Chemical Speciation Network (CSN)
Annual Quality Report

Samples Collected January 1, 2022 through December 31, 2022

Prepared for:
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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 and hybrid integrating plate/sphere (HIPS) for filter absorption.
- 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, 2022 through December 31, 2022 (batches 87-98, 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), Section 4.3 (UC Davis Thermal Optical Analysis Laboratory), and Section 4.4 (UC Davis Optical Absorption Laboratory).

Across the network, completeness — determined by the total number of valid samples relative to the total number of scheduled samples — was 92.5% for PTFE filters, 92.5% for nylon filters, and 90.3% 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 2022 data reporting period.

2. Summary of Laboratory Operation Issues

This section of the report covers operational issues for each measurement processes. These are high-level challenges or major changes to the labs. Specific quality incidents or failures will be discussed in Section 3.2 of the report.

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 Purchase of New Bruker S2-Puma EDXRF Instruments

During the previous 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 are undergoing extensive testing and qualification to ensure they are fit for use before starting any network sample analysis. That process is still ongoing and is expected to deploy in sampling year 2024.

2.3 UC Davis Thermal Optical Analysis Laboratory

During this reporting period (2022) there were no issues with Thermal Optical Analysis.

During the 2023 sample year, AQRC evaluated two new Thermal Optical Analysis. One was a new instrument for TC measurements made by Analytik Jena. This instrument failed to meet our quality control requirements and was returned to the manufacturer.

The other is an autoloader sold by Sunset for the 5L instruments used by AQRC. The autoloader is undergoing testing on one instrument to decide if it will be used permanently. AQRC has a number of quality control tests as well as operational and performance requirements to pass before the autoloader will pass qualification.

2.4 UC Davis Optical Absorption Laboratory

2.4.1 Instrument Stability Enhancement

Prior to and since moving the HIPS instrument from Jungerman Hall to the new laboratory space at 1560 Drew Ave., the instrument experienced multiple calibration shifts which were traced back to mechanical instability of the mounting system. The HIPS system has four main components (laser, integrating sphere, sample chamber, and integrating plate) that were all mounted on a linear, optical rail system. This creates the issue of the long laser housing not being rigidly attached to the integrating sphere which left it vulnerable to misalignment.

The system was modified to include a fiber-optic cable to transmit laser light from the laser to the integrating sphere. This modification allowed the components to be mounted on an optical breadboard with more modern and sturdier mounts. Additionally, decoupling the laser mechanically from the integrating sphere and mounting the fiber-optic cable directly to the sphere significantly reduced the mechanical instability of the optical path. To focus the laser light from the fiber-optic onto the sample filter, a fixed focal length silvered mirror collimator was used.

This new fiber-optic system and the new mounting were completed and put into use on July 15, 2022. All sampling months except January were analyzed with this modified system.

2.4.2 Collimator Replacement

When the HIPS instrument was switched to the fiber-optical configuration described above, the optical characteristics of the light on the filters changed. A shift of the overall reflectance signal to higher values was noted. While the instrument calibrations accommodated this shift in reflectance and did not affect the HIPS results, it was decided that returning the optical properties to something similar to before the fiber-optics were installed would reduce complication in long-term data comparisons and trend monitoring. Therefore, the fixed focal length mirror collimator was replaced with a focusing lens collimator and the laser spot size incident on the sample was tuned to match the pre-fiber-optic spot size. This resulted in the optical characteristics of the system returning to similar values of the pre-fiber-optic setup.

The new focusing lens collimator was installed and put into service after testing on April 12, 2023. This was after all batches of samples for this report were analyzed, but a few reanalyses, as requested by level 1 validation, were performed with the new collimator.

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.

In Table 3.1-1 below, 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.

Table 3.1-1: Network sample completeness by filter type, January 1, 2022 through December 31, 2022.

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	13,396	12,938	12,391	547	95.8	92.5
Nylon	13,396	12,938	12,397	541	95.8	92.5
Quartz	13,396	12,921	12,092	829	93.6	90.3

Across the network there were seven 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, 2022 through December 31, 2022.

In table 3.1-2 below, the calculation is relative to the number of collected samples and determined for null codes applied at the filter level. 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.

Table 3.1-2: Network sites with less than 75% sample completeness for at least one filter type, January 1, 2022 through December 31, 2022.

AQS ID #	Location	Completeness			Null Codes		
		PTFE	Nylon	Quartz	PTFE	Nylon	Quartz
01-113-0003-5	Phenix City - S. Girard School, AL	69.5%	69.5%	100%	BA (89%) Other (11%)	BA (89%) Other (11%)	---
18-089-0022-5	Gary, IN	95.1%	95.1%	62.3%	AF (33.3%) AG (33.3%) AN (33.3%)	AF (33.3%) AG (33.3%) AN (33.3%)	AH (83%) Other (17%)
28-049-0020-5	Jackson NCore, MS	99.2%	98.4%	33.6%	AG (100%)	AG (50%) AH (50%)	AH (48%) AN (27%) Other (25%)
32-003-0540-5	Jerome Mack Middle School, NV	97.5%	98.4%	67.2%	AN (66.7%) AR (33.3%)	AN (100%)	AH (93%) AV (5%) AP (2%)
37-067-0022-5	Winston-Salem – Hattie Ave., NC	93.4%	98.4%	72.1%	AH (50%) AL (25%) AN (25%)	AL (100%)	AH (76%) BA (12%) Other (12%
37-119-0041-5	Garinger High School, NC	98.4%	98.4%	73.8%	AV (100%)	AV (100%)	AN (75%) AH (13%) Other (12%)
39-081-0017-5	Steubenville, OH	72.1%	73.8%	93.4%	AH (88%) AN (12%)	AH (88%) AN (12%)	AH (75%) AG (25%)

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, 2022 through December 31, 2022. Codes are ordered by frequency of occurrence.

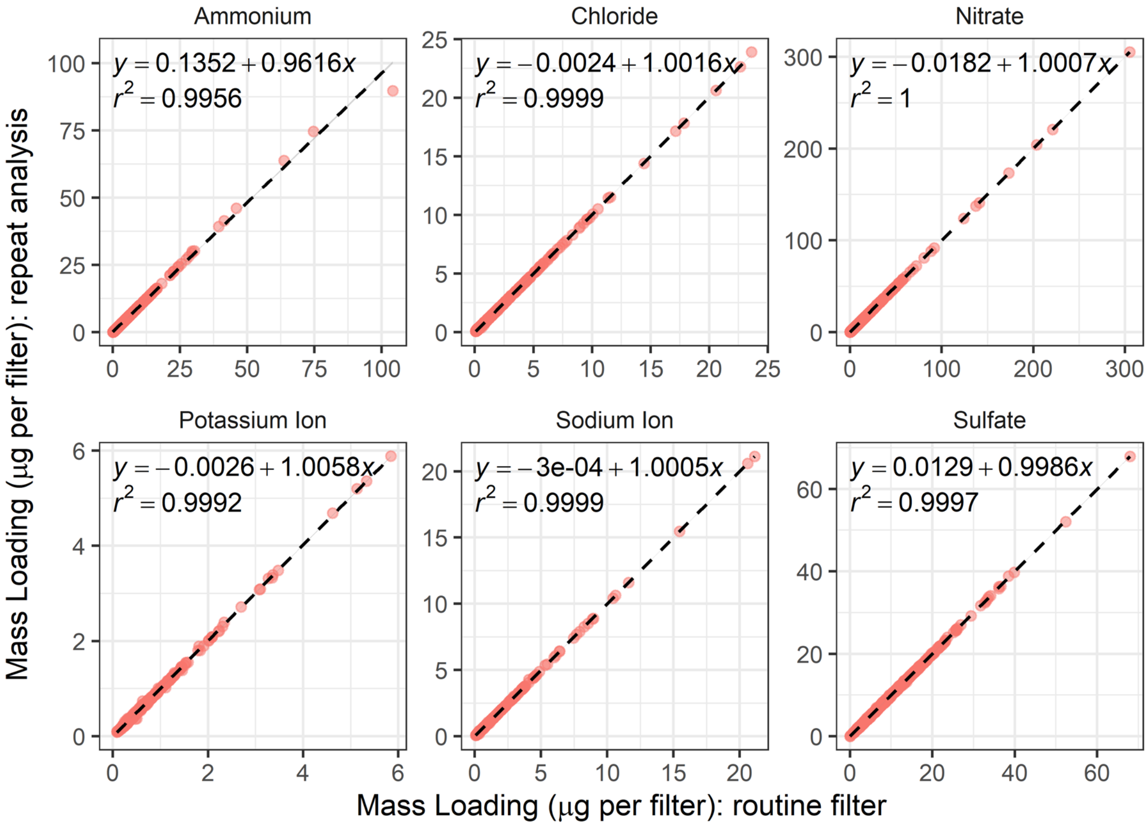
Null Code	SASS PTFE	SASS Nylon	URG Quartz	Total	Null Code Description
AH	114	99	267	480	Sample Flow Rate or CV out of Limits
AN	115	116	202	433	Machine Malfunction
AF	65	66	49	180	Scheduled but not Collected
AV	46	46	77	169	Power Failure
BJ	53	51	29	133	Operator Error
AB	26	26	24	76	Technician Unavailable
BA	20	20	32	72	Maintenance/Routine Repairs
AG	14	14	22	50	Sample Time out of Limits
AO	14	14	17	45	Bad Weather
BI	14	15	15	44	Lost or damaged in transit
AQ	15	23	5	43	Collection Error
BE	9	9	10	28	Building/Site Repair
AK	0	0	23	23	Filter Leak
AD	7	7	9	23	Shelter Storm Damage
AJ	7	7	5	19	Filter Damage
AL	6	6	6	18	Voided by Operator
AR	5	5	8	18	Lab Error
BB	5	5	7	17	Unable to Reach Site
SV	1	2	11	14	Sample Volume Out of Limits
AP	4	4	3	11	Vandalism
AZ	2	2	1	5	Q C Audit
AC	1	1	2	4	Construction/Repairs in Area
AW	2	1	1	4	Wildlife Damage
AI	1	1	1	3	Insufficient Data (cannot calculate)
AS	0	0	3	3	Poor Quality Assurance Results
DA	1	1	0	2	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)

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.

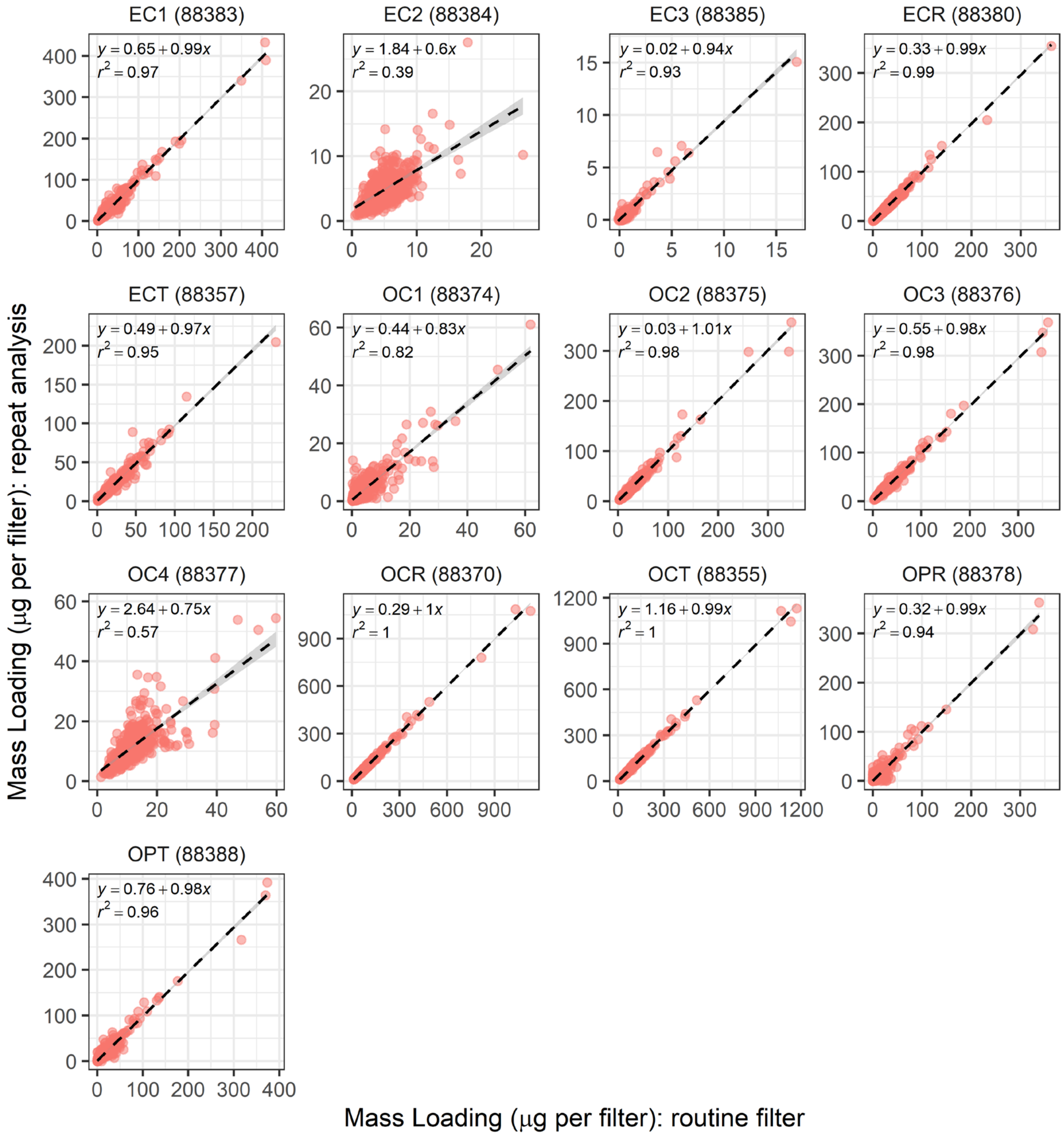
Figure 3.1-1: Ion repeat analysis (replicates and/or duplicates) results; data from valid samples collected January 1, 2022 through December 31, 2022.



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.

In Figure 3.1-2 below, 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.

Figure 3.1-2: Carbon repeat analysis (replicates and/or duplicates) results; data from samples collected during January 1, 2022 through December 31, 2022.



Replicate EDXRF analyses of routine CSN samples were started on December 20, 2020. The data for 2022 is plotted below and each color represents a different analyzer. The method calculates a Z-score that is normalized by uncertainty to plot standard deviations. In the plot, dashed horizontal lines (2 standard deviations) are warnings and solid lines (3 standard deviations) are limits. Cl and Br are not included since they are volatile elements that are lost under vacuum, making repeat analysis impractical.

Step 1: Replicate Precision Estimates Using Legacy Replicate Measurements

The XRF instruments take replicate measurements weekly. To evaluate the process uncertainty, results are compared against the calculated historical precision for that element. This is done for all elements reported that meet certain criteria described next, excluding volatiles like Cl and Br.

Precision using RMS models were calculated for each element. The dataset to calculate precision must be large enough for statistical significance. We use the previous analytical year's 12 months of replicate measurements (estimated to be 5% of all filters*) as the dataset to calculate precision. For new processes or equipment changes, 6 months of data may be used as an initial starting point. Each paired data point for Routine and Replicate measurements, for each measured element, must be ≥ 2x $MDL_{Analytical}$ to avoid statistics dominated by noise and ensure repeatable measurements. Additionally, a minimum of 10 pairs in the dataset is required for each element. Some elements may not reach this requirement due to sparsity in the atmosphere.

*The AQMT process for replicates is to run the filters loaded into the XRF instrument on Friday for a second time. This limitation is due to time and resource constraints, to which AQMT rotates between measuring filters for CSN and IMPROVE. As such, replicates are dependent on which network is in the analyzer on Friday or if it is an even running. However, as far as QC goes, we calculate using the same method, and report the results to the same visualization tool. The datasets are kept separate due to differences in concentrations, but they are plotted and reviewed each week on the same tool, regardless of the network.

Table 3.1-4 Number of pairs above 2x $MDL_{analytical}$ and calculated RMS for each CSN element in legacy dataset used to evaluate 2022 replicate analysis.

Parameter	No. of Pairs	RMS
Ag	264	15.5
Al	1240	9.4
As**	2	37.6
Ba	907	16.4
Br*	NA	NA
Ca	797	7.1
Cd	168	15.3
Ce	655	16.0
Cl*	NA	NA
Co	37	21.0
Cr	1238	16.2
Cs	438	15.8

Parameter	No. of Pairs	RMS
Cu	848	9.5
Fe	1109	5.0
In	361	15.7
K	1225	6.3
Mg	26	20.3
Mn	1106	18.6
Na	61	22.6
Ni	64	17.3
P	23	26.3
Pb	1069	17.1
Rb	46	20.4
S	1022	4.8
Sb	321	14.9
Se	20	17.3
Si	1034	8.9
Sn	500	14.9
Sr	411	18.8
Ti	454	18.7
V**	4	24.2
Zn	398	8.6
Zr	121	13.5

*Volatile elements Cl and Br are excluded from replicate analysis.

**The dataset for As and V do not have enough pairs above 2x MDL to be used for replicate analysis described in Step 2 and plotted in Figure 3.1-3.

Step 2: Replicate Analysis Results (Measured and Reported Each Week)

Once the expected precision for each element is calculated using the previous year's validated data, Z-scores are then calculated in real-time for evaluation by laboratory personnel. The Z-score is the difference between the initial (Routine) and repeated (Replicate) measurements divided by the expected precision. Differences observed within two times the expected precision represent normal operating conditions, while differences greater than three times the precision indicate issues with the EDXRF instruments and are investigated.

The calculated precision for each element in the past reference data set is then applied to each Z-score calculation for real-time replicate measurements. Figure 3.1-3 plots the results as standard deviation from the uncertainty, not from the mean. This was chosen since the difference from uncertainty scales with the measurement quality of each element.

$$Z_e\text{-Score} = \frac{(\text{Routine} - \text{Replicate})/\sqrt{2}}{\text{Uncertainty}}$$

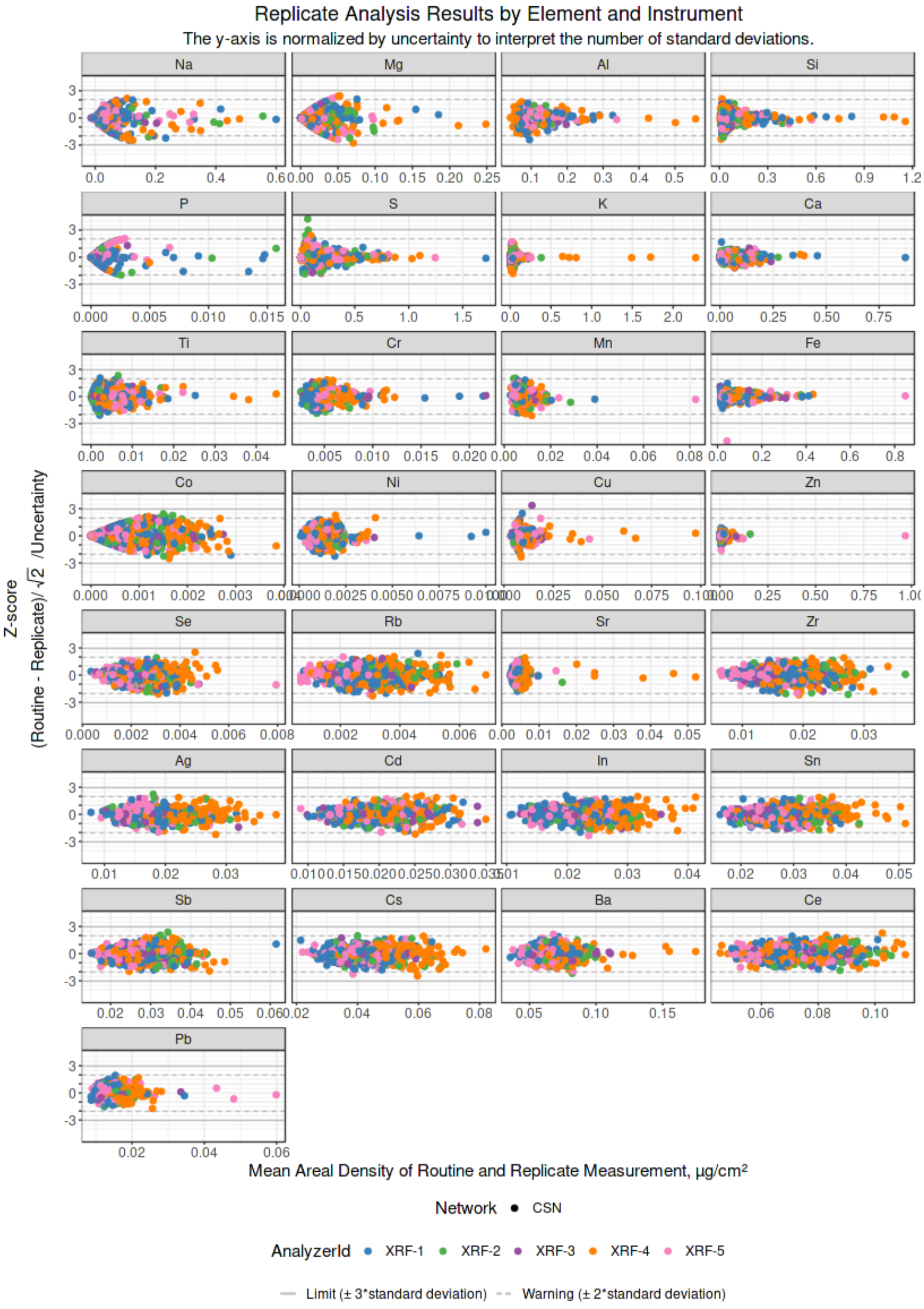
- Z_e = Z-score for each element reported
- Uncertainty = calculated from previous year’s dataset (2021).
- Routine = Areal density of 1st measurement
- Replicate = Areal density of 2nd measurement (not normally reported)

Routine – Replicate was chosen to call attention to any potential bias in the measurements.

Using the statistical data for sample year 2021, we set limits for each measured element. The dataset for sample year 2022 is as follows:

- 579 filters had replicate measurements for sample year 2022, out of 12,391 valid filters (Table 3.1-1), or 4.67% of the network.
    - Each filter measures 33 different elements
        - 31 are used in replicate calculations once Cl and Br are omitted.
- The figure below plots 16,791 replicate measurements. There are a total of 4 points that failed the 3x standard deviation maximum requirement. In these cases, the spectroscopist determines which value should be reported by rerunning a 3rd measurement. Overall, 99.98% of points plotted passed the criteria.
    - Vanadium (V) and arsenic (As) are not plotted because they did not meet the minimum 10 required pairs to calculate precision, described above.

Figure 3.1-3: Replicate Analysis Results by Element and Instrument. Sample year 2022 with 579 replicate measurements.



EDXRF replicates were previously not performed on routine CSN samples due to time limitations, as analyses take approximately 65 minutes per sample. In addition, volatile elements like Cl and Br, and to a lesser extent S, are lost when the sample is analyzed under vacuum on the EDXRF.

In addition to replicates on network filters, EDXRF precision was evaluated by analyzing the same set of samples, which are UCD-made (monthly) multi-element reference materials (see Table 4.2.2) 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 3.1.3.6). 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 3.1.3.7).

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. 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 3.1.3.6) and MDL (Section 3.1.3.7) calculation methods are robust against influence from occasional outliers.

3.1.3.1 Ion Species Field Blanks

Field blank mass loadings for the ion species (Figure 3.1-4 through 3.1-9) are examined in an effort to identify changes that may be occurring in the ions measurement lab. Ions analysis was transitioned from DRI to RTI in October 2018 data and there were clear performance jumps in the data. Starting in Oct 2019, field blank levels increased for ammonium, chloride, potassium ion, and sodium ion.

In the following figures 3.1-4 to 3.1-9, 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 Q3 + 1.5xIQR boundary shown by the horizontal dotted line. All of the data plotted (starting 2019) is from RTI. The transition of ion measurement from DRI to RTI happened in October 2018.

Figure 3.1-4: Time series of ammonium measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

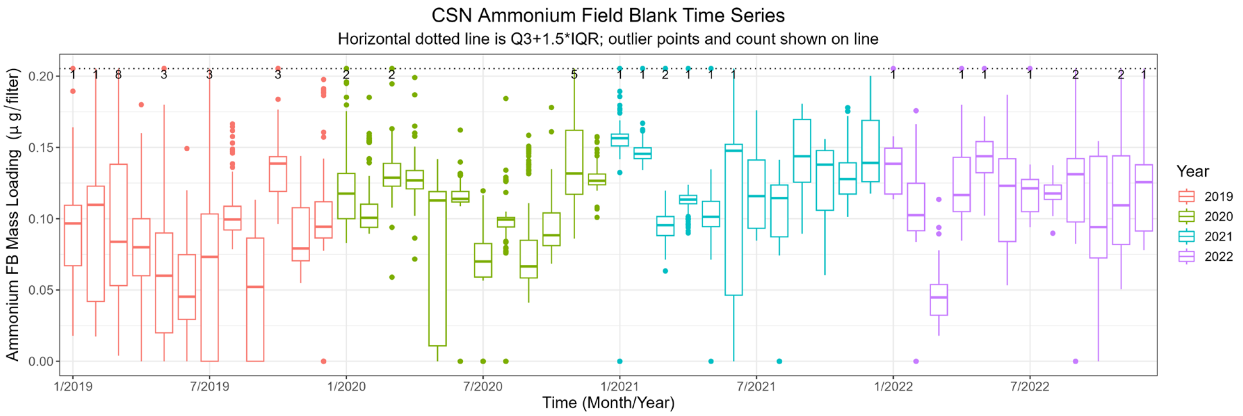


Figure 3.1-5: Time series of chloride measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

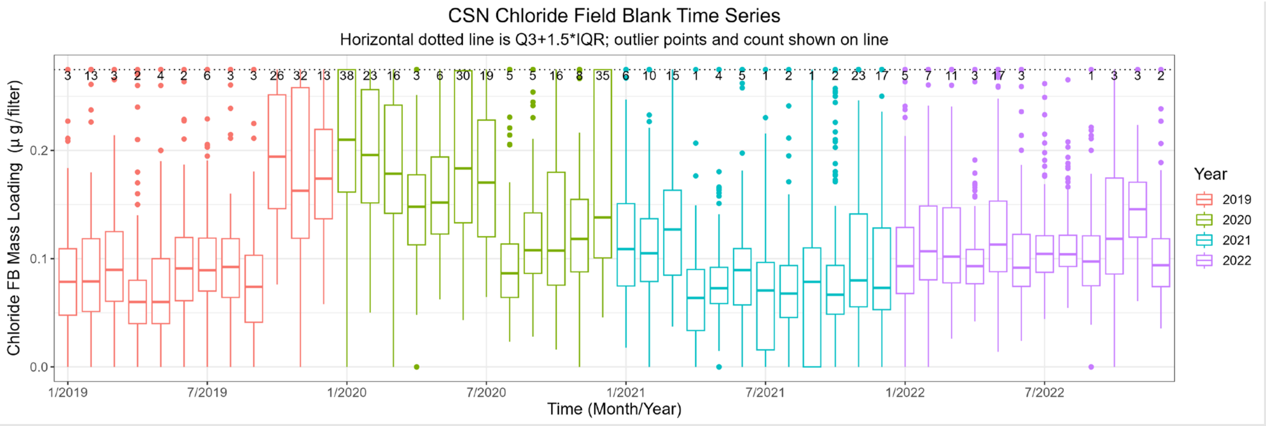


Figure 3.1-6: Time series of nitrate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

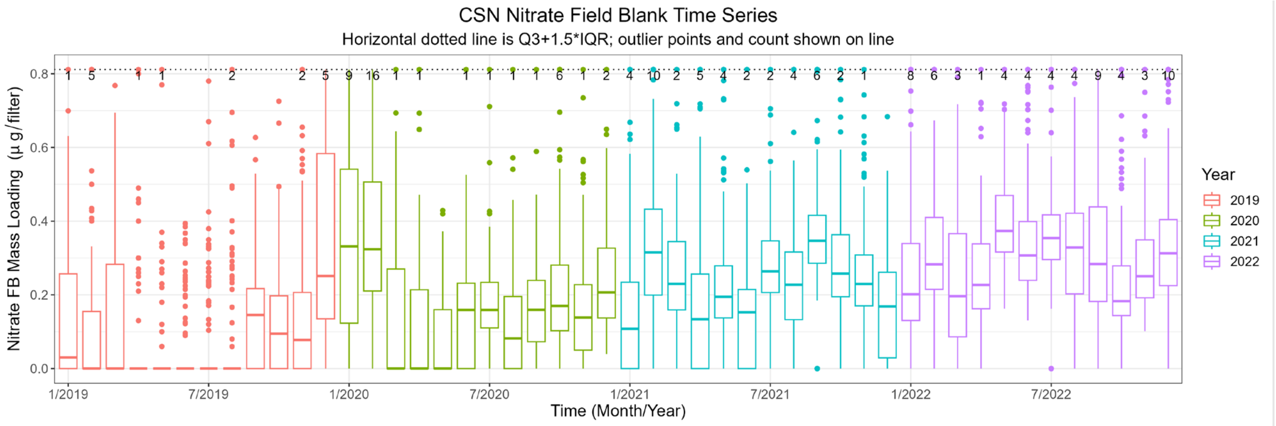


Figure 3.1-7: Time series of potassium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

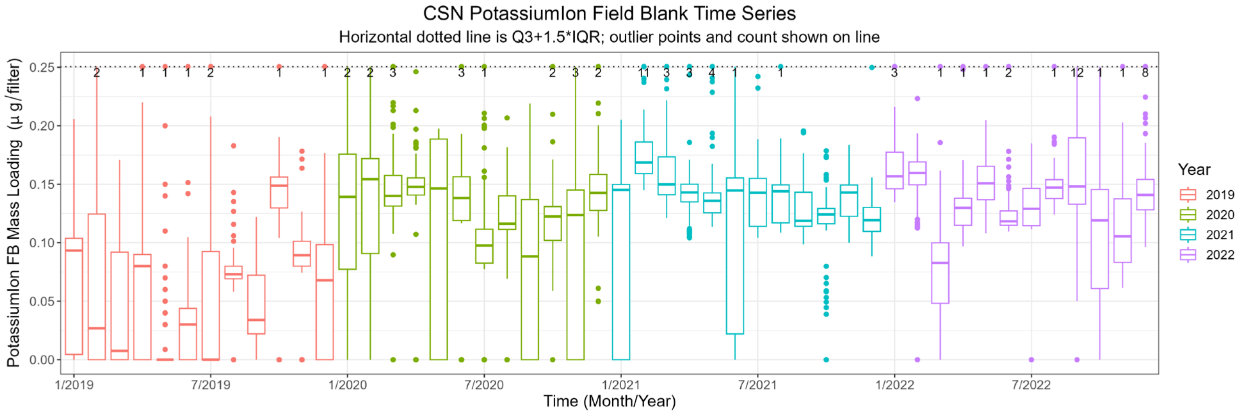


Figure 3.1-8: Time series of sodium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

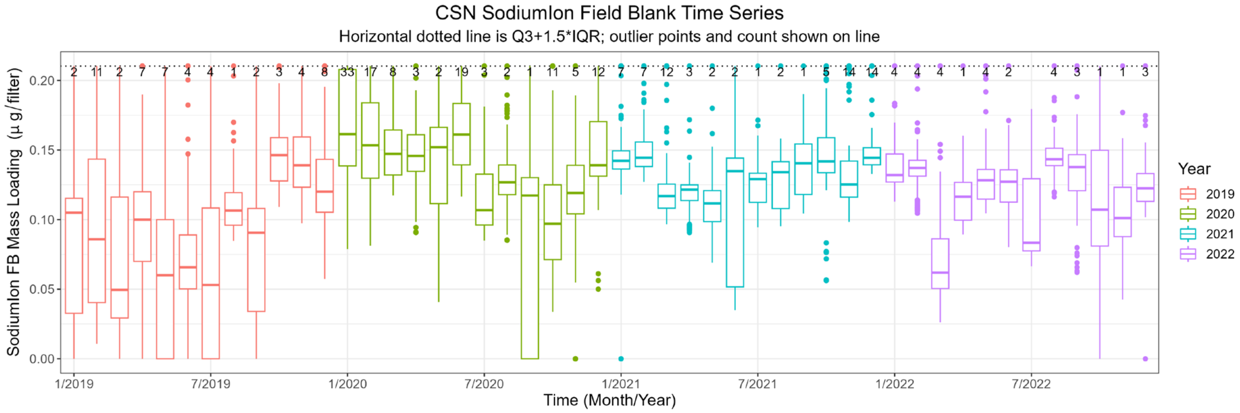
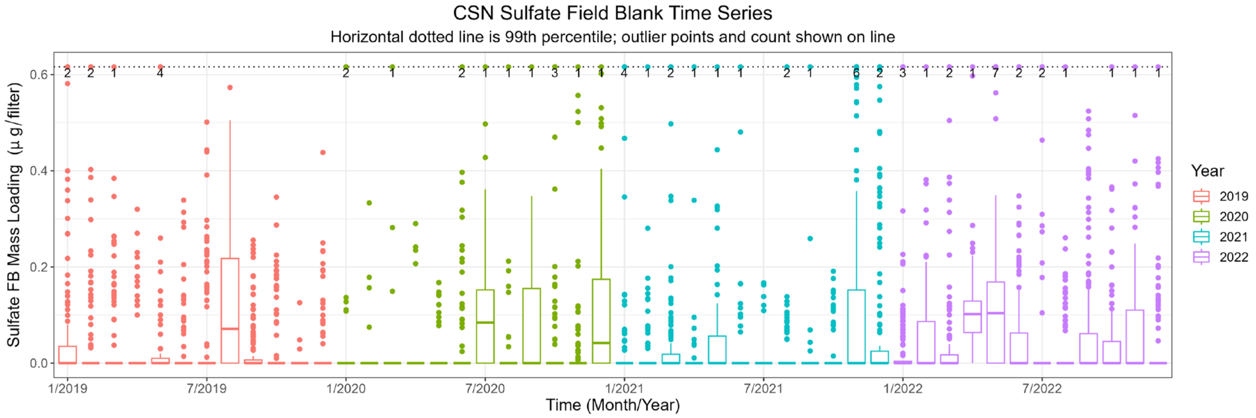


Figure 3.1-9: Time series of sulfate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.



3.1.3.2 Carbon Species Field Blanks

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 occurring in the carbon measurement lab. The lab was transitioned from DRI to RTI in October 2018 and a data advisory was published. The data plotted below is after the transition period and starts January 2019.

The plots for OCR and ECR show some seasonal variability but no performance jumps indicating a large change.

In the following two figures, 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 Q3 + 1.5xIQR boundary shown by the horizontal dotted line. All of the data plotted (starting 2019) is from RTI. The transition of carbon measurement from DRI to RTI happened in October 2018.

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, 2019 through December 31, 2022.

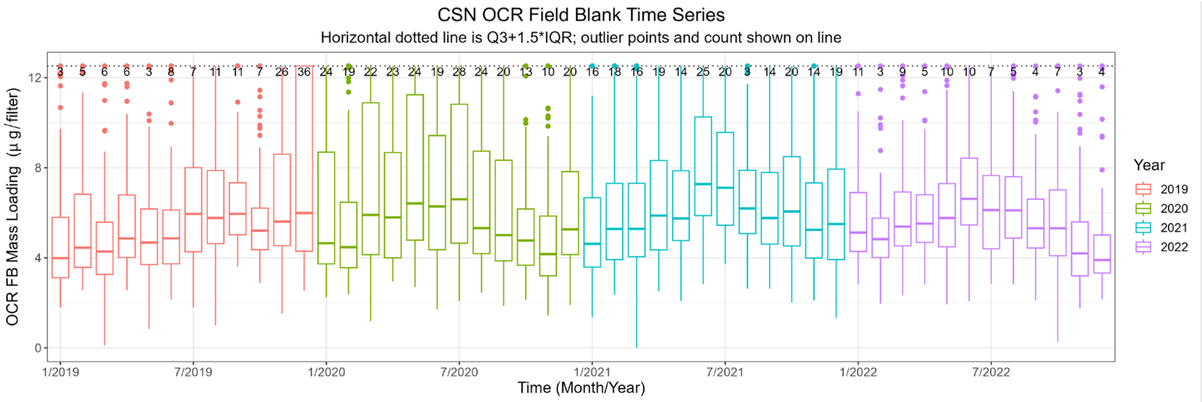
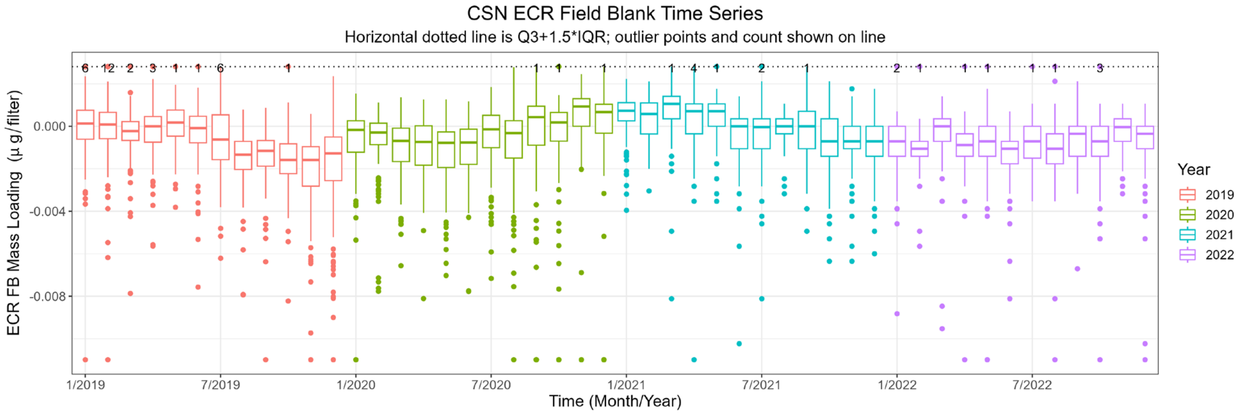


Figure 3.1-11: Time series of elemental carbon by reflectance (ECR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.



3.1.3.3 Elemental Species Field Blanks

Time series of monthly median mass loading of field blanks are shown in Figures 3.1-12 through 3.1-18 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 for 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).
- Silicon (Si; Figure 3.1-12) monthly median field blank mass loadings continue to show 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)
- Sulfur (S; Figure 3.1-13) monthly median field blank mass loadings are very lightly loaded and starting in September 2021, very little sulfur is detected.
- Potassium (K; Figure 3.1-14) monthly median field blank mass loadings are showing more variability since August 2020.

For the following figures, 3.1-12 to 3.1-18, 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 1.5xIQR. Outlier points that are off scale are plotted at the Q3 + 1.5xIQR boundary shown by the horizontal dotted line.

Figure 3.1-12: Time series of silicon (Si) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

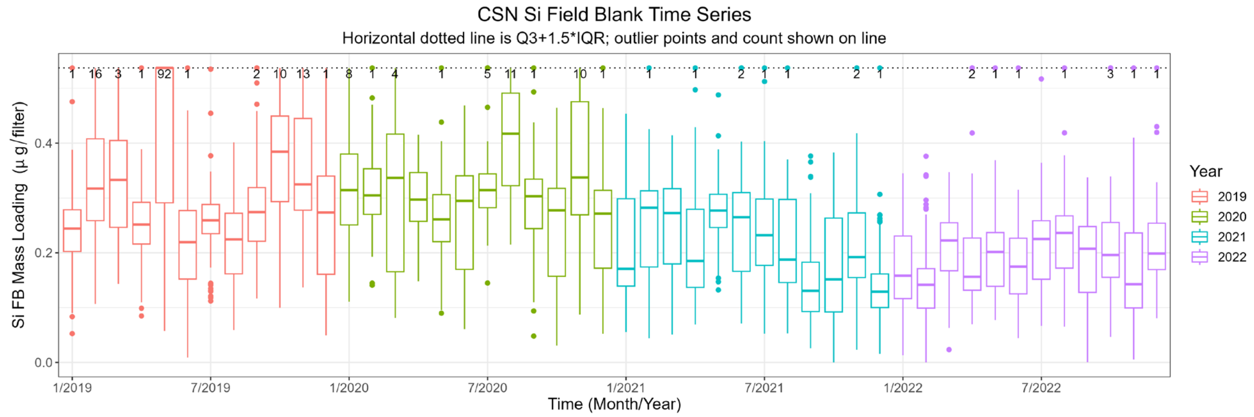


Figure 3.1-13: Time series of sulfur (S) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

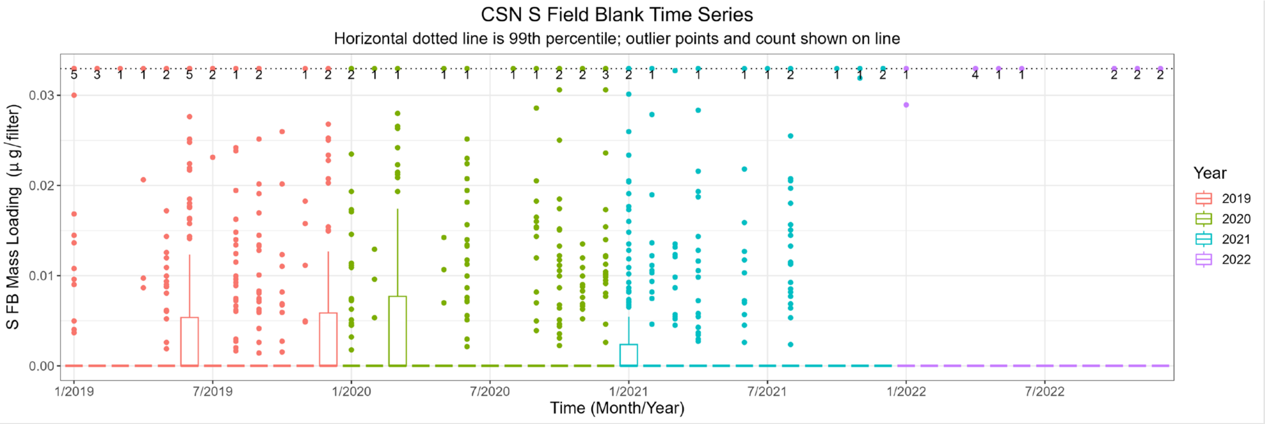


Figure 3.1-14: Time series of potassium (K) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

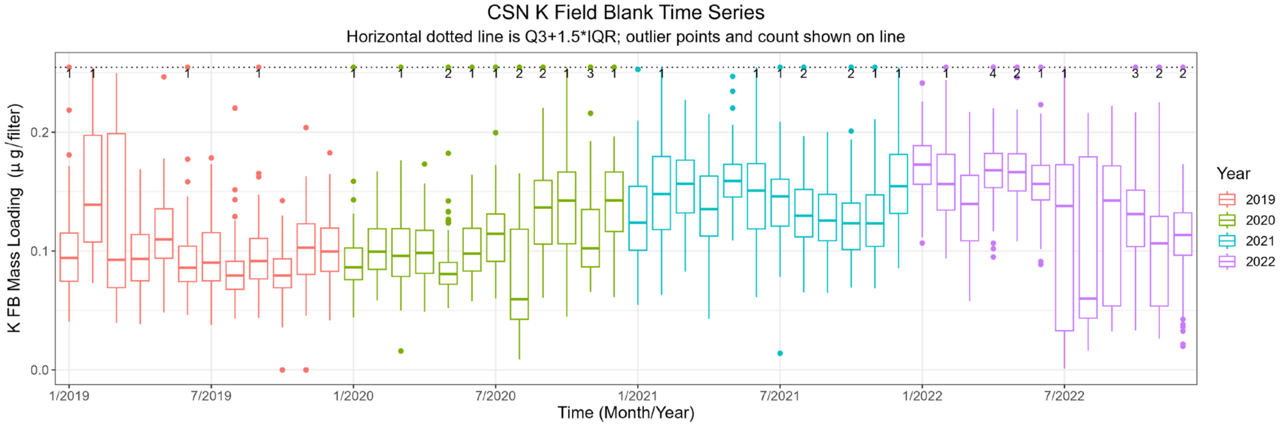


Figure 3.1-15: Time series of calcium (Ca) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

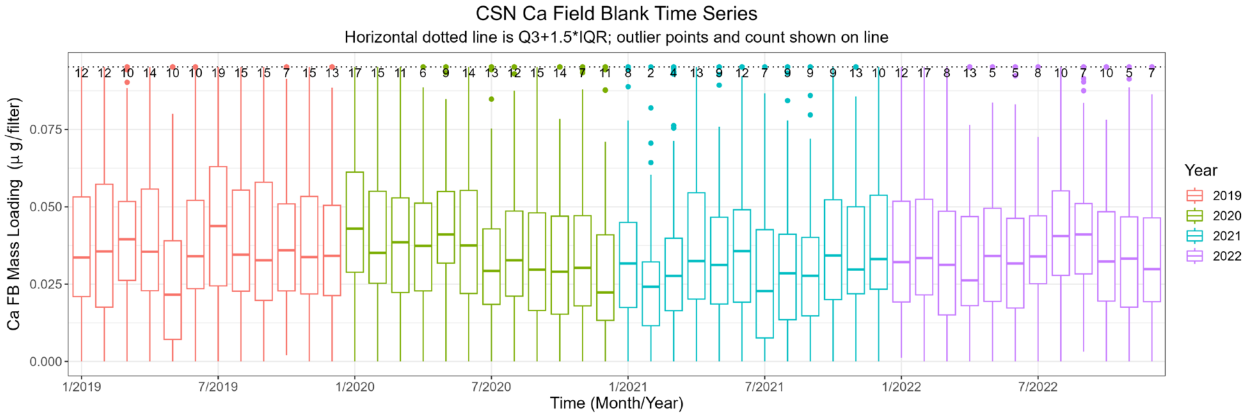


Figure 3.1-16: Time series of titanium (Ti) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

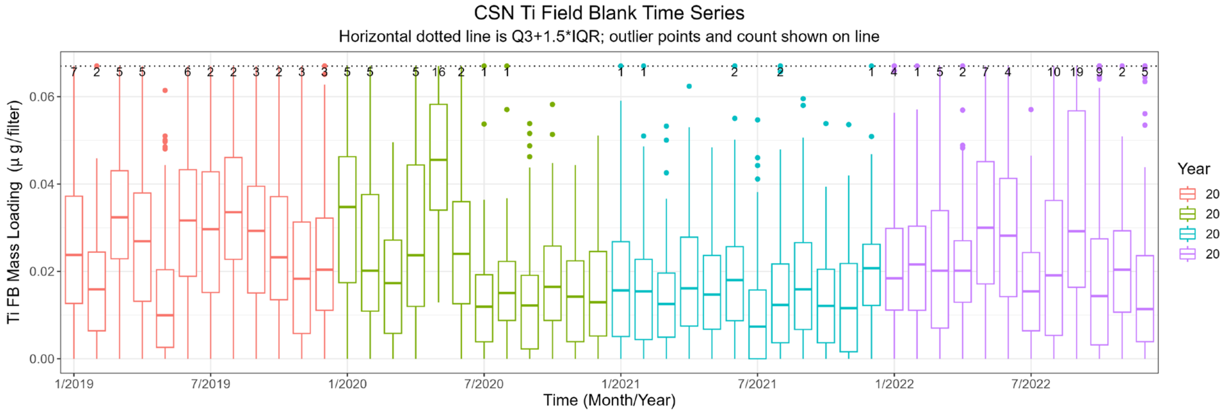


Figure 3.1-17: Time series of iron (Fe) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.

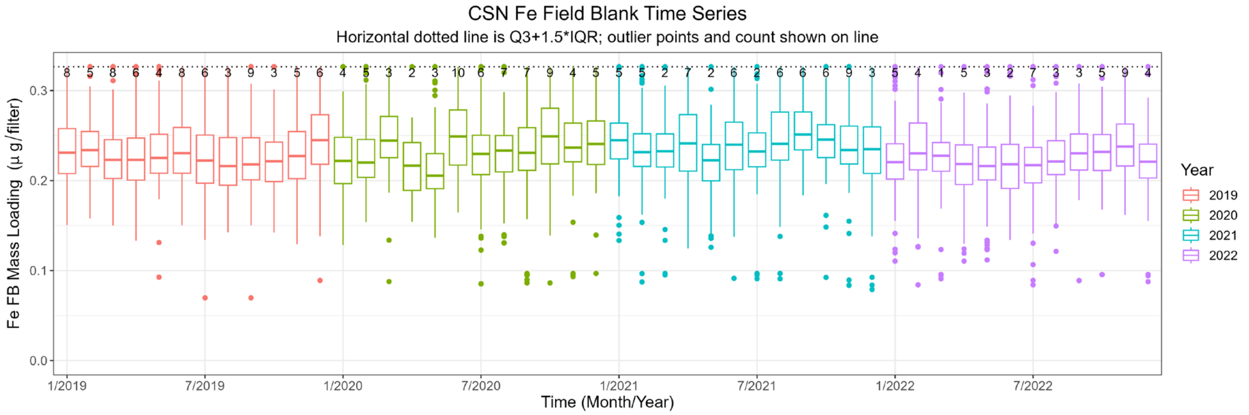
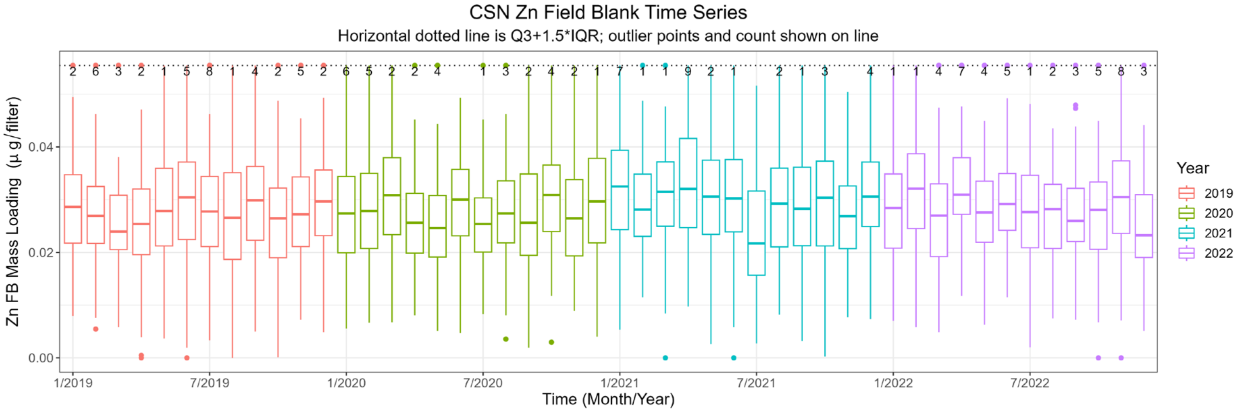


Figure 3.1-18: Time series of zinc (Zn) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2019 through December 31, 2022.



3.1.3.4 Optical Absorption Field Blanks

Field blank mass loadings for tau_633 (Figure 3.1-19) are examined in an effort to identify changes that may be occurring in the optical absorption measurement lab. tau_633 is calculated with HIPS measurements at 633 nm of light from transmittance (t) and reflectance (r) values. It is the optical absorption depth of the deposit. fAbs is calculated using the area of the filter, the sample volume, tau_633, and multiplied by 100 to reach the same order of magnitude as Carbon EC measurements. The general equations are below. There are additional transformations to correct for field blank calibrations and more details are available in *UCD CSN SOP #277: Optical Absorption Analysis*.

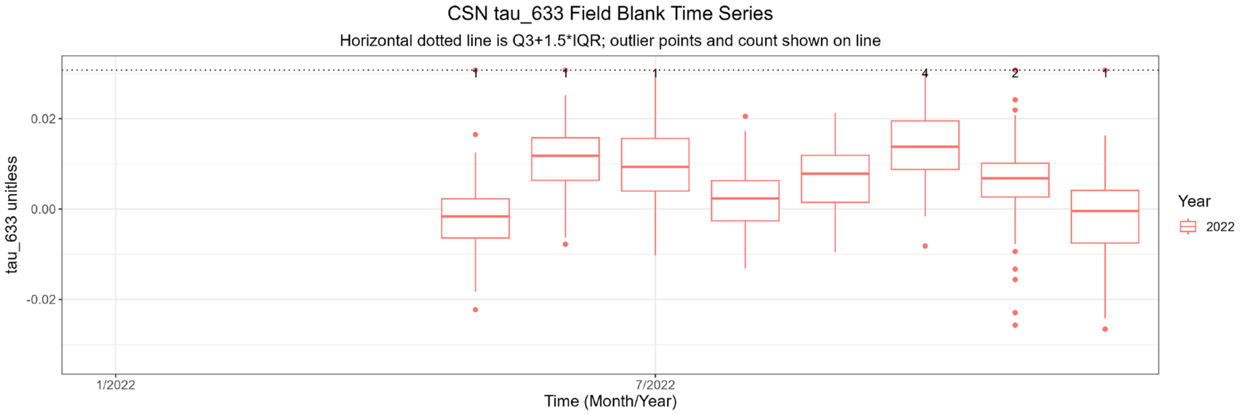
$$\tau_{abs} = \ln\left(\frac{1-r}{t}\right)$$

$$fAbs, Mm^{-1} = \frac{3.53\ cm^2}{Volume,\ m^3} \cdot \tau \cdot 100$$

CSN data was collected for several years but delivery to AQS started May 2022. An effort to validate and deliver past data is underway.

In Figure 3.1-19, 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 Q3 + 1.5xIQR boundary shown by the horizontal dotted line.

Figure 3.1-19: Time series of tau_633 measured on PTFE filter field blanks (FB), for valid field blanks collected May 1, 2022 through December 31, 2022.



3.1.3.5 Laboratory Blanks

Beginning with the shipment to UCD of filters collected in July 2020, the Sample Handling Laboratory, WSP, 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).

3.1.3.6 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.

3.1.3.7 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 95^{th} 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, 2022 through December 31, 2022) are compared to those calculated using the same method from the previous reporting period (samples collected January 1, 2021 through December 31, 2021) (Table 3.1-4). MDLs calculated during this reporting period were within 60% of values from the previous reporting period for all species except elemental carbon species (ECR and ECT). The relative MDL for ECT and ECR increased significantly, but 100% of network samples were still above the reported MDL.

In the following 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 shown in bold have differences ≥ 50% between those reported for the previous reporting period (2021) and the current reporting period (2022). Typical MDLs are from the CSN laboratory analysis contract's statement of work.

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, 2021 through December 31, 2021 (previous reporting period) and January 1, 2022 through December 31, 2022 (current reporting period).

Species	EPA Attachment D	2021 (previous reporting period)		2022 (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	5.3	13	8.9
Al	25	24	58	24	51
As	2.7	0.10	3.3	0.10	0.15
Ba	59	33	8.9	34	9
Br	2.3	0.10	31	0.10	28
Ca	7.6	8.3	93	8.3	93
Cd	23	14	5.1	13	7.2
Ce	88	38	6.1	40	6
Cl	11	3.8	45	3	50
Co	2.0	1.7	3.9	1.7	4
Cr	2.6	2.2	22	2	28
Cs	46	29	4.0	27	7.9
Cu	2.5	4.6	21	4.6	22
Fe	3.3	7.6	97	8.1	97
In	33	16	5.2	15	9.4
K	11	5.1	99	6.1	99
Mg	19	45	16	47	18
Mn	2.9	3.1	25	2.9	28
Na	55	91	28	94	25
Ni	1.9	1.3	18	1.2	23
P	16	1.5	12	2	11
Pb	6.4	7.1	15	6.9	21
Rb	2.6	3.2	5.5	3.2	7.8
S	9.9	0.79	100	0.31	100
Sb	52	17	7.4	17	7.5
Se	2.6	2.6	7.7	2.5	9.9
Si	19	13	90	10	89

Species	EPA Attachment D	2021 (previous reporting period)		2022 (current reporting period)	
	Typical MDL, ng/m^3	Average MDL, ng/m^3	% Above MDL	Average MDL, ng/m^3	% Above MDL
Sn	36	17	7.1	16	8.1
Sr	3.5	3.1	12	2.9	14
Ti	5.3	2.5	61	3.8	46
V	3.9	0.7	8.6	0.46	11
Zn	3.5	2.2	89	2	92
Zr	23	15	5.8	13	8.5
Ammonium	25	13	93	13	93
Chloride	27	30	77	16	83
Nitrate	22	38	99	44	99
Potassium Ion	24	13	80	13	76
Sodium Ion	30	14	61	13	67
Sulfate	35	33	100	31	100
Elemental Carbon (EC1)	95	23	100	26	100
Elemental Carbon (EC2)	63	19	99	14	100
Elemental Carbon (EC3)	63	4.8	82	3.7	84
Elemental Carbon (ECR)	63	0.039	100	0.95	100
Elemental Carbon (ECT)	63	0.52	100	6	100
Organic Carbon (OC1)	63	11	73	13	62
Organic Carbon (OC2)	63	34	99	22	100
Organic Carbon (OC3)	95	300	76	110	96
Organic Carbon (OC4)	95	79	98	54	99
Organic Carbon (OCR)	63	640	90	210	97
Organic Carbon (OCT)	63	640	91	210	97
Organic Pyrolyzed (OPR)	95	66	90	38	88
Organic Pyrolyzed (OPT)	63	66	95	38	94
Soil	NA	---	---	78	96
Reconstructed Mass	NA	---	---	410	96
fAbs	NA	---	---	2.1	85

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, nonconformances, and, if necessary, corrective actions. The following subsections describe significant corrective actions undertaken for data from samples collected during 2022.

Note, AQRC utilizes internal quality reports with an ID system for Nonconformances (NR-####) and Investigations (IR-####). Some may be referenced in the sections below. Please contact AQRC to receive an emailed copy of any requested report.

3.2.1 Elemental Analysis

3.2.1.1 XRF-2 X-ray Intensity Loss

On April 6, 2022 XRF-2 underwent a service by the manufacturer on the sample chamber and cap. Following this service visit there was a general loss of x-ray intensity for the CaF2 target under which Na – Cl are measured. The intensity drop was less than 5% and was not noticed until the monthly SRM QC sample was measured on 4/21/2022. Because the aluminum and potassium values for this SRM were already very near the lower acceptance limit, the slight drop in x-ray intensities caused the concentrations of these elements to drop below acceptable levels and the QC check failed. Analysis was immediately stopped on the instrument and the manufacturer returned to repair the CaF2 target on 5/2/2022. Sample analysis resumed on 5/6/2022 after QC tests confirmed the instrument was operating within specifications for all elements. Additionally, the SRM that failed the QC because concentrations were near the lower limit was replaced with a new SRM which was used in subsequent months.

Results for samples analyzed on XRF-2 from the time the intensity drop occurred after the technician visit on 4/6/2022 and the CaF2 target repair on 5/2/2022 were in question. To assess the impact on the sample results, 5% of samples analyzed between 4/6/2022 and 4/21/2022 when analysis was stopped, were reanalyzed on different XRF analyzers to look for any bias caused by XRF-2's intensity drop. The bias reported from these reanalyses was within expected uncertainty and the results were deemed acceptable. In total 22 CSN filters from Batch 87 (intended use date January 29, 2022) were potentially affected. An analysis-level comment was added those filters. See investigation report IR-0006 for further details.

3.2.1.2 Contamination Issues on XRF-3 and XRF-4

Daily QC measurements on XRF-3 and XRF-4 showed a contamination event beginning late October 2022. The event included Cr, Fe, and Zn contamination on XRF-4's daily QC blank sample and Zn contamination on XRF-3's daily QC ME-RM sample. An investigation determined that the contamination was caused by newly installed gas piston supports for the XRF sample area lids. Due to the position of the QC samples in the XRF sample deck, they are positioned under the gas piston and were therefore susceptible to contamination falling from the pistons. Sampled filters are not positioned under these gas pistons and were not affected by the contamination. Cleaning contaminants off of XRF-4's QC blank returned elemental readings to acceptable blank levels. Visible contaminant particles were found on XRF-3's QC ME-RM, however, they could not be removed, therefore, this QC ME-RM was replaced with a new one. Please see non-conformance report NR-0013 for additional details of these QC failures.

Additionally, the investigation on XRF-3 uncovered further contamination events from the lid hinge, see investigation report IR-0014. No QC or network samples were loaded to the instrument under this faulty hinge until the hinge was replaced by the manufacturer. This prevented any contamination issues from the hinge and no network sample data was affected.

A short time later during the Christmas holiday, XRF-4 experienced another contamination event, this time involving sulfur. No QC failures resulted from this event, but the contamination was noted on the QC blank, and action was immediately taken on 1/3/2023 to clean the analysis chamber which resolved the sulfur contamination. The issue was later discovered by the data validation team when validating CSN sample results from October 2022 sampling that were analyzed on XRF-4 during this time. An investigation was opened, see investigation report IR-0013, which determined the cause was sulfur contamination in the XRF sample analysis chamber due to vacuum pump oil which migrated there during a power outage which was noted around the time the samples were analyzed. This contamination affects the analysis chamber of the XRF, not the samples, but does cause the sulfur x-ray signal to increase. After cleaning the chamber, the issue was resolved. All samples analyzed during the suspected period of contamination (34 filters sampled October 5th, 2022) were reanalyzed and the original results were invalidated.

3.2.1.3 Aluminum and Chlorine Interference

In February 2022, some anomalously high aluminum results were found in some samples by the validation team. When the XRF lab investigated these findings, it was determined that an interference of the aluminum K-alpha line by the chlorine K-alpha-escape peak was not being properly corrected by the calibration of at least one XRF instrument. Because of the lack of reference materials available with suitable chlorine and aluminum concentrations to test this interference, the problem cannot be positively identified in any particular XRF instrument or calibration. However, some general guidelines for identifying results where the aluminum concentration may be misreported due to this interference can be provided. A data advisory on this issue is forthcoming. When the issue was found CSN batch 85 (Nov 2021) had most-recently moved through the XRF lab. The root cause was corrected starting with batch 88 (Feb 2022).

3.2.2 Ion Analysis

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

For previous reporting periods, 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 3.1.3.7, 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

ECT measurement from many Field Blanks were elevated because an analyzer (Delta) laser housing was mis-aligned for batch 96. The laser housing on Delta had loosened over time, leading to misalignment. None of the daily QC blanks throughout this period showed any EC. Only about 50% of the batch 96 field blanks analyzed on Delta showed EC, making it an intermittent problem. The laser housing on Delta was adjusted twice. After the 2nd adjustment, 12 blanks were run and none of them had ECT issue on Delta. Subsequently, daily QC passed. The lab reinstated active monitoring of field blanks to catch this type of issue sooner. After review we do not believe samples were affected. See NR-0015 for details.

On the morning of 7/11/2022, Delta failed the weekly power constant (PC) ECR check twice. After adjusting Delta's power constant, the test was repeated on all 6 instruments with good results. A few samples from the previous week were reanalyzed with results comparable to the original results. The weekly PC test passed on Delta in the next two weeks after this adjustment. See IR-0007 for more details.

On the morning of June 9th, 2022, the quartz refrigerator was found to be slightly outside our approved operating temperature range of 4 °C or less at 5.6 °C because the refrigerator door was slightly ajar. The refrigerator temperature has been within tolerance and normal since that date. The impact to organic carbon would be negligible considering the filters are taken out and reach room temperature during the analysis day. See NR-0008 for more details.

Temperatures were not logged on 6/28/22 for the HIPS or Quartz refrigerators. Temperature checks logged for 6/27/2022 and 6/29/2022 were within acceptable range. To correct this issue going forward, we assign certain lab personnel to ensure this daily task is completed, checked, and if someone is unavailable, there are other lab persons who will take over the task. See NR-0009 for more details.

The quartz refrigerator did not have the temperature recorded on April 11 and 12, 2023. The dates recorded before and after were under 4 degrees C. Moving Forward, each set of refrigerators will become one person's responsibility, with upper lab staff overseeing the log completions daily. See NR-0022 for more details.

Half of batch 97 quartz tray 9 (25 filters) was left out of the refrigerator overnight. The operator is experienced but made a mistake. See NR-0016 for more details.

The Data Validation & Reporting group found qualifiers missing from carbon records reported to AQS due to a bug in the datvalCSN code. There are six carbon species (ECTT (88381), ECTTraw (88357), OCTT (88382), OCTTraw (88355), OPTT (88379), OPTTraw(88388)) which are not reported with the LJ qualifier in AQS. A total of 312 parameter records were found, denoting results for 52 samples. The datvalCSN code was updated to version 1.25.1 to fix the bug and begin storing qualifiers of all data when delivering to DART, following *UCD CSN SOP #801: Processing and Validating Raw Data*. The new version was first used with batch 93 (July 2022) data. Past data were corrected in AQS. See NR-0012 for more details.

3.2.4 Optical Absorption

Temperatures were not logged on 6/28/2022 for the HIPS or Quartz refrigerators. Temperature checks logged for 6/27/2022 and 6/29/2022 were within acceptable range. To correct this issue going forward, we assign certain lab personnel to ensure this daily task is completed, checked, and if someone is unavailable, there are other lab persons who will take over the task. See NR-0009 for more details.

3.2.5 Data Processing

3.2.5.1 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.

3.2.5.2 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.

3.2.6 Technical System Audit

The EPA did not conduct an audit during the time when 2022 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.

3.2.7 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 2024.

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 87 through 98, covering the sampling period January 1, 2022 through December 31, 2022. Routine analysis of these samples was performed March 17, 2022 through March 15, 2023. Both routine analysis and reanalysis was performed March 17, 2022 through April 19, 2023. Using ion chromatography, RTI analyzed for both anions (chloride [Cl^-], nitrate [NO_3^-], and sulfate [SO_4^{2-}]) and cations (sodium [Na^+], ammonium [NH_4^+], 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 (2022)	Analysis Batch #	IC Analysis Dates
January	87	3/17/2022 - 5/11/2022
February	88	4/8/2022 - 6/14/2022
March	89	5/10/2022 – 7/9/2022
April	90	6/21/2022 – 8/12/2022
May	91	7/18/2022 – 9/17/2022
June	92	8/15/2022 – 10/12/2022
July	93	9/17/2022 – 11-14-2022
August	94	10/01/2022 – 12/14/2022
September	95	11/14/2022 – 1/17/2023
October	96	12/11/2022 – 2/14/2023
November	97	1/12/2023 – 3/13/2023
December	98	2/17/2023 – 4/19/2023

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

Activity	Frequency	Acceptance Criteria	Corrective Action
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_2O and/or eluent); at least one per day	No limit set; the data is compiled for comparability studies; < 10 times MDL	Investigate; reanalyze
Round Robin (External QA by USGS)	4 per month	Not applicable; data reported and compared annually	Investigate
Reanalysis	5% per of all samples, reanalyzed on different day and as requested	MDL to10 times MDL: RPD up to 200%, 10 to 100 times MDL: RPD < 20%, >100 times MDL: differences within 10%	Investigate 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 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022).

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

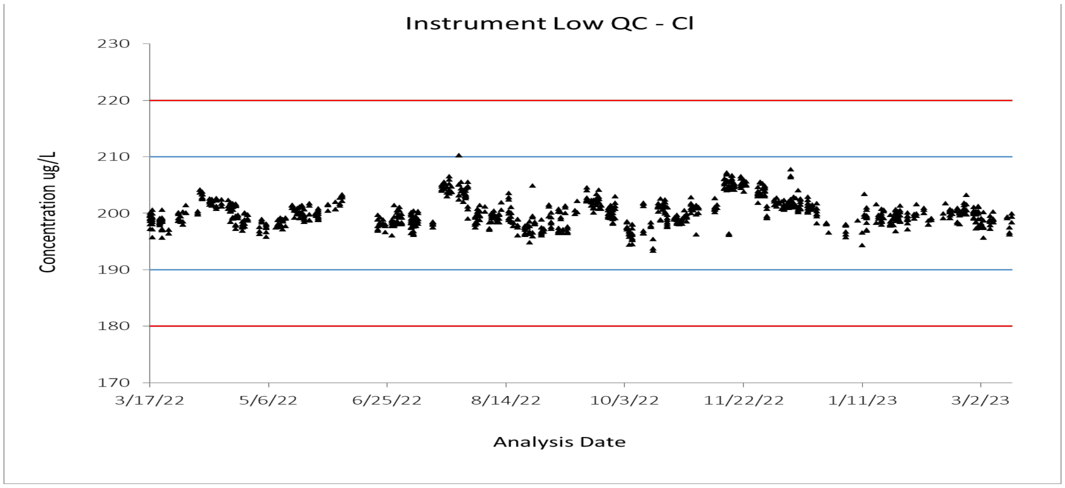
Table 4.1-4: Target concentrations of cation CCV check standards for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022).

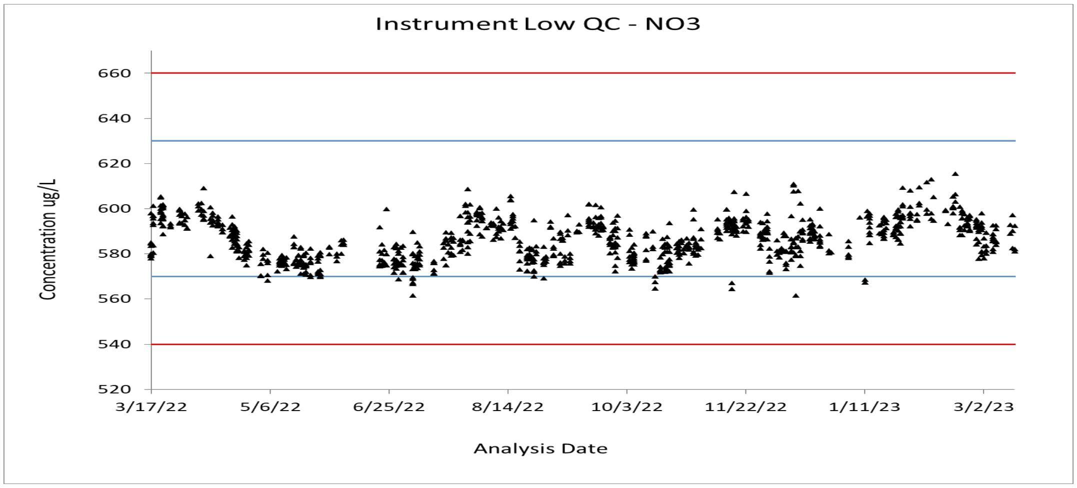
QC Sample	Na^+ (ppb)	NH_4^+ (ppb)	K^+ (ppb)
Instrument Low QC	20	20	20
Instrument Medium QC	250	250	250
Instrument Medium-High QC	750	750	750
Instrument High QC	2000	2000	2000

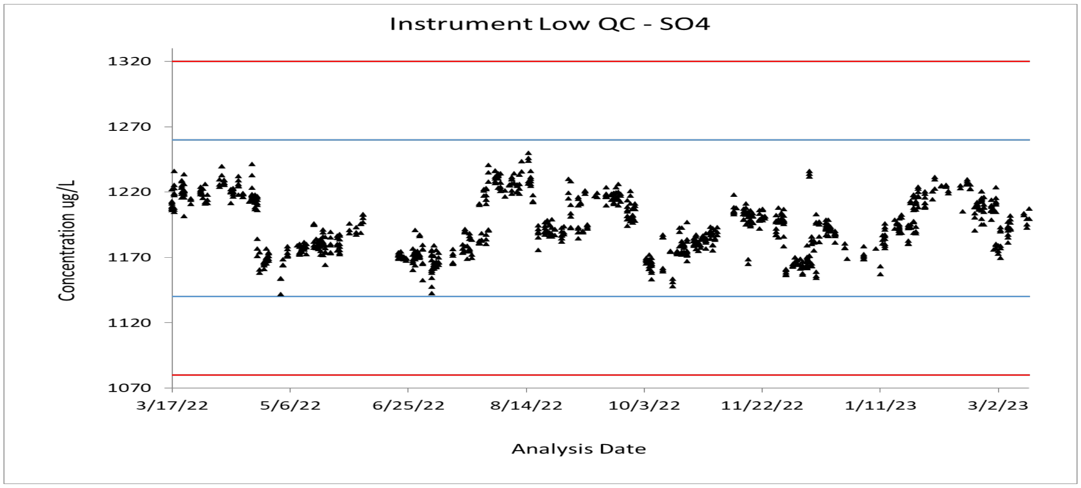
At least two CCV check standards are analyzed immediately after the calibration standards and a single CCV check standard is analyzed after every ten samples. When an instrument CCV check standard fails the acceptance criteria by falling outside of the control limits, impacted samples are reanalyzed. 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.

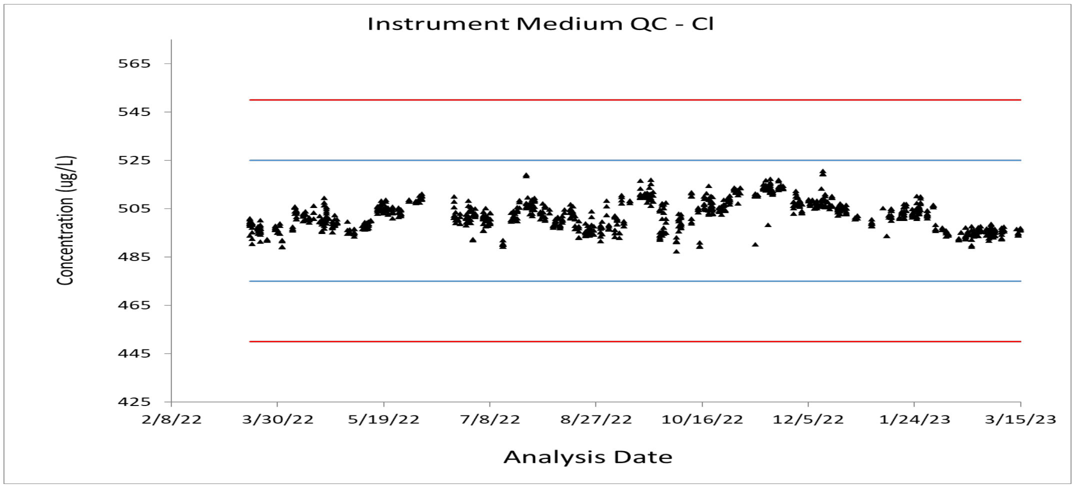
In the below control chart figures, red lines show upper and lower control limits set at ±10% of the nominal concentrations for the low, medium, medium-high, and high standards. Blue lines show upper and lower warning limits.

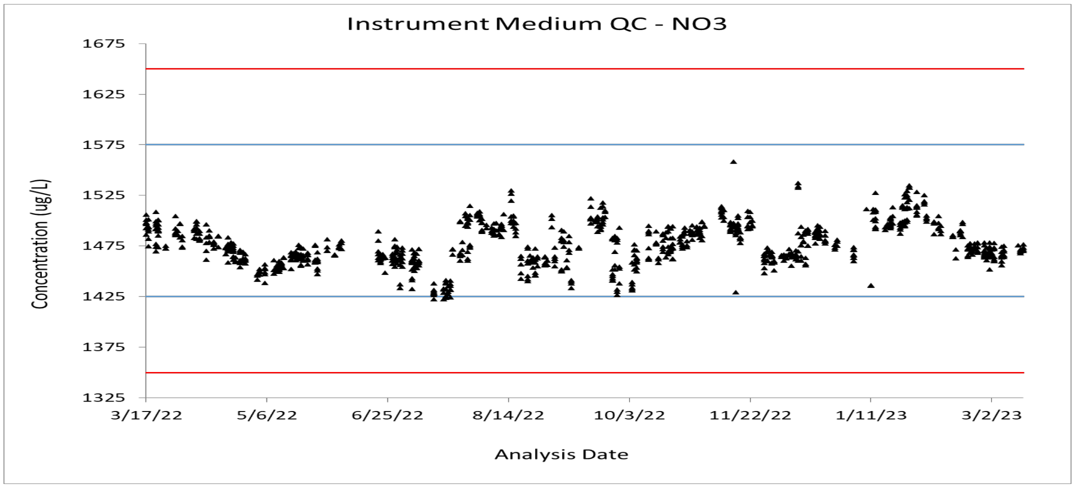
Figure 4.1-1: Control charts for anion CCV check standards at low, medium, medium-high, and high concentrations measured in units of µg/L (see Table 4.1-3) for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022).

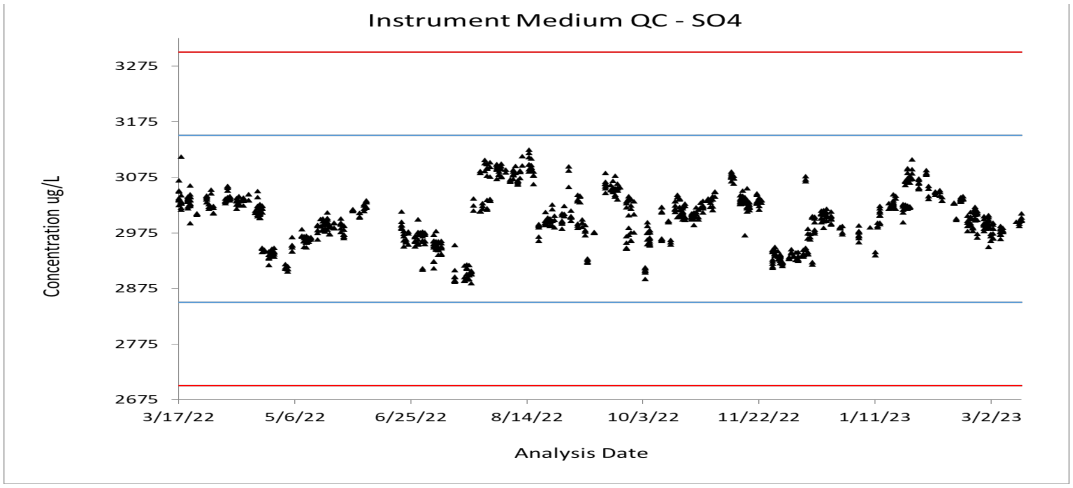


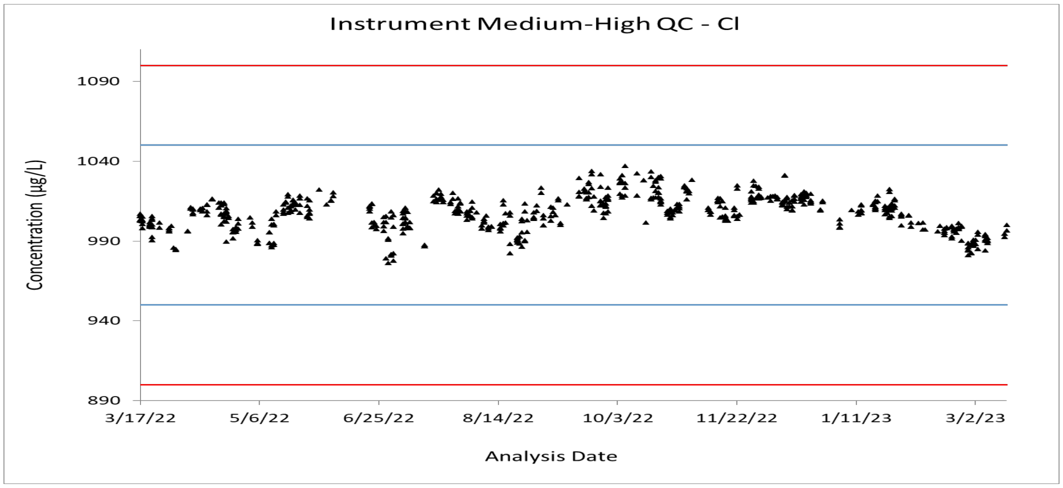


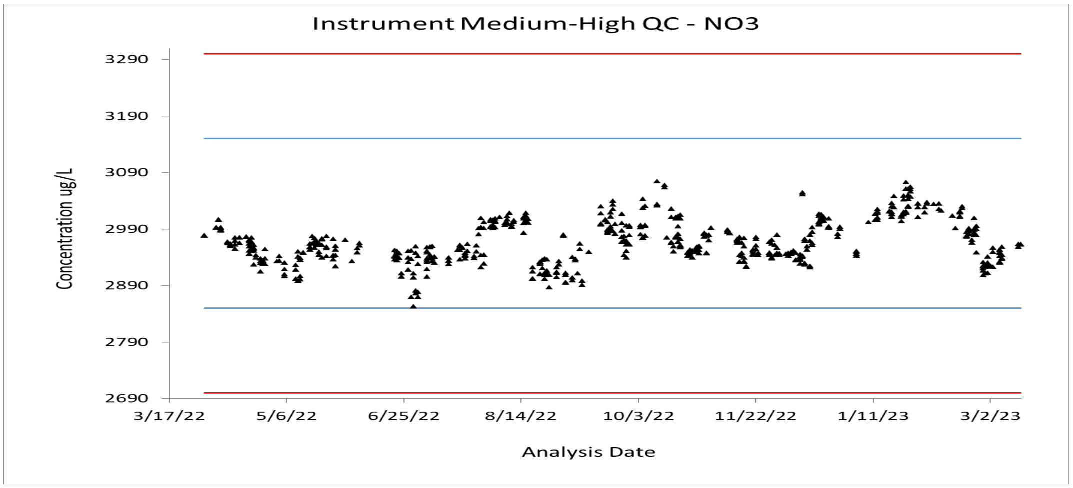


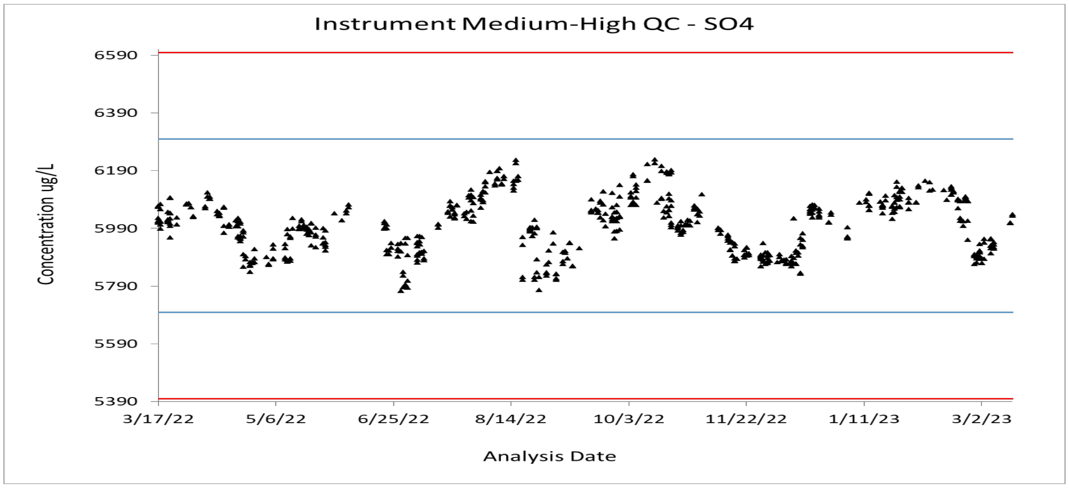

Instrument Medium QC - Cl
Concentration (ug/L)
565
545
525
505
485
465
445
425
2/8/22
3/30/22
5/19/22
7/8/22
8/27/22
10/16/22
12/5/22
1/24/23
3/15/23
Analysis Date

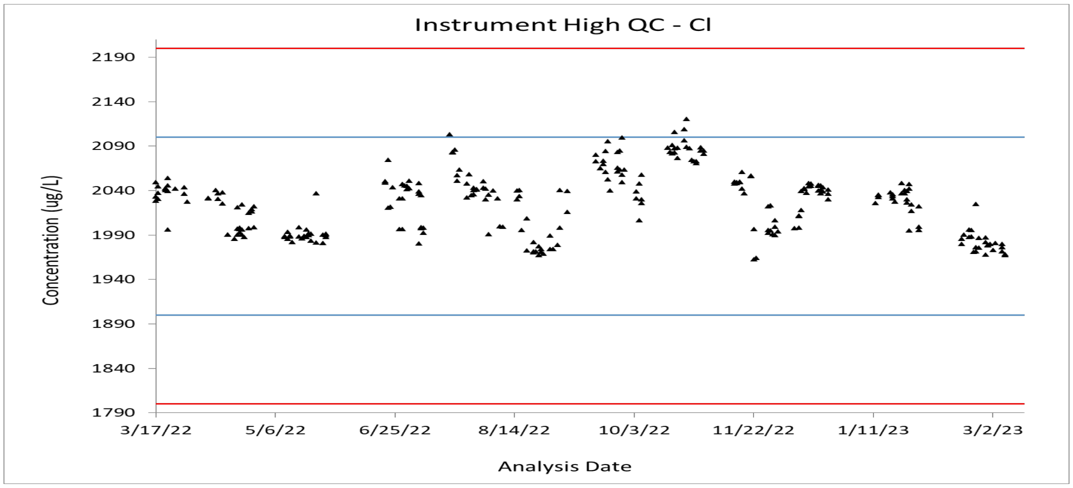

Instrument Medium QC - NO3
Concentration (ug/L)
1675
1625
1575
1525
1475
1425
1375
1325
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

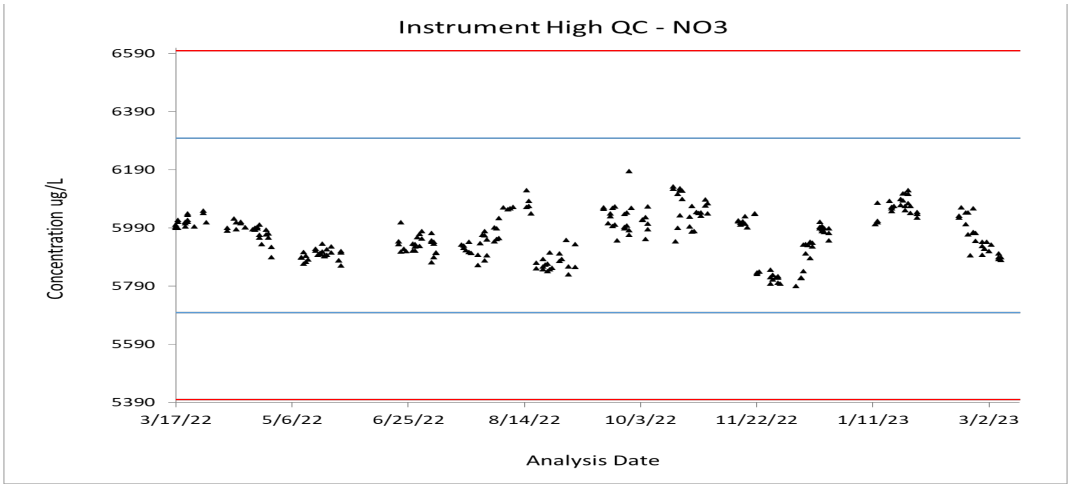

Instrument Medium QC - SO4
Concentration ug/L
3275
3175
3075
2975
2875
2775
2675
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

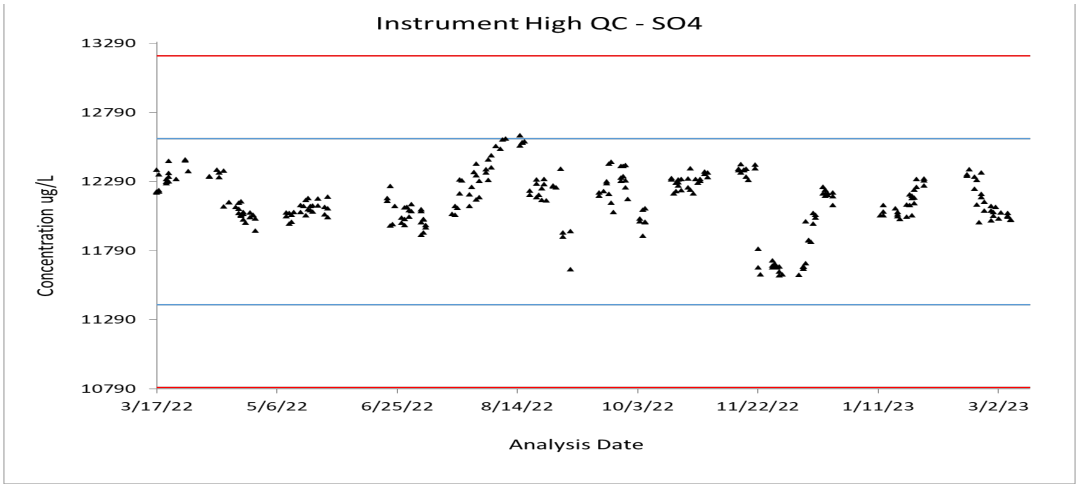

Instrument Medium-High QC - Cl
Concentration (µg/L)
1090
1040
990
940
890
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Instrument Medium-High QC - NO3
Concentration ug/L
3290
3190
3090
2990
2890
2790
2690
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Instrument Medium-High QC - SO4
Concentration ug/L
6590
6390
6190
5990
5790
5590
5390
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

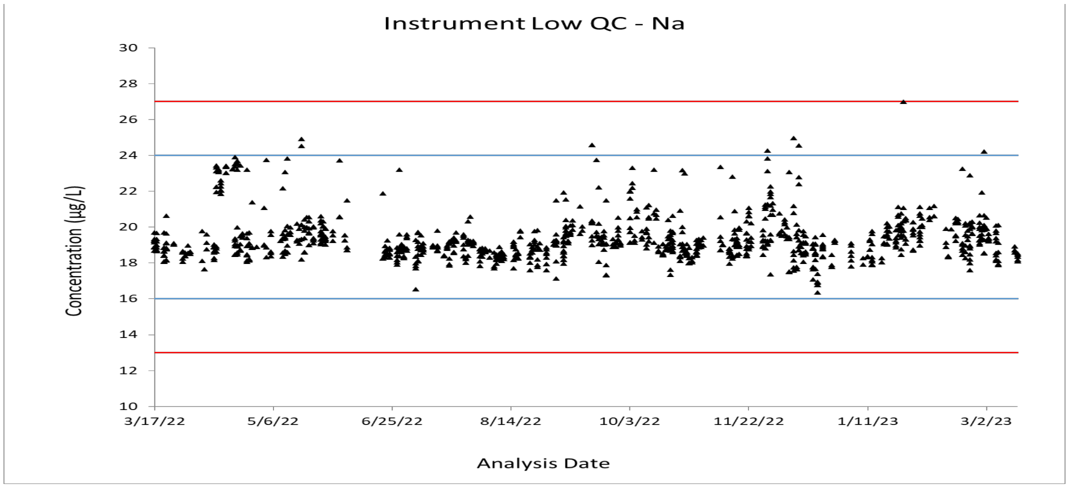


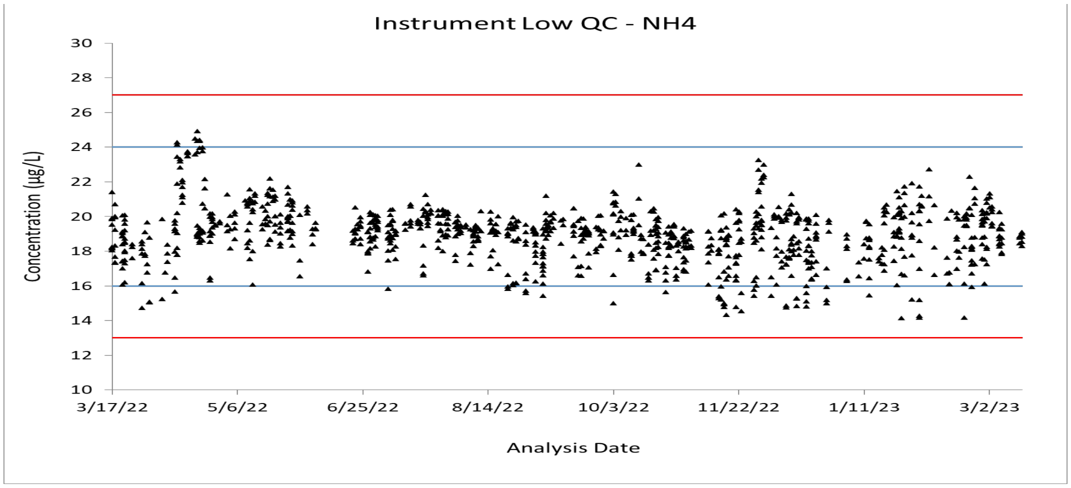


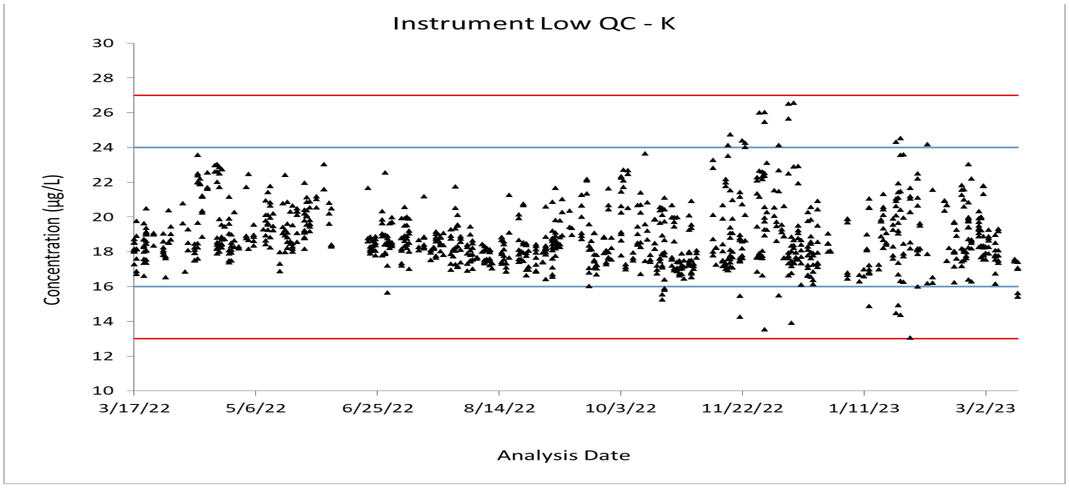


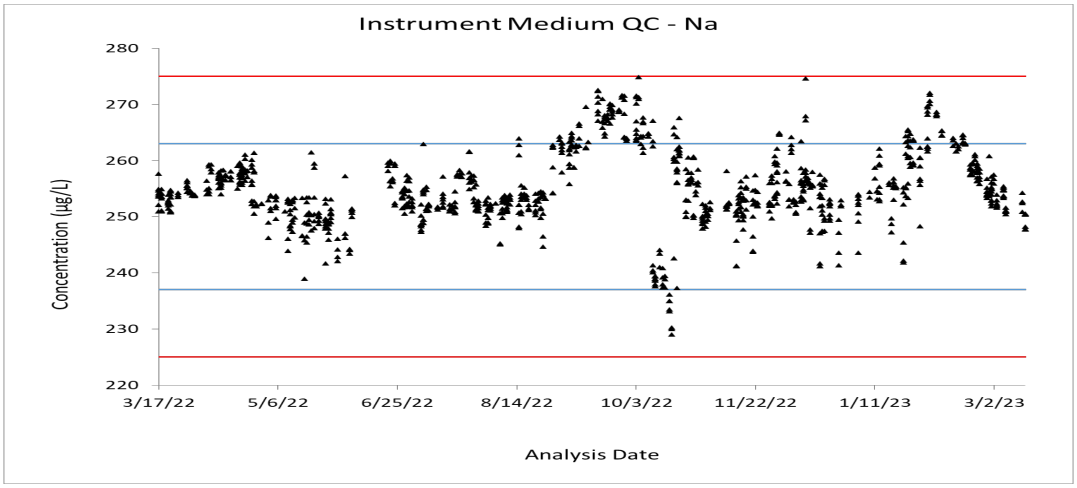
In the below control chart figures, red lines show upper and lower control limits set at ±35% of the nominal concentrations for the low standards and ±10% of the nominal concentrations for the medium, medium-high, and high standards. Blue lines show upper and lower warning limits.

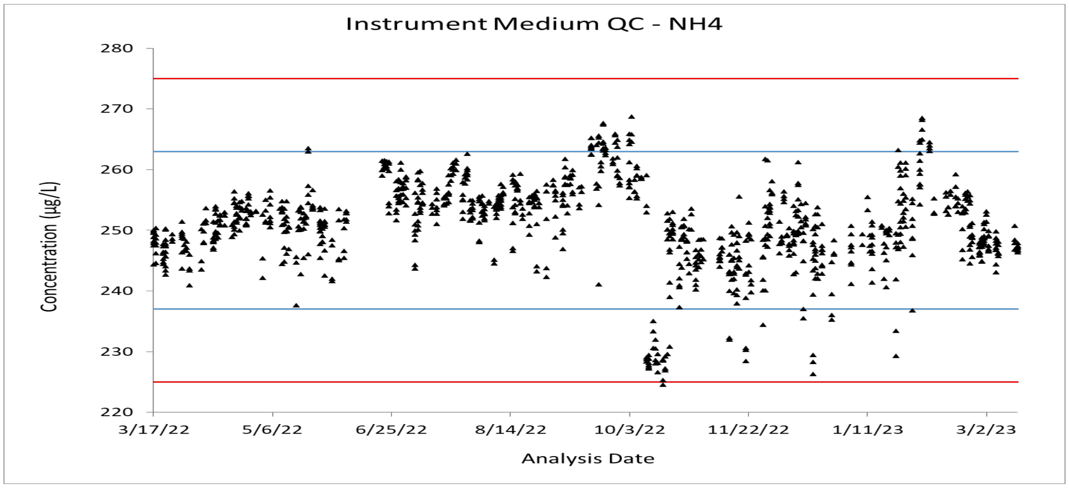
Figure 4.1-2: Control charts for cation CCV check standards at low, medium, medium-high, and high concentrations measured in units of µg/L (see Table 4.1-4) for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022).

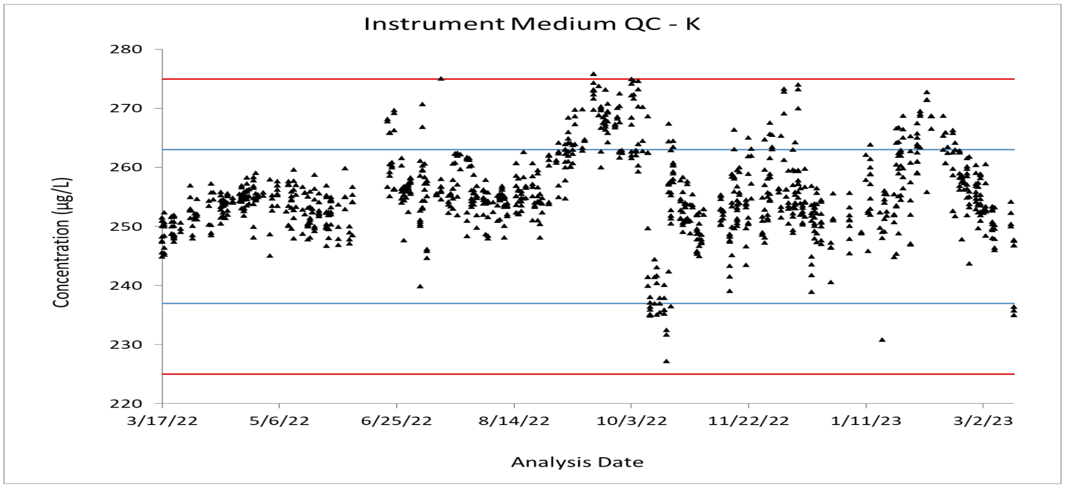


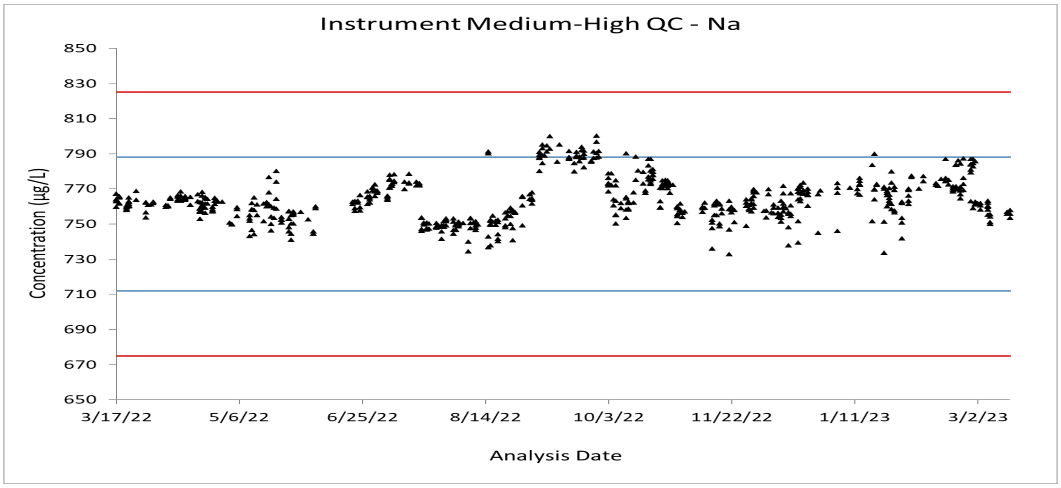


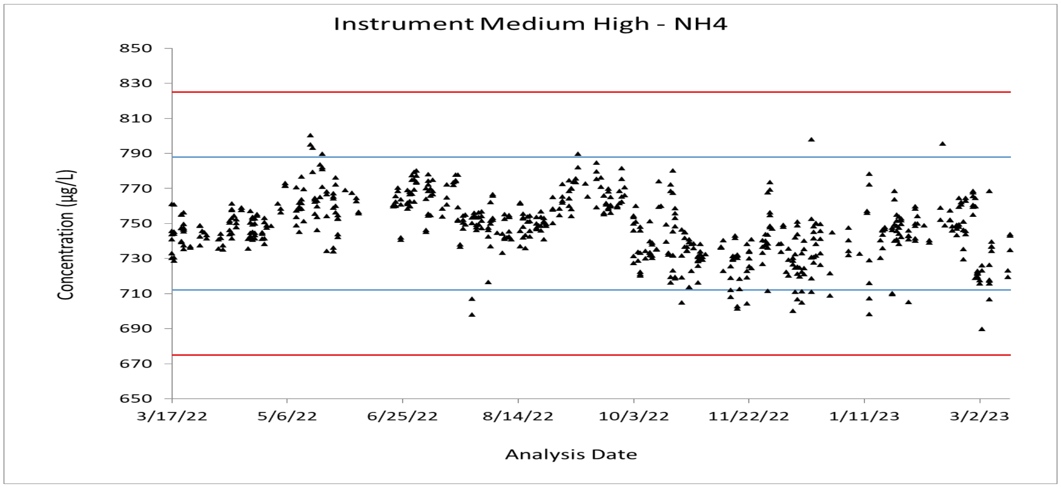


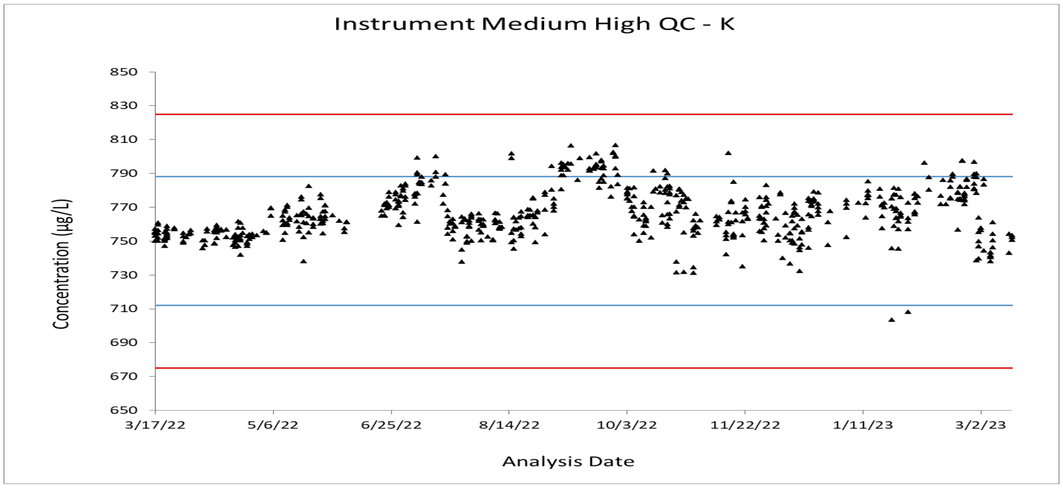

Instrument Medium QC - Na
280
270
260
250
240
230
220
Concentration (µg/L)
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

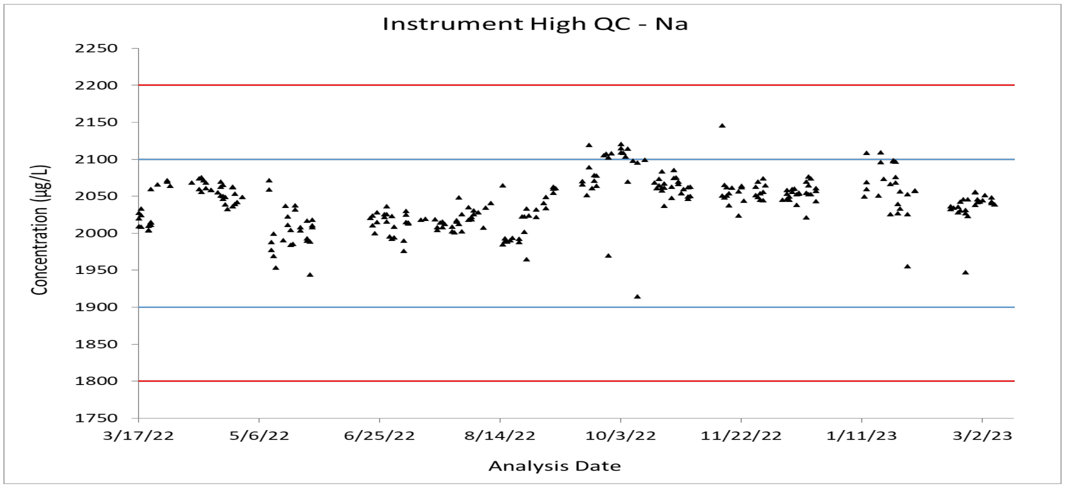

Instrument Medium QC - NH4
280
270
260
250
240
230
220
Concentration (µg/L)
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

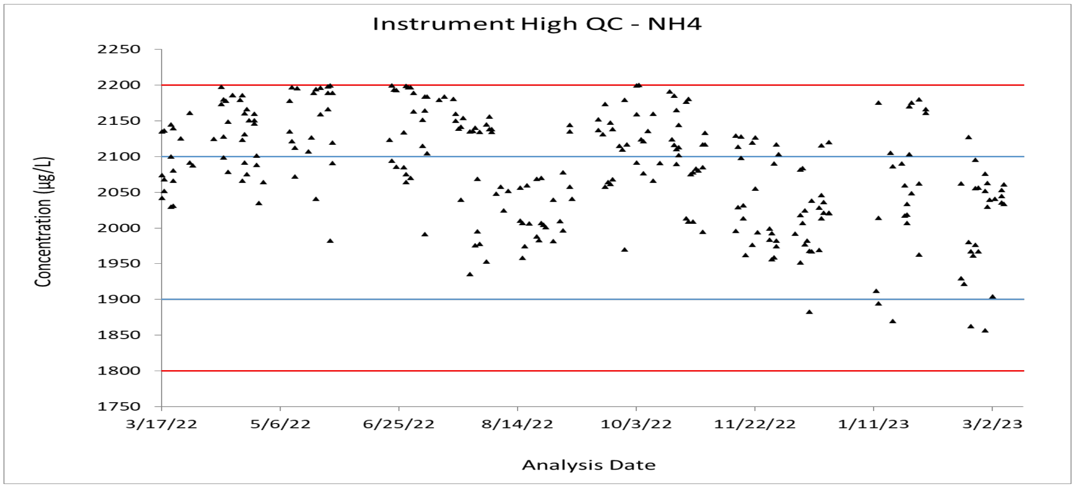

Instrument Medium QC - K
280
270
260
250
240
230
220
Concentration (µg/L)
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

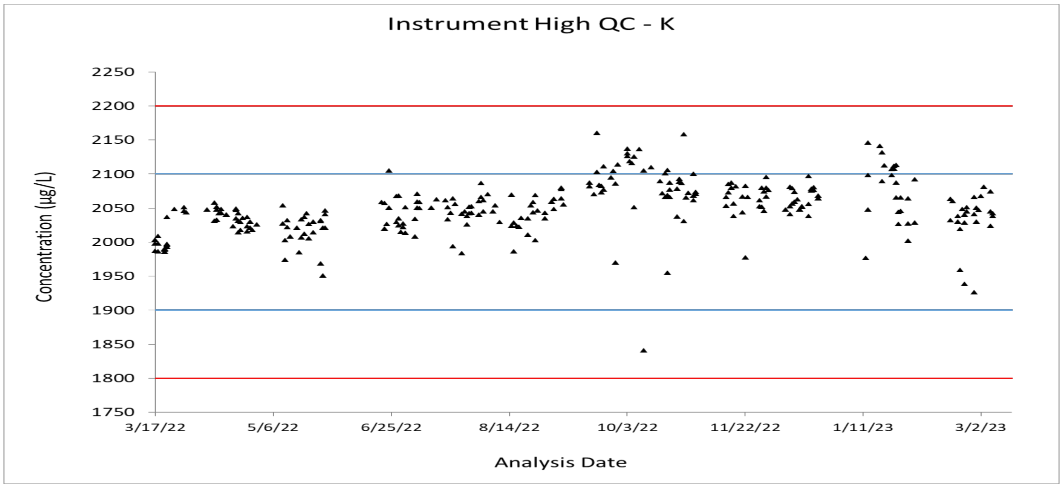

Instrument Medium-High QC - Na
850
830
810
790
770
750
730
710
690
670
650
Concentration (µg/L)
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Instrument Medium High - NH4
850
830
810
790
770
750
730
710
690
670
650
Concentration (µg/L)
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Instrument Medium High QC - K
850
830
810
790
770
750
730
710
690
670
650
Concentration (µg/L)
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date



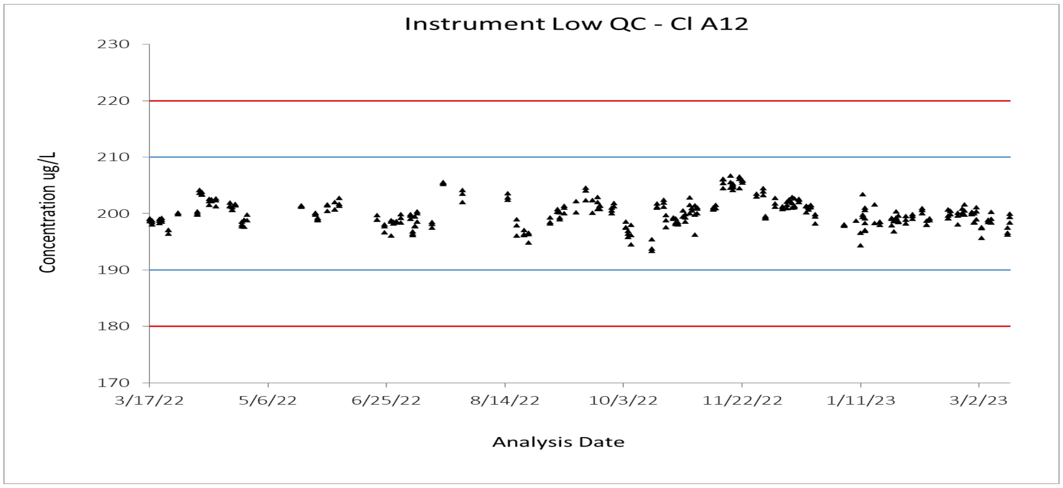


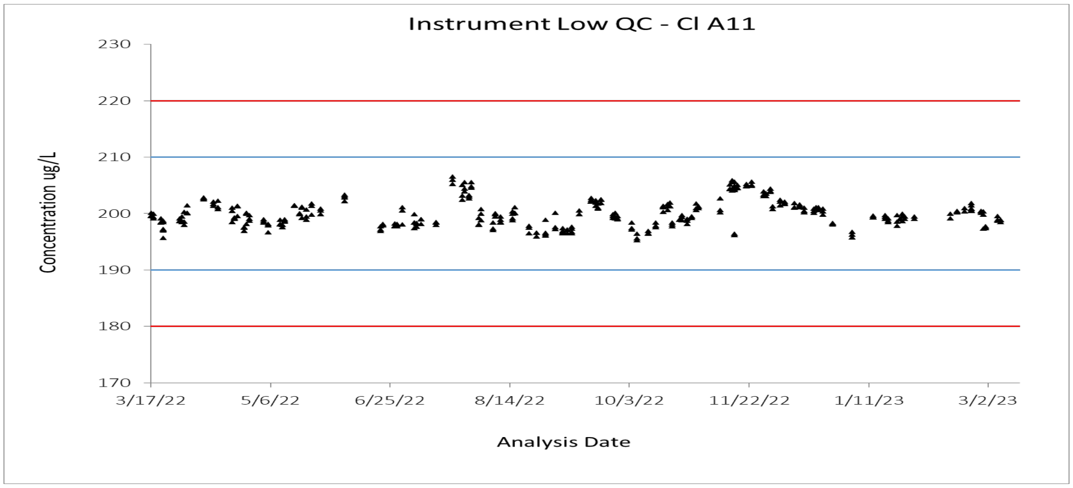


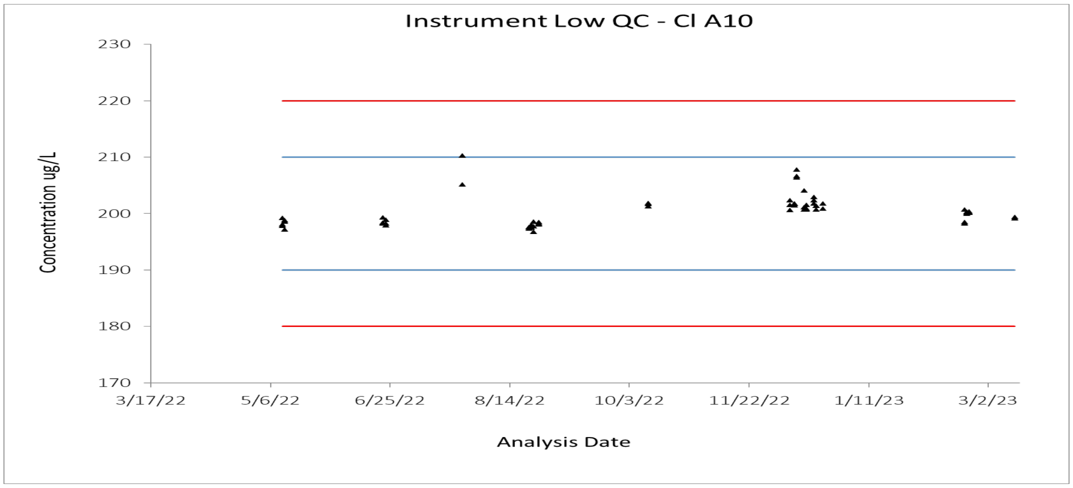
For the purpose of demonstrating instrument-to-instrument performance, control charts for the lowest CCV check standards were generated, where instruments A11, A12, A9, A10, and A8 are compared for anions (Figure 4.1-3) and instruments C9, C10, and C3 are compared for cations (Figure 4.1-4). The control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

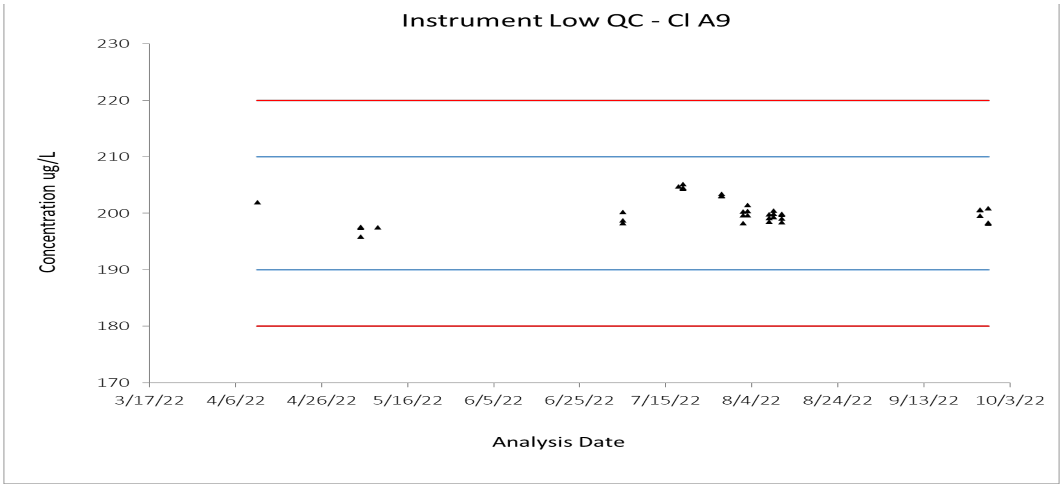
In the below control chart figures, red lines show upper and lower control limits set at ± 10% of the nominal concentrations. Blue lines show upper and lower warning limits.

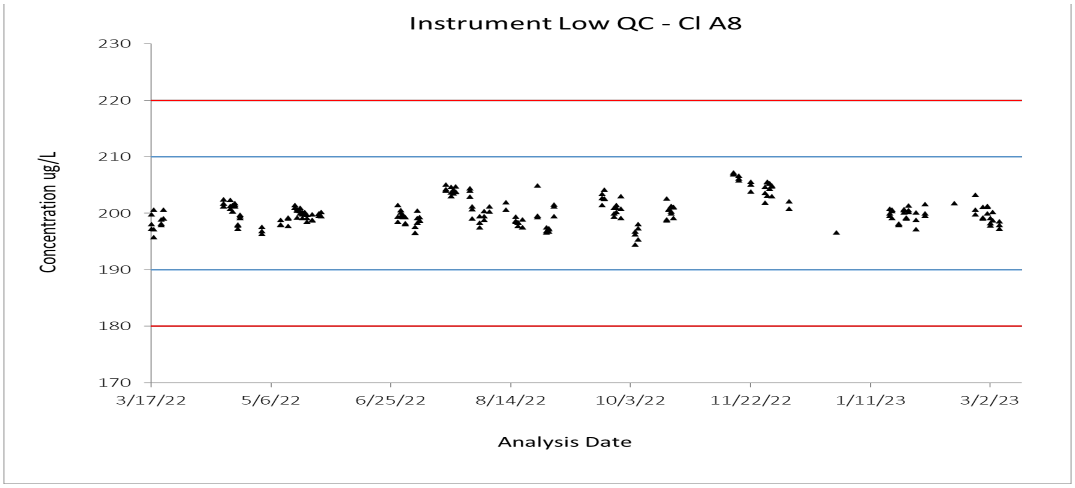
Figure 4.1-3: Control charts for anion CCV check standards showing comparability between instruments (A11 and A12, Thermo Dionex Aquion systems; A9, A10, and A8 Thermo Dionex ICS-3000 systems) at low concentrations (see Table 4.1-3) for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022). Note that A9 and A10 were not utilized as often for CSN sample analysis as these two systems are part of a dual system configured for anion only analysis. It is more efficient to combine single anion/cation systems for CSN analysis.

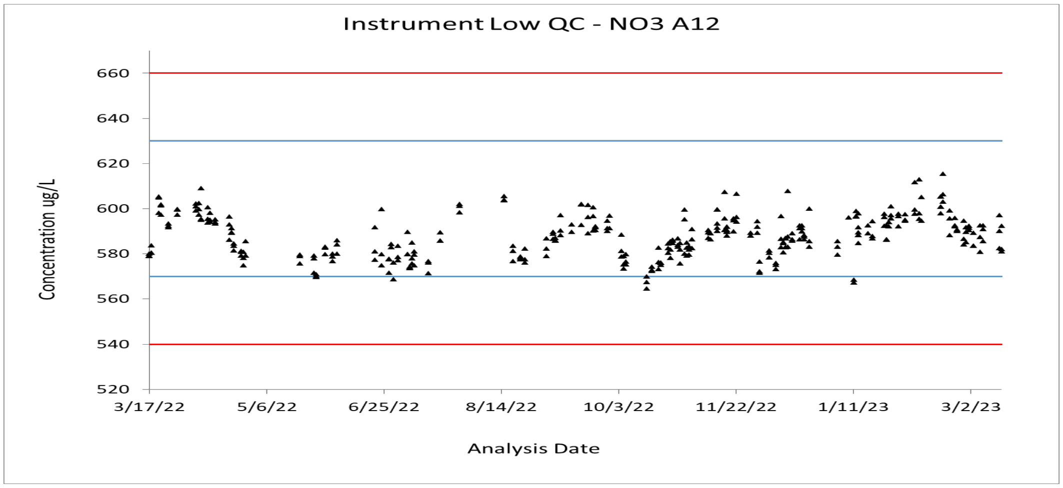


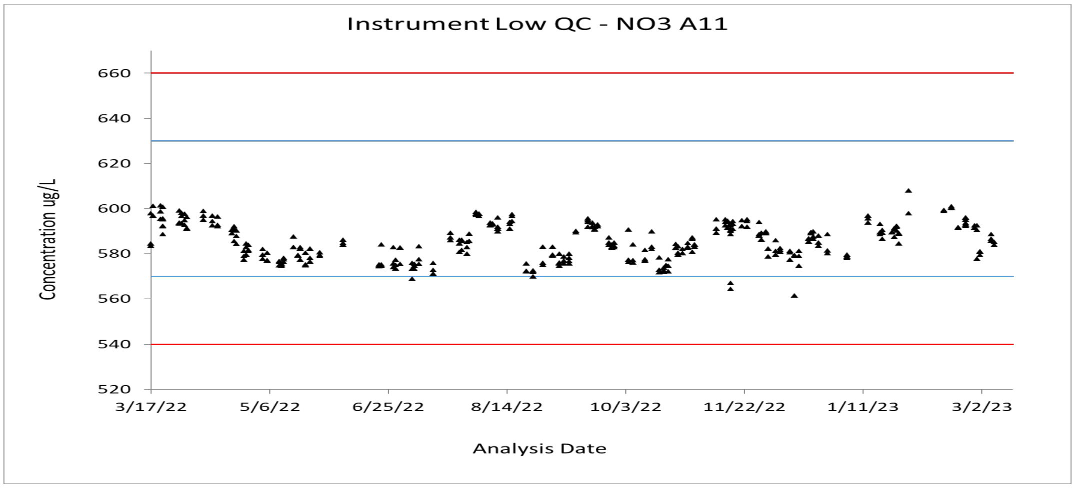


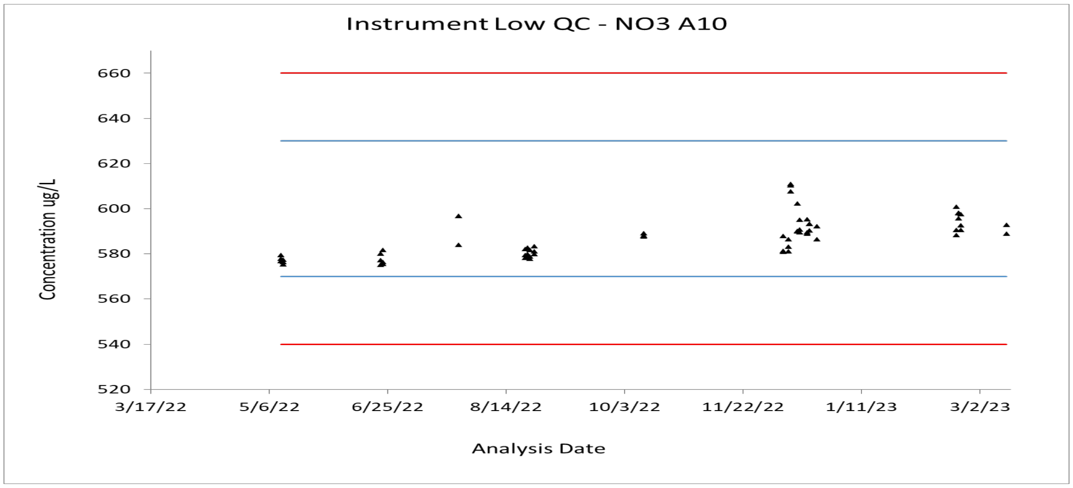

Instrument Low QC - Cl A10
Concentration ug/L
230
220
210
200
190
180
170
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

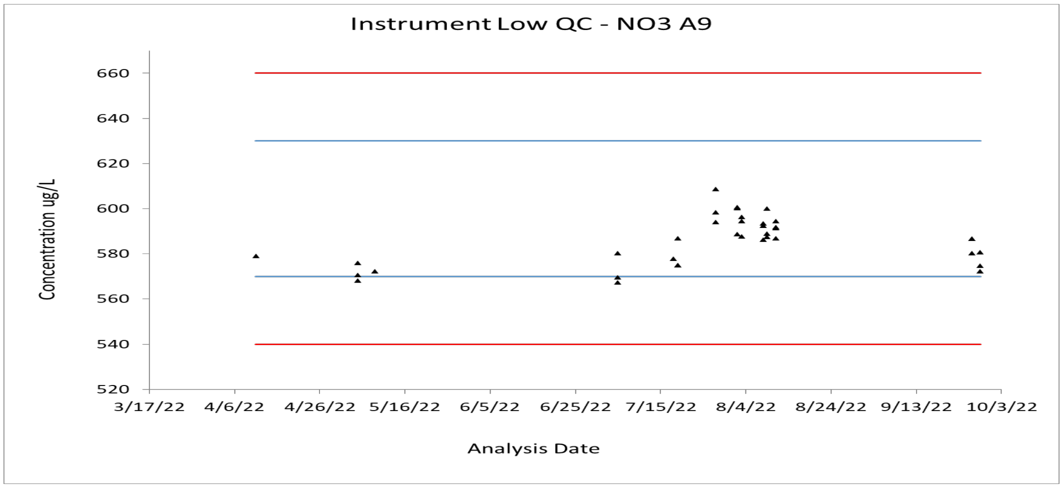

Instrument Low QC - Cl A9
Concentration ug/L
230
220
210
200
190
180
170
3/17/22
4/6/22
4/26/22
5/16/22
6/5/22
6/25/22
7/15/22
8/4/22
8/24/22
9/13/22
10/3/22
Analysis Date

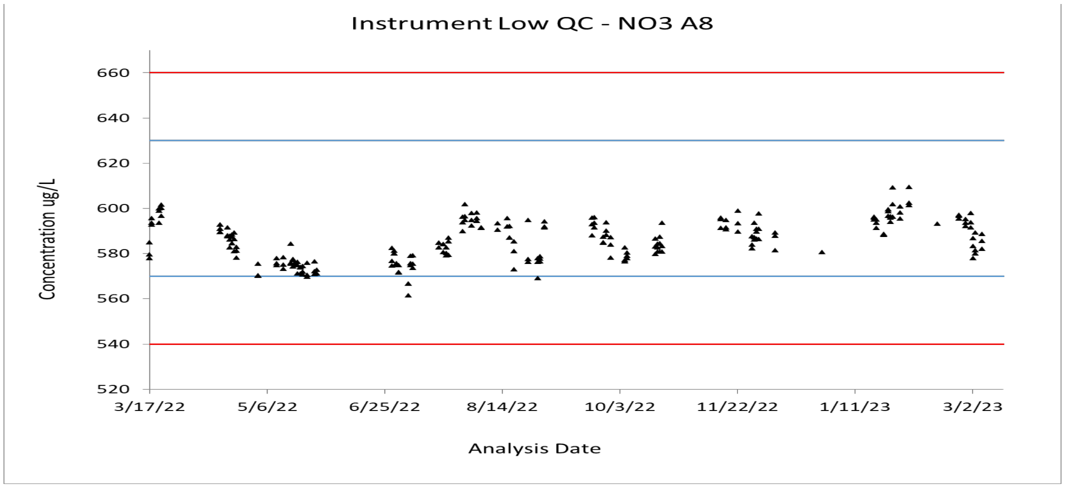

Instrument Low QC - Cl A8
Concentration ug/L
230
220
210
200
190
180
170
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

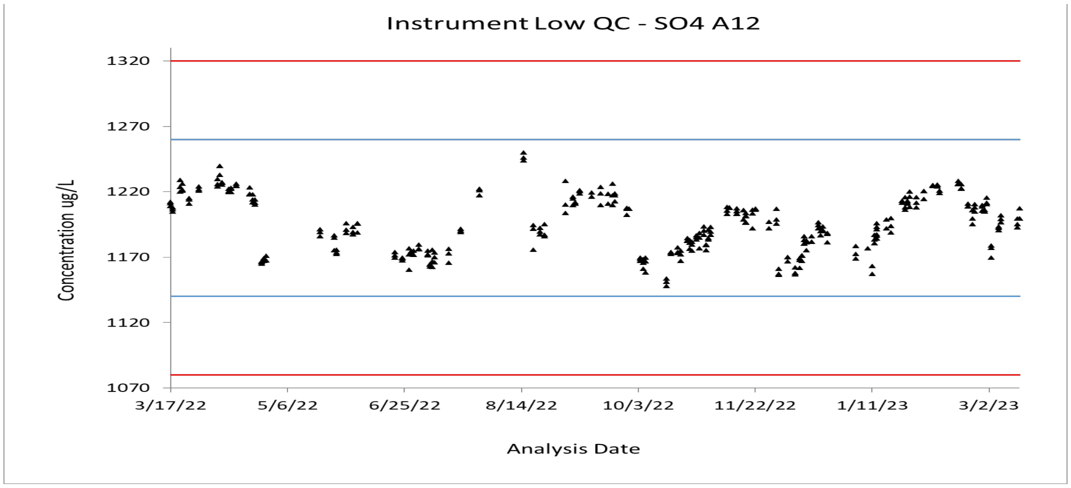

Instrument Low QC - NO3 A12
660
640
620
600
580
560
540
520
Concentration ug/L
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

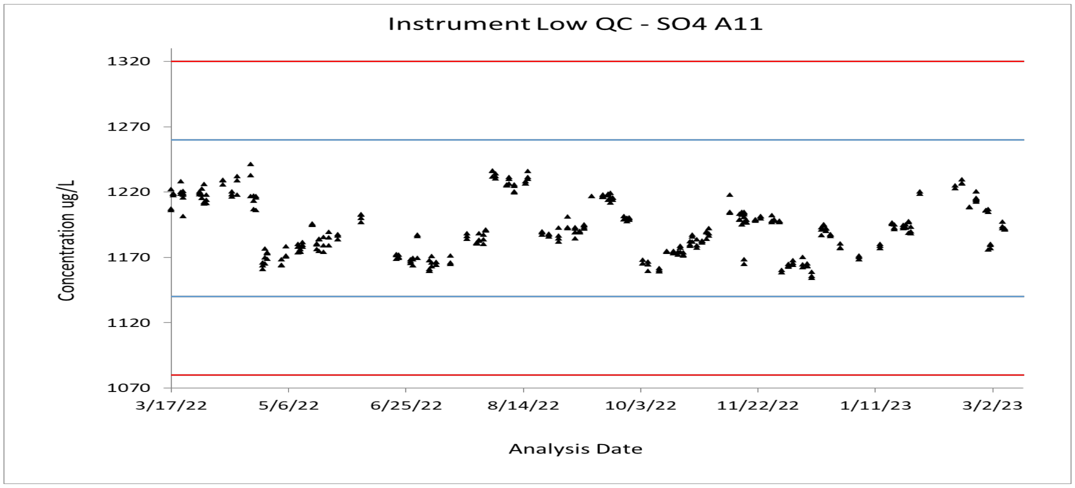

Instrument Low QC - NO3 A11
660
640
620
600
580
560
540
520
Concentration ug/L
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

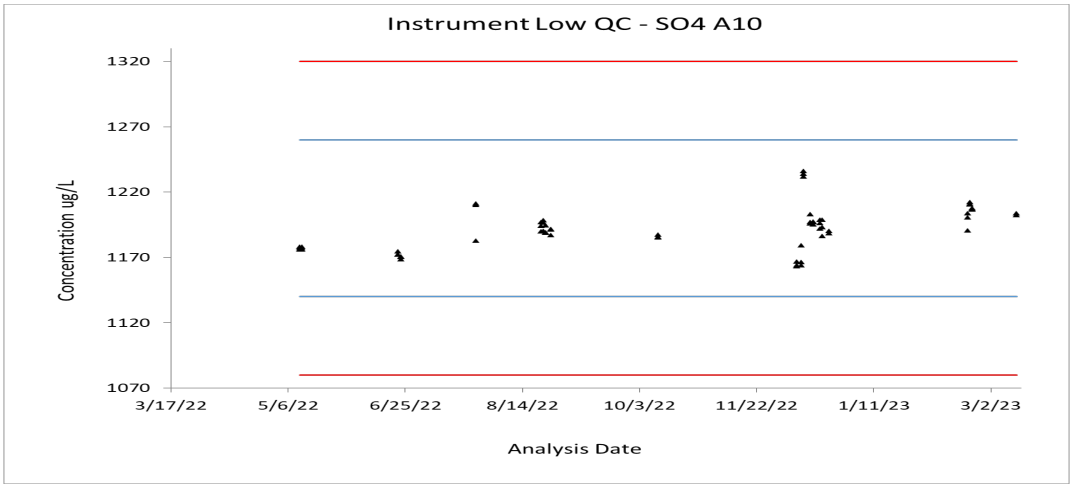

Instrument Low QC - NO3 A10
660
640
620
600
580
560
540
520
Concentration ug/L
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

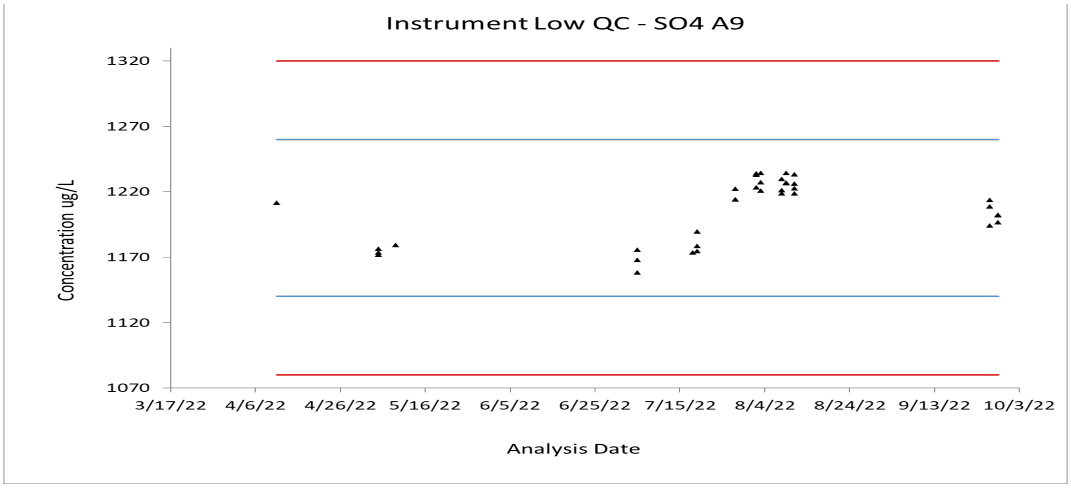

Instrument Low QC - NO3 A9
Concentration ug/L
660
640
620
600
580
560
540
520
3/17/22
4/6/22
4/26/22
5/16/22
6/5/22
6/25/22
7/15/22
8/4/22
8/24/22
9/13/22
10/3/22
Analysis Date

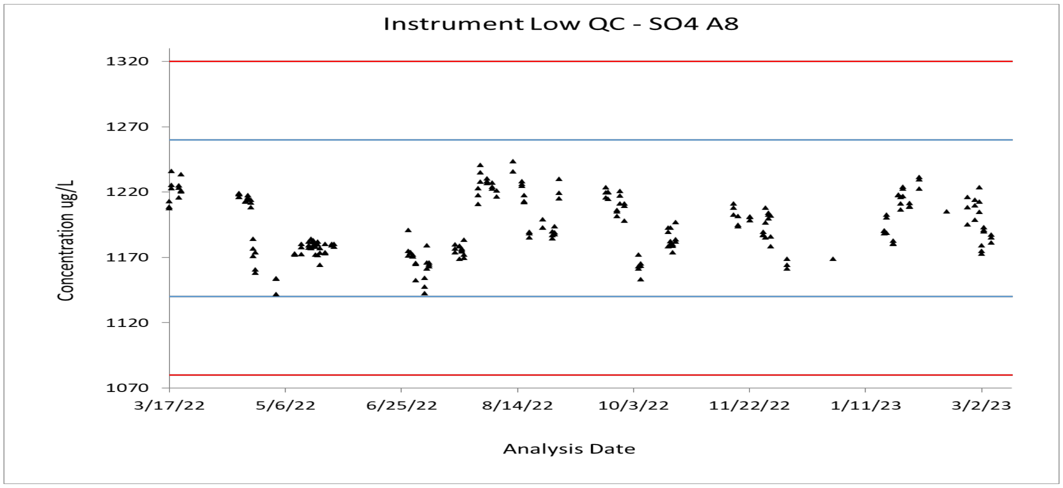

Instrument Low QC - NO3 A8
Concentration ug/L
660
640
620
600
580
560
540
520
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Instrument Low QC - SO4 A12
Concentration ug/L
1320
1270
1220
1170
1120
1070
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Instrument Low QC - SO4 A11
Concentration ug/L
1320
1270
1220
1170
1120
1070
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

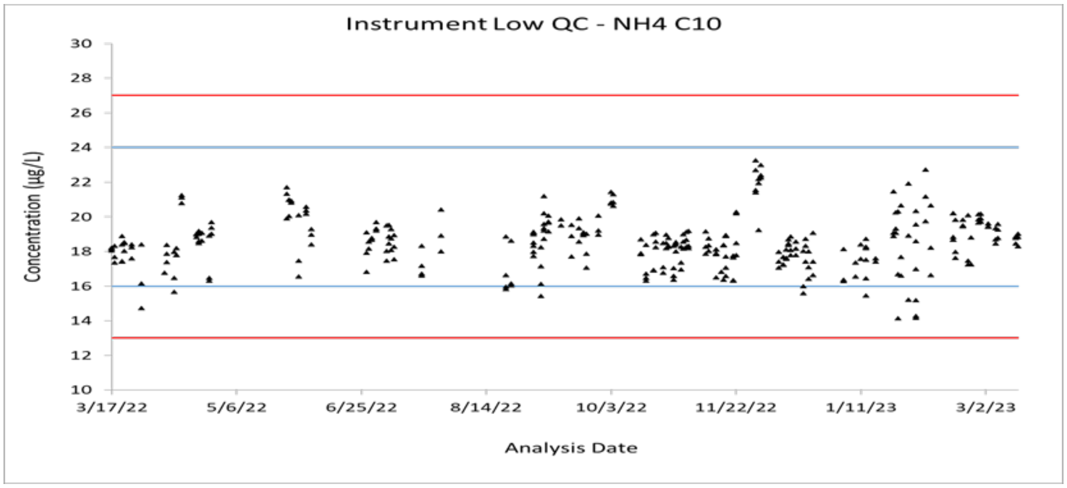

Instrument Low QC - SO4 A10
Concentration ug/L
1320
1270
1220
1170
1120
1070
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

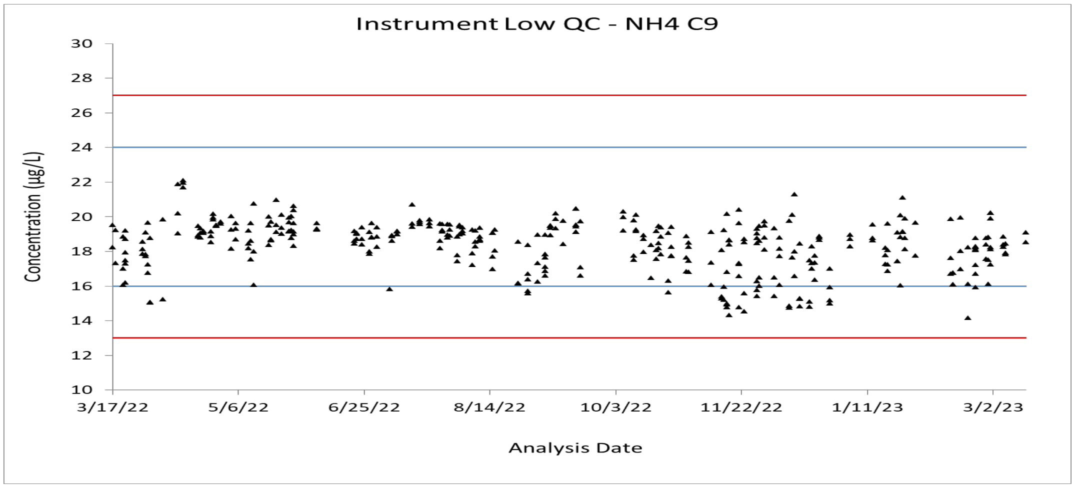

Instrument Low QC - SO4 A9
Concentration ug/L
1320
1270
1220
1170
1120
1070
3/17/22
4/6/22
4/26/22
5/16/22
6/5/22
6/25/22
7/15/22
8/4/22
8/24/22
9/13/22
10/3/22
Analysis Date

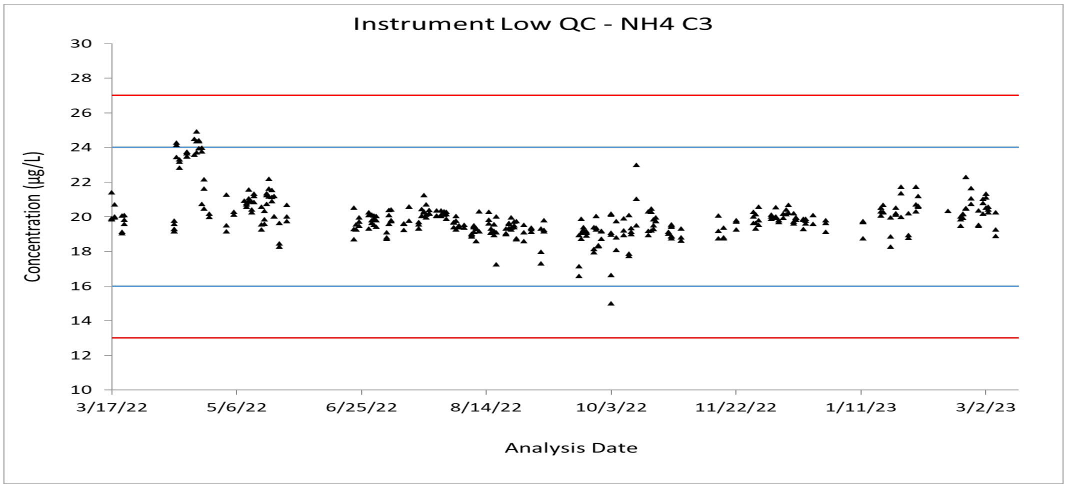


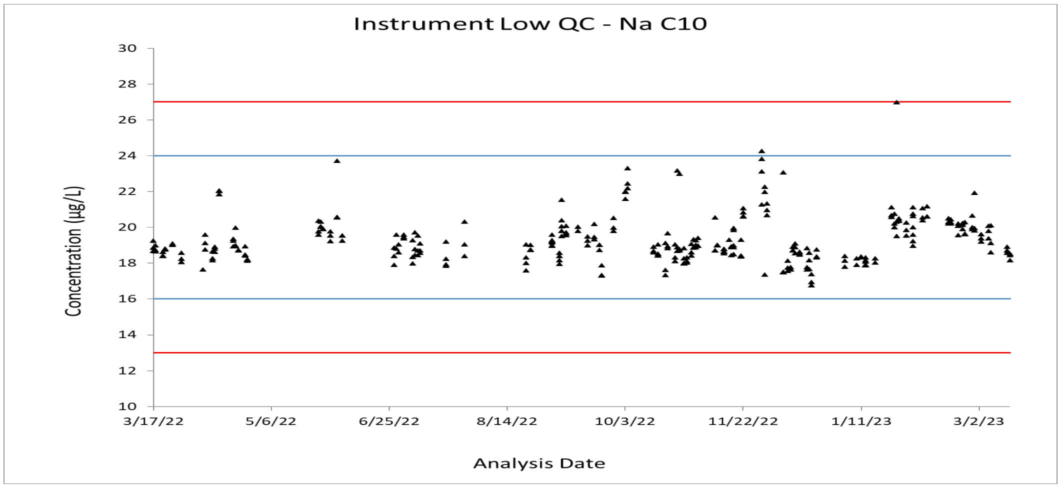
In the following control chart figures, red lines show upper and lower control limits set at ± 35% of the nominal concentrations. Blue lines show upper and lower warning limits.

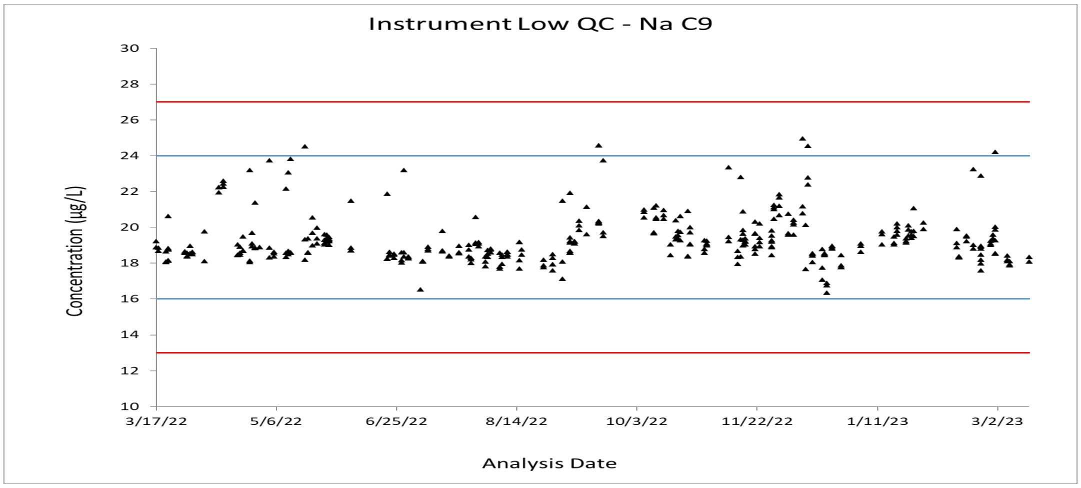
Figure 4.1-4: Control charts for cation CCV check standards showing comparability between instruments (C9 and C10, Thermo Dionex Aquion systems; C3 Thermo Dionex ICS-2000 systems) at low concentrations (see Table 4.1-4) for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022).

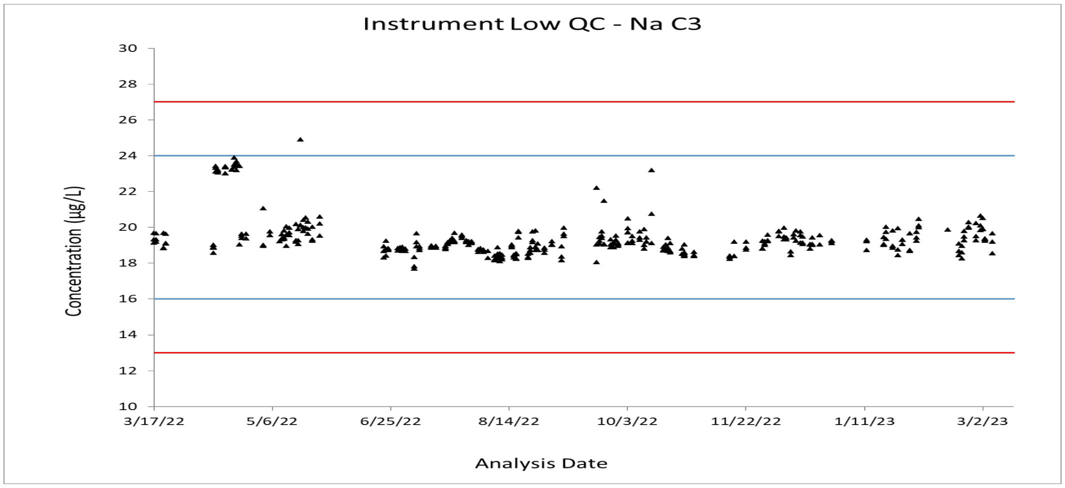


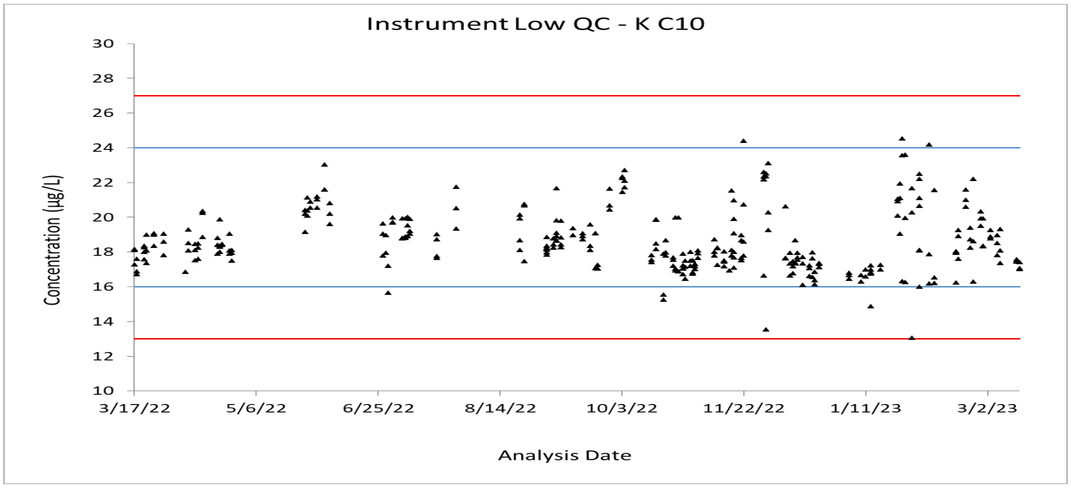

Instrument Low QC - NH4 C9
30
28
26
24
22
20
18
16
14
12
10
Concentration (µg/L)
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

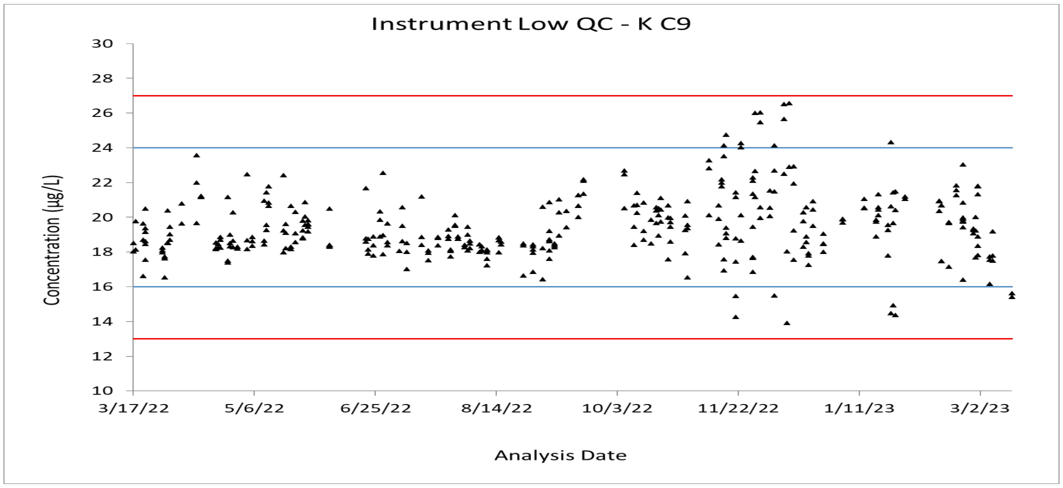

Instrument Low QC - NH4 C3
30
28
26
24
22
20
18
16
14
12
10
Concentration (µg/L)
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

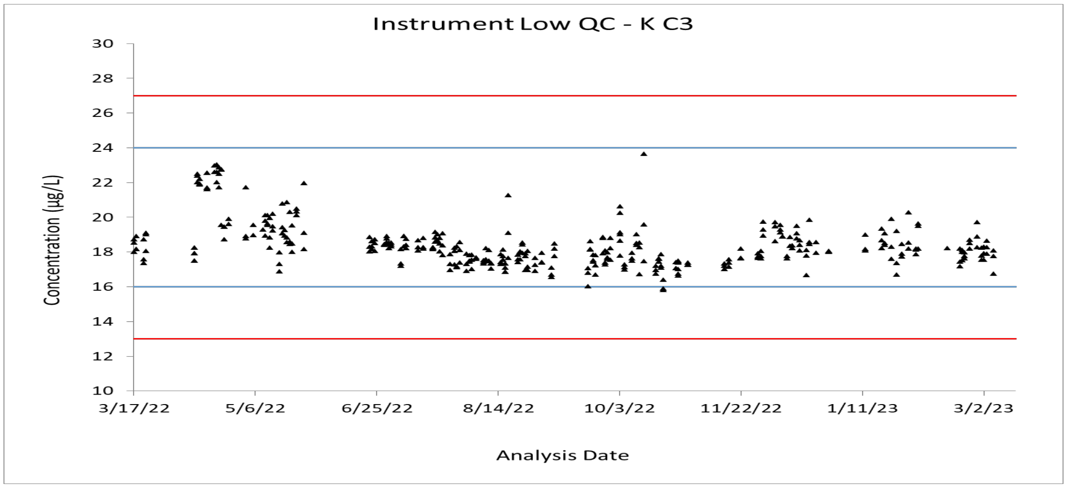

Instrument Low QC - Na C10
30
28
26
24
22
20
18
16
14
12
10
Concentration (µg/L)
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Instrument Low QC - Na C9
Concentration (µg/L)
30
28
26
24
22
20
18
16
14
12
10
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Instrument Low QC - Na C3
Concentration (µg/L)
30
28
26
24
22
20
18
16
14
12
10
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Instrument Low QC - K C10
Concentration (µg/L)
30
28
26
24
22
20
18
16
14
12
10
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

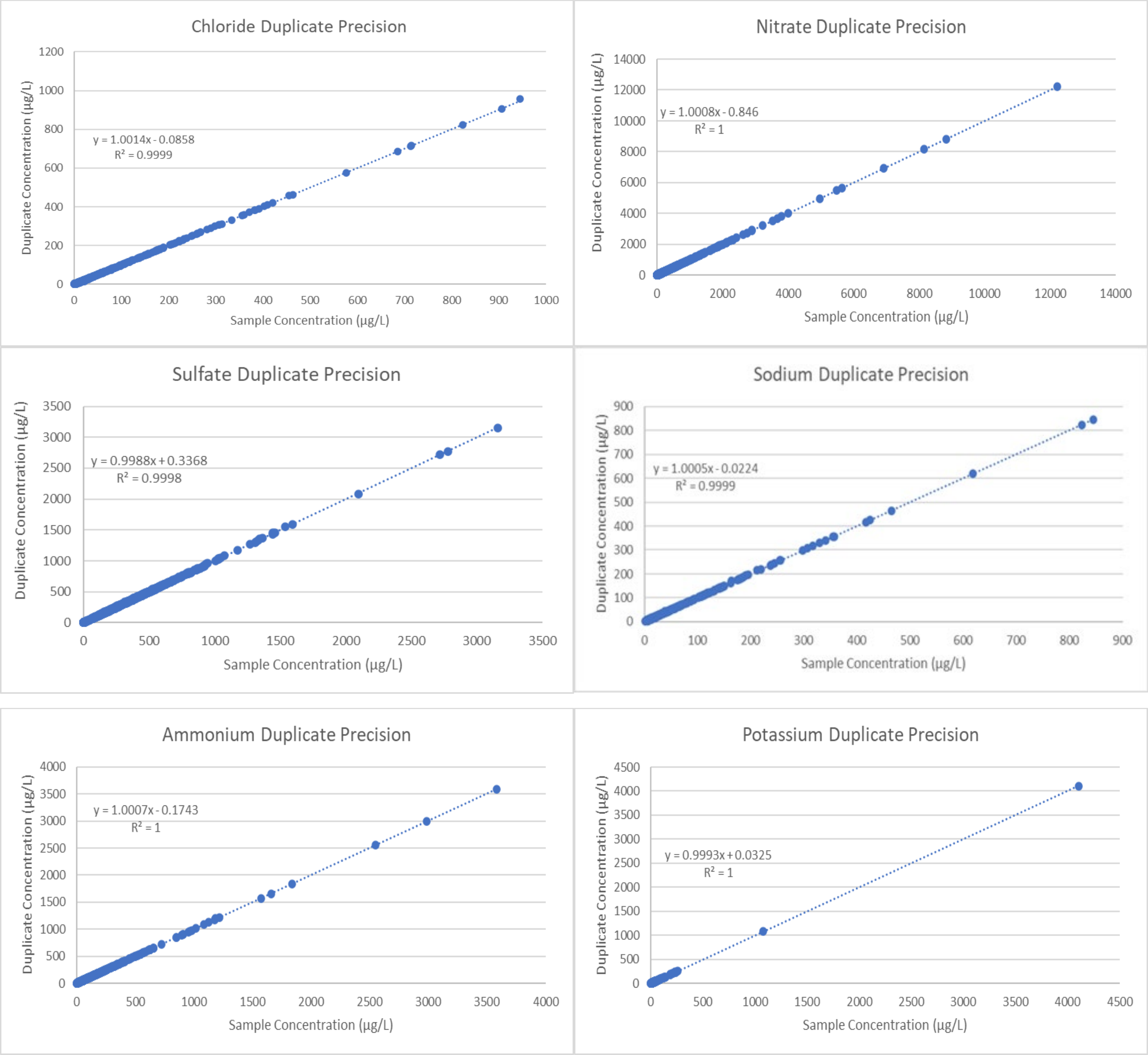




4.1.2.3 Duplicate Samples

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 ± 10% when sample concentrations are greater than ten times the analytical MDL and within ± 100% when sample concentrations are at or up to ten times the analytical MDL. During the analysis period when samples collected during 2022 were analyzed (March 17, 2022 through March 15, 2023), there were a total of 915 duplicate samples analyzed for anions (Figure 4.1-5), there were seven cases where the RPD did not meet the acceptance criteria. Also during this analysis period, there were a total of 912 duplicate samples analyzed for cations (Figure 4.1-5), with five cases where the RPD did not meet the acceptance criteria. 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 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 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.

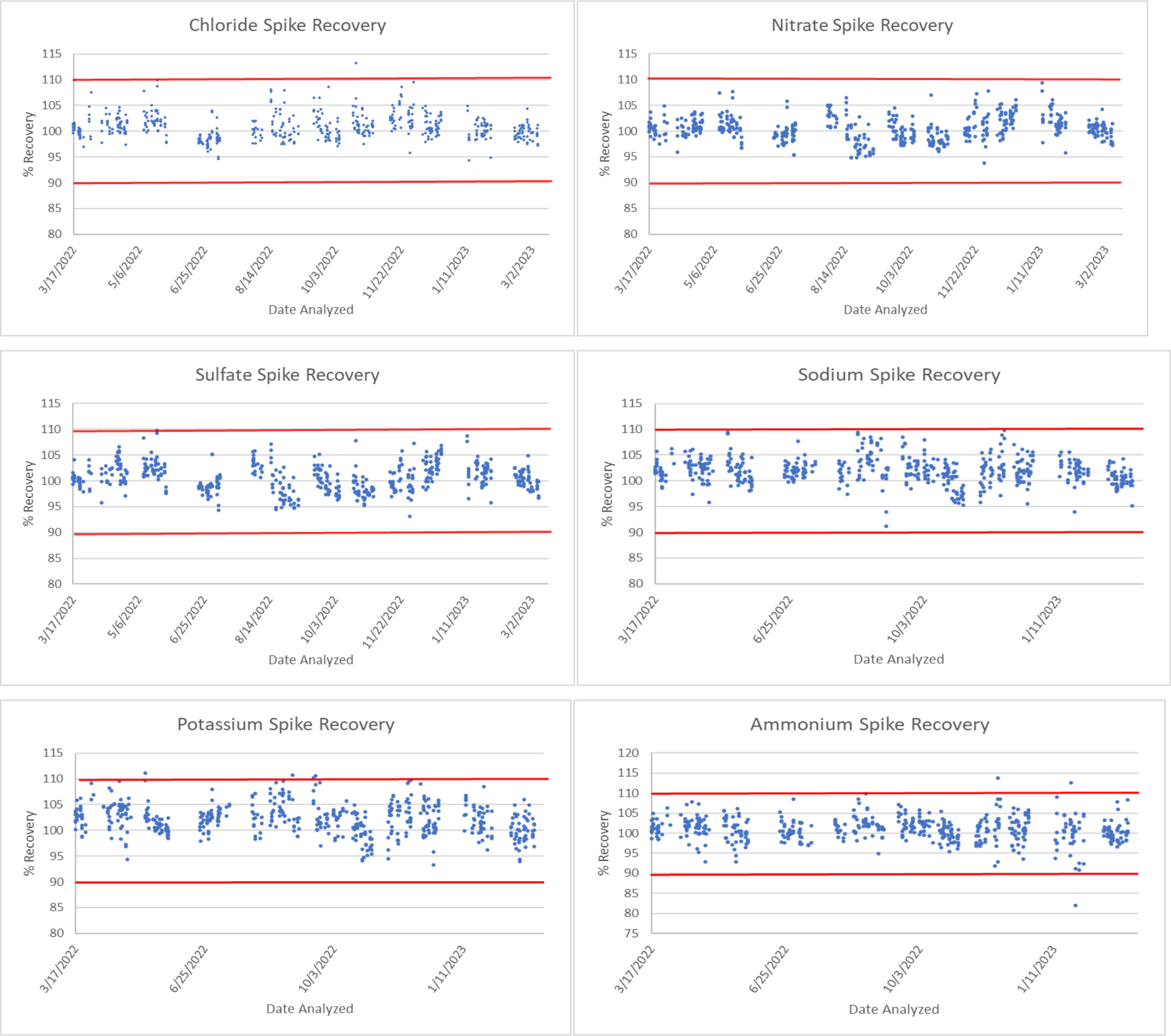


4.1.2.4 Spiked Sample Extracts

Matrix spikes are performed on 4% (two per set of 50 samples) of the samples analyzed. The matrix is deionized (DI) water, and spike samples typically meet the acceptance criteria with failures most likely resulting from introduced contamination. A total of 578 matrix spikes were analyzed for anions. There were two cases where either chloride, nitrate, or sulfate failed spike recovery criteria (Figure 4.1-6); samples were reanalyzed for all cases. A total of 575 matrix spikes were analyzed for cations. There were ten 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. In the below figures, the red lines are drawn to indicate the acceptable recovery limits of 90% to 110%.

Figure 4.1-6: Time series of recovery (%) for anion and cation of matrix spikes for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022).



4.1.2.5 Reagent Blanks and Spikes

All analyses begin with the injection of two DI water instrument blanks which clean the sample loop prior to injection of calibration standards. Method blanks and laboratory control spikes (LCS) are used to measure the background contamination that could be introduced during the extraction, sample handling, or analysis processes. At the time of filter extraction, an empty extraction vial is included as a method blank at a rate of 1 for every 50 samples. Empty extraction vials are also spiked with exact volumes of concentrated solutions for both anions and cations a rate of 1 for every 25 samples for LCS analysis. The same volume of water (25.0 mL) is added to the method blank and LCS vials as is added to the vials with the filter samples to be extracted.

Figure 4.1-7: Concentrations of anions and cations in DI water blanks for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022). Black line indicates the analytical method detection limit.

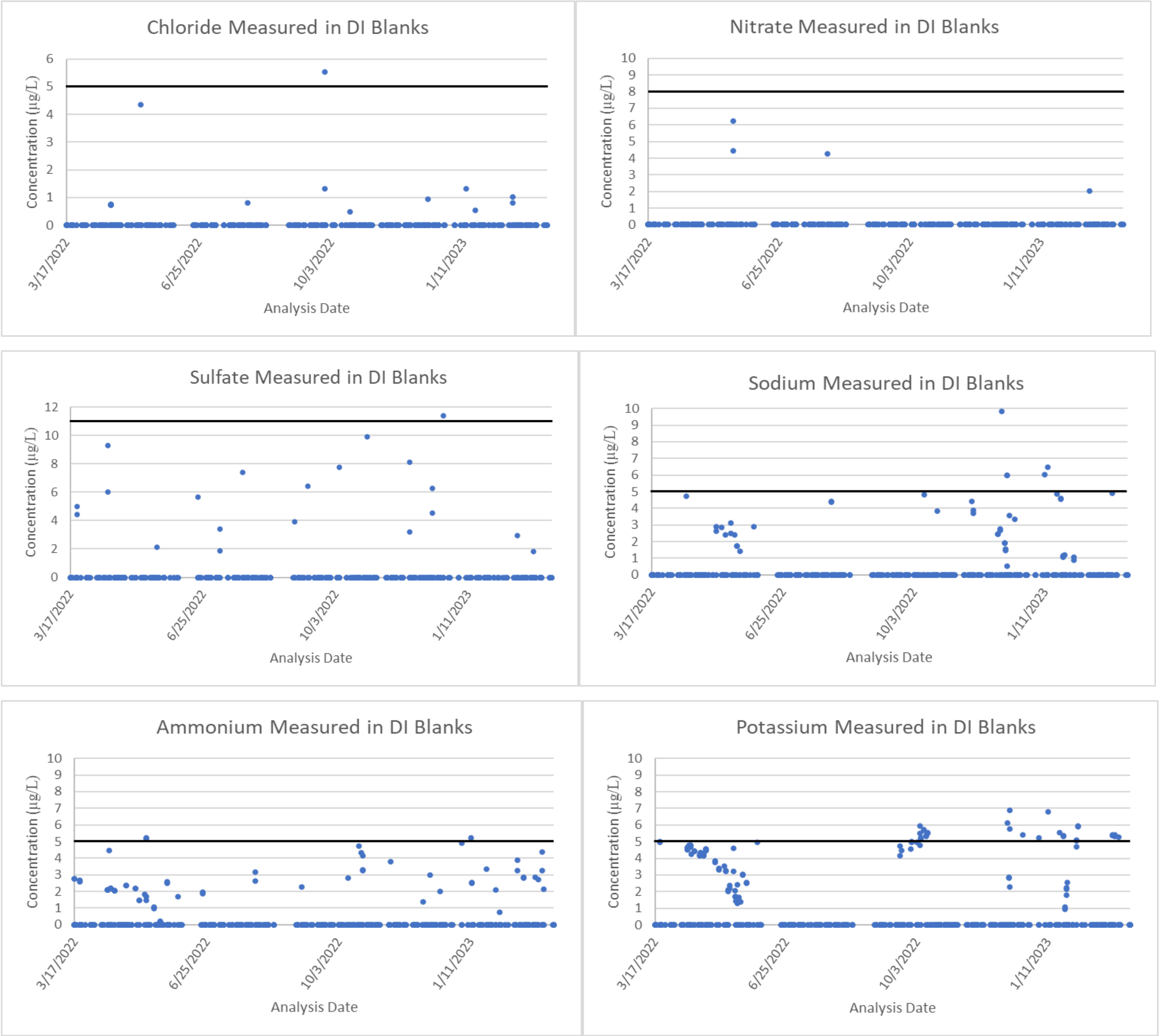
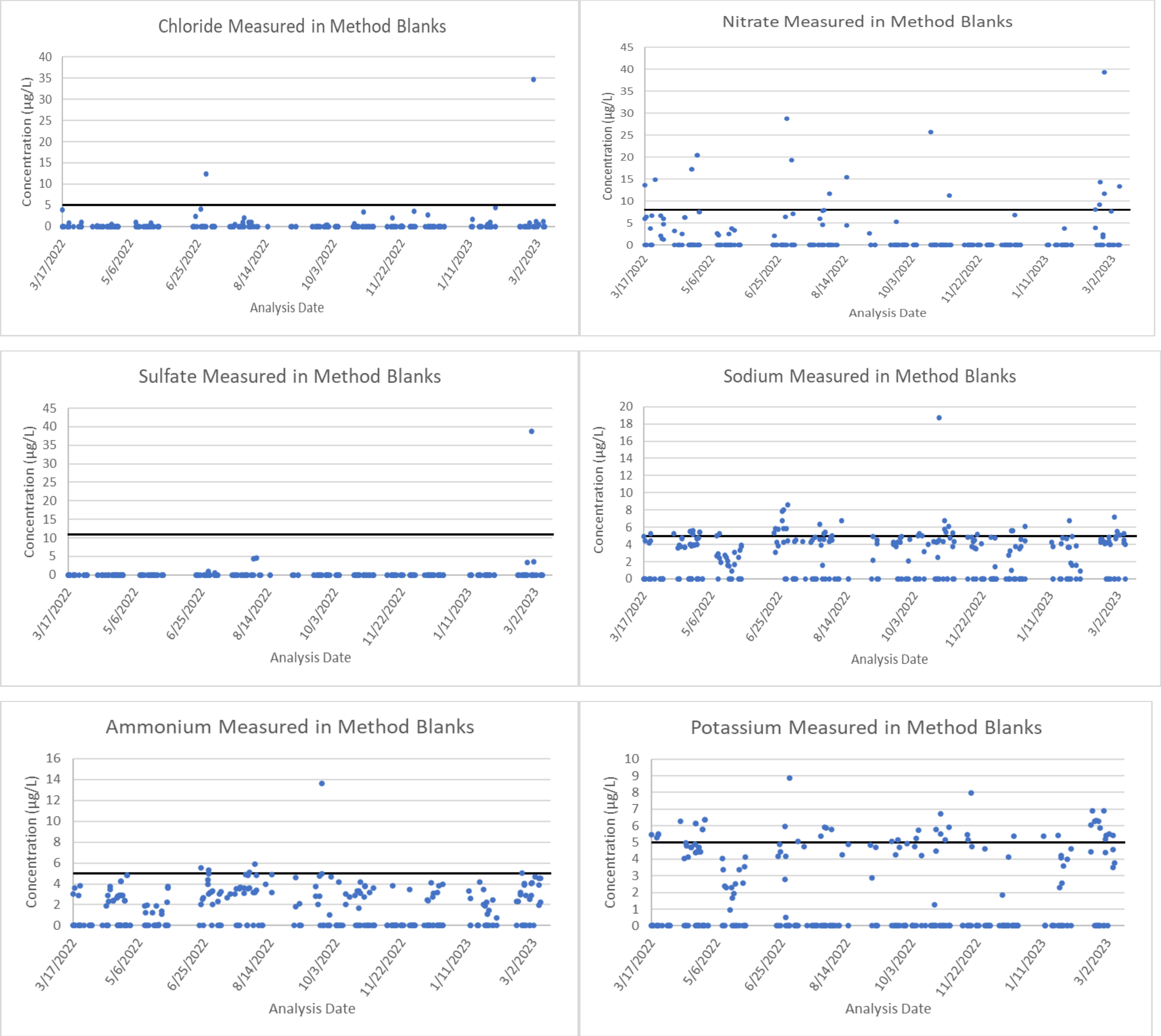


Figure 4.1-8: Concentrations of anions and cations in method blanks for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022). Black line indicates the analytical method detection limit.



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 03/17/2022 through 03/15/2023 (samples collected 1/1/2022 through 12/31/2022).

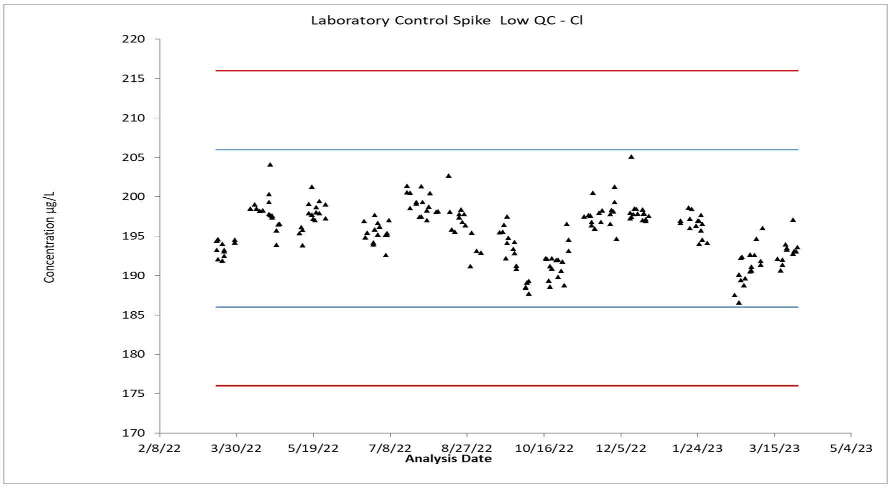
QC Sample	Cl^- (ppb)	NO_3^- (ppb)	SO_4^{2-} (ppb)
LCS Low	196	588	1180
LCS Medium	476	1430	2860
LCS High	2000	6000	12000

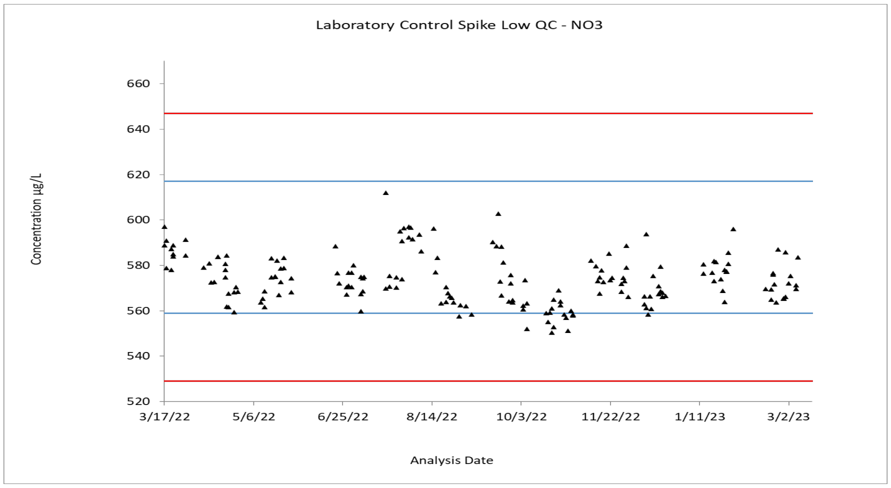
Table 4.1-6: Target concentrations for cation LCS for the analysis period 3/16/2021 through 03/7/2021 (samples collected 1/1/2021 through 12/31/2021).

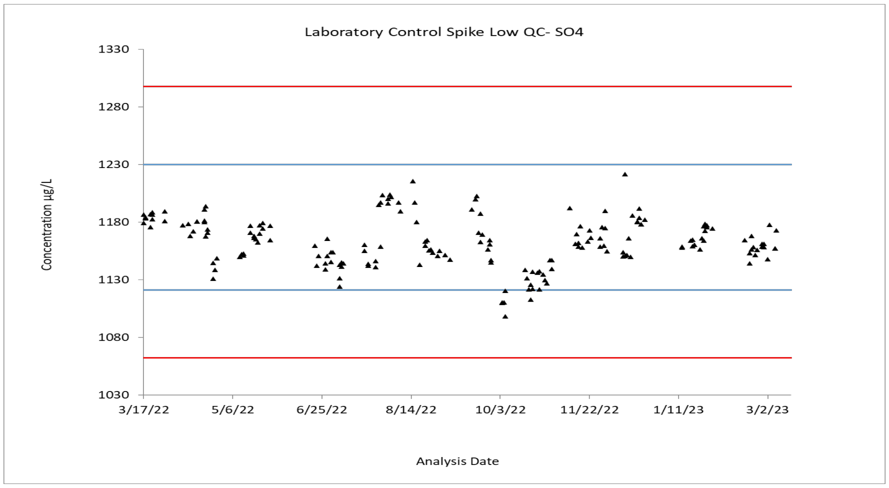
QC Sample	Na^+ (ppb)	NH_4^+ (ppb)	K^+ (ppb)
LCS Low	20	20	20
LCS Medium	276	276	276
LCS High	769	769	769

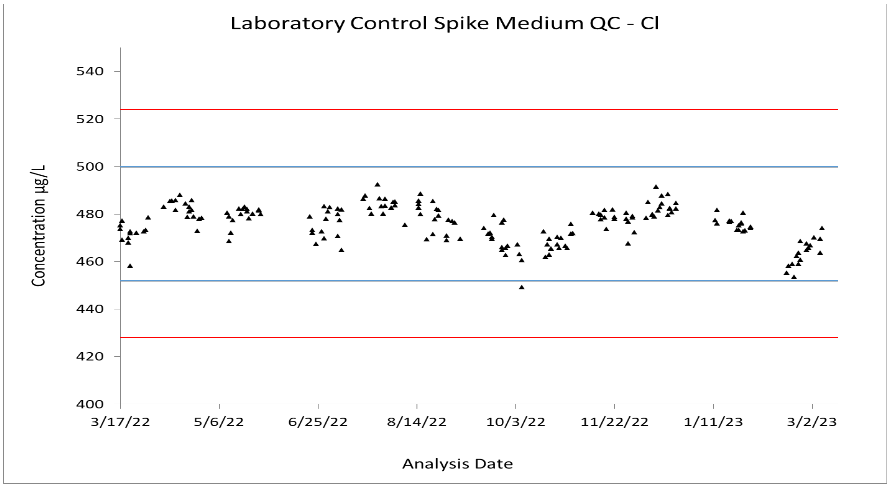
In figures 4.1-9 and 4.1-10 below, red lines show upper and lower control limits per the CCV check standard acceptance criteria. Blue lines show upper and lower warning limits.

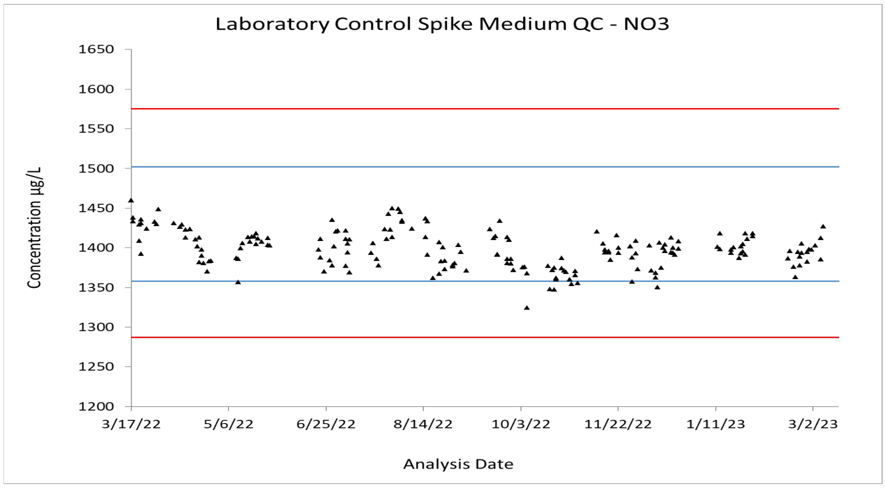
Figure 4.1-9: Control charts for anion LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022).

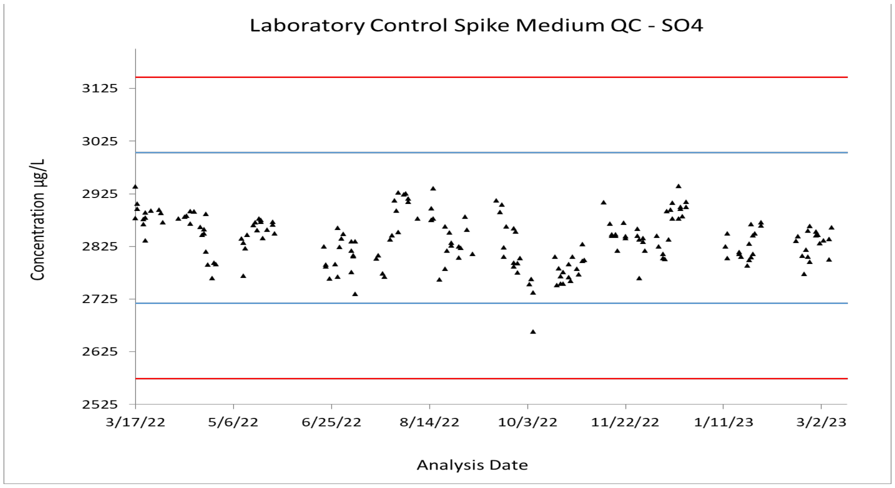


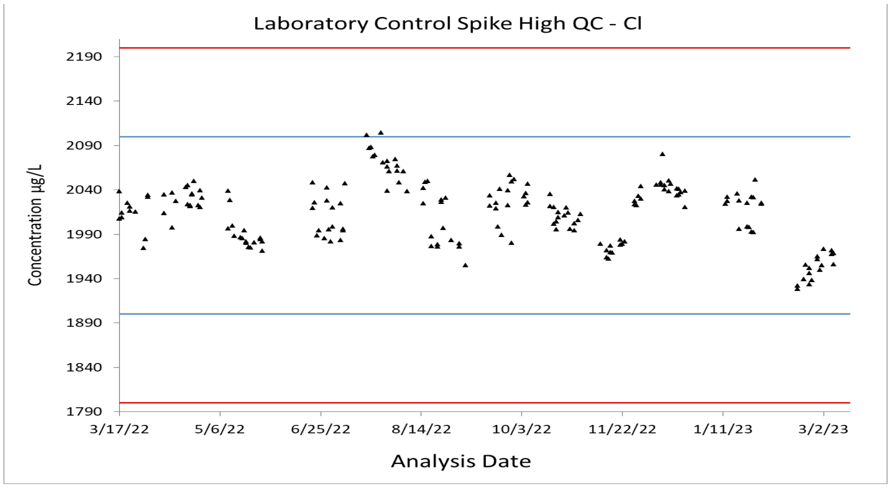

Laboratory Control Spike Low QC - NO3
Concentration µg/L
660
640
620
600
580
560
540
520
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

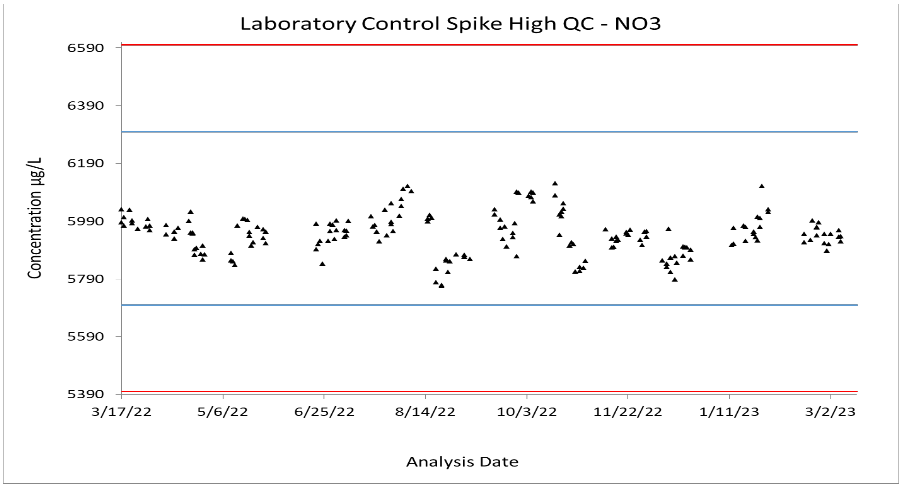

Laboratory Control Spike Low QC- SO4
Concentration µg/L
1330
1280
1230
1180
1130
1080
1030
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike Medium QC - Cl
Concentration µg/L
540
520
500
480
460
440
420
400
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike Medium QC - NO3
1650
1600
1550
1500
1450
1400
1350
1300
1250
1200
Concentration µg/L
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike Medium QC - SO4
3125
3025
2925
2825
2725
2625
2525
Concentration µg/L
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike High QC - Cl
2190
2140
2090
2040
1990
1940
1890
1840
1790
Concentration µg/L
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike High QC - NO3
6590
6390
6190
5990
5790
5590
5390
Concentration µg/L
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

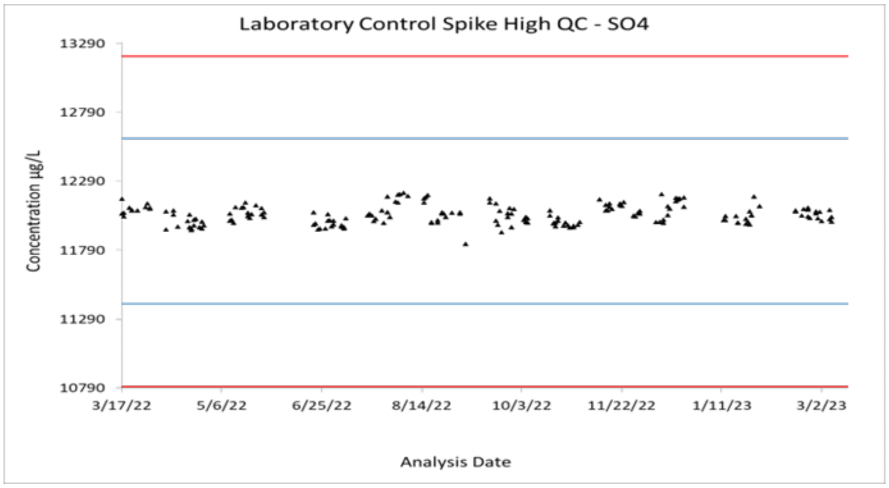
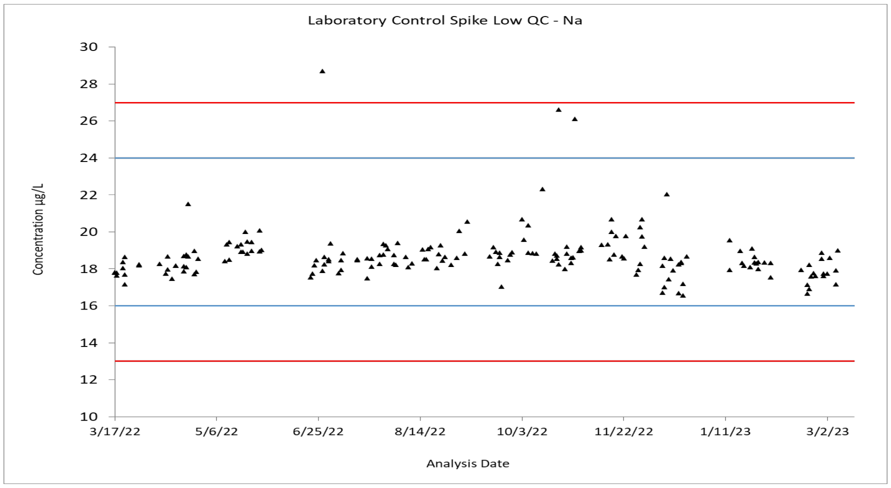
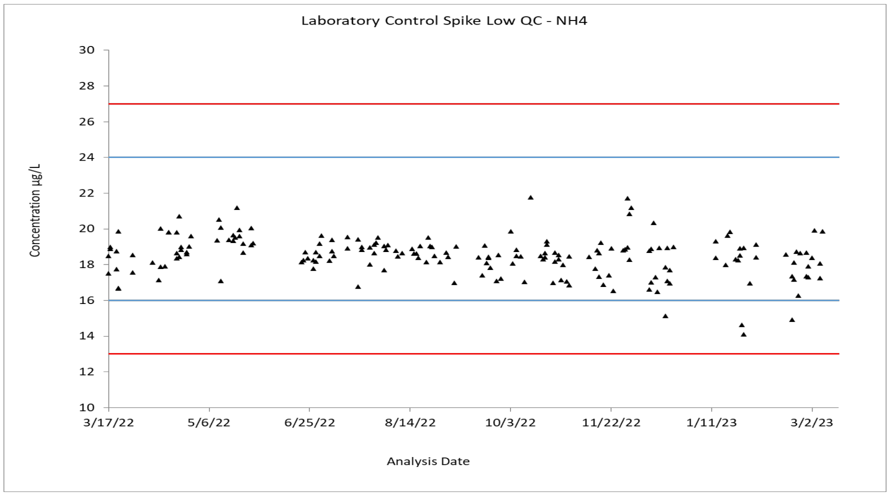
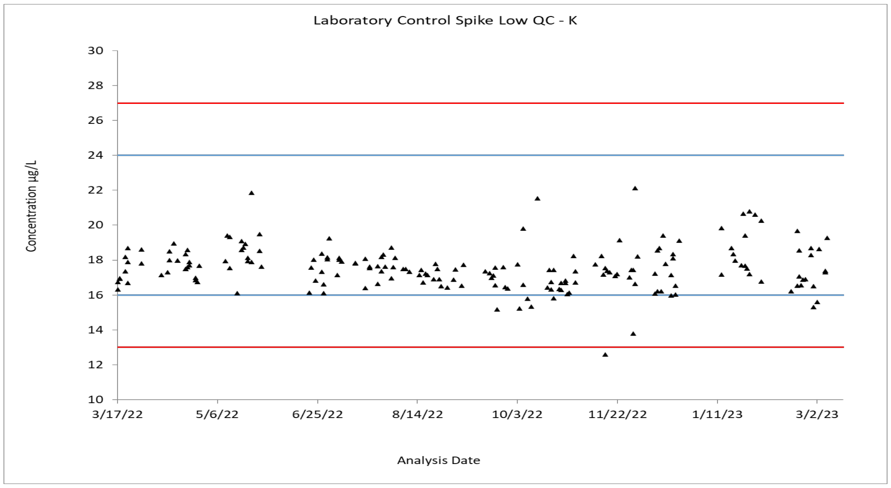
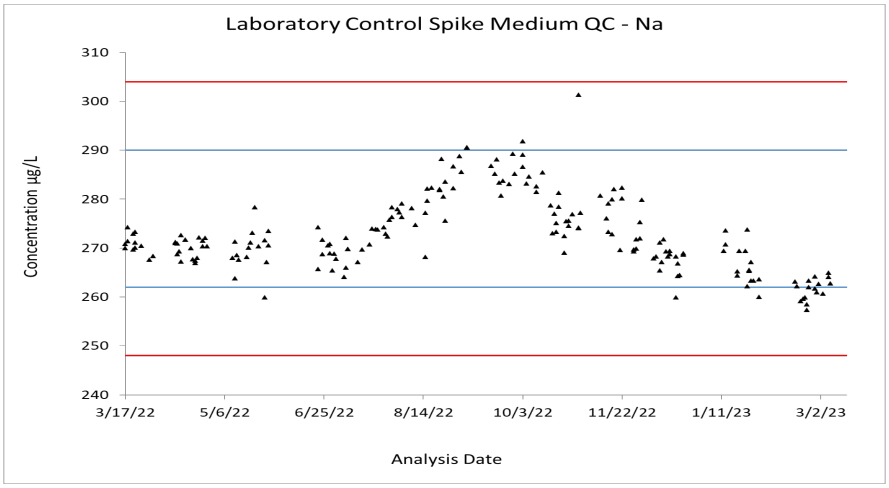

Laboratory Control Spike High QC - SO4
13290
12790
12290
11790
11290
10790
Concentration µg/L
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

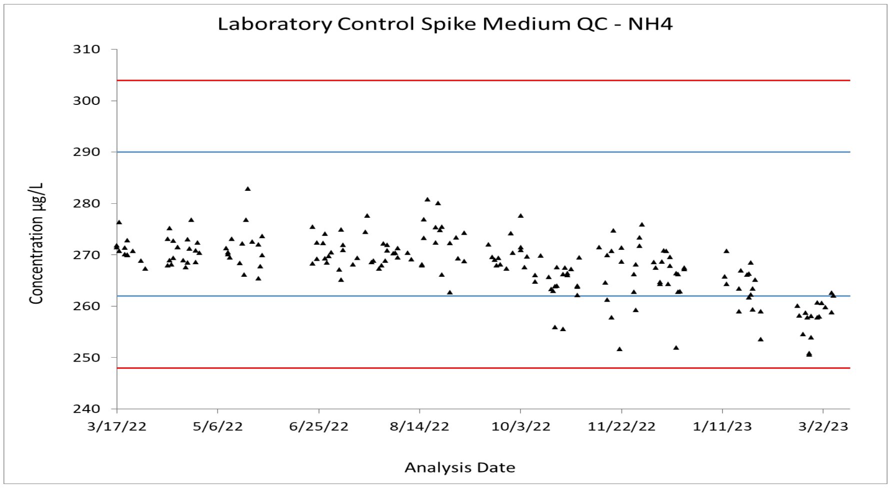
Figure 4.1-10: Control charts for cation LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022).

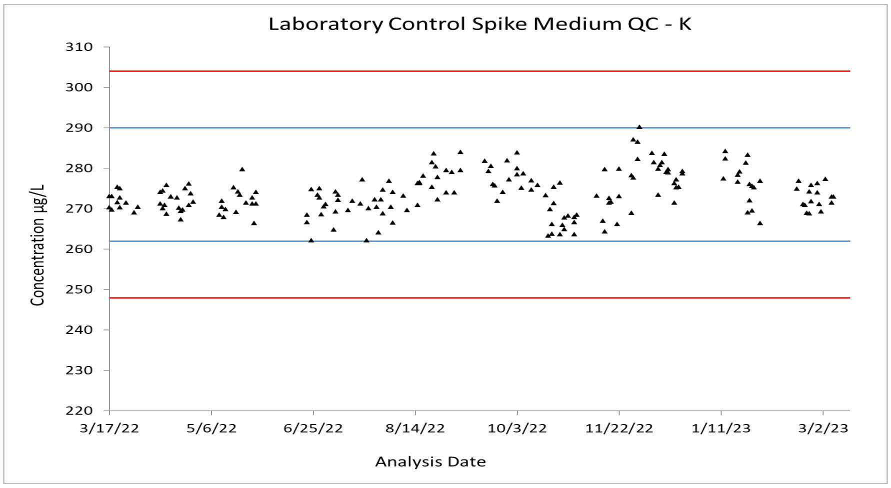


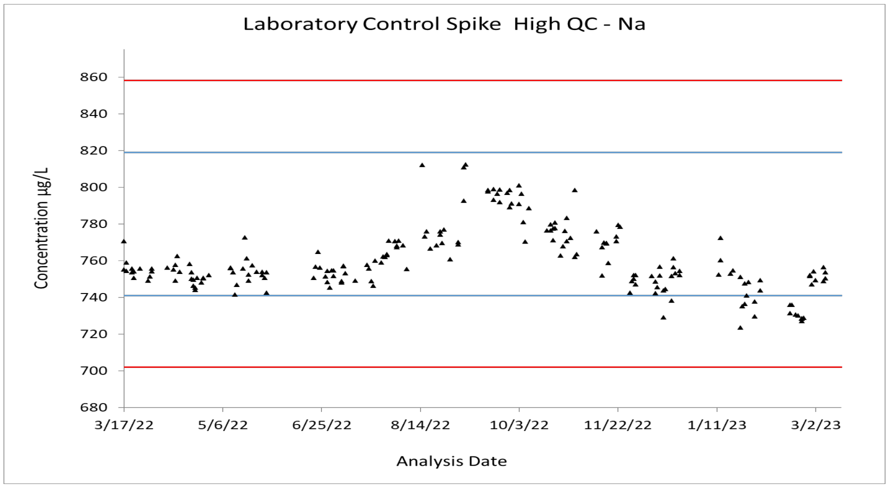


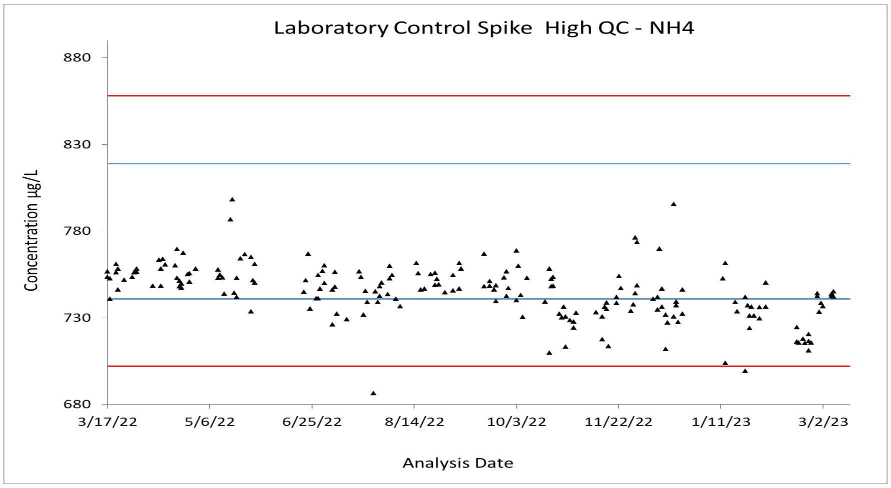


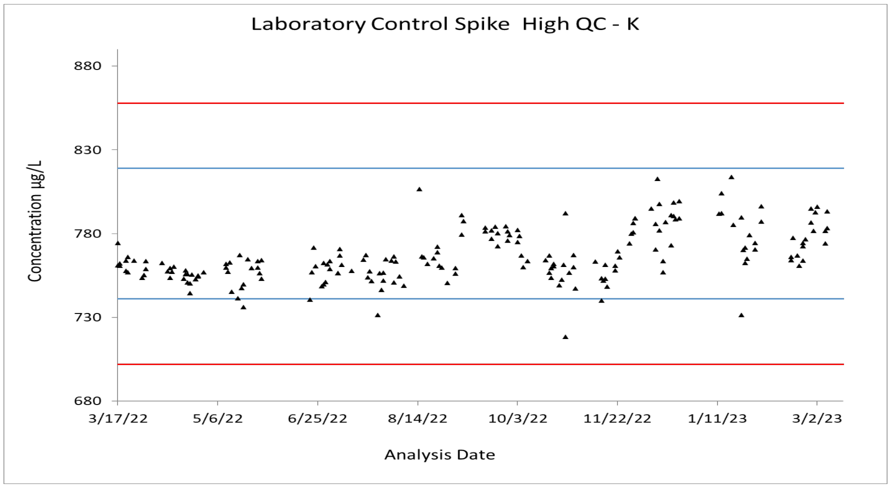

Laboratory Control Spike Medium QC - Na
Concentration µg/L
310
300
290
280
270
260
250
240
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike Medium QC - NH4
Concentration µg/L
310
300
290
280
270
260
250
240
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike Medium QC - K
Concentration µg/L
310
300
290
280
270
260
250
240
230
220
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike High QC - Na
Concentration µg/L
860
840
820
800
780
760
740
720
700
680
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike High QC - NH4
Concentration µg/L
880
830
780
730
680
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date


Laboratory Control Spike High QC - K
Concentration µg/L
880
830
780
730
680
3/17/22
5/6/22
6/25/22
8/14/22
10/3/22
11/22/22
1/11/23
3/2/23
Analysis Date

4.1.2.6 Round Robin (USGS)

The RTI Ions Chromatography Laboratory participated in the National Atmospheric Deposition Program/Mercury Deposition Network Interlaboratory Comparison Program. The program is administered by the United States Geological Survey (USGS) Branch of Quality Systems. Four samples per month were sent to participating laboratories for analysis.

Results may be viewed using this URL:
https://bqs.usgs.gov/PCQA/Interlaboratory_Comparison/graphOutput.php?page=start

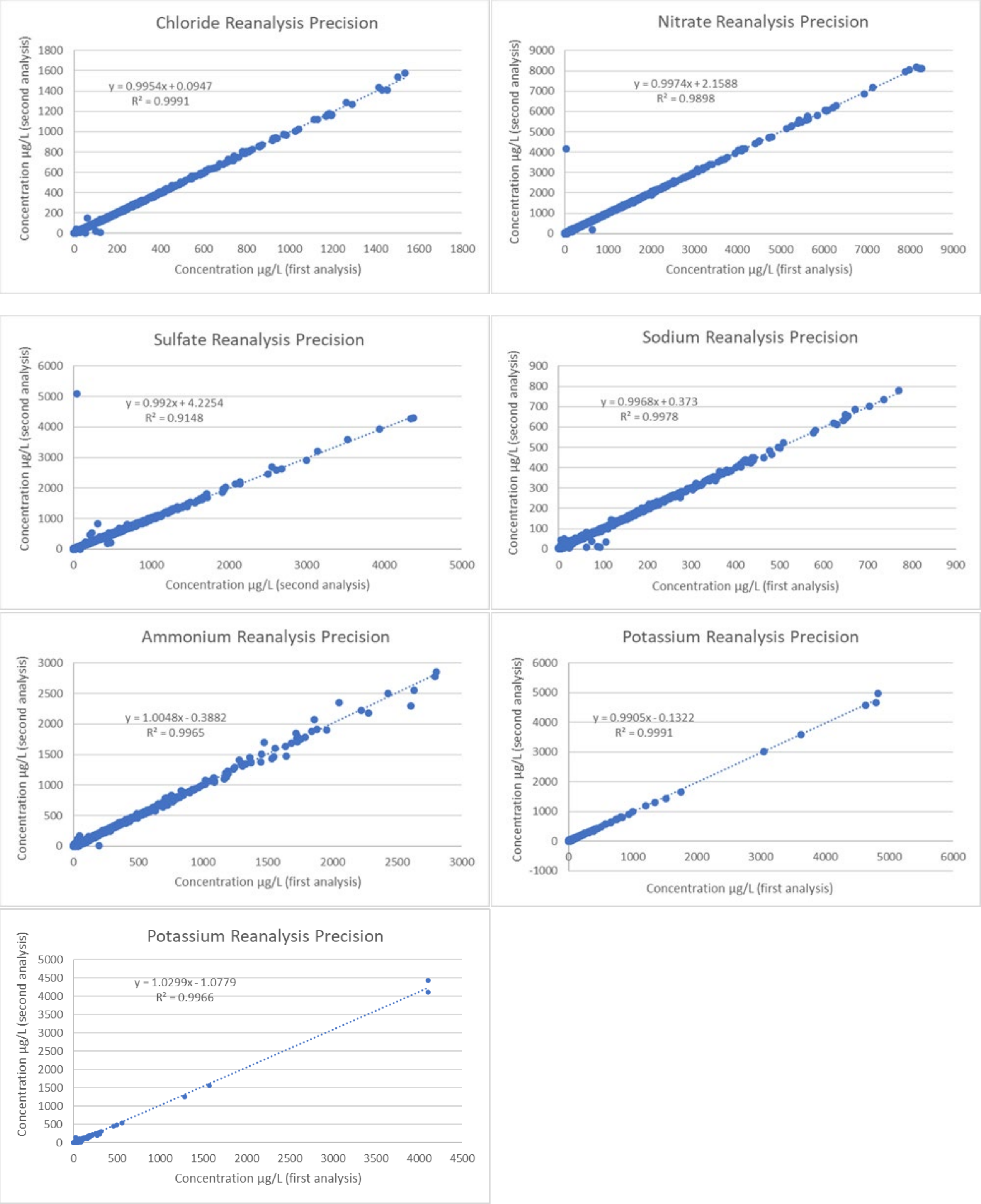
Data from previous years may also be reviewed using this URL.

4.1.2.7 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 2,476 samples reanalyzed for anions and 2,681 samples reanalyzed for cations (Figure 4.1-11). Less than 0.8% and 1.0% 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 3/17/2022 through 3/15/2023 (samples collected 1/1/2022 through 12/31/2022).



4.1.3 Determination of Uncertainties and Method Detection Limits

For discussion of Method Detection Limits (MDLs) see Section 3.1.3.7.

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

4.1.4 Audits, Performance Evaluations, Training, and Accreditations

4.1.4.1 System Audits

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

4.1.4.2 Performance Evaluations

No performance evaluations were conducted during this reporting period.

4.1.4.3 Training

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

4.1.4.4 Accreditations

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

4.1.5 Summary of Filter Blanks

4.1.5.1 Field Blanks

Over the sampling period (January 1, 2022 through December 31, 2022) there were 1,627 valid nylon filter field blanks. Table 4.1-7 and Table 4.1-8 summarize the field blank statistics.

Table 4.1-7: Nylon filter field blank statistics in µg/mL for the analysis period 3/22/2022 through 3/7/2023 (samples collected 1/1/2022 through 12/31/2022).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl^-	1627	0.004	0.005	0.000	0.191	0.008
NO_3^-	1627	0.012	0.014	0.000	0.888	0.029
SO_4^{2-}	1627	0.000	0.004	0.000	0.570	0.023
Na^+	1627	0.005	0.005	0.000	0.121	0.005
NH_4^+	1627	0.005	0.005	0.000	0.218	0.006
K^+	1627	0.006	0.006	0.000	0.054	0.003

Table 4.1-8: Nylon filter field blank statistics in µg/filter (extraction volume 25 mL) for the analysis period 3/22/2022 through 3/7/2023 (samples collected 1/1/2022 through 12/31/2022).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl^-	1627	0.104	0.130	0.000	4.767	0.196
NO_3^-	1627	0.288	0.351	0.000	22.187	0.724
SO_4^{2-}	1627	0.000	0.090	0.000	14.244	0.568
Na^+	1627	0.126	0.127	0.000	3.022	0.133
NH_4^+	1627	0.120	0.120	0.000	5.443	0.151
K^+	1627	0.137	0.137	0.000	1.343	0.064

4.1.5.2 Laboratory Blanks

As described in Section 3.1.3.5, 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 4.1-9 and Table 4.1-10 summarize the laboratory blank statistics.

Table 4.1-9: Nylon filter laboratory blank statistics in µg/mL for the analysis period 3/31/2022 through 3/8/2023 (samples collected 1/1/2022 through 12/31/2022).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl^-	60	0.005	0.005	0.002	0.010	0.002
NO_3^-	60	0.003	0.004	0.000	0.020	0.005
SO_4^{2-}	60	0.009	0.012	0.000	0.057	0.013
Na^+	60	0.005	0.005	0.003	0.007	0.001
NH_4^+	60	0.005	0.005	0.000	0.012	0.002
K^+	60	0.000	0.002	0.000	0.017	0.005

Table 4.1-10: Nylon filter laboratory blank statistics in µg/filter (extraction volume 25 mL) for the analysis period 3/31/2022 through 3/8/2023 (samples collected 1/1/2022 through 12/31/2022).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl^-	60	0.003	0.004	0.000	0.020	0.005
NO_3^-	60	0.009	0.012	0.000	0.057	0.013
SO_4^{2-}	60	0.000	0.002	0.000	0.017	0.005
Na^+	60	0.005	0.005	0.000	0.012	0.002
NH_4^+	60	0.005	0.005	0.003	0.007	0.001
K^+	60	0.005	0.005	0.002	0.010	0.002

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, 2022 through December 31, 2022. UC Davis performed analysis for 33 elements using energy dispersive X-ray fluorescence (EDXRF) instruments. These analyses were performed during an analysis period from March 26, 2022 through April, 20, 2023, 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 2022 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	87	2022-03-27 - 2022-05-19	2022-04-20 - 2022-04-21	NA	2022-03-26 - 2022-04-24	2022-04-21 - 2022-04-25
February	88	2022-04-26 - 2022-06-16	NA	NA	2022-05-01 - 2022-05-22	2022-05-02 - 2022-05-20
March	89	2022-05-23 - 2022-07-08	2022-05-26 - 2022-06-08	2022-05-26 - 2022-06-01	2022-05-24 - 2022-06-08	2022-05-25 - 2022-06-09
April	90	2022-06-26 - 2022-08-17	NA	NA	2022-06-26 - 2022-07-23	2022-07-13 - 2022-07-23
May	91	2022-07-23 - 2022-08-19	NA	NA	2022-07-23 - 2022-09-21	2022-08-06 - 2022-08-17
June	92	2022-08-19 - 2022-09-13	NA	NA	2022-08-19 - 2022-09-13	2022-08-30 - 2022-09-14
July	93	2022-09-23 - 2022-11-18	2022-09-23 - 2022-10-06	2022-09-23 - 2022-10-06	2022-09-23 - 2022-10-07	2022-09-23 - 2022-10-07
August	94	2022-10-27 - 2022-12-15	2022-10-26 - 2022-11-08	2022-10-26 - 2022-11-08	2022-10-26 - 2022-11-08	2022-10-27 - 2022-11-08
September	95	2022-11-24 - 2022-12-06	2022-11-23 - 2022-12-07	2022-11-24 - 2022-12-06	2022-11-23 - 2022-12-07	2022-11-23 - 2022-12-07
October	96	2022-12-21 - 2023-02-21	2022-12-21 - 2023-02-21	2022-12-21 - 2023-02-21	2022-12-21 - 2023-02-21	2022-12-21 - 2023-02-21
November	97	2023-01-20 - 2023-03-22	2023-01-25 - 2023-02-04	2023-01-26 - 2023-02-06	2023-01-23 - 2023-02-04	2023-01-25 - 2023-02-04
December	98	2023-02-23 - 2023-04-20	2023-02-28 - 2023-03-14	2023-02-28 - 2023-03-14	2023-02-28 - 2023-03-13	2023-02-28 - 2023-03-14
All Months	87-98	2022-03-27 – 2023-04-20	2022-04-20 – 2023-03-14	2022-05-26 – 2023-03-14	2022-03-26 - 2023-03-13	2022-04-21 - 2023-03-14

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* and later during this reporting period *UCD CSN TI #904B* which replaced TI 302B. Samples are analyzed using Malvern-Panalytical Epsilon 5 EDXRF instruments following *UCD CSN SOP #302*. Calibration of the EDXRF instruments is performed annually and as needed to address maintenance or performance issues (e.g. an X-ray tube or detector is replaced). Quality control procedures are described in *UCD CSN TI #302D* and are summarized in Table 4.2-2.

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

Analysis	Frequency	Criterion	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	• XRF software automatically adjusts the energy channels
Laboratory Blank	Daily	≤ acceptance limits with exceedance of any elements not to occur in more than two consecutive days	• 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	• 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	Replicate uncertainty is within 3x analytical uncertainty for each element. Elements checked = all reported elements excluding Cl and Br (volatiles)	• Repeat replicate to look for agreement. • Investigate filter integrity and visual quality. • Investigate instrument.
Reanalysis samples	Monthly	z-score between ± 1 for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb	• Check sample for damage/contamination • Further cross-instrumental testing • Replace QC sample if necessary • Reanalyze network samples since last passing QC as needed.
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 4.2-1 and Figure 4.2-2 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 cleaned or 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 twenty-four samples from 2022 were reanalyzed for suspected zinc contamination. Of those, sixteen 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-4 had elevated values for Cr, Fe, and Zn which failed acceptance from 10/26/2022 to 11/10/2022. This extended time of failure was not caught earlier because at the time of failure the XRF instrument calibrations where still being calculated so no QC results could be displayed for review. Once the calibrations were finalized this data became available and the failures were noted. A nonconformance report was completed for this event, NR-0013. The issue resulted from contamination of the QC blank sample from newly installed gas piston supports for the XRF sample deck lid which sit directly above the storage position for the QC blank sample. The gas piston was monitored for further contamination after this, but none was noticed indicating likely a single event after the gas piston was installed. The QC blank sample was cleaned by canned air which returned all elemental results to acceptable blank levels. No CSN sample were affected by this issue. Additional discussion of this issue can be found in section 3.2.1.2.

Figure 4.2-1: Analysis results from daily PTFE blanks for the analysis period 3/26/2022 through 4/20/2023 (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 3/26/2022 through 4/20/2023 (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.

XRF-3 failed QC criteria for Zn from 11/2/2022 to 11/17/2022, see Table 4.2-5. Unfortunately, this QC failure occurred after the yearly calibration was performed but before the calibration was finalized, meaning no areal densities could be calculated so QC results were not visible which delayed the observation of this failure. Once the calibration was finalized the areal densities were processed and this QC failure was immediately reported. A nonconformance report, NR-0013 was filed and the investigation found the cause was contamination to the daily QC ME-RM from the hinge for the XRF sample deck lid, see investigation report IR-0014. All QC and network samples were moved to areas of the XRF sample deck which were not underneath this hinge which stopped the Zn contamination. The manufacturer was contacted and a new hinge was installed which remedied the problem. The QC ME-RM was replaced with a new one due to the contamination. The validation team was notified of the issue to monitor sample results for elevated zinc and request reanalysis if contamination was suspected.

Table 4.2-3: Descriptive statistics of XRF-1 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 393.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	2.057	1.709	2.438	0	0	1.6
Si	0.875	0.751	1.159	0	0	1.9
S	17.049	15.746	19.245	0	0	1.0
K	2.393	2.204	2.694	0	0	0.7
Ca	2.405	2.143	2.619	0	0	0.7
Cr	0.996	0.895	1.094	0	0	1.0
Fe	2.850	2.501	3.057	0	0	1.2
Zn	0.356	0.305	0.373	0	0	1.2
As	0.683	0.609	0.745	0	0	0.8
Se	0.469	0.439	0.536	0	0	1.0
Rb	0.234	0.210	0.256	0	0	1.5
Sr	0.227	0.203	0.248	0	0	1.5
Cd	0.302	0.271	0.331	1.3	0	3.9
Sn	0.353	0.315	0.396	1.0	0	3.9
Pb	0.088	0.063	0.105	0	0	7.3

Table 4.2-4: Descriptive statistics of XRF-2 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 150.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.637	1.296	1.877	0	0	2.8
Si	0.730	0.543	0.892	0	0	2.9
S	13.601	12.021	14.692	0	0	2.2
K	1.904	1.712	2.092	0	0	2.1
Ca	1.843	1.646	2.011	0	0	1.0
Cr	0.772	0.694	0.848	0	0	0.9
Fe	2.163	1.933	2.362	0	0	1.1
Zn	0.265	0.228	0.279	0.7	0	2.9
As	0.528	0.474	0.580	0	0	1.1
Se	0.380	0.343	0.419	0	0	1.4
Rb	0.184	0.164	0.201	0	0	2.0
Sr	0.179	0.160	0.195	0	0	2.0
Cd	0.238	0.204	0.274	3.3	0	4.9
Sn	0.280	0.239	0.317	0	0	4.7
Pb	0.078	0.059	0.099	0.7	0	8.7

Table 4.2-5: Descriptive statistics of XRF-3 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 142.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.530	1.160	1.685	0	0	2.1
Si	1.005	0.795	1.124	0	0	1.7
S	12.243	11.099	13.565	0	0	1.4
K	1.685	1.530	1.870	0	0	0.9
Ca	1.587	1.431	1.749	0	0	1.0
Cr	0.665	0.599	0.732	0	0	0.8
Fe	1.847	1.659	2.027	0	0	1.0
Zn	0.372	0.304	0.372	4.9	2.1	39.4
As	0.464	0.412	0.504	0	0	1.4
Se	0.332	0.302	0.369	0	0	1.4
Rb	0.159	0.142	0.174	0	0	2.3
Sr	0.158	0.142	0.173	0	0	2.1
Cd	0.212	0.182	0.248	0.7	0	5.6
Sn	0.254	0.205	0.309	0	0	5.0
Pb	0.161	0.133	0.182	0.7	0	5.7

Table 4.2-6: Descriptive statistics of XRF-4 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 307.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.762	1.620	2.268	0	0	1.9
Si	0.974	0.672	1.104	0	0	3.0
S	16.053	14.499	17.721	0	0	0.8
K	2.289	2.067	2.526	0	0	0.8
Ca	2.360	2.075	2.536	0	0	0.9
Cr	0.987	0.869	1.062	0	0	0.8
Fe	2.752	2.404	2.938	0	0	0.9
Zn	0.365	0.315	0.385	1.3	0	1.3
As	0.679	0.599	0.732	0	0	1.1
Se	0.482	0.433	0.529	0	0	1.2
Rb	0.233	0.206	0.251	0	0	1.8
Sr	0.224	0.198	0.241	0	0	1.8
Cd	0.298	0.256	0.332	0.3	0	4.3
Sn	0.347	0.305	0.382	0.7	0	3.9
Pb	0.084	0.064	0.103	1.3	0	8.8

Table 4.2-7: Descriptive statistics of XRF-5 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 234.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.750	1.438	2.083	0	0	1.9
Si	0.687	0.565	0.932	0	0	2.3
S	14.917	13.643	16.674	0	0	1.3
K	2.107	1.941	2.373	0	0	1.2
Ca	2.050	1.872	2.288	0	0	1.3
Cr	0.880	0.792	0.968	0	0	1.2
Fe	2.425	2.220	2.713	0	0	1.6
Zn	0.320	0.272	0.332	2.1	0	2.2
As	0.607	0.547	0.669	0	0	1.7
Se	0.443	0.397	0.485	0	0	1.7
Rb	0.207	0.187	0.228	0	0	1.9
Sr	0.202	0.182	0.223	0	0	1.7
Cd	0.271	0.231	0.309	0	0	3.8
Sn	0.317	0.273	0.370	0	0	3.9
Pb	0.080	0.061	0.103	0	0	7.7

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 June 2022. 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 my 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 4/20/2023.

Table 4.2-8: Descriptive statistics of XRF-1 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 62.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.146	0.899	1.312	0	0	2.3
Si	1.101	0.945	1.308	0	0	1.7
S	9.346	8.841	10.806	2.0	0	3.0
K	1.286	1.144	1.399	0	0	0.6
Ca	1.152	1.019	1.246	0	0	1.4
Cr	0.467	0.422	0.516	0	0	1.2
Fe	1.305	1.169	1.428	0	0	1.0
Zn	0.363	0.323	0.395	0	0	1.2
As	0.323	0.289	0.353	0	0	1.4
Se	0.233	0.209	0.255	0	0	1.3
Rb	0.114	0.103	0.126	0	0	2.9
Sr	0.117	0.105	0.128	0	0	2.4
Cd	0.159	0.130	0.187	0	0	5.8
Pb	0.226	0.205	0.251	0	0	3.1

Table 4.2-9: Descriptive statistics of XRF-2 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 62.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.147	0.899	1.312	0	0	3.3
Si	1.166	0.945	1.308	0	0	2.5
S	9.608	8.841	10.806	0	0	3.7
K	1.292	1.144	1.399	0	0	2.4
Ca	1.147	1.019	1.246	0	0	1.4
Cr	0.466	0.422	0.516	0	0	1.3
Fe	1.313	1.169	1.428	0	0	1.3
Zn	0.364	0.323	0.395	0	0	1.3
As	0.323	0.289	0.353	0	0	2.0
Se	0.234	0.209	0.255	0	0	1.5
Rb	0.114	0.103	0.126	0	0	2.6
Sr	0.116	0.105	0.128	0	0	2.7
Cd	0.156	0.130	0.187	0	0	5.7
Pb	0.225	0.205	0.251	0	0	3.6

Table 4.2-10: Descriptive statistics of XRF-3 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 58.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.213	0.899	1.312	0	0	2.1
Si	1.197	0.945	1.308	0	0	1.4
S	9.459	8.841	10.806	0	0	2.4
K	1.266	1.144	1.399	0	0	0.6
Ca	1.149	1.019	1.246	0	0	1.2
Cr	0.469	0.422	0.516	0	0	0.9
Fe	1.293	1.169	1.428	0	0	0.8
Zn	0.361	0.323	0.395	0	0	1.1
As	0.326	0.289	0.353	0	0	1.8
Se	0.232	0.209	0.255	0	0	1.5
Rb	0.114	0.103	0.126	0	0	2.5
Sr	0.116	0.105	0.128	0	0	2.2
Cd	0.158	0.130	0.187	0	0	6.3
Pb	0.228	0.205	0.251	0	0	3.5

Table 4.2-11: Descriptive statistics of XRF-4 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 61.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.002	0.899	1.312	0	0	2.3
Si	1.176	0.945	1.308	0	0	2.7
S	9.528	8.841	10.806	0	0	3.3
K	1.295	1.144	1.399	0	0	0.9
Ca	1.167	1.019	1.246	0	0	1.1
Cr	0.476	0.422	0.516	0	0	1.4
Fe	1.344	1.169	1.428	0	0	1.0
Zn	0.367	0.323	0.395	0	0	1.0
As	0.330	0.289	0.353	0	0	1.6
Se	0.238	0.209	0.255	0	0	2.0
Rb	0.116	0.103	0.126	0	0	2.3
Sr	0.118	0.105	0.128	0	0	2.9
Cd	0.158	0.130	0.187	0	0	5.6
Pb	0.228	0.205	0.251	0	0	3.3

Table 4.2-12: Descriptive statistics of XRF-5 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/26/2022 through 4/20/2023 (see Table 4.2-1 for corresponding sampling dates), N = 62.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.102	0.899	1.312	0	0	2.2
Si	1.071	0.945	1.308	0	0	2.1
S	9.311	8.841	10.806	0	0	2.2
K	1.265	1.144	1.399	0	0	1.5
Ca	1.120	1.019	1.246	0	0	2.5
Cr	0.463	0.422	0.516	0	0	1.2
Fe	1.282	1.169	1.428	0	0	1.7
Zn	0.357	0.323	0.395	0	0	2.2
As	0.317	0.289	0.353	0	0	2.1
Se	0.231	0.209	0.255	0	0	2.1
Rb	0.112	0.103	0.126	0	0	2.5
Sr	0.114	0.105	0.128	0	0	1.8
Cd	0.156	0.130	0.187	0	0	5.7
Pb	0.220	0.205	0.251	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. 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:

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

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,

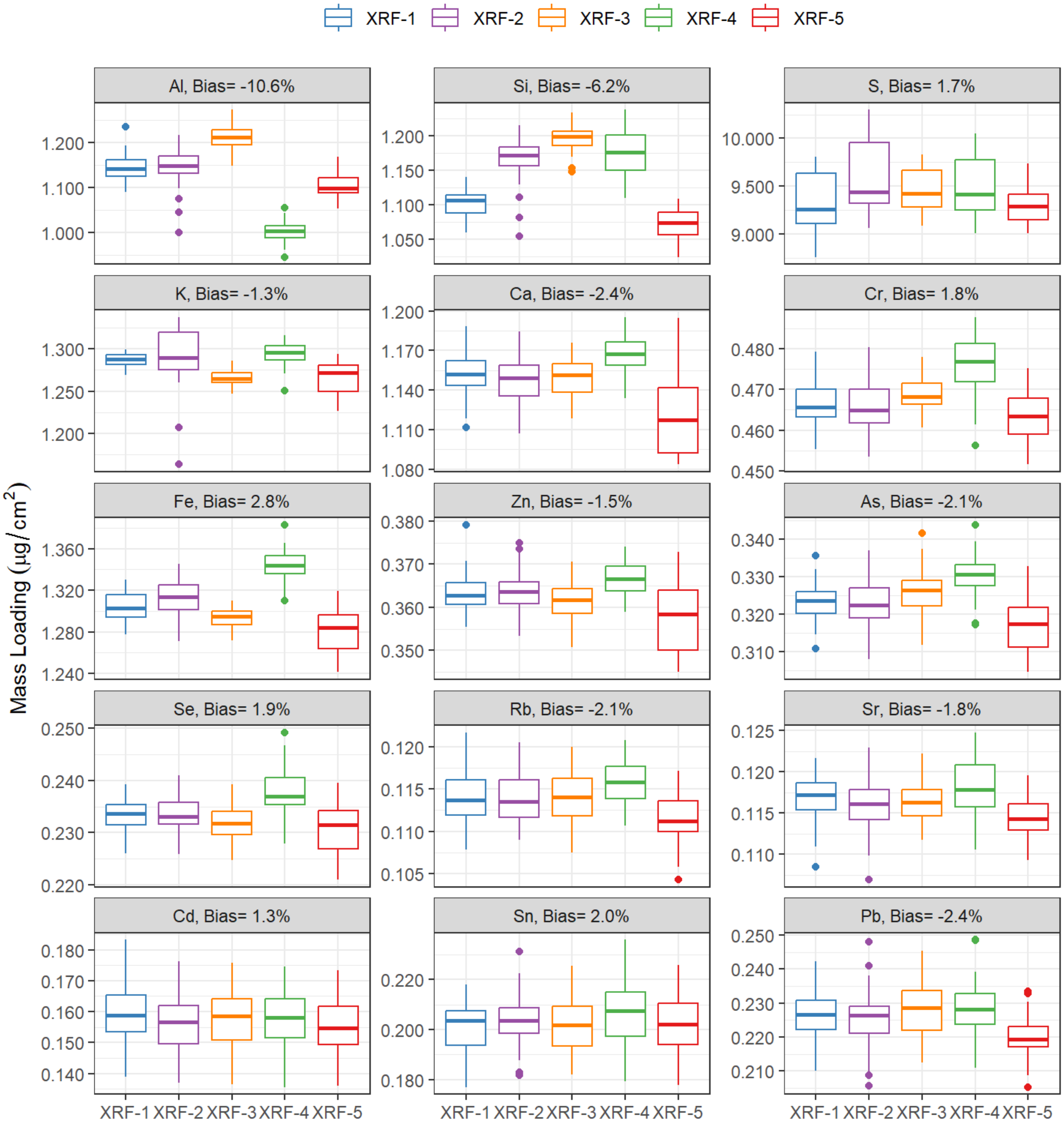
$$Precision_i = \sqrt{\frac{n\sum_{j=1}^{n} d_{i,j}^2 - \left(\sum_{j=1}^{n} d_{i,j}\right)^2}{n(n-1)}}$$

The results from this analysis, for the elements listed for the weekly ME-RM in Table 4.2-2, averaged over the UC Davis ME-RM samples 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 4.2-3 for the weekly ME-RM sample. In that figure, 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 1.5xIQR.

Table 4.2-13: Precision and bias of all EDXRF instruments from the weekly UC Davis ME-RM calculated for the analysis period 3/26/2022 through 4/20/2023 (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	1.7	1.2	7.2	9.8	-0.5	2.2	3.3	2.6	2.0	2.3
Si	-2.9	1.8	3.6	2.8	-4.8	1.9	2.4	1.3	2.1	1.7
S	-0.9	1.3	-0.3	1.0	-1.0	1.8	3.1	1.5	2.1	1.6
K	0.0	0.1	-0.1	0.8	-0.9	0.6	2.4	0.6	0.8	1.2
Ca	0.4	-0.3	0.0	1.9	-1.8	1.4	1.3	1.3	1.2	1.7
Cr	-0.4	-0.9	0.0	1.7	-0.5	1.1	1.0	0.9	1.4	1.1
Fe	-0.6	0.5	-0.7	2.6	-1.7	0.9	1.1	0.8	0.9	1.3
Zn	0.2	-0.3	-0.1	1.3	-1.1	1.2	1.1	1.2	0.9	1.8
As	0.5	-1.0	0.3	1.6	-1.5	1.4	2.0	1.9	1.6	1.7
Se	-0.1	-0.3	-0.6	1.5	-0.5	1.4	1.2	1.5	2.1	1.9
Rb	0.6	0.2	-0.7	2.1	-2.0	2.9	2.9	2.7	2.5	2.1
Sr	-0.1	-0.1	-0.5	1.6	-0.7	2.2	3.5	2.3	2.5	2.0
Cd	1.6	-1.9	-0.6	1.0	-0.2	6.3	5.0	4.8	6.0	4.8
Sn	0.0	1.1	-2.8	3.2	-1.1	4.5	4.6	5.2	6.5	5.5
Pb	0.9	-1.0	1.3	1.1	-2.2	3.1	3.4	4.0	2.9	2.5

Figure 4.2-3: Instrumental comparison using the weekly UC Davis ME-RM.



4.2.2.4 Long-Term Stability, Reproducibility, and Inter-Instrument Performance

A set of filters are reanalyzed monthly to monitor the long-term instrument performance. The set consists of 16 UC Davis produced ME-RMs and covers a range of mass loadings simulating the range of real CSN samples. In order to compare multiple filters with different mass loadings, the results of reanalysis are first converted to z-scores. For a given month, the z-score for the i^{th} element and j^{th} filter is

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

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

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

Every month, 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 4.2-4 shows the mean z-score plots during the analysis period. No issues were observed in the z-scores for this analysis period.

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 +/- the root-mean-squared-relative error plus three times the standard deviation for a set of monthly measurements (n=44); see *UCD CSN TI #302D* for further detail.

The NIST SRM 2783 results from this analysis period (3/26/2022 through 4/20/2023) are shown in Figure 4.2-5, and Table 4.2-14 summarizes the calibrations performed during this analysis period. All EDXRF instruments underwent routine annual calibrations in November/December 2021 and October 2022. Calibrations required after maintenance repairs are listed. Note XRF-4 was recalibrated on April 29, 2022, this was not due to a maintenance issue, but rather to correct an issue with the chlorine escape peak overlap on the aluminum peak, see section 3.2.1.3 for details. The results from the monthly NIST SRM 2783 analyses show failures for Al and K on XRF-2 in April 2022 and XRF-5 in July 2022. In both instances, the SRM was reanalyzed with a passing result indicating the calibration was functioning properly; these were just statistical anomalies due to the results being so near the lower QC limit. The event in July 2022 prompted a change in the SRM 2783 filter which was being analyzed from serial number 1617 to serial number 1616. There were no other issues with monthly SRM QC results indicating the 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 3/26/2022 through 4/20/2023.

Table 4.2-14: Dates for calibrations performed on each EDXRF instrument during this analysis period (3/26/2022 through 4/20/2023).

EDXRF Instrument	Calibration Date	Reason for Calibration	Range of Sample Dates Analyzed
XRF-4	2021-11-24	Annual Calibration	2022-01-05 – 2022-01-29
XRF-2	2021-11-26	Annual Calibration	2022-01-29 – 2022-07-31
XRF-3	2021-12-02	Annual Calibration	2022-03-12 – 2022-03-24
XRF-5	2022-02-11	Annual Calibration delayed for maintenance	2022-01-01 – 2022-07-31
XRF-1	2022-02-17	X-ray tube replaced	2022-01-02 – 2022-07-31
XRF-4	2022-04-29	Al/Cl overlap fixed	2022-02-04 – 2022-07-31
XRF-3	2022-06-23	X-ray tube replaced	2022-07-02 – 2022-07-31
XRF-1	2022-10-19	Annual Calibration	2022-07-10 – 2022-12-31
XRF-2	2022-10-19	Annual Calibration	2022-08-01 – 2022-12-31
XRF-3	2022-10-20	Annual Calibration	2022-08-03 – 2022-12-28
XRF-4	2022-10-21	Annual Calibration	2022-08-12 – 2022-12-31
XRF-5	2022-10-24	Annual Calibration	2022-08-09 – 2022-12-31

4.2.3 Determination of Uncertainties and Method Detection Limits

For discussion of Method Detection Limits (MDLs) see Section 3.1.3.7.

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, 2022 through December 31, 2022) there were 1,628 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 2022 sampling analysis period 4/14/2022 through 4/20/2023 (samples collected 1/1/2022 through 12/31/2022).

Species	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)
Ag	1628	0.018	0.019	0.007	0.045	0.006
Al	1628	0.074	0.077	0.043	0.642	0.023
As	1628	0.000	0.000	0.000	0.000	0.000
Ba	1628	0.064	0.066	0.027	0.121	0.015
Br	1628	0.000	0.000	0.000	0.002	0.000
Ca	1628	0.003	0.007	0.000	2.323	0.073
Cd	1628	0.019	0.020	0.006	0.042	0.006
Ce	1628	0.073	0.074	0.027	0.151	0.018
Cl	1628	0.002	0.002	0.000	0.182	0.008
Co	1628	0.001	0.001	0.000	0.004	0.001
Cr	1628	0.004	0.004	0.002	0.025	0.001
Cs	1628	0.043	0.044	0.015	0.090	0.012
Cu	1628	0.009	0.008	0.003	0.020	0.003
Fe	1628	0.019	0.021	0.007	0.906	0.028
In	1628	0.021	0.022	0.006	0.059	0.007
K	1628	0.013	0.012	0.000	0.267	0.013
Mg	1628	0.009	0.015	0.000	0.341	0.020
Mn	1628	0.006	0.006	0.001	0.048	0.002
Na	1628	0.000	0.017	-0.011	0.249	0.029
Ni	1628	0.001	0.001	0.000	0.009	0.001
P	1628	0.000	0.000	0.000	0.015	0.001
Pb	1628	0.013	0.013	0.007	0.027	0.003
Rb	1628	0.003	0.003	0.000	0.008	0.001
S	1628	0.000	0.001	0.000	0.423	0.021
Sb	1628	0.027	0.028	0.010	0.057	0.008
Se	1628	0.002	0.002	0.000	0.007	0.001
Si	1628	0.016	0.019	0.000	1.697	0.058
Sn	1628	0.027	0.028	0.011	0.059	0.007
Sr	1628	0.004	0.004	0.002	0.012	0.001
Ti	1628	0.002	0.002	0.000	0.088	0.003
V	1628	0.000	0.000	0.000	0.002	0.000
Zn	1628	0.002	0.003	0.000	0.053	0.002
Zr	1628	0.017	0.017	0.004	0.053	0.006

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 4.2-16 summarizes the laboratory blank statistics.

Table 4.2-16: PTFE filter laboratory blank statistics for the 2022 sampling analysis period 4/21/2022 through 3/13/2023 (samples collected 1/1/2022 through 12/31/2022).

Species	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)
Ag	60	0.020	0.020	0.009	0.040	0.006
Al	60	0.076	0.074	0.052	0.102	0.011
As	60	0.000	0.000	0.000	0.000	0.000
Ba	60	0.066	0.069	0.038	0.108	0.014
Br	60	0.000	0.000	0.000	0.000	0.000
Ca	60	0.002	0.002	0.000	0.005	0.001
Cd	60	0.017	0.018	0.008	0.037	0.007
Ce	60	0.077	0.075	0.041	0.120	0.017
Cl	60	0.001	0.001	0.000	0.003	0.001
Co	60	0.001	0.001	0.000	0.003	0.001
Cr	60	0.004	0.004	0.002	0.013	0.002
Cs	60	0.044	0.046	0.024	0.088	0.013
Cu	60	0.005	0.007	0.003	0.014	0.003
Fe	60	0.019	0.021	0.008	0.187	0.022
In	60	0.020	0.021	0.011	0.034	0.006
K	60	0.011	0.010	0.002	0.017	0.004
Mg	60	0.008	0.014	0.000	0.080	0.017
Mn	60	0.006	0.006	0.003	0.009	0.001
Na	60	0.000	0.013	0.000	0.092	0.023
Ni	60	0.001	0.001	0.000	0.003	0.001
P	60	0.000	0.000	0.000	0.003	0.001
Pb	60	0.012	0.012	0.009	0.018	0.002
Rb	60	0.002	0.003	0.001	0.006	0.001
S	60	0.000	0.000	0.000	0.000	0.000
Sb	60	0.027	0.027	0.012	0.054	0.008
Se	60	0.002	0.002	0.001	0.006	0.001
Si	60	0.018	0.017	0.007	0.026	0.005
Sn	60	0.026	0.027	0.014	0.042	0.007
Sr	60	0.004	0.004	0.002	0.007	0.001
Ti	60	0.002	0.002	0.000	0.007	0.002
V	60	0.000	0.000	0.000	0.001	0.000
Zn	60	0.002	0.003	0.000	0.048	0.006
Zr	60	0.016	0.017	0.006	0.034	0.007

4.3 UC Davis Thermal Optical Analysis Laboratory

The UC Davis Thermal Optical Analysis (TOA) Laboratory received and analyzed quartz filters from batches 87 through 98, covering the field sampling period beginning from January 2, 2022 through December 29, 2022. Analyses of these samples were performed April 1, 2022 through March 14, 2023. Six 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 2022 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 (2022)	Analysis Batch #	TOA Analysis Dates
January	87	04/01/2022 - 05/16/2022
February	88	05/02/2022 - 05/27/2022
March	89	05/25/2022 - 07/01/2022
April	90	06/23/2022 - 08/11/2022
May	91	07/20/2022 - 09/15/2022
June	92	08/12/2022 - 10/14/2022
July	93	09/14/2022 - 11/15/2022
August	94	10/12/2022 - 12/13/2022
September	95	11/09/2022 - 01/17/2023
October	96	12/07/2022 - 02/15/2023
November	97	01/11/2023 - 02/03/2023
December	98	02/15/2023 - 03/14/2023
All months	87-98	04/01/2022 - 03/14/2023

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* and later during this reporting period *CSN TI #904A* which replaced 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	≤1.0 µg 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 µg C/cm^2	Repeat analysis. If same result, check instrument and gas lines for possible contamination
Single-point Sucrose Standard Check	Beginning of analysis day	Within ±7% of the calculated value	Repeat analysis. If same result, run a different sucrose solution to determine if the problem is with the solution or instrument. If former, make new sucrose solution. If latter, perform multi-point calibration to determine new calibration constant
Calibration Peak Area Check	Every analysis	Within ±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 20th network sample analysis	Within ±10% RPD when TC >10 µg C /cm^2 within ±20% RPD when ECR > 2.5 µg C /cm^2 or Within ±1 µg/cm^2 when TC ≤10 µg C /cm^2 Within ±0.5 µg/cm^2 when ECR ≤2.5 µg C/cm^2.	Investigate instrument and sample anomalies. Analyze the third punch on a different analyzer
Inter-instrument Comparison Check	Weekly	Within ± 10 % RPD* when TC > 10 µg C/cm^2 Within ± 20 % RPD when EC > 2.5 µg C/cm^2 or Within ± 1 µg/cm^2 when TC ≤ 10 µg C/cm^2 Within ± 0.5 µg/cm^2 when EC ≤ 2.5 µg 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, thermograms are to be 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. However, the thermogram reviews were not being performed for every sample analysis but were instead only being done when indicated by an issue reported by the QC webapp or lab analyst or during a level 1 data validation or when the Spectroscopist felt there was need to monitor the instrument due to some maintenance that may have been recently done. More details about this lapse in thermogram review are being documented in nonconformance report, NR-0026.

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 4/01/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022).

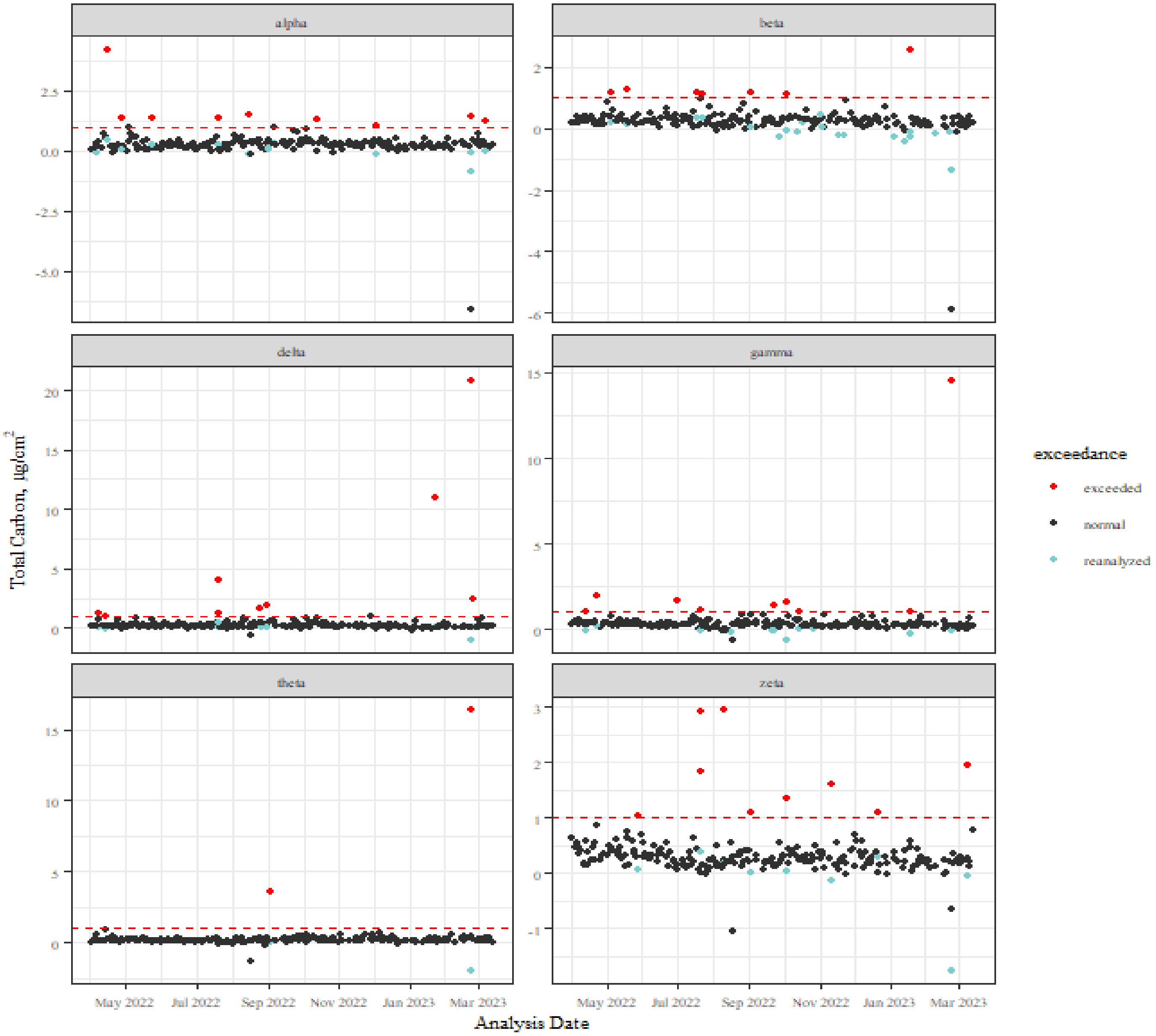
Blank Type	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St.Dev. (µg/cm^2)	# Exceedance
Laboratory Blank	1310	0.23	0.33	-6.59	20.87	0.97	44
Laboratory Blank - R*	68	-0.01	-0.06	-1.94	1.82	0.49	1
Instrument Blank	1327	-0.04	-0.05	-1.29	1.17	0.13	33
Instrument Blank - R*	38	-0.12	-0.12	-0.48	0.16	0.15	3

*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/cm^2, 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. Unstable FID baselines can occur after a methanator oven change or a HeOx or H_2 gas cylinder change. After changes such as these the laboratory blanks were repeated multiple 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.

In the following figure, red dashed horizontal line indicates the acceptance criteria of 1.0 µg C/cm^2 for total carbon areal density. For cases when the acceptance criteria were exceeded (red points), a repeat analysis (blue points) was performed.

Figure 4.3-1: Total carbon results of daily quartz filter laboratory blanks from each analyzer for the analysis period 4/01/2022 through 03/14/2023 (samples collected 1/2/2022 through 12/29/2022).

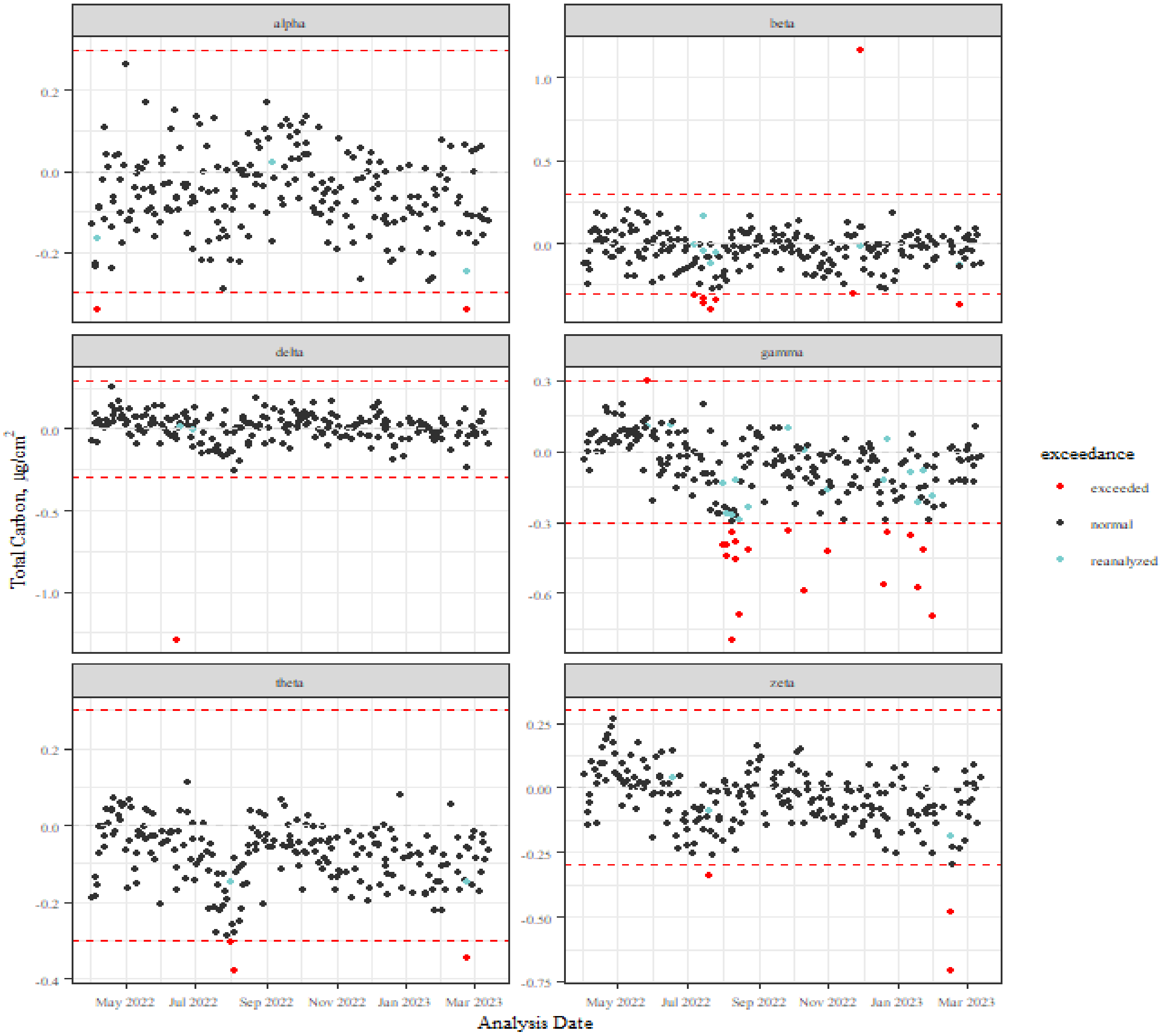


Instrument blank (IB) analysis is performed following the laboratory blank analysis by reusing the sample punch. The instrument blank acceptance criteria is TC (total carbon) within ± 0.3 µg/cm^2. When the instrument blank fails to meet the QC criteria (red points in Figure 4.3-2), analysis is repeated (blue points in Figure 4.3-2). If the Instrument Blank-R analysis still exceeds the acceptance limit (three 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. Gamma IB failed many times because the FID baseline was low. After changing FID igniter battery to a new one on 8/11/2022, performing autozero on 8/15/2022 and 8/22/2022, the IB recovered. The IB failure on Gamma does not impact the CSN samples because the IB, daily sucrose and weekly instrument inter-comparison were passed before the CSN samples were analyzed. Replicates were run to compare the results of Gamma with other instruments to ensure that the CSN sample analysis results are repeatable.

In the following figure, horizontal dash lines in red color indicate the acceptance criteria of ± 0.3 µg C/cm2 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.

Figure 4.3-2: Results of daily instrument blanks from each analyzer for the analysis period 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022).



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 µL 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 µg C/cm^2 through 210.5 µg 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/cm^2.

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 and 17.5†

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

† Starting from 9/7/2022, the sucrose|17 is 17.5 µg C/cm^2 because the old sucrose|17 is expired and replaced with a new one

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 98 exceedances out of the 1,427 sucrose analyses during the report period. All repeat-analyses of the sucrose solution showed acceptable results (Figure 4.3-3).

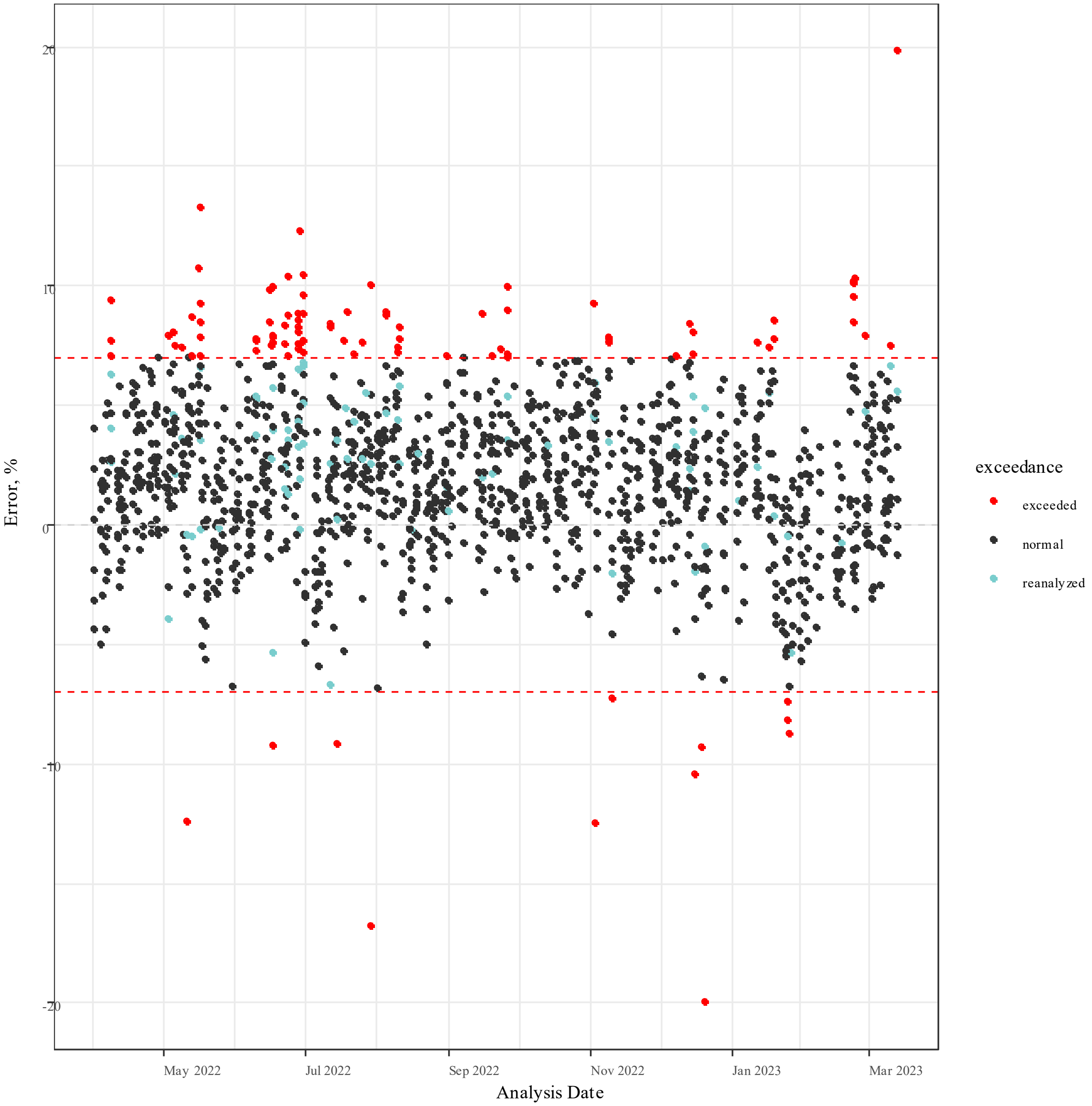
$$Error\ (\%) = \left(\frac{Measured\ TC - Calculated\ TC}{Calculated\ TC}\right) \times 100\% \tag{Eq. 4.3-1}$$

Table 4.3-5: Statistics of daily single-point sucrose standard total carbon analyses on all carbon analyzers for the analysis period 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022).

Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
1427	1.97	1.95	-19.95	19.83	3.35	98

In the following figure, Red dashed lines indicate the acceptance criteria of ±7% error. For cases when original measured sucrose value (red points) exceeded the acceptance criteria, a repeated analysis was performed (blue points).

Figure 4.3-3: Results of daily single-point sucrose calibration standard check for the analysis period 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022) for all instruments.



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 ± 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 33 exceedances during this reporting period. All affected samples were reanalyzed with acceptable results. Twelve exceedances occurred due to FID ignition being off during the analysis. Four exceedances occurred due to the FID baseline being too low, which all happened on Theta analyzer. Fourteen calibration peak area exceedances occurred when pressure was lower than normal, probably because the clamp that connects the oven front cap was not sufficiently tightened. Ten out of the fourteen exceedances due to pressure low happened on Theta analyzer. On 6/14/2022 the methanator oven was replaced due to a decrease in calibration area readings on Zeta. On 2/10/2023 the methanator oven was replaced on Gamma and Zeta due to a decrease in calibration area reading. Similarly, on 2/23/2023 the methanator oven was replaced on Beta due to a decrease in calibration area.

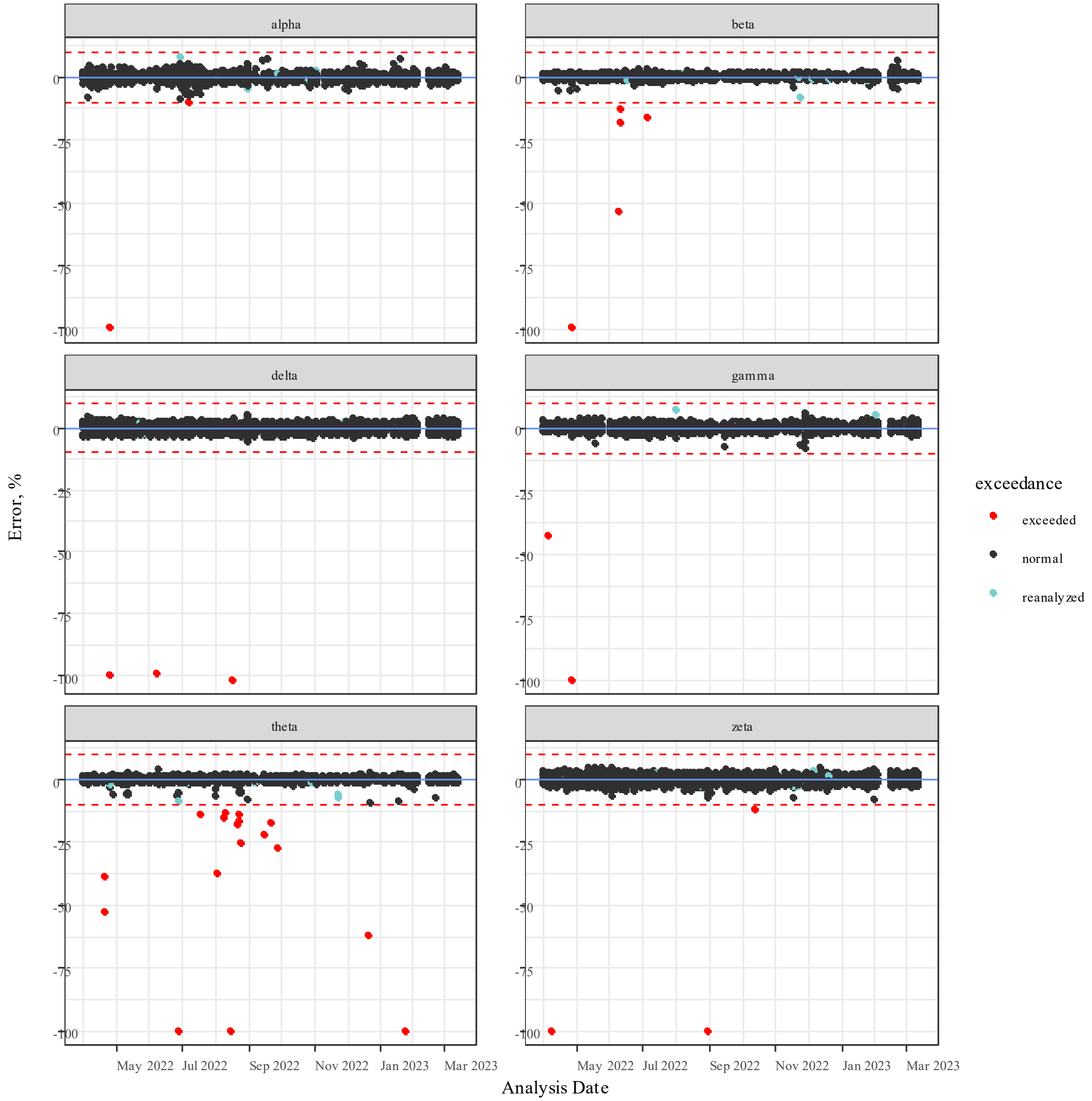
$$Error\ (\%) = \left(\frac{Cal.Peak - Average\ Cal.Peak}{Average\ Cal.Peak}\right) \times 100\%$$

(Eq. 4.3-2)

Table 4.3-6: Statistics of internal calibration peak area check on all carbon analyzers for the analysis period 4/1/2022 through 3/14/2023(samples collected 1/2/2022 through 12/29/2022).

Analyzer	Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
Alpha	2532	0.05	-0.04	-99.97	7.66	2.46	2
Beta	2475	0.01	-0.12	-99.95	6.25	3.21	6
Delta	2448	0.14	-0.12	-101.53	5.05	3.85	3
Gamma	2492	-0.02	-0.05	-99.91	7.29	2.51	2
Theta	2458	0.02	-0.29	-99.98	4.19	4.29	17
Zeta	2527	0.08	-0.08	-99.98	4.76	3.27	3

Figure 4.3-4: Results of internal calibration area check for the analysis period 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022). Red dashed lines indicate the acceptance criteria of ±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).

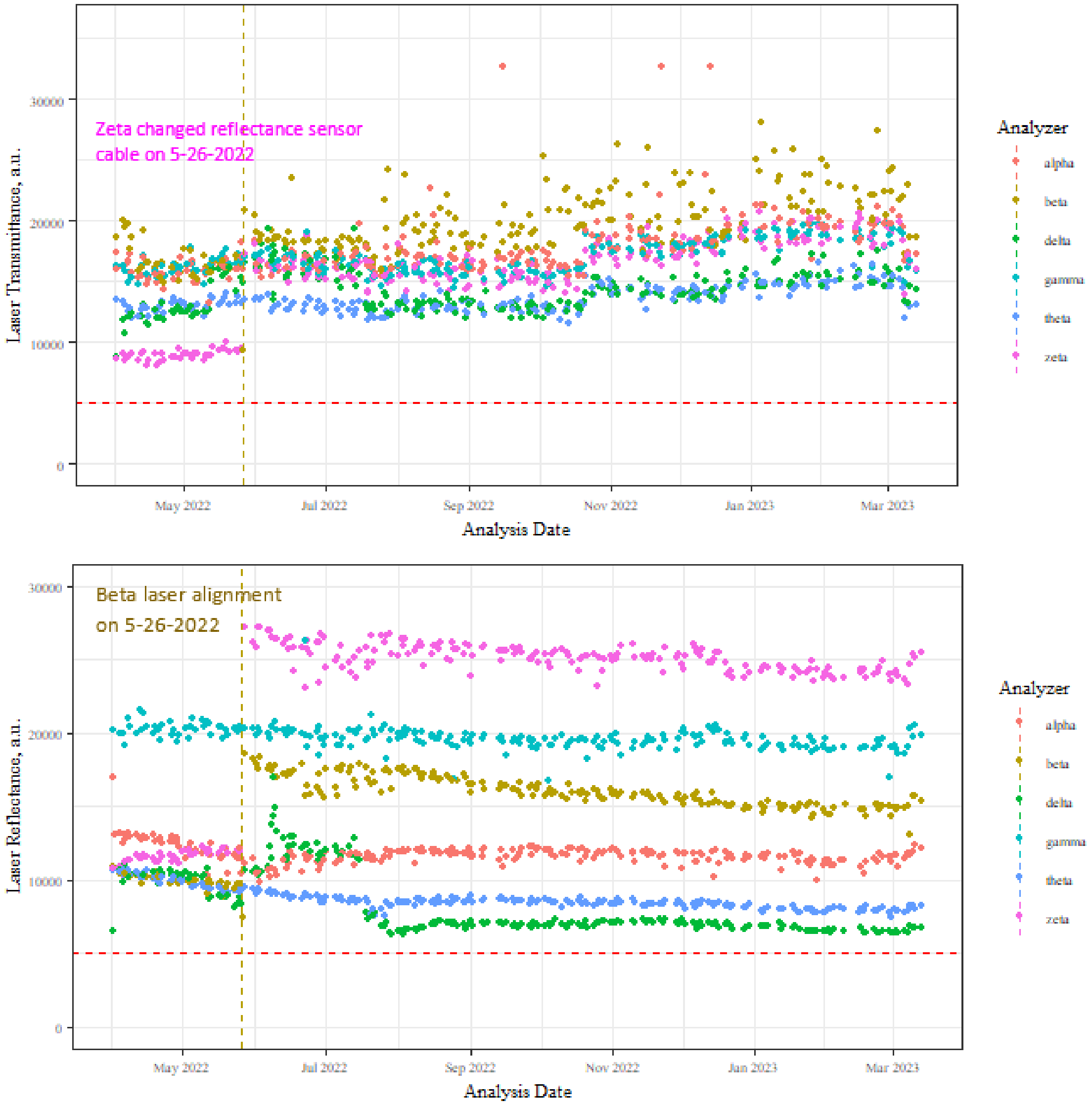


4.3.2.4 *Laser Performance Check*

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. Beta had a laser source alignment on 5/26/2022. Zeta changed reflectance sensor cable on 5-26-2022. During this report period, there were no exceedances of laser reflectance signal.

In the following figure, the 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.

Figure 4.3-5: Laser initial readings (top: Transmittance; bottom: Reflectance) of the instrumental blank analysis for the analysis period 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022).



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 15,002 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 4.3-6 shows the results of the replicate analyses. There was a total of 51 TC exceedances and 56ECR 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.

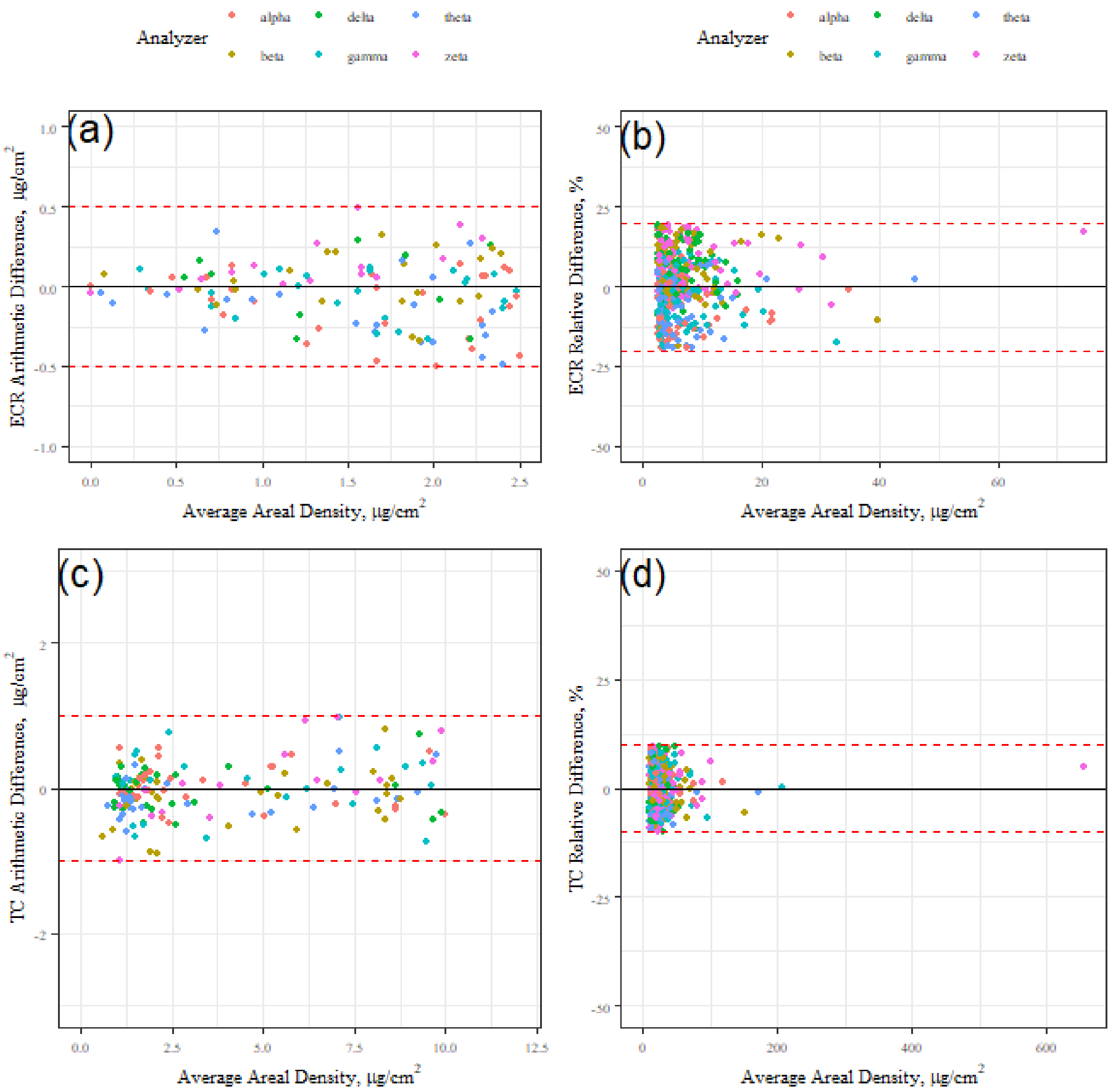
Table 4.3-7: Acceptance criteria and the summary statistics of the replicate analyses for the analysis period 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022).

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	666	51	51
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	666	56	56

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

In the following figure, the red dashed lines in each panel represents the acceptance criteria. These plots include passing retests of exceedances, the original failures are not plotted.

Figure 4.3-6: Results of CSN replicate analysis for ECR (Panel a and b) and TC (Panel c and d) for the analysis period 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022).

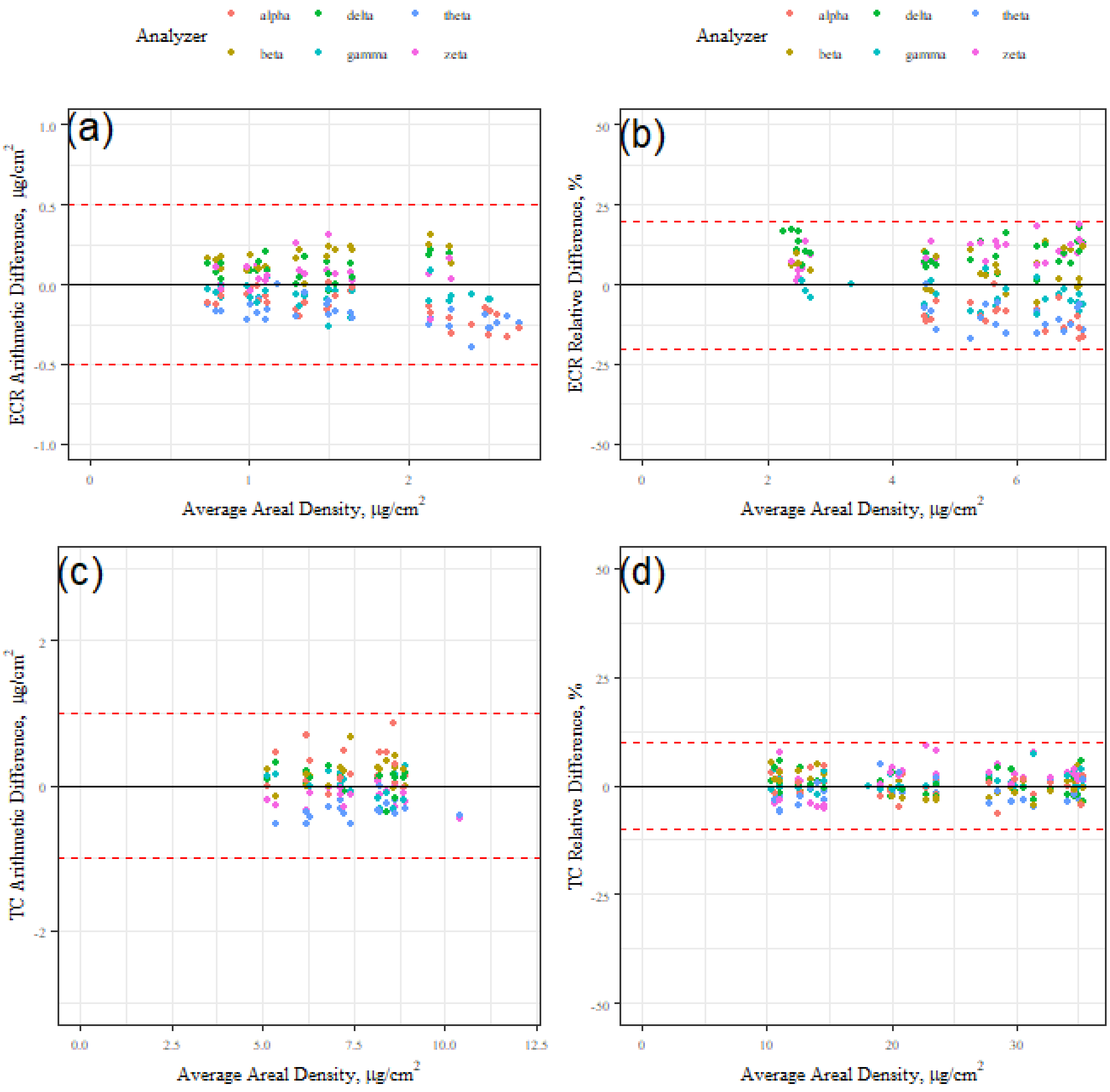


4.3.2.6 Inter-Instrument Comparison Check

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 53 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 4.3-7 shows the results of the weekly PC samples for each analyzer.

In the following figure, 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.

Figure 4.3-7: 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 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022).



The measured carbon areal density from each analyzer (Ax) 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 µg C/cm^2 and ECR > 2.5 µg C/cm^2) 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:

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

The acceptance criteria for inter-instrument comparison at low filter loadings (TC ≤ 10 µg C/cm^2 and ECR ≤ 2.5 µg C/cm^2) 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 zero 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 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022).

	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	20	-10.17	-10.04	4.18	32	0.03	-0.26	2.59
Beta	27	5.00	4.64	5.21	32	-0.49	-0.12	2.64
Delta	29	9.59	10.04	4.44	33	0.14	0.34	2.57
Gamma	24	-4.39	-3.87	3.91	33	-0.11	0.55	1.98
Theta	20	-11.74	-10.73	4.36	31	-1.99	-1.86	2.51
Zeta	27	9.90	9.82	4.38	31	2.30	1.57	3.82
	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	30	-0.13	-0.14	0.09	18	0.13	0.25	0.27
Beta	23	0.16	0.16	0.07	18	0.21	0.17	0.19
Delta	22	0.09	0.10	0.07	18	0.10	0.06	0.16
Gamma	27	-0.07	-0.08	0.07	18	-0.01	-0.01	0.17
Theta	30	-0.19	-0.18	0.08	19	-0.34	-0.34	0.13
Zeta	23	0.06	0.06	0.10	19	-0.13	-0.15	0.15

NA: Not available.

4.3.2.7 Multi-point Sucrose Calibration

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 calibration performed for the analysis period 4/1/2022 through 3/14/2023 (samples collected 1/2/2022 through 12/29/2022).

Analyzer	Calibration Date	Slope	r^2	Calibration Constant
Alpha[1]	3/28/2023	0.98	1	21.5709
Alpha[1]	9/13/2022	1.0026	0.9998	20.9243
Beta[1]	3/28/2023	0.96	1	22.3927
Beta[1]	9/13/2022	0.9857	0.9997	21.414
Delta[1]	3/28/2023	0.99	1	20.9346
Delta[1]	9/13/2022	1.0156	1	20.6388
Gamma[1]	3/28/2023	0.99	1	20.7785
Gamma[1]	9/13/2022	1.0173	0.9998	20.4683
Theta[1]	3/28/2023	0.98	1	20.6745
Theta[1]	9/13/2022	1.0258	1	20.2062
Zeta[1]	3/28/2023	0.97	1	21.68
Zeta[1]	9/13/2022	1.0474	0.9998	21.0079

[1] Semi-annual sucrose calibration after calibration gas cylinder was replaced.

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 04/01/2022 through 03/14/2023 (samples collected 01/02/2022 through 12/29/2022). 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]	5/25/2022	no	-26	-46	-51	-54	-20	-29
Alpha1	11/4/2022	no	-28	-51	-55	-59	-25	-34
Beta[1]	5/25/2022	no	-7	-10	-7	-6	-5	-16
Beta1	11/4/2022	no	-4	-5	-3	-4	-5	-17
Gamma[1]	7/20/2022	no	-14	-19	-7	-5	1	-6
Gamma1	1/9/2023	no	-15	-21	-3	-3	-2	-7
Delta[1]	7/13/2022	no	16	24	7	-4	-10	-21
Delta1	1/9/2023	no	28	36	15	6	-11	-19
Zeta[1]	5/25/2022	no	-16	-27	-20	-21	7	-6
Zeta[1]	11/4/2022	no	-14	-21	-8	-8	13	-1
Theta[1]	7/20/2022	no	11	19	32	30	12	3
Theta[1]	1/9/2023	No	12	18	34	30	12	4

[1] Semi-annual temperature calibration

4.3.3 Determination of Uncertainties and Method Detection Limits

For determination of Method Detection Limits (MDLs) see Section 3.1.3.7.

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 participated in ERLAP 2023 OCEC Interlaboratory Comparison. The results showed no systematic bias in all factors including TC, OC, or EC. The AQRC measurements compared well with other labs that participated. See references section of this report to find citation (JRC133803).

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, 2022 through December 31, 2022) there were 1623 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 04/01/2022 through 03/14/2023 (samples collected 01/02/2022 through 12/29/2022). 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 ($\mu g/cm^2$)	Average ($\mu g/cm^2$)	Min ($\mu g/cm^2$)	Max ($\mu g/cm^2$)	St. Dev. ($\mu g/cm^2$)
EC1	1623	0.06	0.09	-0.14	1.45	0.12
EC2	1623	0.09	0.11	-0.06	0.90	0.07
EC3	1623	0.01	0.02	-0.21	1.20	0.04
ECR	1623	0.00	0.00	-0.01	0.59	0.02
ECT	1623	0.00	0.01	-0.31	0.41	0.04
OC1	1623	0.17	0.17	-0.01	1.62	0.10
OC2	1623	0.33	0.36	0.12	3.22	0.16
OC3	1623	0.55	0.71	0.17	8.74	0.63
OC4	1623	0.23	0.30	-0.34	1.74	0.23
OCR	1623	1.50	1.75	0.07	11.91	1.02
OCT	1623	1.50	1.75	0.39	11.91	1.02
OPR	1623	0.17	0.21	-0.32	1.96	0.19
OPT	1623	0.16	0.21	-0.31	1.96	0.19

4.3.5.2 Laboratory Blanks Supplied by WSP

Five quartz laboratory blanks are shipped from the Sample Handling Laboratory (WSP) 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 WSP 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 4.3 -12 summarizes the laboratory blank statistics.

Table 4.3-12: Quartz filter laboratory blank statistics for the analysis period 04/01/2022 through 03/14/2023 (samples collected 01/02/2022 through 12/29/2022). 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	240	-0.00	0.01	-0.06	0.26	0.04
EC2	240	0.02	0.03	-0.02	0.28	0.04
EC3	240	0.01	0.01	-0.03	0.10	0.02
ECR	240	0.00	0.00	-0.00	0.09	0.01
ECT	240	0.00	0.00	-0.00	0.00	0.00
OC1	240	0.06	0.07	0.01	0.36	0.07
OC2	240	0.07	0.09	0.03	0.28	0.06
OC3	240	0.10	0.16	0.02	0.84	0.15
OC4	240	-0.00	0.02	-0.14	0.51	0.09
OCR	240	0.29	0.39	-0.07	1.91	0.33
OCT	240	0.29	0.39	-0.07	1.91	0.33
OPR	240	0.03	0.05	-0.08	0.56	0.08
OPT	240	0.03	0.05	-0.08	0.56	0.08

4.4 UC Davis Optical Absorption Laboratory

The UC Davis Optical Absorption Laboratory received and analyzed PTFE filters from batches 91 through 98, covering the field sampling period beginning from May 2, 2022 through December 29, 2022. Analyses of these samples were performed August 25, 2022 through May 4, 2023. The Hybrid Integrating Plate and Sphere (HIPS) instrument was used for all analysis. This instrument uses a 633nm laser that shines a light at the filter. Detectors are set up to collect the light that transmits (T) through the filters and reflects off the filter (R). What is not collected was absorbed (A) by the filter. The parameter reported is filter absorption, fAbs, in the inverse megameter unit (Mm-1).

Table 4.4-1: Sampling months in 2022 and corresponding HIPS 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 (2022)	Analysis Batch #	HIPS Analysis Dates
May	91	2022-08-25 - 2022-09-22
June	92	2022-09-14 - 2022-10-19
July	93	2022-10-10 - 2022-11-18
August	94	2022-11-10 - 2022-12-20
September	95	2022-12-13 - 2023-02-08
October	96	2023-01-09 - 2023-01-09
November	97	2023-02-08 - 2023-03-10
December	98	2023-03-16 - 2023-05-04
All months	87-98	2022-08-25 - 2023-05-04

4.4.1 Summary of QC Checks and Statistics

No standards for light absorption of particulate matter on filter media exist. Therefore, all quality control checks for the HIPS optical absorption instrument are performed on sampled filters. Reference values for these filters are determined by multiple measurements performed over multiple days. Consistency is paramount when no standards exist to check accuracy. To maintain this consistency, the raw detector response to a static set of filters (referred to as the Verification Set) is checked to be within ± 3% of the reference values. Then another static set of filters (the Reanalysis Set) is measured and calibrated results are checked against reference values. Only after these checks pass all acceptance criteria are samples analyzed on the system. A final review of the sample results is performed to check for instrument drift or individual filter issues prior to finalizing the results. HIPS QC tests and acceptance criteria are outlined in Table 4.4-2.

Table 4.4-2: UC Davis quality control measures for carbon analysis by HIPS.

Analysis	**Frequency**	**Criterion**	**Corrective Action**
Verification Set	Daily	Within ± 3 % of their reference values	• Visually inspect filter for damage or contamination. • If no damage is found, rotate filter. • Ensure sample was loaded correctly • Re-register detectors • Reanalysis required
Reanalysis Set	Once at the beginning of analysis and once at the end of total analysis for the day.	Linearity coefficient of determination must be greater than 0.95 and the slope must be within 0.95 and 1.0. Long-term reanalysis acceptable mean z-scores are ≤ 1	• Visually inspect filter for damage or contamination. • If no damage is found, rotate filter. • Ensure sample was loaded correctly • Re-register detectors • Reanalysis required
Registration filter	Once at the beginning of the day, and once every 200 samples, or 5 full trays.	Within ± 1 % of the accepted values	Reanalysis required

The Verification Set is used to determine whether the optical system, consisting of the light source, integrating sphere and plate, and detectors are operating as expected. The Reanalysis Set is used to determine if the system can be calibrated correctly. A calibration is generated using field blanks (N=80) from the same manufacturing lots as the Reanalysis Set filters. The field blanks are measured a total of six times, three times each day over two days. The calibration coefficients are taken as the slope and y-intercept of the linear regression of these transmittance and reflectance values. The Reanalysis Set samples are then measured a total of ten times (5 times each over two days). The tau value (optical absorption depth) is calculated from each of the 22 samples using this calibration and the results must lie within ± 2 X uncertainty. The standard deviations for transmittance and reflectance as well as the uncertainty of the linear regression coefficients from the calibration are used to determine the expanded uncertainty of the final Reanalysis Set tau values. The relevant equations are shown below.

$$\tau_{abs} = \ln\left(\frac{1-r}{t}\right)$$

where τ_{abs} is the field blank corrected absorption optical depth, r is the field blank corrected reflectance value given by $r = -a_1R/a_0$, with a_0 as the intercept and a_1 is the slope of the linear regression of the field blank results to the line, $r + t = 1$ and t is the field blank corrected transmittance value given by $t = T/a_0$. T and R are the registered (power normalized) transmittance and reflectance measurements reported by the HIPS instrument, respectively.

$$U(\tau_{abs}) = k\sqrt{\left(\frac{u(r)}{1-r}\right)^2 + \left(\frac{u(t)}{t}\right)^2}$$

where,

$$u(r) = \sqrt{\left(\frac{R}{a_0}u(a_1)\right)^2 + \left(\frac{a_1 R}{a_0^2}u(a_0)\right)^2 + \left(\frac{a_1}{a_0}u(R)\right)^2}$$

and

$$u(t) = \sqrt{\left(\frac{1}{T}u(a_0)\right)^2 + \left(\frac{a_0}{T^2}u(T)\right)^2}$$

$u(r)$ and $u(t)$ are the uncertainties of the blank corrected reflectance and transmittance measurements while $u(a_0)$ and $u(a_1)$ are the standard errors in the intercept and slope of the linear regression of field blanks and $u(R)$ and $u(T)$ are the uncertainties of the raw reflectance and transmittance values estimated as the median standard deviation from seven measurements of the reanalysis filters. k is the coverage factor that sets the confidence of the uncertainty. We apply a value of k=2, which corresponds to a 95 % confidence interval.

4.4.2 Summary of QC Results

QC tests conducted over the course of the analysis period showed good overall control of the instrument 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.

4.4.2.1 Detector Response Verification

The Verification Set is used to determine whether the optical system, consisting of the light source, integrating sphere and plate, and detectors are operating as expected. All samples in the Verification Set must lie within ± 3 % of their respective reference values, with one exception. The registration filter (QcSampleId=3), which is used for converting the raw power readings from the detectors to historically consistent normalized values, must lie within ± 1 % of its reference values. The reference values are determined as the mean transmittance and reflectance values from 12 measurements over the course of two days (6 measurements on each day).

The detector response verification QC check passed 100% of the time during the period reported here.

4.4.2.2 Reanalysis Check

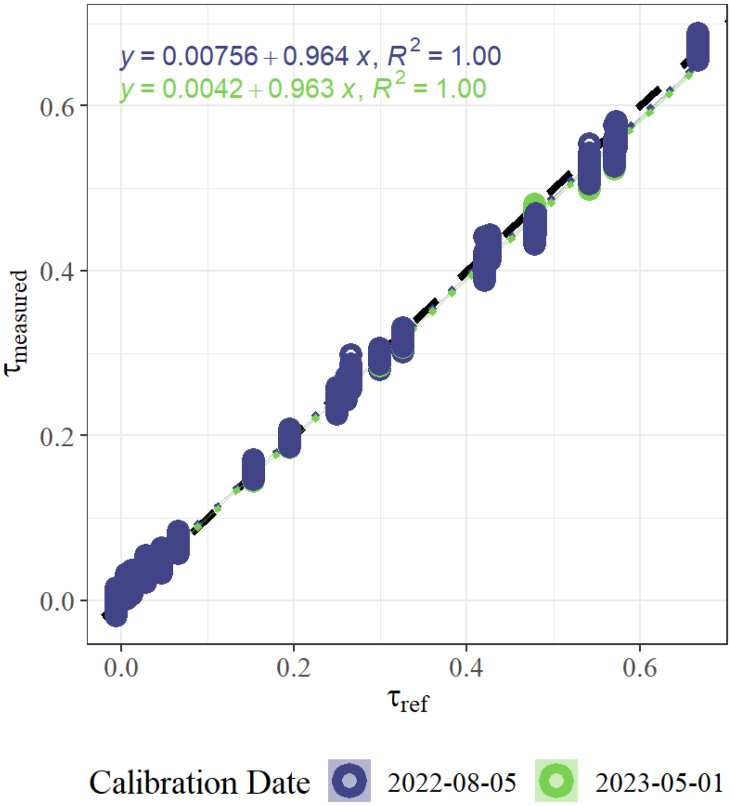
The Reanalysis Set verification check is predicated on a field blank calibration using field blanks representative of the sample filters chosen for reanalysis. This linear calibration is used to calculate the unitless absorption optical depth parameter (τ_{abs}). The measurement results of the Reanalysis Set samples must lie within ± 2 times the uncertainty of τ_{abs}. Additionally, the calibration of the Reanalysis Set must have a linearity, as determined by the coefficient of determination (COD), greater than 0.95. Similarly, the measured τ_{abs} values must correlate with their respective reference values with a COD greater than 0.95 and a slope between 0.95 and 1.0.

Calibration of the QC materials are summarized in Table 4.4-3 below and the comparison of τ_{abs} with reference values is shown after in Figure 4.4-1.

Table 4.4-3: Summary of QC materials calibration results.

Calibration Date	Linearity
2022-08-05	0.985
2023-05-01	0.987

Figure 4.4-1: HIPS linearity check of the Reanalysis Filter set.



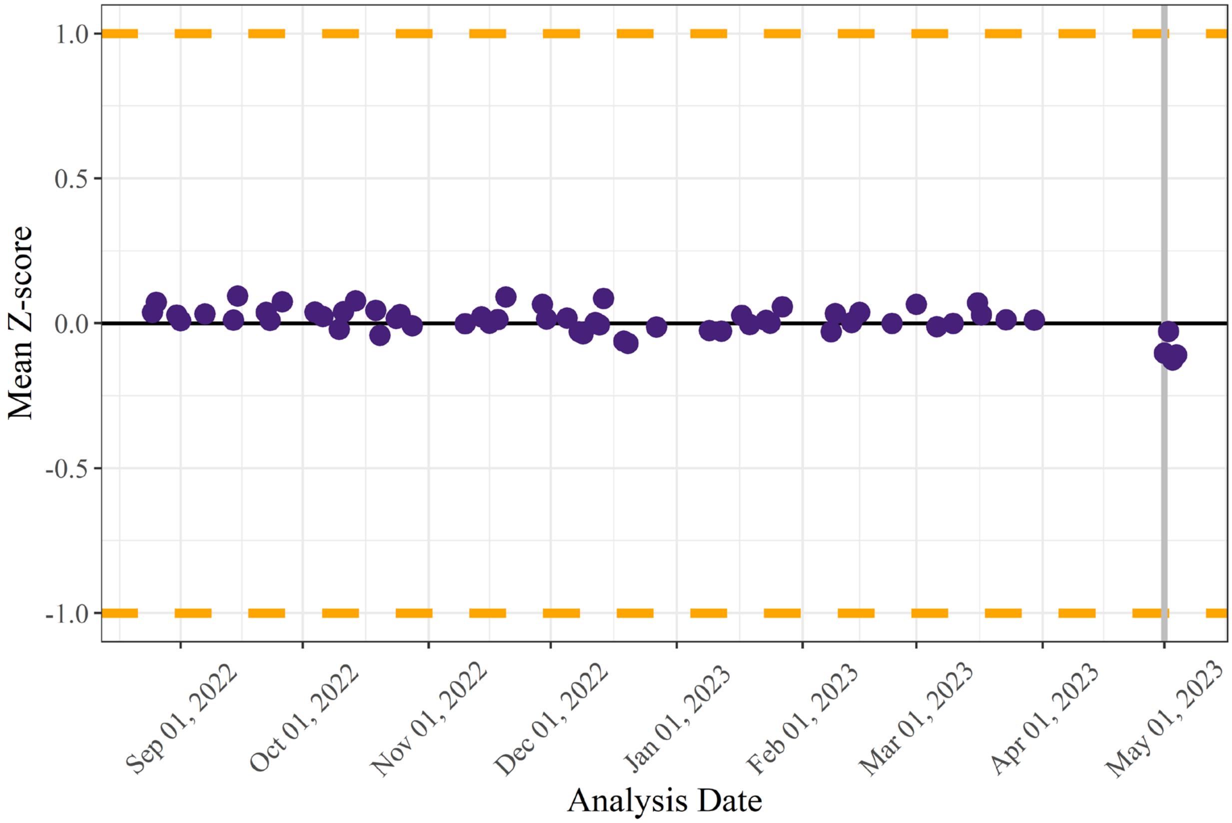
The linearity check passed for all calibrations of the Reanalysis Set. The HIPS instrument had a 100 % passing rate for the reanalysis set measurements within the uncertainty bounds, ± 2 X $U_{\tau_{abs}}$.

The long-term trend of the reanalysis results is monitored using the z-score. The z-score for each reanalysis sample is calculated as

$$z\text{-}score = \frac{\tau_{abs,i} - \tau_{abs,accepted}}{\sqrt{U(\tau_{abs,i})^2 + U(\tau_{abs,accepted})^2}}$$

while the mean z-score is calculated for each day of analysis. Mathematically, $mean\ z\text{-}score = \frac{1}{n}\sum_i z\text{-}score_i$. The absolute value of the mean z-score must remain ≤1 and any sudden shifts in the plotted mean z-score value compared to previous values must be investigated. The mean z-scores from this reporting period are shown below in Figure 4.4-2.

Figure 4.4-2: HIPS reanalysis mean z-score. Vertical lines identify calibration dates. Horizontal lines demarcate the QC limits of the z-scores.



4.4.3 Determination of Uncertainties and Method Detection Limits

For determination of Method Detection Limits (MDLs) see Section 3.1.3.7.

For uncertainty estimates see Section 6.5.

4.4.4 Audits, Performance Evaluations, Training, and Accreditations

4.4.4.1 System Audits

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

4.4.4.2 Performance Evaluations

No performance evaluations were conducted during this reporting period.

4.4.4.3 Training

Training of all personnel who assist with or operate the HIPS instrument is mandatory through UC Davis.

Only personnel listed in *UC Davis CSN Quality Assurance Project Plan (QAPP)*, trained on the appropriate SOPs and Technical Information materials (*CSN SOP 277* and *CSN TI 277A-C and si*), and authorized by the Laboratory Manager can perform HIPS analysis on CSN samples.

4.4.4.4 Accreditations

There are no accreditations for optical absorption analysis on aerosol filters by HIPS.

4.4.5 Summary of Filter Blanks

4.4.5.1 Field Blanks

Over the sampling period (May 1, 2022 through December 31, 2022) there were 1,077 valid PTFE filter field blanks. Table 4.4-4 summarizes the field blank statistics.

Table 4.4-4: PTFE filter field blank statistics for the 2022 sampling analysis period 8/25/2022 through 5/4/2023 (samples collected 5/1/2022 through 12/31/2022). Values are expressed as optical depth, which is unitless.

Species	Count	Median	Average	Min	Max	St. Dev.
fAbs	1077	0.721	0.765	-3.281	25.604	1.500

4.4.5.2 Laboratory Blanks

Five PTFE laboratory blanks are shipped with each batch of routine filters to the analysis laboratory and analyzed. A total of 35 PTFE laboratory blanks were analyzed during the current reporting period. Table 4.4-5 summarizes the laboratory blank statistics.

Table 4.4-5: PTFE filter laboratory blank statistics for the 2022 sampling analysis period 8/25/2022 through 5/4/2023 (samples collected 5/1/2022 through 12/31/2022). Values are expressed as optical depth, which is unitless.

Species	Count	Median	Average	Min	Max	St. Dev.
fAbs	35	-0.748	-0.541	-2.409	1.682	1.023

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, 2022 through December 31, 2022. 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, 2022 through December 31, 2022.

Sampling Month (2022)	Analysis Batch #	Filter Receipt Date	AQS Delivery Date	Days
January	87	March 9, 2022	July 1, 2022	114
February	88	April 6, 2022	August 4, 2022	120
March	89	May 5, 2022	September 1, 2022	119
April	90	June 15, 2022	October 13, 2022	120
May	91	July 13, 2022	November 10, 2022	120
June	92	August 10, 2022	December 8, 2022	120
July	93	September 14, 2022	January 12, 2023	120
August	94	October 12, 2022	February 8, 2023	119
September	95	November 9, 2022	March 8, 2023	119
October	96	December 7, 2022	April 6, 2023	120
November	97	January 11, 2023	May 11, 2023	120
December	98	February 15, 2023	June 15, 2023	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; QAPP revision (1.5) was delivered to the EPA for review on October 28, 2022, titled the CSN 2022 QAPP, revised again on December 12, 2022, and accepted by the EPA on January 17, 2023.

Shortly after v1.5 was released, the next CSN contract was awarded to AQRC (68HERH23D0004). Version 1.6 of the QAPP document was released on November 20th, 2023.

RTI, a subcontractor to AQRC, also released Revision 0 of their QAPP for Filter Handing, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography on November 20th, 2023.

However, these latest versions from AQRC and RTI would not have been in effect during 2022 sampling. Filter Handling, Acceptance Testing, and Gravimetric Analysis was handled by WSP (formerly Wood) under their own QAPP and direct contract with EPA for 2022 filters.

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 2023 revisions were delivered to EPA along with the revised QAPP. This round of revisions included integrating the new contract requirements such as transferring sample-handling from WSP to RTI and changing the data flow.

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 (WSP) 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, WSP gravimetric mass result files are received via email from WSP 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 to 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.

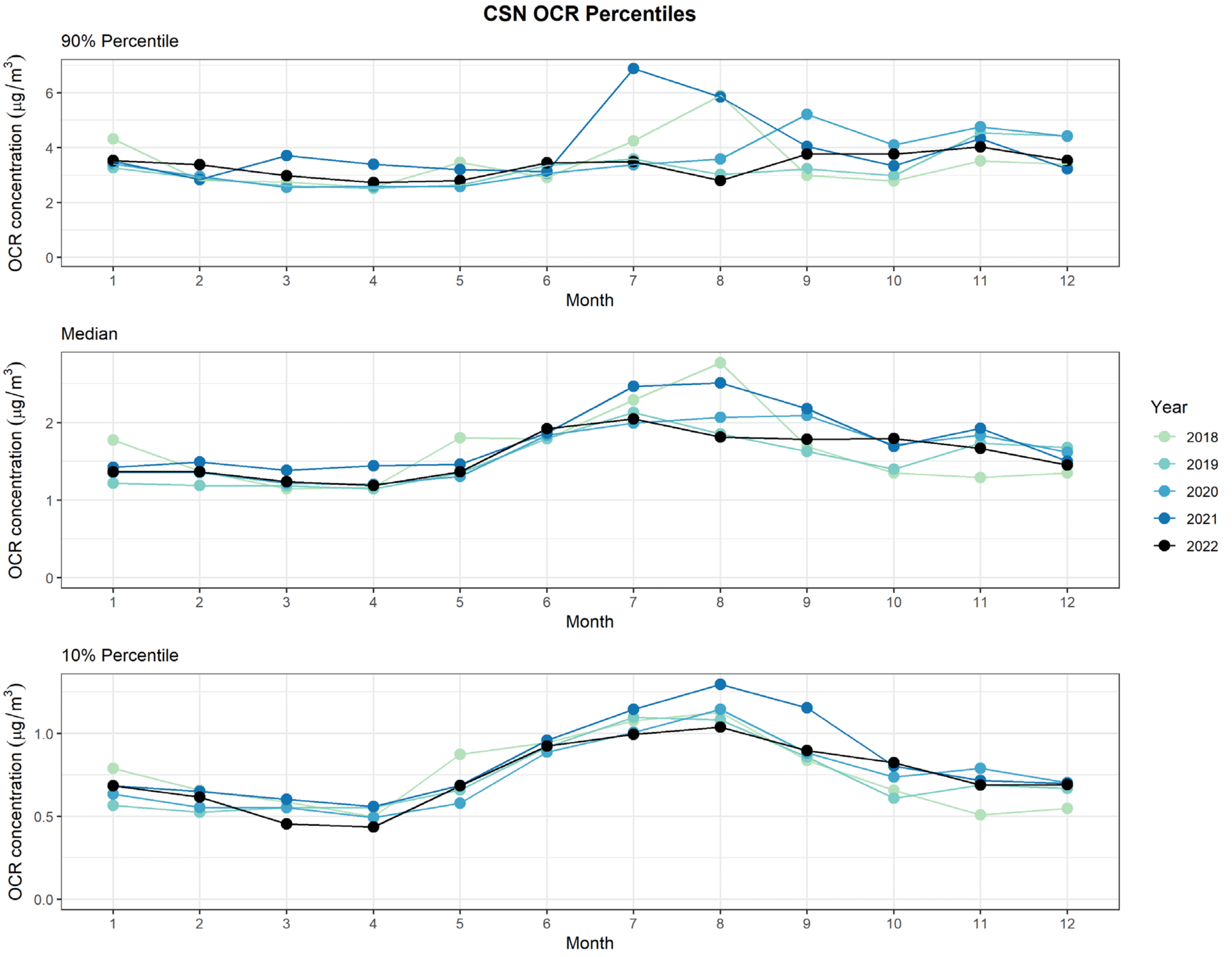
6.4.1 Summary of Monthly Data Validation Review Results

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.

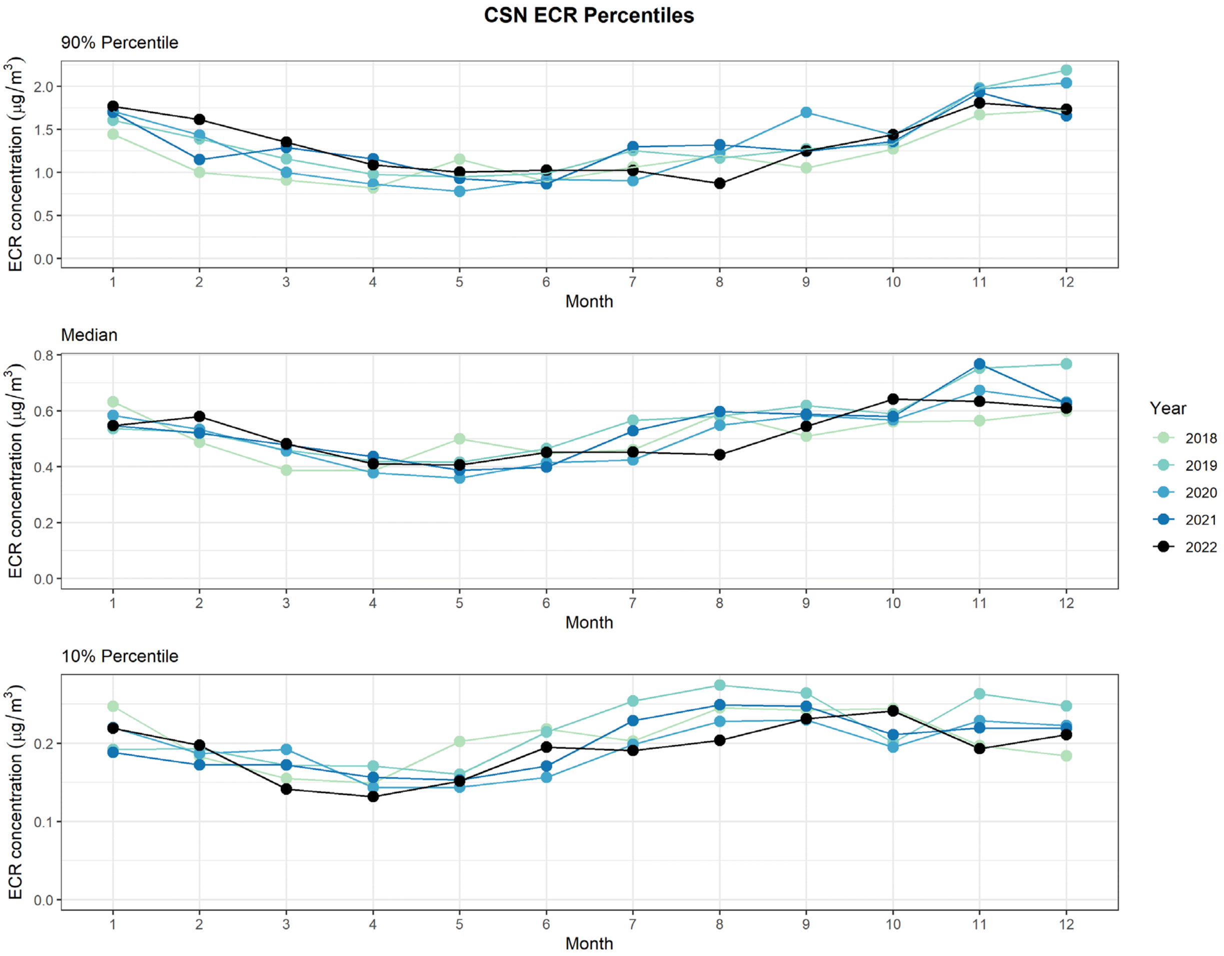
Figure 6.4-1 shows time series for the network-wide 90th percentile, median (50th percentile), and 10th percentile concentrations of organic carbon by reflectance (OCR). This figure shows concentration data without blank correction to enable comparison across a wider timeframe. The carbon fraction OCR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



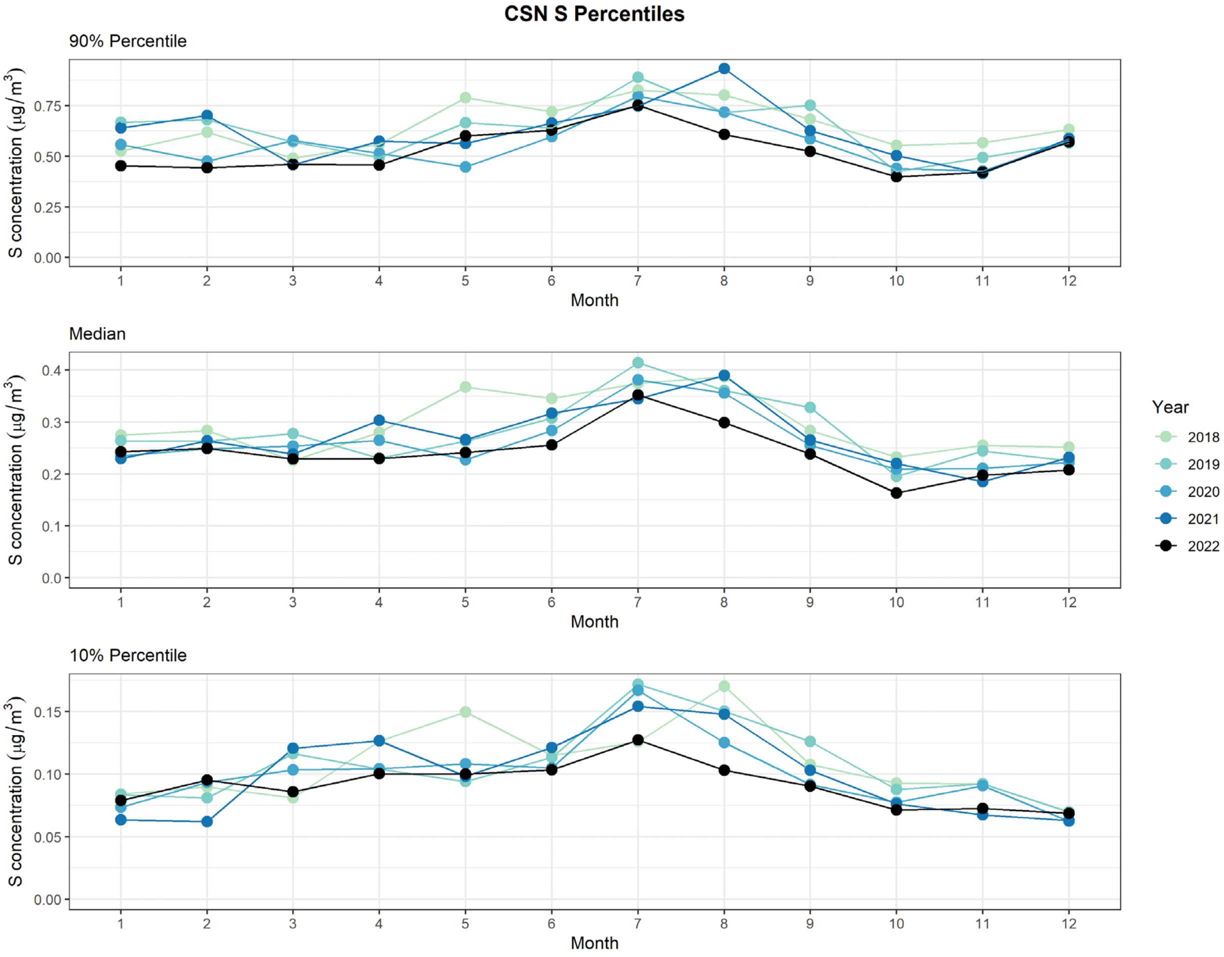
The OC4 plot in Figure 6.4-2 indicates when AQRC changed the OC4 time setting to be 580s for every analysis. This is seen in the 10th percentile plot as a jump in Sept 2020 when the change was implemented. This change allowed analyzers to collect all the OC4 without cutting the analysis short. The change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

Figure 6.4-2: Multi-year time series of network-wide elemental carbon by reflectance concentrations (ECR; raw data without blank correction).



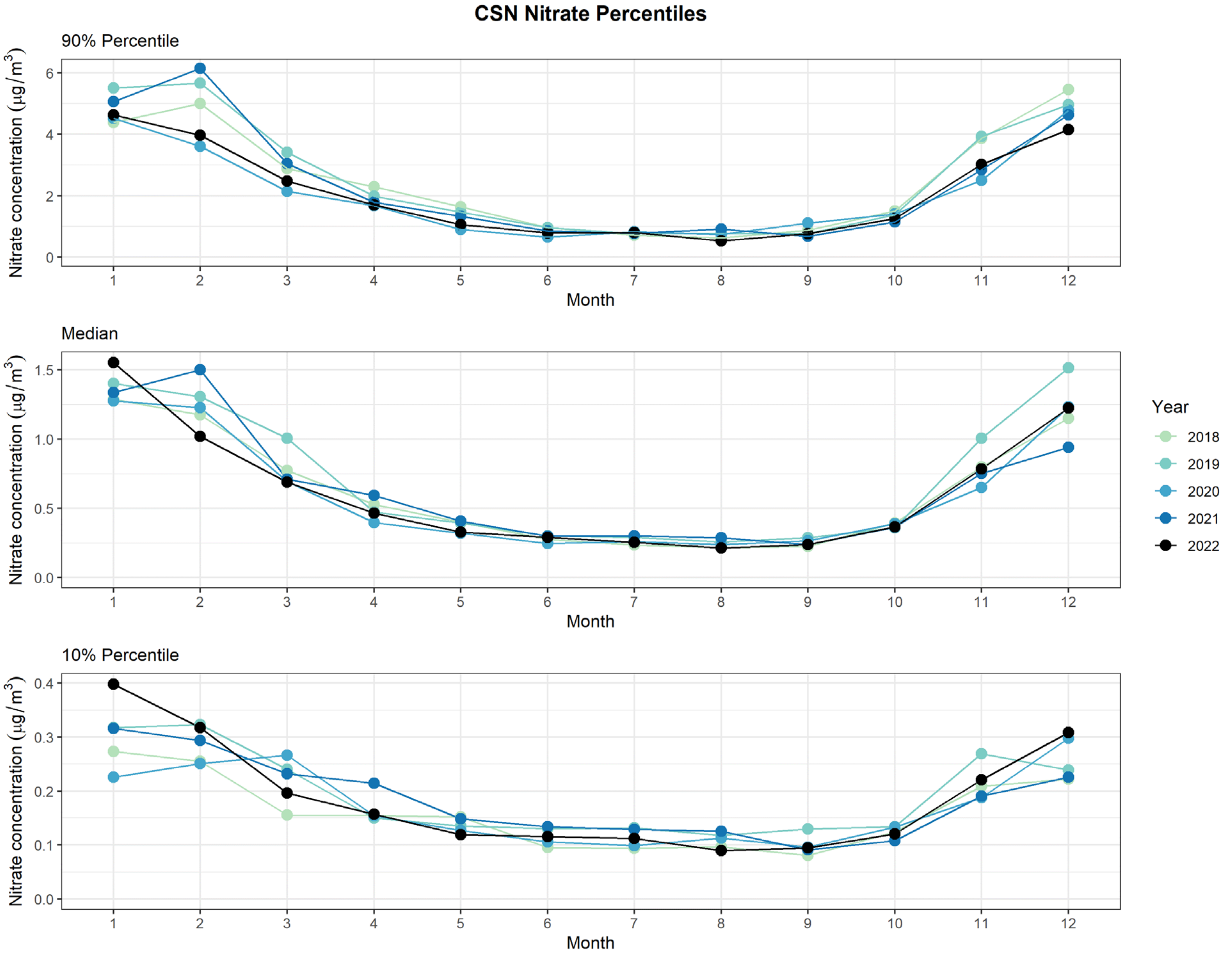
Similar to recent years, the 2022 sulfur concentrations generally continue to be low (Figure 6.4-3), with reduced seasonal variability.

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



The 2022 nitrate concentrations continue to show strong seasonality with elevated winter concentrations (Figure 6.4-4).

Figure 6.4-4: Multi-year time series of network-wide nitrate concentrations.



As discussed in Section 6.4.1.6, 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 2019 through 2022 RCM and soil results are shown in Figure 6.4-5 and 6.4-6, respectively.

Figure 6.4-5: Multi-year time series of network-wide composite variable reconstructed mass (RCM) concentrations.

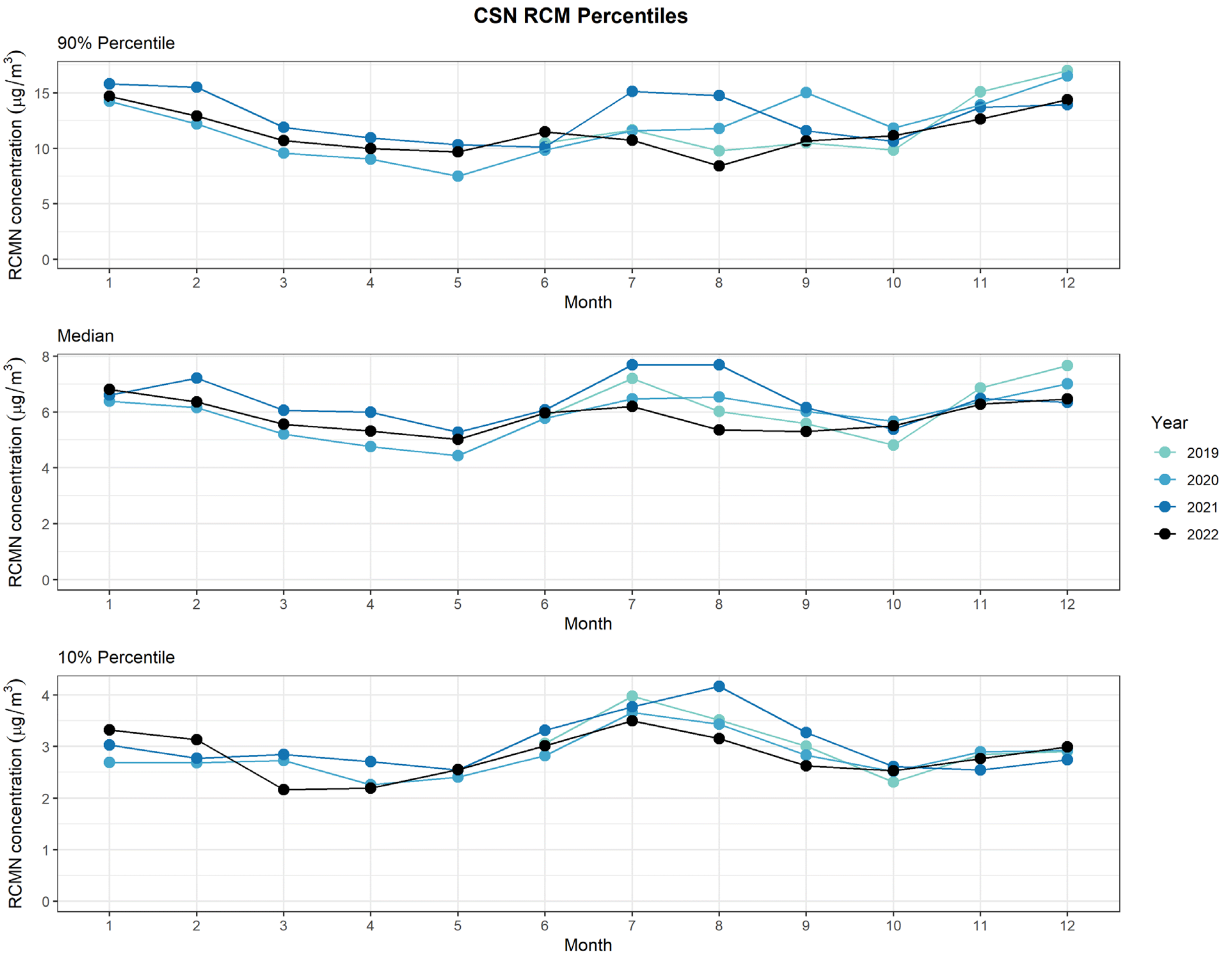
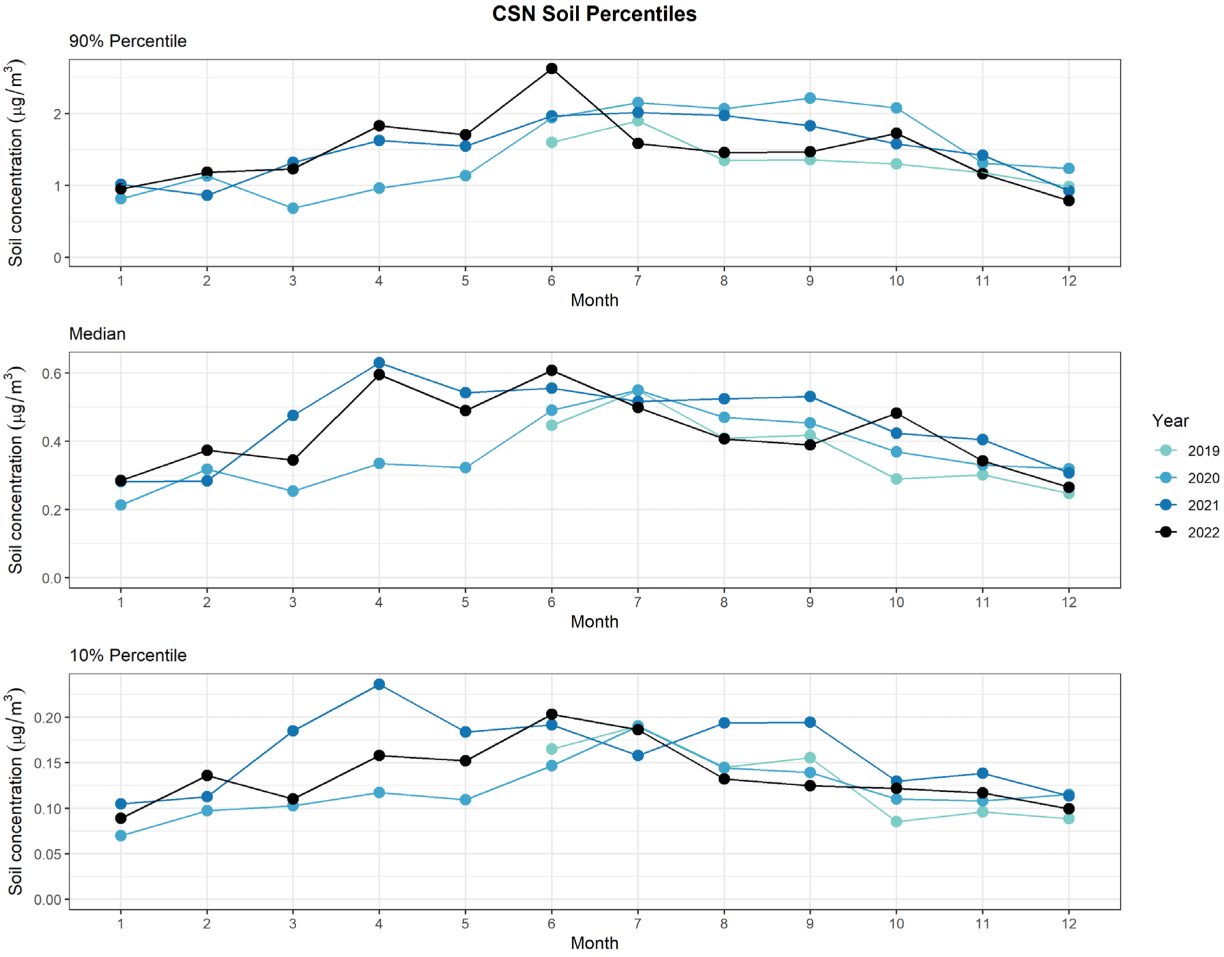
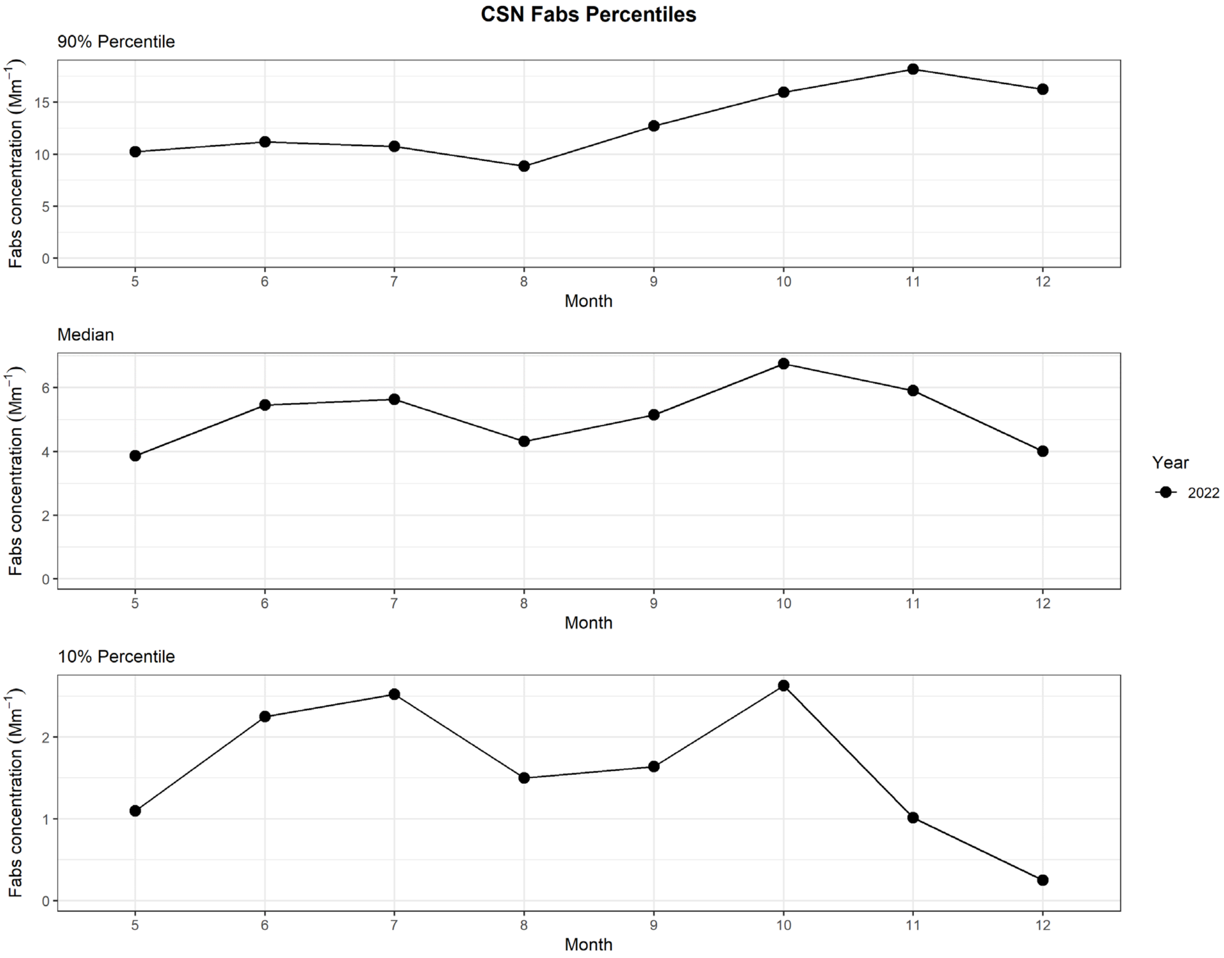


Figure 6.4-6: Multi-year time series of network-wide composite variable soil concentrations.



Starting in May 2022, AQRC began delivering fAbs measurements off of the HIPS instrument. fAbs is a measurement of light absorption on a filter which characterizes the darkness of the sample deposit and correlates with EC measurements on the Carbon instruments. The unit reported is inverse Megameters (Mm-1). Figure 6.4-7 below has 2022 data, which starts in May when we began delivering validate fAbs measurements. The delivery of available fAbs data from previous years is underway.

Figure 6.4-7: Single-year time series of network-wide fAbs 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×S)/SO_4 should be one if all particulate sulfur is present as water-soluble sulfate. In practice, ambient measurements often yield a ratio slightly greater than one, especially in the summer months, 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 shows that S and SO_4 are generally well correlated with a correlation coefficient of 0.95. Figure 6.4-9 shows that the ratio of (3xS)/ SO_4 has been trending down over the past six years, with the median ratio below 1 toward the end of 2022. Interestingly, the ratio of (3xS)/ SO_4 for the IMPROVE network exhibits an opposite increasing trend over the past few years (Figure 6.4-10).

Figure 6.4-8: Scatter plot of (3×S) versus SO_4, samples collected January 1, 2022 through December 31, 2022 (2020-2021 data are plotted in gray for comparison). Number of observations (complete pairs) is 12,304. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.

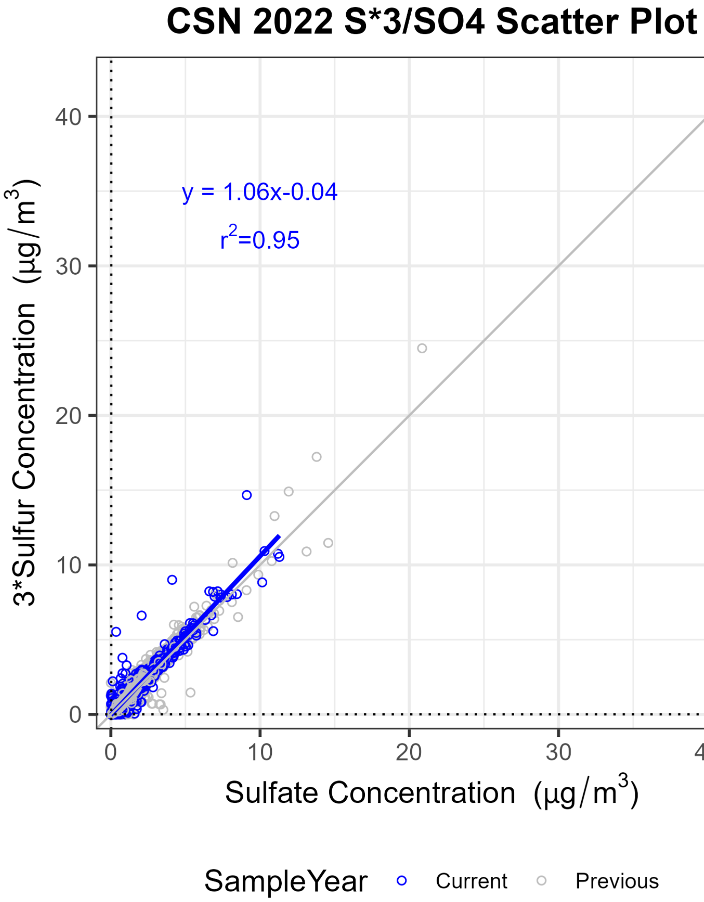


Figure 6.4-9: Timeseries of CSN monthly ratio of (3xS) versus SO_4, samples collected from 2017 to 2022.

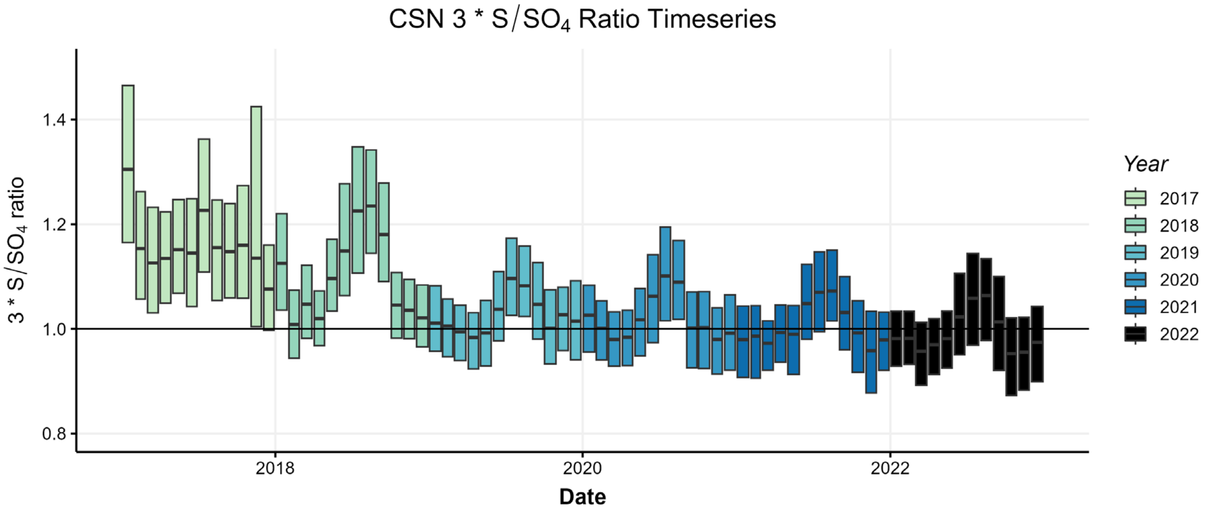
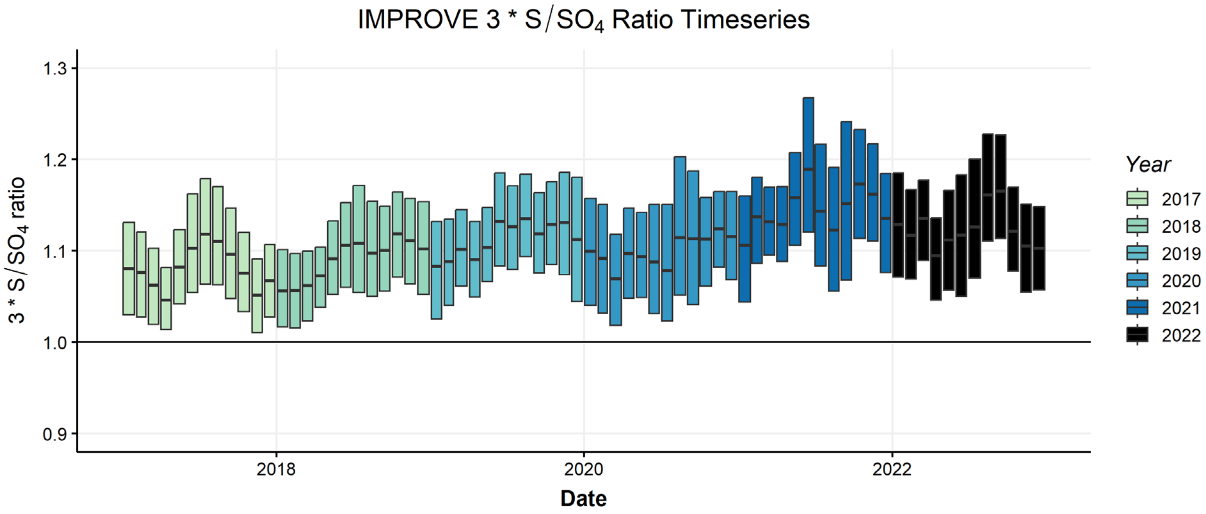


Figure 6.4-10: Timeseries of IMPROVE monthly ratio of (3xS) versus SO_4, samples collected from 2017 to 2022.



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/SO_4 ratio relationship, the potassium/potassium ion ratio can be used to identify measurement bias as well as atmospherically unusual events. In a scenario where all the particulate potassium is present as water-soluble potassium ion, the potassium/potassium ion ratio is expected to be near one. This scenario is not universal, so the potassium vs. potassium ion relationship presents some variability, especially at the lower concentration end (Figure 6.4-11).

Figure 6.4-11: Scatter plot of potassium versus potassium ion, samples collected January 1, 2022 through December 31, 2022 (2020-2021 data are plotted in gray for comparison). Number of observations (complete pairs) is 12,304. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit. Both y- and x-axis are set to be (0,15 µg/m^3) with 2 outlier points excluded.

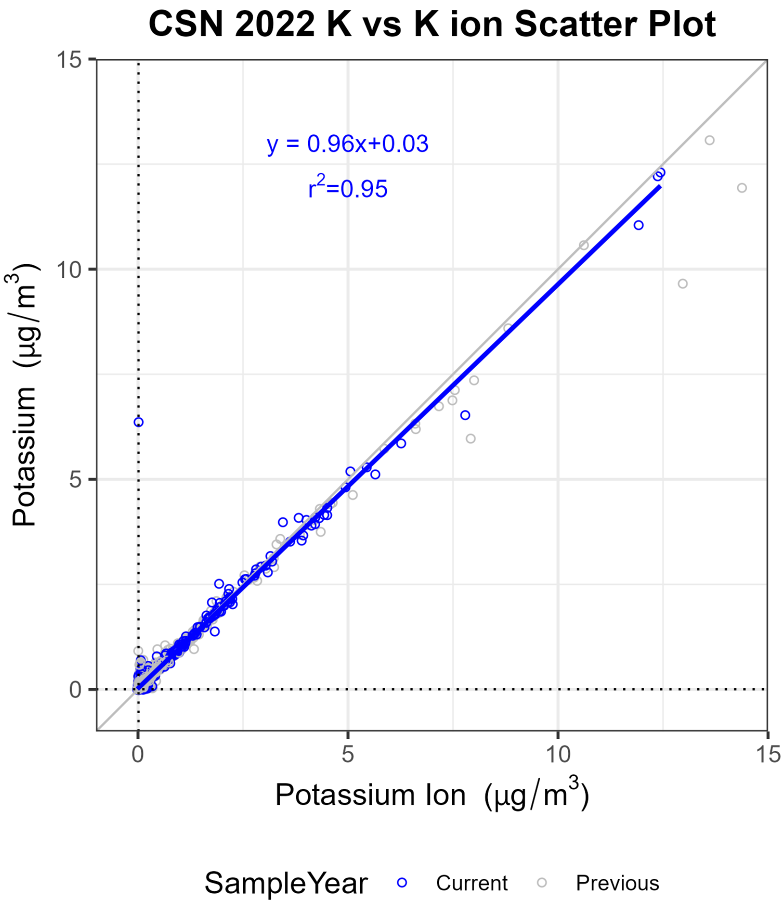
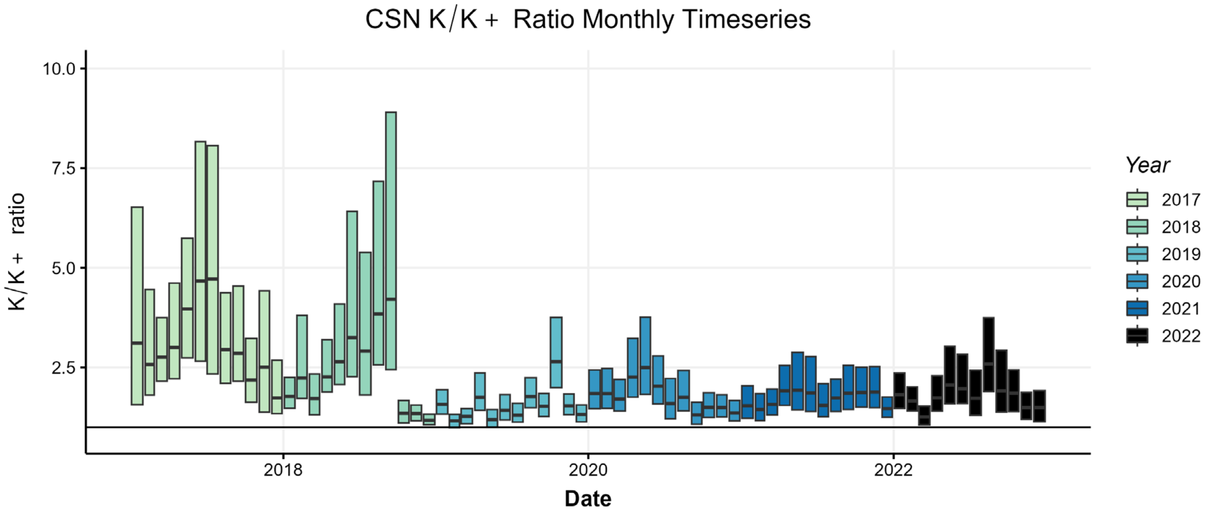


Figure 6.4-12 shows the multi-year timeseries of monthly ratio of K/K$^+$ over the past years. The ratio decreased sharply after the October 2018 Ions lab change from DRI to RTI. K$^+$ measurement was suspected to be biased low when DRI was performing ion analysis.

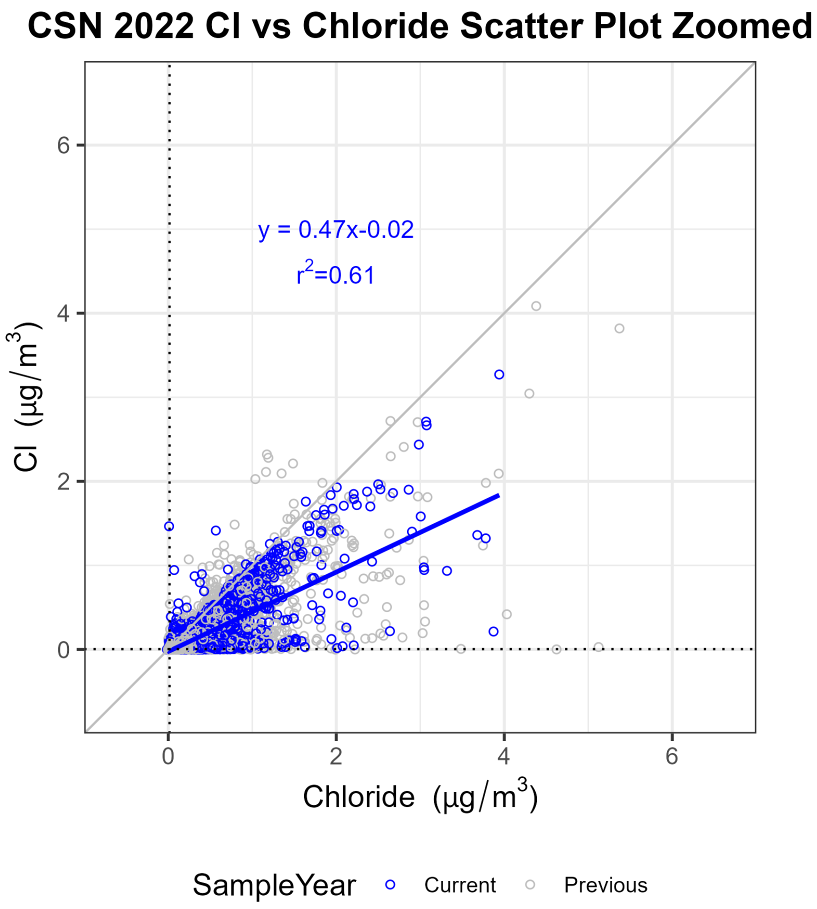
Figure 6.4-12: Timeseries of CSN monthly ratio of K versus K^+, samples collected from 2017 to 2022.



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. Similar 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 6.4-13).

Figure 6.4-13: Scatter plot of chlorine versus chloride ion, samples collected January 1, 2022 through December 31, 2022 (2020-2021 data are plotted in gray for comparison). Number of observations (complete pairs) is 12,248. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit. Both y- and x-axis are set to be (0,7 µg/m^3) with 2 outlier points excluded.



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 case where valid measurements are available for all needed variables, reconstructed mass is the following sum:

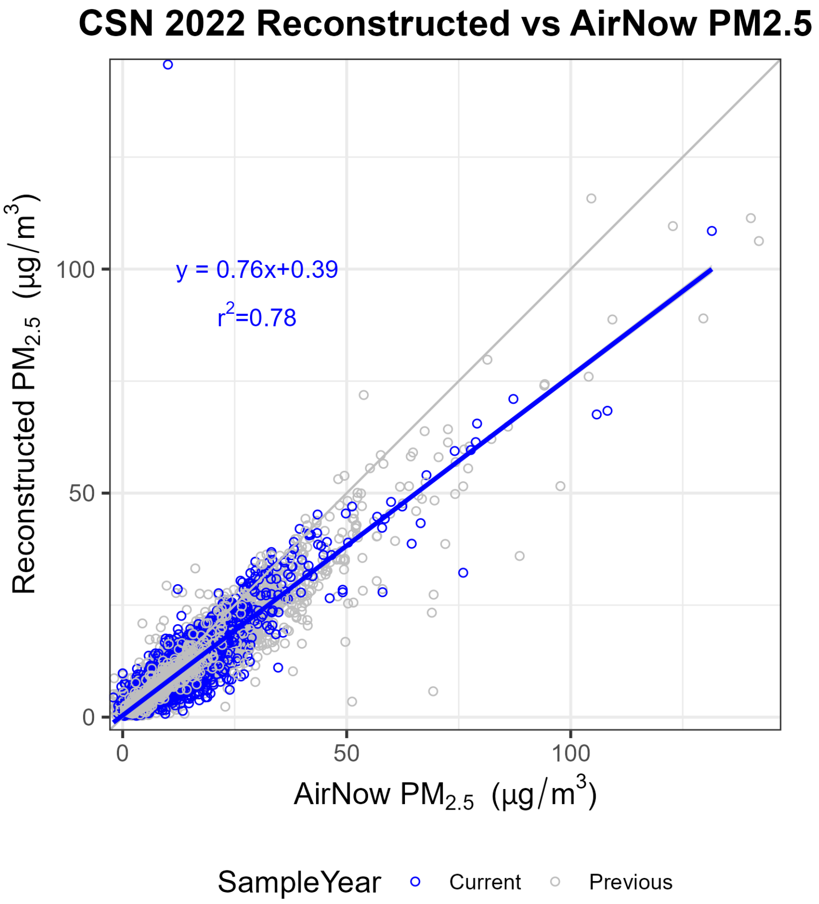
$$RCM = (4.125 \times S) + (1.29 \times NO_3^-) + (1.4 \times OC) + (EC) +$$
$$(2.2 \times Al + 2.49 \times Si + 1.63 \times Ca + 2.42 \times Fe + 1.94 \times Ti) + (1.8 \times chloride)$$

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

Since gravimetric analysis is not routinely performed using CSN filters, for comparison purposes, 24 hour average PM2.5 mass data (AQS parameter code 88101) from AirNow are used as part of the validation process in DART. The data provided by AirNow is not final and is only available after 2019-1-1, 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 mass ratio is expected to be near one. The RCM and AirNow mass generally correlate, but RCM tends to underestimate FRM mass (Figure 6.4-14).

Figure 6.4-14: Scatter plot of reconstructed mass (RCM) versus AirNow $PM_{2.5}$ mass, samples collected January 1, 2022 through December 31, 2022 (2020-2021 data are plotted in gray for comparison). Number of observations (complete pairs) is 9,525. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.



6.4.1.7 *fAbs Versus Carbon Measurements*

In the figures below, we plot a comparison of the HIPS measurement fAbs with carbon measurement ECR (Reflectance) as well as black carbon (BC), estimated from the initial and final laser readings of the TOA. Currently, fAbs data has been validated and delivered to AQS starting in May 2022. Previous data is being validated and will be delivered in the future, which will allow more historical comparisons to be plotted.

Figure 6.4-15: Timeseries of monthly ratio of fAbs versus ECR samples collected in 2022.

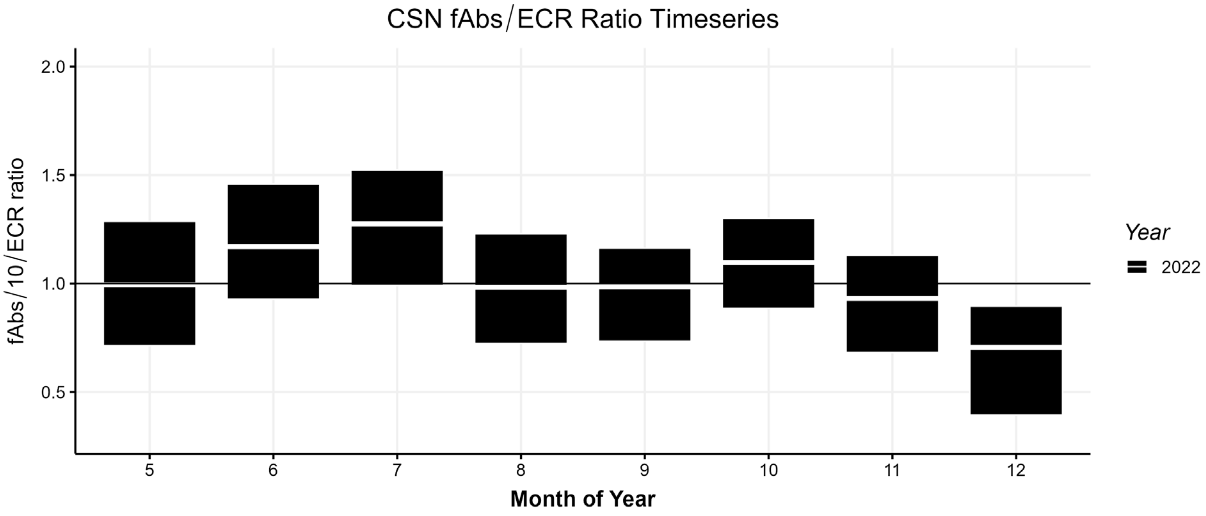
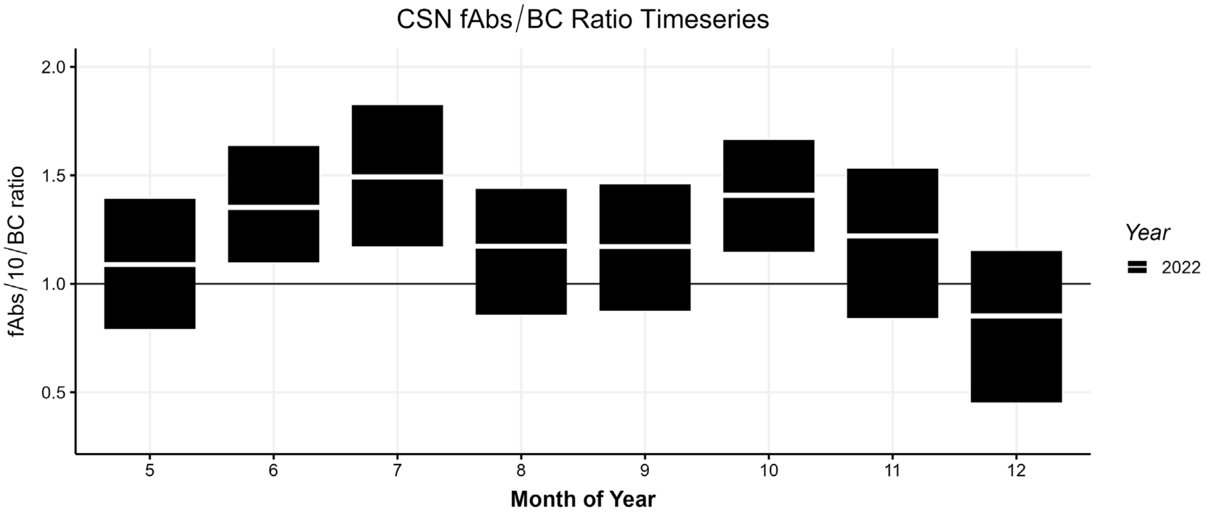


Figure 6.4-16: Timeseries of monthly ratio of fAbs versus BC samples collected in 2022.



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). Data from the previous two years (2020-2021, gray triangles) are plotted together with the current year (2022) to allow for direct comparison.

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

The scaled relative differences are ±√2, when one of the two measurements is zero and vary between these limits at concentrations close to the detection limit. 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, 2022 through December 31, 2022). Dotted vertical lines indicate MDL. Data from the previous two years (2020-2021) is plotted as grey triangles.

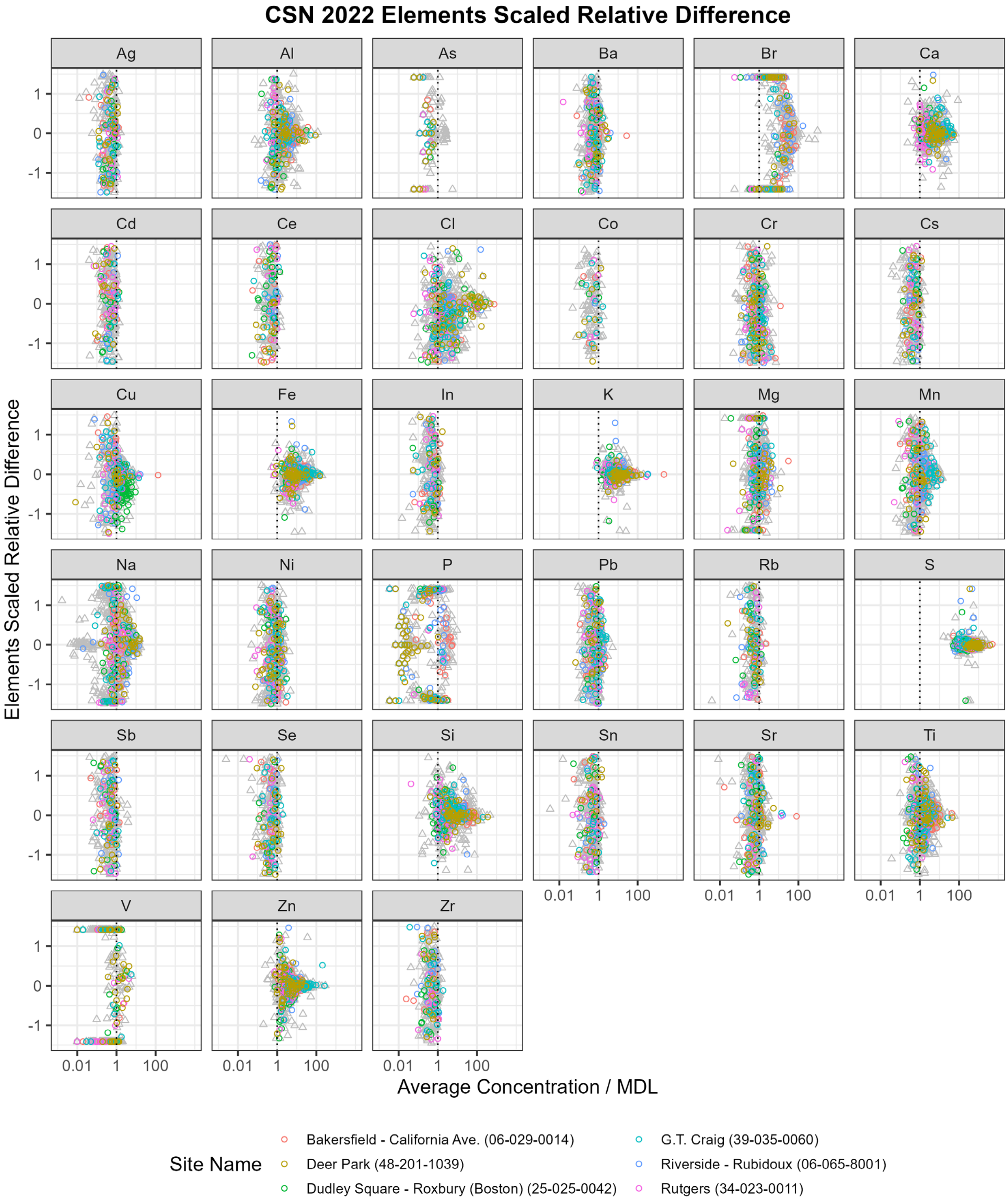


Figure 6.5-2: Scaled relative differences for ion measurements at sites with collocated samplers across the network (January 1, 2022 through December 31, 2022). Dotted vertical lines indicate MDL. Data from the previous two years (2020-2021) is plotted as gray triangles.

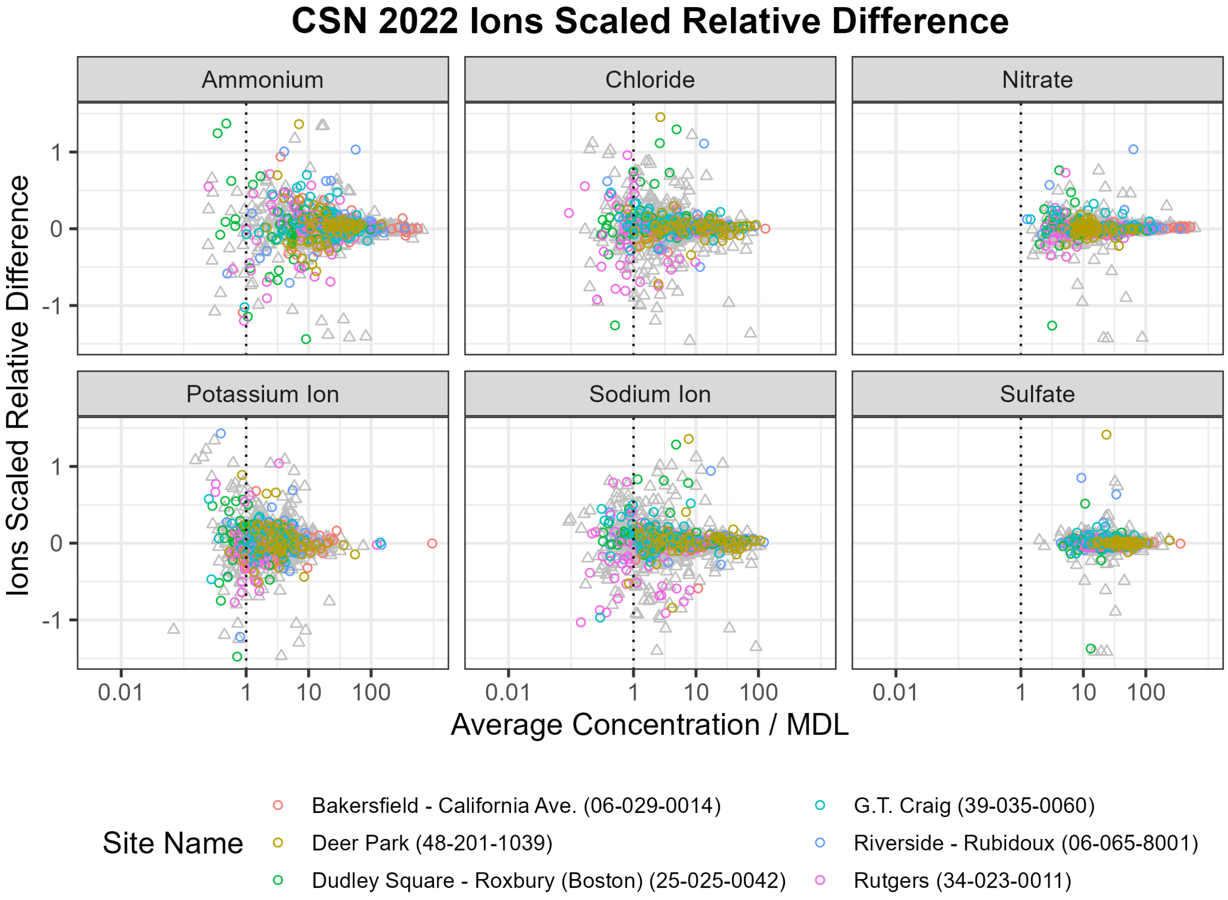
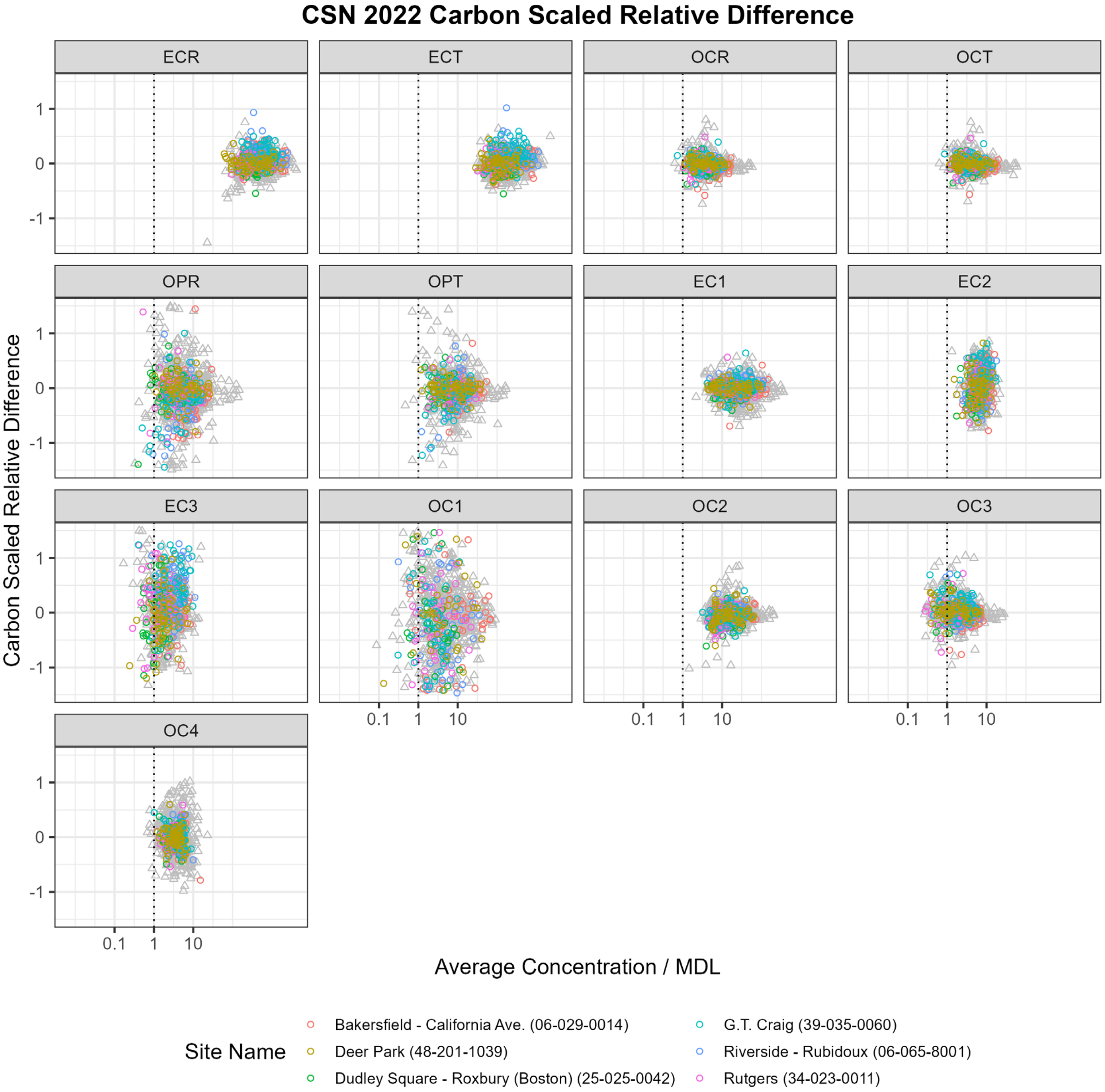


Figure 6.5-3: Scaled relative differences for carbon measurements at sites with collocated samplers across the network (January 1, 2022 through December 31, 2022). Dotted vertical lines indicate MDL. Data from the previous two years (2020-2021) is plotted as grey triangles. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolized (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).



Collocated precision is reported 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.

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

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 3.1.3.7) 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.

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

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.

$$Relative\ Percent\ Difference\ (RPD_i) = \frac{X_i - Y_i}{X_i + Y_i/_2} x100\% \qquad \text{(Eq. 6.5-4)}$$

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

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:

$$CV = \sqrt{\frac{n.\sum_{i=1}^{n} RPD_i^2 - (\sum_{i=1}^{n} RPD_i)^2}{2n(n-1)}} \times \sqrt{\frac{n-1}{X_{0.1,n-1}^2}}$$

(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), Table 6.5-3 (carbon), and Table 6.5-4 (optical) list median CV calculated using Equations 6.5-4 and 6.5-5 from collocated samples collected during 2022 (current reporting period) as well as 2021 (previous reporting period). The CFR CV calculated using Equations 6.5-4 and 6.5-6 from collocated samples collected during 2022 (current reporting period) and 2021 (previous reporting period) is also included.

In the following tables 6.5-1 to 6.5-5, the following explanations and data limits apply, unless otherwise noted before the table.

- For the previous 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 the current reporting period, *f* is calculated from samples collected June 1, 2019 through May 31, 2021 and used in relevant calculations for samples between January 1, 2022 through December 31, 2022 and CV is calculated from samples collected January 1, 2022 through December 31, 2022.
- 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.

Table 6.5-1: Fractional uncertainty (*f*), median coefficient of variation (CV), and CFR coefficient of variation (CFR CV) for element species.

	2021 (previous reporting period)						**2022 (current reporting period)**					
Species	***f*** **(%)**	**Pairs**	**CV (%)**	**Pairs**	**CFR CV (%)**	**Pairs**	***f*** **(%)**	**Pairs**	**CV (%)**	**Pairs**	**CFR CV (%)**	**Pairs**
Ag	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Al	17.4	89	12.0	95	26.8	95	16.4	127	10.4	77	20.9	77
As	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Ba	25.0	0	---	0	---	0	25.0	0	---	4	15.5	4
Br	25.0	23	34.6	91	55.1	91	53.4	108	40.0	72	58.1	72
Ca	13.6	371	7.9	247	21.2	247	13.6	408	6.8	240	18.8	240
Cd	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Ce	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Cl	32.9	173	19.8	85	39.4	85	36.1	169	19.6	103	37.8	103
Co	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Cr	25.0	0	---	0	---	0	25.0	0	---	1	---	1
Cs	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Cu	25.0	6	---	18	---	18	25.0	24	---	15	28.2	15
Fe	11.8	386	5.9	319	16.7	319	10.9	492	7.8	298	18.8	298
In	25.0	0	---	0	---	0	25.0	0	---	0	---	0
K	8.2	595	5.3	340	13.2	340	7.5	600	4.8	304	11.3	304
Mg	25.0	8	---	2	---	2	25.0	9	---	9	43.4	9
Mn	25.0	19	---	21	---	21	25.0	30	---	23	21.1	23
Na	18.8	67	---	32	---	32	17.9	64	---	38	19.9	38
Ni	25.0	0	---	1	---	1	25.0	1	---	0	---	0
P	25.0	3	---	12	53.5	12	25.0	16	---	5	31.5	5
Pb	25.0	0	---	1	---	1	25.0	1	---	0	---	0
Rb	25.0	0	---	0	---	0	25.0	0	---	0	---	0
S	5.4	658	3.5	353	7.7	353	5.2	640	3.5	341	11.9	341
Sb	25.0	0	---	2	---	2	25.0	1	---	0	---	0
Se	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Si	14.5	327	7.0	241	20.2	241	13.8	377	8.3	222	20.6	222
Sn	25.0	0	---	0	---	0	25.0	0	---	0	---	0
Sr	25.0	0	---	0	---	0	25.0	1	---	4	8.6	4
Ti	15.5	86	10.7	101	24.1	101	16.6	125	---	52	16.7	52
V	25.0	0	---	3	---	3	25.0	2	---	6	64.1	6
Zn	10.0	281	8.6	260	16.2	260	11.2	387	7.9	240	16.9	240
Zr	25.0	0	---	0	---	0	25.0	0	---	0	---	0

In the following Table 6.5-2, For the previous reporting period, absorption was not reported and has no relevant fractional uncertainty, median CV or CFR. This overrides the statement made for all tables in this section.

Table 6.5-2: Fractional uncertainty (*f*), median coefficient of variation (CV), and CFR coefficient of variation for filter absorption (fAbs).

	2021 (previous reporting period)						2022 (current reporting period)					
Species	***f*** **(%)**	**Pairs**	**CV (%)**	**Pairs**	**CFR CV (%)**	**Pairs**	***f*** **(%)**	**Pairs**	**CV (%)**	**Pairs**	**CFR CV (%)**	**Pairs**
fAbs	---	---	---	---	---	---	25.0	---	6.5	75	14.5	75

Table 6.5-3: Fractional uncertainty (*f*), median coefficient of variation (CV), and CFR coefficient of variation for ion species.

	2021 (previous reporting period)						2022 (current reporting period)					
Species	***f*** **(%)**	**Pairs**	**CV (%)**	**Pairs**	**CFR CV (%)**	**Pairs**	***f*** **(%)**	**Pairs**	**CV (%)**	**Pairs**	**CFR CV (%)**	**Pairs**
Ammonium	10.8	626	4.9	309	12.5	309	8.2	582	7.2	288	20.6	288
Chloride	10.1	432	4.0	219	14.9	219	8.8	420	3.7	238	13.6	238
Nitrate	5.5	636	2.9	342	8.1	342	4.9	622	2.6	319	9.9	319
Potassium Ion	25.0	38	5.8	153	14.6	153	10.9	249	6.8	126	12.9	126
Sodium Ion	11.1	414	4.0	188	16.8	188	9.0	362	3.8	183	16.6	183
Sulfate	4.1	656	2.1	352	4.8	352	4.0	640	1.9	343	8.2	343

In the following Table 6.5-4, 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).

Table 6.5-4: Fractional uncertainty (f), median coefficient of variation (CV), and CFR coefficient of variation for carbon species.

	2021 (previous reporting period)						**2022 (current reporting period)**					
Species	**f(%)**	**Pairs**	**CV (%)**	**Pairs**	**CFR CV (%)**	**Pairs**	**f(%)**	**Pairs**	**CV (%)**	**Pairs**	**CFR CV (%)**	**Pairs**
Elemental Carbon (EC1)	9.5	643	10.5	336	18.9	336	11.2	621	7.9	329	14.4	329
Elemental Carbon (EC2)	20.6	535	20.4	322	31.0	322	21.7	532	20.5	317	29.7	317
Elemental Carbon (EC3)	23.9	78	---	40	---	40	20.8	102	20.7	109	33.6	109
Elemental Carbon (ECR)	11.0	644	7.7	336	15.2	336	10.6	623	10.8	329	17.3	329
Elemental Carbon (ECT)	12.5	644	9.8	336	16.3	336	12.5	624	11.6	329	19.0	329
Organic Carbon (OC1)	33.5	290	23.4	155	41.4	155	31.9	268	23.6	91	44.8	91
Organic Carbon (OC2)	12.8	620	8.1	331	12.7	331	13.1	606	9.1	328	15.2	328
Organic Carbon (OC3)	10.9	312	7.0	115	11.8	115	10.8	141	8.1	245	14.9	245
Organic Carbon (OC4)	19.2	176	13.1	246	24.4	246	22.8	225	10.0	282	18.3	282
Organic Carbon (OCR)	7.5	469	5.4	247	9.3	247	6.8	361	5.7	302	11.4	302
Organic Carbon (OCT)	6.4	484	4.7	260	8.4	260	6.3	384	5.1	307	10.1	307
Organic Pyrolyzed (OPR)	17.2	437	15.8	210	30.3	210	18.6	382	15.9	215	26.6	215
Organic Pyrolyzed (OPT)	13.2	560	13.6	291	27.7	291	14.5	514	10.2	296	21.4	296

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