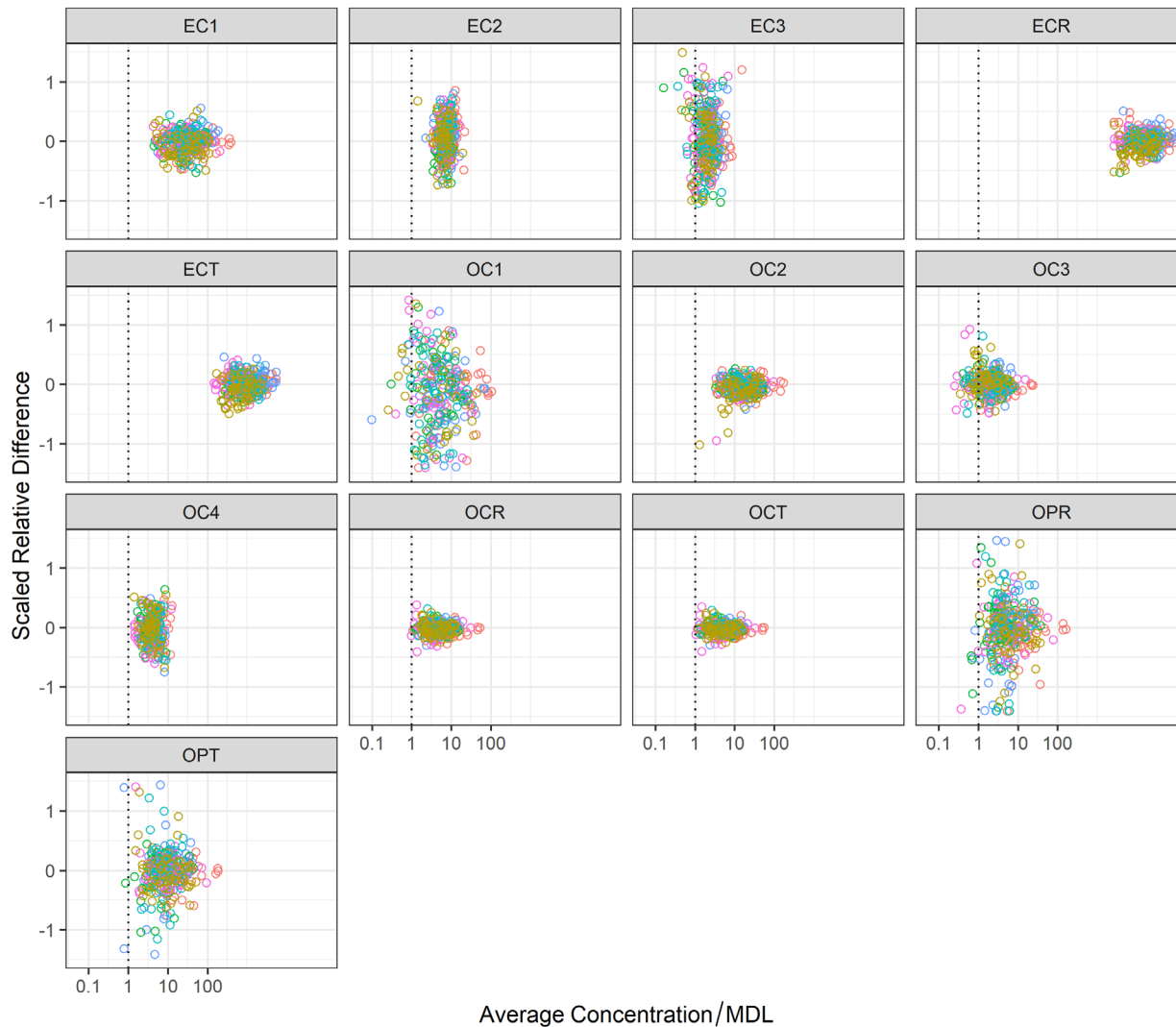


Figure 6.5-3: Scaled relative differences for carbon measurements at sites with collocated samplers across the network (January 1, 2020 through December 31, 2021). Dotted vertical lines indicate MDL. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).



Site

- Bakersfield - California Ave. (06-029-0014)
- Deer Park (48-201-1039)
- Dudley Square - Roxbury (Boston) (25-025-0042)
- G.T. Craig (39-035-0060)
- Riverside - Rubidoux (06-065-8001)
- Rutgers (34-023-0011)

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, 2021 through December 31, 2021) the

fractional uncertainty is calculated from sample pairs collected at CSN collocated sites June 1, 2018 through May 31, 2020, 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 (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.

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

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 (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.

Using the methodology as shown in Rice and Landis (2016), CV is calculated as the median (P_{50th}) relative percent difference (RPD) from sample pairs (i) collected at collocated sites, using the subset of observations with concentrations at least three times the MDL, as shown in Equation 6.5-4 and Equation 6.5-5.

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

$$CV = P_{50th} \left(\frac{|RPD_i|}{\sqrt{2}} \right) \quad (\text{Eq. 6.5-5})$$

where X_i and Y_i are the measurements from routine and collocated sites, respectively, for the i^{th} pair of measurements.

Using the methodology in the Code of Federal Regulations (CFR) Appendix A to Part 58 – Quality Assurance Requirements for Monitors used in Evaluations of National Ambient Air Quality Standards (available at https://www.law.cornell.edu/cfr/text/40/appendix-A_to_part_58), precision is estimated from duplicate measurements from collocated samplers. Here, only the subset of observations with concentrations at least three times the MDL are used. For each

collocated pair, the relative percent difference is calculated using Equation 6.5-4. The CV upper bound is calculated using Equation 6.5-6:

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^n RPD_i^2 - (\sum_{i=1}^n RPD_i)^2}{2n(n-1)}} \times \sqrt{\frac{n-1}{X_{0.1, n-1}^2}} \quad (\text{Eq. 6.5-6})$$

Where n is the number of valid data pairs being aggregated, and $X_{0.1, n-1}^2$ is the 10th percentile of a chi-squared distribution with $n-1$ degrees of freedom. The factor of 2 in the denominator adjusts for the fact that each RPD_i is calculated from two values with error.

Table 6.5-1 (elements), Table 6.5-2 (ions), and Table 6.5-3 (carbon) list median CV calculated using Equations 6.5-4 and 6.5-5 from collocated samples collected during 2021 (current reporting period) as well as 2020 (previous reporting period). The CFR CV calculated using Equations 6.5-4 and 6.5-6 from collocated samples collected during 2021 (current reporting period) and 2020 (previous reporting period) is also included.

Table 6.5-1: Fractional uncertainty (f), median coefficient of variation (CV), and CFR coefficient of variation (CFR CV) for element species. For the previous reporting period, f is calculated from samples collected June 1, 2017 through May 31, 2019 and used in relevant calculations for samples between January 1, 2020 through December 31, 2020 and CV is calculated from samples collected January 1, 2020 through December 31, 2020. For the current reporting period, f is calculated from samples collected June 1, 2018 through May 31, 2020 and used in relevant calculations for samples between January 1, 2021 through December 31, 2021 and CV is calculated from samples collected January 1, 2021 through December 31, 2021. 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; the adopted value of 25% for f are shown in the table.

Species	2020 (previous reporting period)						2021 (previous reporting period)					
	f (%)	Pairs	CV (%)	Pairs	CFR CV (%)	Pairs	f (%)	Pairs	CV (%)	Pairs	CFR CV (%)	Pairs
Na	17.6	68	---	25	---	25	18.8	67	---	32	---	32
Mg	25.0	10	---	4	---	4	25.0	8	---	2	---	2
Al	15.3	91	---	58	---	58	17.4	89	12.0	95	26.8	95
Si	14.2	329	9.8	170	24.6	170	14.5	327	7.0	241	20.2	241
P	25.0	7	---	15	---	15	25.0	3	---	12	53.5	12
S	5.7	654	3.0	292	8.7	292	5.4	658	3.5	353	7.7	353
Cl	35.1	179	25.5	85	43.3	85	32.9	173	19.8	85	39.4	85
K	8.4	567	5.0	271	10.8	271	8.2	595	5.3	340	13.2	340
Ca	13.4	263	6.9	174	23.8	174	13.6	371	7.9	247	21.2	247
Ti	15.5	98	8.0	62	16.6	62	15.5	86	10.7	101	24.1	101
V	25.0	0	---	1	---	1	25.0	0	---	3	---	3
Cr	25.0	1	---	0	---	0	25.0	0	---	0	---	0
Mn	25.0	16	---	19	---	19	25.0	19	---	21	---	21
Fe	13.2	328	6.1	237	16.6	237	11.8	386	5.9	319	16.7	319
Co	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Ni	25.0	0	---	0	---	0	25.0	0	---	1	---	1
Cu	25.0	6	---	17	---	17	25.0	6	---	18	---	18
Zn	9.8	245	6.2	223	16.7	223	10.0	281	8.6	260	16.2	260
As	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Se	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Br	25.0	1	35.6	70	57.6	70	25.0	23	34.6	91	55.1	91
Rb	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Sr	25.0	0	---	1	---	1	25.0	0	---	0	---	0
Zr	-25.0	0	---	0	---	0	25.0	0	---	0	---	0
Ag	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Cd	25.0	0	---	0	---	0	25.0	0	---	0	---	0
In	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Sn	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Sb	25.0	0	---	0	---	0	25.0	0	---	2	---	2
Cs	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Ba	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Ce	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Pb	25.0	0	---	0	---	0	25.0	0	---	1	---	1

Table 6.5-2: Fractional uncertainty (f), median coefficient of variation (CV), and CFR coefficient of variation for ion species. For the previous reporting period, f is calculated from samples collected June 1, 2017 through May 31, 2019 and used in relevant calculations for samples between January 1, 2020 through December 31, 2020 and CV is calculated from samples collected January 1, 2020 through December 31, 2020. For the current reporting period, f is calculated from samples collected June 1, 2018 through May 31, 2020 and used in relevant calculations for samples between January 1, 2021 through December 31, 2021 and CV is calculated from samples collected January 1, 2021 through December 31, 2021. 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; the adopted value of 25% for f are shown in the table.

Species	2020 (previous reporting period)						2021 (current reporting period)					
	f (%)	Pairs	CV (%)	Pairs	CFR CV (%)	Pairs	f (%)	Pairs	CV (%)	Pairs	CFR CV (%)	Pairs
Ammonium	15.9	591	4.6	263	14.0	263	10.8	626	4.9	309	12.5	309
Chloride	11.4	403	5.4	173	17.5	173	10.1	432	4.0	219	14.9	219
Nitrate	7.9	628	3.1	284	13.4	284	5.5	636	2.9	342	8.1	342
Potassium Ion	25.0	11	7.7	126	16.8	126	25.0	38	5.8	153	14.6	153
Sodium Ion	14.1	411	5.0	163	19.2	163	11.1	414	4.0	188	16.8	188
Sulfate	5.8	654	2.9	292	11.2	292	4.1	656	2.1	352	4.8	352

Table 6.5-3: Fractional uncertainty (f), median coefficient of variation (CV), and CFR coefficient of variation for carbon species. For previous reporting period, f is calculated from samples collected June 1, 2017 - May 31, 2019 and used in relevant calculations for samples between January 1, 2020 - December 31, 2020 and CV is calculated from samples collected January 1, 2020 - December 31, 2020. For the current reporting period, f is calculated from samples collected June 1, 2018 - May 31, 2020 and used in relevant calculations for samples between January 1, 2021 - December 31, 2021 and CV is calculated from samples collected January 1, 2021 - December 31, 2021. 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; the adopted value of 25% for f are shown in the table. 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	2020 (previous reporting period)						2021 (current reporting period)					
	f (%)	Pairs	CV (%)	Pairs	CFR CV (%)	Pairs	f (%)	Pairs	CV (%)	Pairs	CFR CV (%)	Pairs
Elemental Carbon (EC1)	12.1	653	7.9	292	17.7	292	9.5	643	10.5	336	18.9	336
Elemental Carbon (EC2)	27.4	509	13.1	243	22.7	243	20.6	535	20.4	322	31.0	322
Elemental Carbon (EC3)	25.0	18	---	32	---	32	23.9	78	---	40	---	40
Elemental Carbon (ECR)	13.5	650	6.5	293	14.3	293	11.0	644	7.7	336	15.2	336
Elemental Carbon (ECT)	15.4	649	8.0	294	15.6	294	12.5	644	9.8	336	16.3	336
Organic Carbon (OC1)	32.5	399	24.1	124	40.5	124	33.5	290	23.4	155	41.4	155
Organic Carbon (OC2)	11.6	643	7.9	286	18.5	286	12.8	620	8.1	331	12.7	331
Organic Carbon (OC3)	12.2	530	---	34	---	34	10.9	312	7.0	115	11.8	115
Organic Carbon (OC4)	19.1	461	12.7	101	27.5	101	19.2	176	13.1	246	24.4	246
Organic Carbon (OCR)	8.5	614	5.7	141	8.8	141	7.5	469	5.4	247	9.3	247
Organic Carbon (OCT)	7.4	619	4.9	154	8.1	154	6.4	484	4.7	260	8.4	260
Organic Pyrolyzed (OPR)	23.7	421	15.7	183	24.3	183	17.2	437	15.8	210	30.3	210
Organic Pyrolyzed (OPT)	20.1	597	9.6	238	21.5	238	13.2	560	13.6	291	27.7	291

7. References

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