Chemical Speciation Network (CSN)
Annual Quality Report

Samples Collected January 1, 2023 through December 31, 2023

Prepared for:
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. Executive Summary

1.1 Introduction

The University of California, Davis (UC Davis) Air Quality Research Center (AQRC) summarizes quality assurance (QA) annually in this report as a contract deliverable for the Chemical Speciation Network (CSN) program (contract #EP-D-15-020 & 68HERH23D0004). 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, 2023 through December 31, 2023 (WSP batches 99-104, and RTI batches 23-05 to 23-12), where each batch corresponds with a single calendar month).

During the time period of January 1, 2023 through December 31, 2023, the shipping and handling and gravimetric components of the program transitioned from the contractor WSP to RTI International under subcontract to UC Davis. As will be discussed in more detail later, the transition started with the filter set collected May 6, 2023 and the transition was completed by June 8, 2023. The transition period includes WSP batches 103-104 and RTI batches 23-05 to 23-06, where each batch corresponds with a single calendar month.

1.2 Data Quality Overview and Issues

Section 3 of this report provides laboratory performance details for each of the analytical measurement techniques. The laboratory performance is detailed in Section 3.2 (RTI Ion Chromatography Laboratory), Section 3.3 (UC Davis X-ray Fluorescence Laboratory), Section 3.4 (UC Davis Thermal Optical Analysis Laboratory), and Section 3.5 (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 91.8% for PTFE filters, 91.8% for nylon filters, and 88.3% 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 2023 data reporting period.

Neither the EPA nor UC Davis conducted a Technical Systems Audit (TSA) of the SHAL laboratory during the 2023 data reporting period. Select staff from UC Davis did visit the shipping and handling and gravimetry operation area in Research Triangle Park, NC prior to the start of work.

2. Summary of Field Operation Issues

2.1 Chemical Speciation Site Changes

Changes at each CSN site are detailed in a quarterly metadata report. The report contains information on shipping and handling as well as laboratory operations. Details of changes from project start (5/23/23) through the end of the calendar year (12/31/23) are summarized in Table 2-1. Information in Table 2-1 does contain additional information not captured in the quarterly metadata reports.

Table 2-1: CSN site changes.

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
5/25/23	481130069 Hinton, TX	Operator James Hayes reached out and asked the shipment location for coolers be changed to his home address for the foreseeable future.	NA	NA	NA
5/25/23	481130069 Hinton, TX	Operator James Hayes reached out and asked we pause sending URG cassettes until the URG sampler is repaired.	Completeness	All or partial	Yes
5/26/23	100032004 Wilmington (MLK), DE	Site requested sampling pause due to lack of site operator. Missed 5Q/6Q sampling events scheduled for 6/8 and 6/11.	Completeness	All or partial	Yes
6/1/23	multiple	RTI started shipping samples to field sites under new contract.	Completeness	All or partial	NA
6/1/23	multiple	RTI started performing gravimetric analysis of samples under new contract.	Completeness	All or partial	NA
6/1/23	multiple	RTI started using Nylon Lot 710 filters.	Completeness	All or partial	NA
6/1/23	multiple	RTI started using PTFE Lot 240 filters.	Completeness	All or partial	NA
6/1/23	multiple	RTI started using quartz Lot 21642 filters.	Completeness	All or partial	NA

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
6/7/23	multiple	Several sites indicated through emails, phone calls, and messages on the COC forms that the SASS modules were not received with the screws all the way tightened. **Additional Information:** Many of the site operators tightened modules prior to sampling. A noticeable jump in %CV was observed for the canisters suspected to have arrived loose without tightening.	Completeness	All or partial	Yes
6/8/23	multiple	End of receipt of filters at WSP.	Completeness	All or partial	NA
6/14/23	multiple	RTI started using Nylon Lot 711 filters.	Completeness	All or partial	NA
6/14/23	100032004 Wilmington (MLK), DE	Site requested sampling restart. Sample collection restarted on 6/14.	Completeness	All or partial	Yes
6/14/23	481130069 Hinton, TX	URG sampling restarted with 6/14 sampling event.	Completeness	All or partial	NA
6/16/23	Multiple TX	Susan Simonet asked we include: Neal Penney neal.penney@tceq.texas.gov, Susan Simonet susan.simonet@tceq.texas.gov, Romeo Rubiano romeo.rubiano@tceq.texas.gov, Stephanie Ma stephanie.ma@tceq.texas.gov, and Holly Landuyt Holly.Landuyt@tceq.texas.gov in future communications with TX site operators	NA	NA	NA
6/21/23	multiple	Several sites indicated through emails, phone calls, and messages on the COC forms that the quartz filters were not loaded correctly into the URG cartridges. **Additional Information:** This issue was attributable to one staff member and was corrected upon discovery, however there was a lag between receiving the information and correcting the issue, so several sites had filters incorrectly loaded.	Completeness	All or partial	Yes
6/21/23	multiple	Several sites indicated through emails, and messages on the COC forms that the quartz filters were not loaded correctly into the URG cartridges. **Additional Information:** This issue continues to cause problems, though the frequency of non loaded cassettes is decreasing over time as staff become more familiar with processes.	Completeness	All or partial	Yes
6/23/23	50-007-0012 Burlington; VT	Site location was moved, no more sampling at this site after 6/20/23 **Additional Information:** Site was moved, all sampling occurring at new location	Completeness	All or partial	No

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
6/23/23	50-007-0014 Burlington - Main St.; VT	Site location was moved, new AQS Site code was assigned. **Additional Information:** Site was moved, all sampling occurring at new location.	Completeness	All or partial	No
6/26/23	multiple	The shipment calendar was setup to have sites ship sampled 4a filters back on July 3rd for delivery on July 5th. An email communication was sent out requesting sites ship on July 5th for a delivery date of July 6th. **Additional Information:** Only ~3 shipments were received on July 5th.	Completeness	All or partial	NA
6/26/23	295100085 Blair Street; MO	Location of where to ship samples was requested changed starting July 3rd	NA	NA	NA
7/24/23	270530963 Minneapolis – Philips; MN	Site temporarily shut down due to power loss, stopped beginning with 7/29/23 scheduled sample	Completeness	All or partial	NA
7/27/23	391530023 Akron – 5 Points; OH	Site temporarily shut down due to roof repair, stopped beginning with 8/10/23 scheduled sample	Completeness	All or partial	NA
7/28/23	420290100 New Garden; PA	Changed shipping location and addressee	NA	NA	NA
7/28/23	421290008 Greensburg; PA	Site restart. Scheduled sampling to begin on 8/10/23 6a/7a.	Completeness	All or partial	NA
7/28/23	20900035 Hurst Road – North Pole; AK	Site indicated they have been receiving Nylon modules with no denuder for three events. **Additional Information:** Denuder was added to module after the information was provided.	Completeness	All or partial	Yes
8/4/23	60670006 Del Paso Manor; CA	Site request we resume URG shipments to this site starting on 9/3/23	Completeness	Partial	Yes
8/8/23	multiple	Some sites reported the Lab Out section of the FSCOC was not filled out.	NA	NA	NA
8/8/23	250250042 Roxbury (collocated); MA	This site does not have two functioning controllers for their two URG samplers. Instead they use one controller and share between the two samplers. This requires an additional filter to be loaded into the single event collocated sampler. When this filter is not loaded it leads to an invalid event. This has occurred multiple times.	Completeness	Partial	Yes

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
8/22/23	Multiple Roxbury, Roxbury (collocated), Chicopee; MA	Site complained their coolers were being received above 4C at the lab for three sites during the month of March. **Additional Information:** New coolers have been purchased and deployed to the program to assist with better temperature receipts.	Completeness	Partial	Yes
8/25/23	391130038 Sinclair Community College; OH	Site emailed 8/25/23 indicating their URG sampler was down. We continued to send samples and the sampler was collecting again starting 9/21/23. **Additional Information:** Even though the site requested this pause, it didn't take effect in time. Site operator writing on the Field COC form indicated repair of equipment was nearly completed.	Completeness	Partial	Yes
8/30/23	420010001 Arendtsville; PA	Changed shipping location and addressee	NA	NA	NA
8/31/23	multiple	Due to a mix up of shipping labels, five sites received the wrong boxes for sampling. All information was corrected upon receipt of the samples, and no data was lost and no events were deemed invalid. **Additional Information:** Events were flagged with a qualifier code only.	Completeness	Partial	Yes
9/6/23	270530963 Minneapolis – Philips; MN	Site back online starting with 9/6/23 sampling event	Completeness	All or partial	NA
9/18/23	160010010 St Lukes Hospital – Meridian; ID	Site has a need for scheduled pickup to ensure temperature requirements are met. Starting on 9/18/23, scheduled pickups for this one site were re-introduced.	NA	NA	NA
9/27/23	530770015 Toppenish – Ward Rd; WA	Site started sampling 9/27/23	Completeness	All or partial	NA
10/27/23	multiple	Sites: Gary, IN, Toppenish, WA and Yakima, WA were added to the scheduled pick-up process at the sites requests.	NA	NA	NA
11/1/23	420030008 Lawrenceville; PA	Changed shipping location and addressee	NA	NA	NA
11/1/23	420030064 Liberty; PA	Changed shipping location and addressee	NA	NA	NA

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
11/9/23	420010001 Arendtsville; PA	Changed shipping location and addressee	NA	NA	NA
11/9/23	420750100 Lebanon; PA	Changed shipping location and addressee	NA	NA	NA
11/14/23	multiple	UCD has become concerned with the amount of mismatched filter IDs to aliquots IDs for PTFE filters. **Additional Information:** The database used for the processing is being revised to require and entry before loading and an entry after disassembly.	Completeness	All or partial	NA
11/20/23	multiple	RTI implemented a change to the above issue. Database process now involves staff entering PTFE filter ID's before and after sampling and compares the values in an attempt to catch more typos by staff.	Completeness	All or partial	NA
11/20/23	20900035 Hurst Road – North Pole; AK	In reviewing June's data, the site inquired about why a TS code was applied to their gravimetry data. We are currently reviewing the process to determine if the code is necessary, or should be excluded from future data. Since June there have been no instances where a TS code needed to be applied to this site's data.	Completeness	Gravimetry	Yes
11/21/23	multiple	Calendar for 2024 sampling, shipping and receiving was approved and posted to AMTIC site.	Completeness	All or partial	NA
11/28/23	multiple	Several sites emailed and indicated they had not received their 6a packages, but expected them to be delivered. RTI followed the published calendar and all shipments went out on time. It appears there was an earlier version of the calendar which had the packages arriving sooner. RTI does not have access to this previous version of the calendar.	Completeness	All or partial	NA
11/28/23	multiple	A manager at an environmental branch, pointed out the calendar for 1-in-6 day shipments would require two trips to sites for exchanging the modules between events; the sites had previously been able to make one trip to allow for setup and take down at the same time. With the approval from EPA, a new calendar was created and will be utilized for 2024 that was different than the initial 1-in-6 calendar.	Completeness	All or partial	NA

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
12/5/23	multiple	Printed calendar and request for updated contact information was included in the packages which were sent to all the sites.	Completeness	All or partial	NA
12/20/23	multiple	It was noticed by UCD that the volumes in datafiles provided for data processing were missing a digit on the volume. After some research it was determined it was a computer settings issue, which was quickly resolved. All the data was resent with the updated and correct number of decimal places for the months of June, July, August, September, and October. Data from November on should not be affected as the change has been implemented.	Completeness	All or partial	NA
12/20/23	180970078 Indianapolis – Washington Park; IN	Site indicated they are having issues with their URG sampler and are going to send it for repairs. They asked we pause URG samples at the site. The pause started with the 1/4/24 sampling event.	Completeness	All or partial	NA

3. Summary of Laboratory Operation Issues

This section of the report covers operational issues for each measurement process. 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.

3.1 RTI Sample Handling Lab

The RTI Sample Handling Lab responsibilities include purchasing filters from suppliers, performing quality control checks, shipping and receiving filters to and from sites, weighing filters as needed for FRM sites, coordinating with the main CSN contractor, UC Davis AQRC, and other activities as needed that do not fall into laboratory analysis. The lab also pre-fires quartz filters to remove possible contamination, then sends the test samples to UC Davis for verification.

During this reporting period (2023), both UC Davis and RTI observed a potential filter integrity issue involving flaking of the 25 mm quartz filters. It is not suspected the filters were degrading, however it was believed the edges of the filters were shedding and potentially covering parts of the ambient sampling collection portion of the filter. An inquiry was made to Cytiva in 2024, as they purchased the original supplier Pall Corporation, and a response will be provided in the 2024 report. There is currently no available data to suggest the excess flaking from the filters are causing an adverse effect, however further data evaluation in 2024 should lead to final conclusions.

The only significant data quality issues involved two instances of invalidation of gravimetric data due to holding times being exceeded for post-weighing of filters. It was discussed with EPA that holding times of non-FRM filters may be relaxed, but the decision was made to keep the holding times which follow the Quality Assurance Guidance Document 2.12 Monitoring $PM_{2.5}$ in Ambient Air Using Designated Reference or Class I Equivalent Methods (January 2016).

3.2 RTI Ion Analysis Laboratory

There were no operational issues reported during this period.

3.3 UC Davis X-ray Fluorescence Laboratory

3.3.1 Purchase of New Bruker S2-Puma EDXRF Instruments

During the previous reporting period, 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 the 2024 sampling year.

3.4 UC Davis Thermal Optical Analysis Laboratory

During this reporting period (2023) there were no operating issues with the existing Thermal Optical Analysis 5L analyzers. Two new devices were tested but failed to meet operational standards.

One new device under evaluation was the Analytik Jena multi EA 5000 analyzer for fast total carbon (TC) measurements. The instrument failed to achieve comparability with the existing Sunset 5L analyzers and was returned to the manufacturer after the trial period.

The other device is an autoloader manufactured by Sunset for the 5L analyzers used by AQRC. AQRC has a number of quality control measures as well as operational and performance requirements that must be met before the autoloader can be implemented for network analysis. After extensive testing, it was concluded that the autoloader had a major misalignment issue and was sent back to Sunset for inspection and repair.

3.5 UC Davis Optical Absorption Laboratory

3.5.1 Collimator Replacement

When the HIPS instrument was switched to the fiber-optical configuration in 2022, 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 values which were similar to the pre-fiber-optic setup.

The new focusing lens collimator was installed and put into service after testing on April 12, 2023. This was completed before analysis of the 2023 sampling year samples began, so all 2023 sample analyses were performed with the new collimator.

4. Quality Issues and Corrective Actions

4.1 Data Quality

4.1.1 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 4-1). 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 4-1 and Table 4-2 do not include placeholder records generated for samples that were scheduled but not collected. The completeness is comparable for PTFE and nylon filters which are both collected by the Met One SASS / Super SASS sampler; however, the number of invalid samples is higher for quartz filters, which are collected by the URG sampler.

In Table 4-1 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 4-1: Network sample completeness by filter type (1/1/23 – 12/31/23).

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	13,144	12,576	12,064	512	95.9	91.8
Nylon	13,144	12,572	12,064	508	96.0	91.8
Quartz	13,144	12,519	11,600	919	92.7	88.3

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 4-2), considering samples collected January 1, 2023 through December 31, 2023.

In table 4-2 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 4-3.

Table 4-2: Network sites > 75% sample completeness for at least one filter type (1/1/23 – 12/31/23).

AQS ID # / Location	Completeness			Null Codes		
	PTFE	Nylon	Quartz	PTFE	Nylon	Quartz
12-073-0012-5 Tallahassee Community College, FL	56.7%	56.7%	73.3%	AN (96%) AH (4%)	AN (96%) AH (4%)	AH (50%) AN (25%) Other (25%)
13-245-0091-5 Augusta, GA	100%	100%	70%	---	---	AH (94%) AG (5%)
28-049-0020-5 Jackson NCore, MS	98.3%	98.3%	40.5%	AO (100%)	AO (100%)	AH (81%) AN (14%) Other (5%)
30-093-0005-5 Butte Greeley School, MT	93.3%	93.3%	58.3%	AH (50%) AI (25%) AN (25%)	AH (50%) AI (25%) AN (25%)	AN (32%) AH (28%) Other (40%)
46-099-0009-5 SF-USD, SD	85.1%	85.1%	73.9%	AF (39%) AN (33%) Other (28%)	AF (39%) AN (33%) Other (28%)	AN (64%) AF (23%) Other (13%)
47-157-0075-6 Shelby Farms – Memphis, TN	93.4%	95.9%	42%	AH (63%) AV (25%) AN (12%)	AH (40%) AV (40%) AN (20%)	AH (96%) AV (3%) AG (1%)
48-113-0069-5 Hinton, TX	71.1%	71.1%	78.8%	AH (60%) AN (34%) Other (6%)	AH (60%) AN (34%) Other (6%)	AN (48%) AH (20%) Other (32%)

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 4-3). Additional null and qualifier codes may be applied to individual parameters for issues such as species-specific contamination. In the table below, number and type of null codes are applied at the filter level; codes are ordered by frequency of occurrence.

Table 4-3: Number and type of null codes applied to SASS and URG samples from 1/1/23 – 12/31/23.

Null Code	SASS PTFE	SASS Nylon	URG Quartz	Total	Null Code Description
AH	89	77	307	473	Sample Flow Rate or CV out of Limits
AN	127	130	192	449	Machine Malfunction
AV	63	63	69	195	Power Failure
AF	46	46	73	165	Scheduled but not Collected
BJ	39	39	27	105	Operator Error
AG	18	18	50	86	Sample Time out of Limits
AR	14	19	46	79	Lab Error
BA	3	3	50	56	Maintenance/Routine Repairs

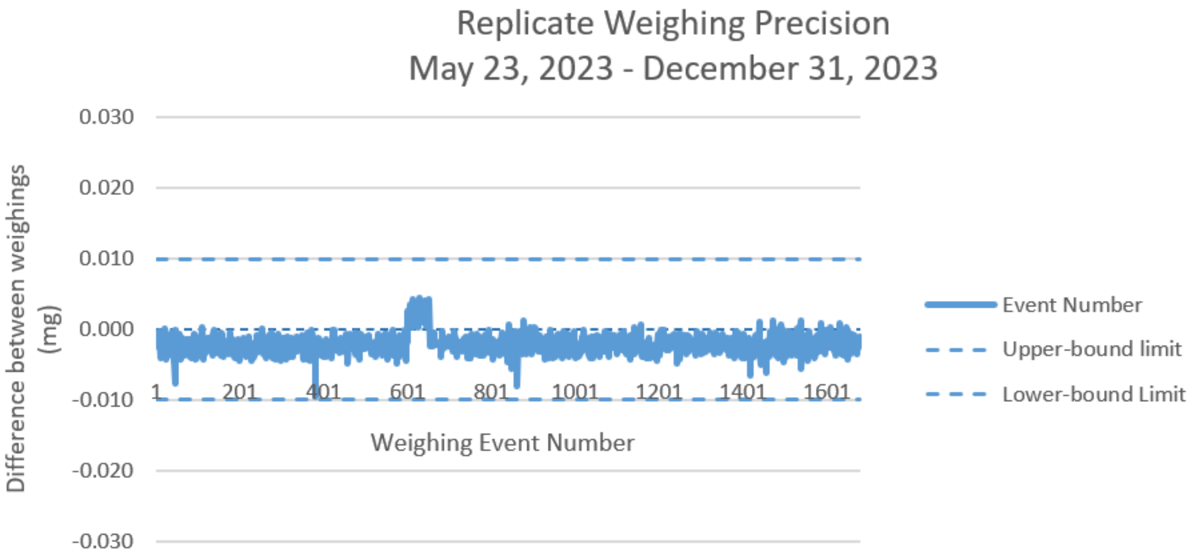
Null Code	SASS PTFE	SASS Nylon	URG Quartz	Total	Null Code Description
AO	14	13	17	44	Bad Weather
AB	12	12	13	37	Technician Unavailable
BI	11	9	11	31	Lost or damaged in transit
AI	9	11	10	30	Insufficient Data (cannot calculate)
BE	9	9	9	27	Building/Site Repair
AJ	4	5	13	22	Filter Damage
AS	13	9	0	22	Poor Quality Assurance Results
AL	6	6	7	19	Voided by Operator
BB	6	6	5	17	Unable to Reach Site
DA	6	9	1	16	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)
SV	5	5	5	15	Sample Volume Out of Limits
AQ	3	4	7	14	Collection Error
AC	5	5	0	10	Construction/Repairs in Area
AP	2	2	3	7	Vandalism
TS	2	2	2	6	Holding Time Or Transport Temperature Is Out Of Specs.
AW	3	2	0	5	Wildlife Damage
AD	1	1	1	3	Shelter Storm Damage
AK	1	1	1	3	Filter Leak
AE	1	1	0	2	Shelter Temperature Outside Limits
SA	0	0	2	2	Storm Approaching
AM	0	1	0	1	Miscellaneous Void

4.1.2 Comparability and Analytical Precision

4.1.2.1 Gravimetric Mass

Gravimetric filter weighing is performed in duplicate for all pre-sampled and post-sampled filters. There were no instances of duplicate weighings, which fell outside the permissible ± 10 µg criteria. Results are provided in Figure 4-1 below, which include filters analyzed as part of the CSN network and the additional filters which are analyzed under the CSN contract from Puerto Rico and the Virgin Islands.

Figure 4-1: Replicate weighing precision.

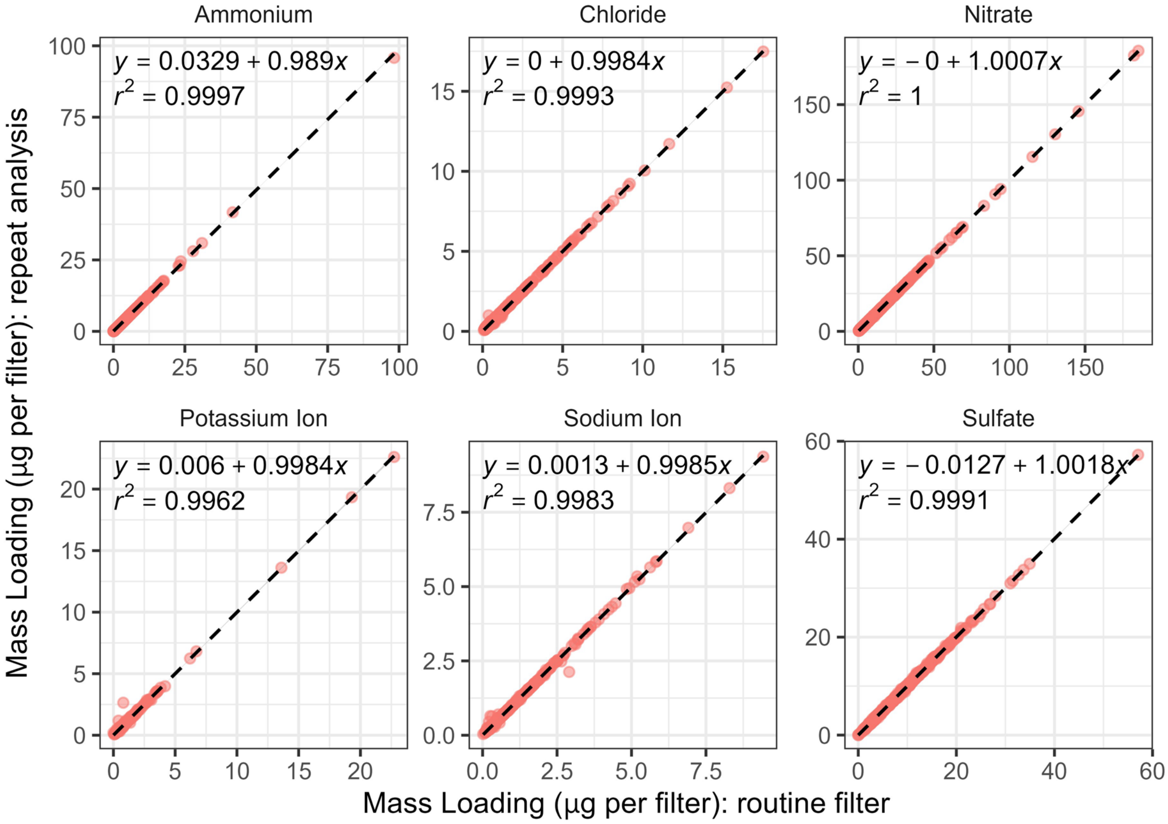


4.1.2.2 Ion Analysis

Analytical precision is evaluated by comparing data from repeat analyses, where two analyses are performed on the same sample extract using the same instrument and identified as duplicates in the ion analysis batch queue. These samples may also be identified as replicate samples in tables and charts below to demonstrate precision. The IC laboratory also conducts a reanalysis of samples on approximately 10% of the total batch of samples to check the analytical precision across instruments as an additional check for good laboratory practices. The IC laboratory does not report these results but flags them in the database as “RS” so that UC Davis staff are aware that a reanalysis was conducted. The IC laboratory does report the duplicate or replicate sample results to UC Davis for precision calculations. 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 7.5) 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 4-2). Eight different IC instruments were used for routine and repeat analyses where both replicate and duplicate analyses are performed using the same extract.

Figure 4-2: Ion repeat analysis (replicates and/or duplicates) results; data from valid samples collected 1/1/23 – 12/31/23.



4.1.2.3 Elemental Analysis

Replicate EDXRF analyses of routine CSN samples were started on December 20, 2020. The data for 2023 is plotted in figure 4-3 below, where the number of pairs above 2x $MDL_{analytical}$ and the calculated RMS for each CSN element in the legacy dataset are used to evaluate the 2023 replicate analysis.

Step 1: Replicate Precision Estimates Using Legacy Replicate Measurements

Each week, the XRF instruments take replicate measurements. 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 root mean square (RMS) models were calculated for each element. The dataset to calculate precision needs to be large enough to be statistically significant. 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.

* Due to time and resource constraints, the AQMT process for replicates is to run the filters loaded into the XRF instrument on Friday for a second time. EDXRF replicate quantities are kept small because it takes approximately 65 minutes per sample. The XRF lab rotates between measuring filters for CSN and IMPROVE, as such, filters from either network could be in the analyzers on Fridays. Therefore, 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 4-4: Pairs above 2x MDL$_{\text{analytical}}$ and calculated RMS for each legacy CSN element.

Parameter	No. of Pairs	RMS		Parameter	No. of Pairs	RMS
Ag	264	15.5		**Mn**	1106	18.6
Al	1240	9.4		**Na**	61	22.6
As**	2	37.6		**Ni**	64	17.3
Ba	907	16.4		**P**	23	26.3
Br*	NA	NA		**Pb**	1069	17.1
Ca	797	7.1		**Rb**	46	20.4
Cd	168	15.3		**S**	1022	4.8
Ce	655	16.0		**Sb**	321	14.9
Cl*	NA	NA		**Se**	20	17.3
Co	37	21.0		**Si**	1034	8.9
Cr	1238	16.2		**Sn**	500	14.9
Cs	438	15.8		**Sr**	411	18.8
Cu	848	9.5		**Ti**	454	18.7
Fe	1109	5.0		**V****	4	24.2
In	361	15.7		**Zn**	398	8.6
K	1225	6.3		**Zr**	121	13.5
Mg	26	20.3				

*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 4-3.

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, then Z-scores can be 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 4-3 plots the results as standard deviation from the uncertainty, not from the mean. This was chosen because 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)

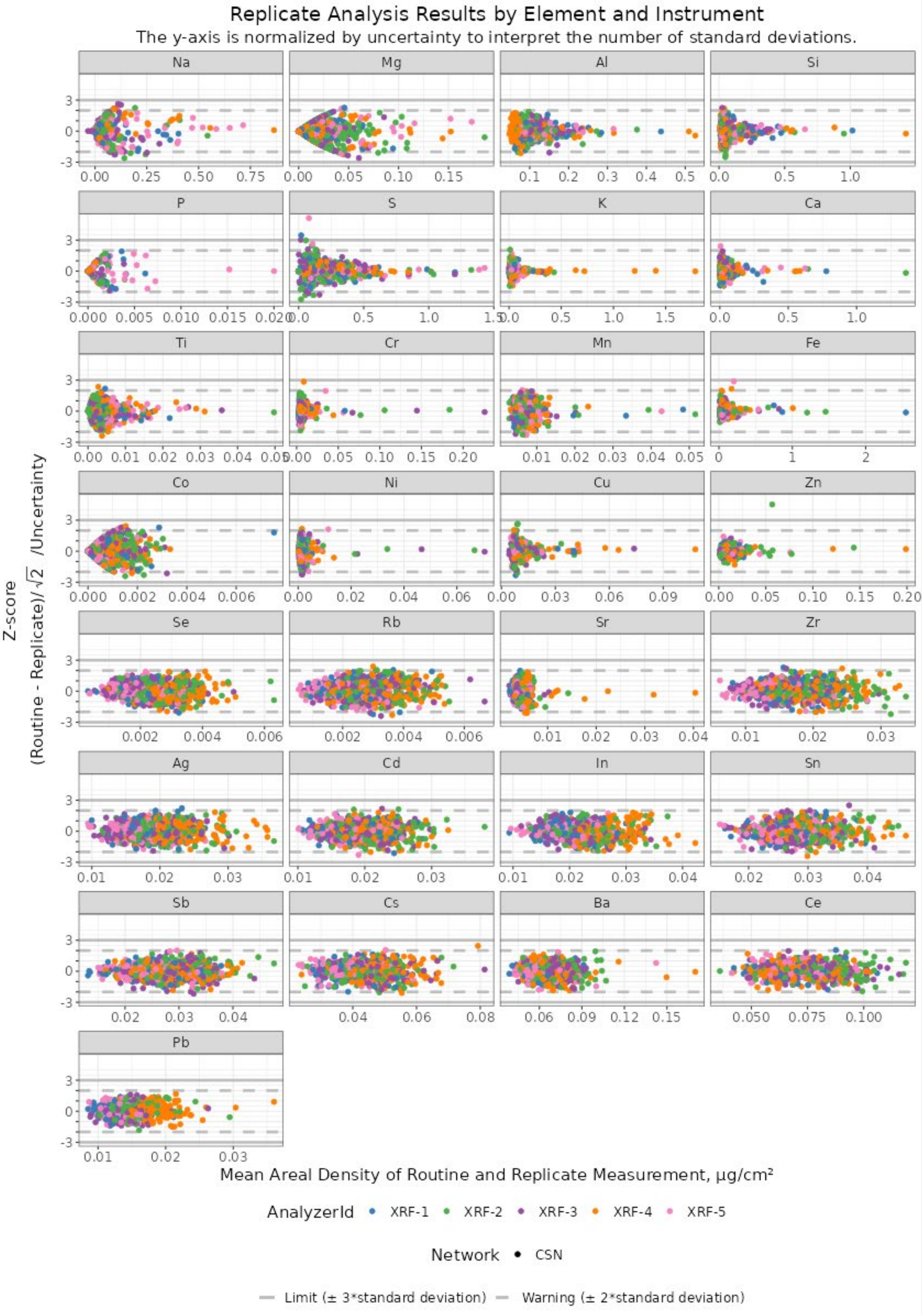
Routine – Replicate was chosen to call attention to any potential bias in the measurements.

Using the statistical data for sample years 2021-2022, we set limits for each measured element. The dataset for sample year 2023 is as follows:

- 639 filters had replicate measurements for sample year 2023, out of 12,064 valid filters (Table 3.1-1), or 5.16 % 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 18,531 (639 x 29 elements) 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 ((18,531-4)/18,531).
  - Vanadium (V) and Arsenic (As) are not plotted because they did not meet the minimum 10 required pairs to calculate precision, described above.

The results are plotted in Figure 4-3. 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.

Figure 4-3: Replicate analysis results by element and instrument for sample year 2023.



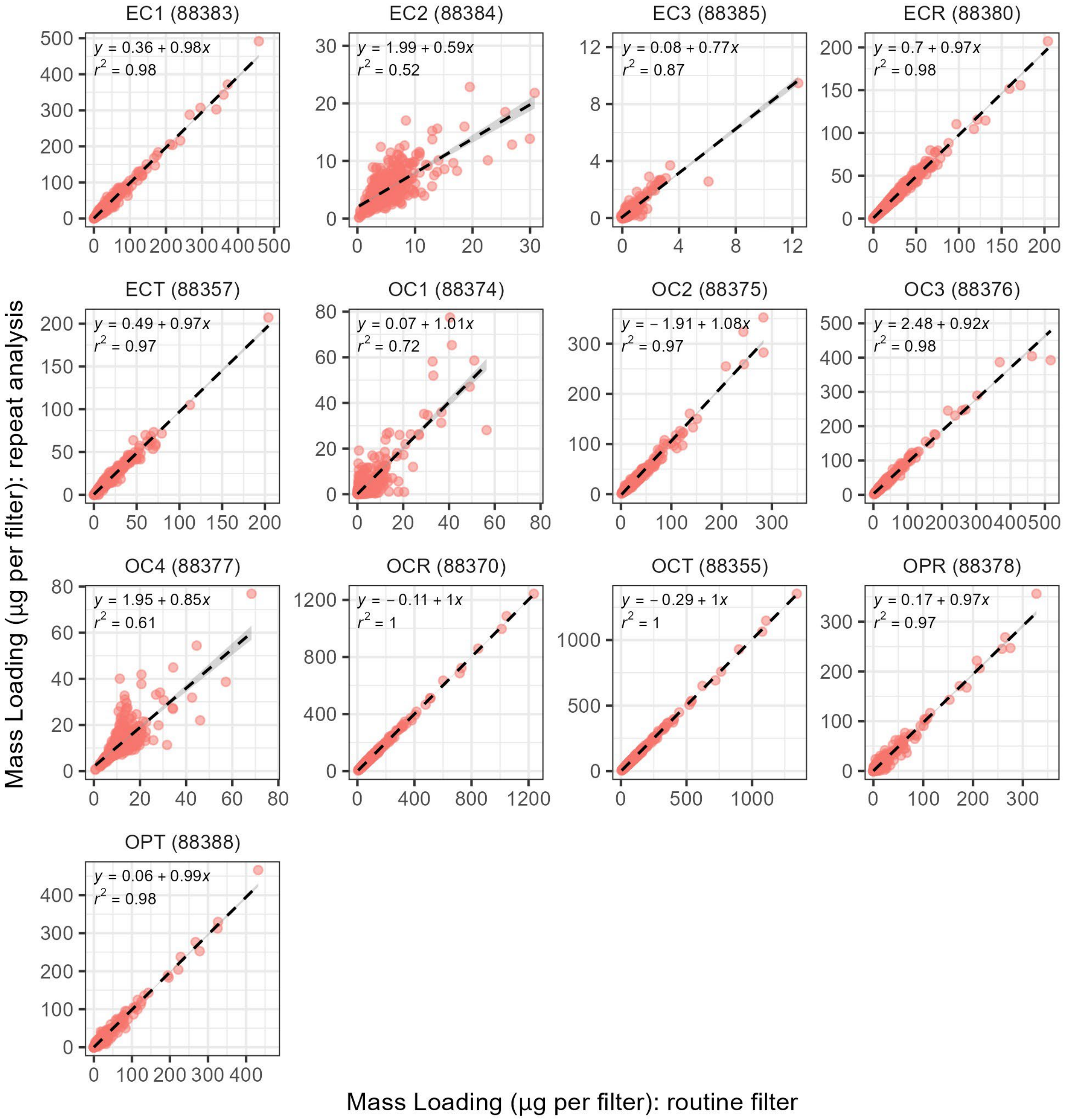
In addition to replicates on network filters, EDXRF precision was evaluated by analyzing the same set of samples, which are UCD-made multi-element reference materials (see Table 5-15). These are analyzed on a monthly basis to assess both the short- and long-term stability of the EDXRF measurements as described in *UCD CSN SOP #302* (see section 5.4.2.4).

4.1.2.4 Carbon Analysis

Comparison of carbon mass loadings from repeat analyses (replicates and/or duplicates) on valid quartz filters analyzed by TOA generally show agreement (Figure 4-4), 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 4-4 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 4-4: Carbon repeat analysis (replicates and/or duplicates) results; data from samples collected during January 1, 2023 through December 31, 2023.



4.1.3 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 4.1.3.7). 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 4.1.3.8).

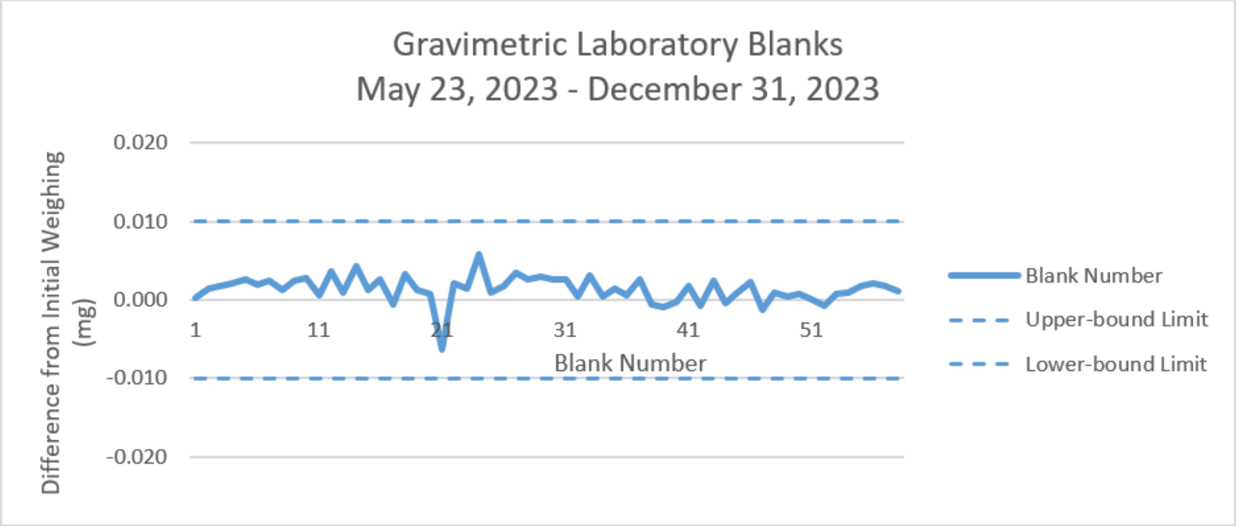
Beginning in May 2017, field blanks are collected once per month for each filter type per site; prior to May 2017 field blanks were collected less frequently.

There is some variability in field blank mass loadings by species. As part of the validation process (see Section 7), field blank outliers are investigated but are only invalidated if there is cause to do so. Artifact correction (Section 4.1.3.7) and MDL (Section 4.1.3.8) calculation methods are robust against influence from occasional outliers.

4.1.3.1 Gravimetric Mass Lab Blanks (RTI)

Gravimetry lab blanks are used to assess chamber suitability over the duration between when the filters are pre-weighed and post-weighed (post collection). During a batch of pre-weighing, a select number of additional filters are selected and pre-weighed with the set to be sampled. These lab blank filters remain in the gravimetry chamber and are post weighed at the same time as the post-weighing of filter returned from the collection at the field sites. Passing criteria for gravimetric lab blanks is ±15µg difference between pre and post – weighing. Results are provided in Figure 4-5.

Figure 4-5: Gravimetric laboratory blanks.

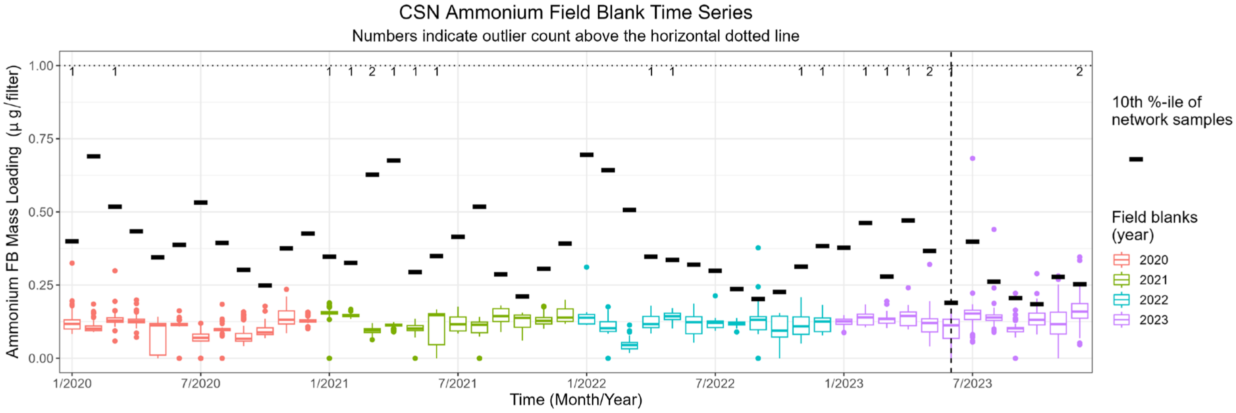


4.1.3.2 Ion Species Field Blanks

Field blank mass loadings for the ion species (Figure 4-6 through 4-11) are examined in an effort to identify changes that may be occurring in the ions measurement lab.

In the following figures 4-6 to 4-11, 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. The vertical dashed line indicates when the sample-handling transitioned from WSP to RTI.

Figure 4-6: Time series of ammonium measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.



In the below figure, we see chloride field blanks have been elevated since RTI took over as sample-handling lab. Cl is not increasing. The cause for this increase is unknown, but chloride field blank loadings have decreased in the first half of 2024 (not shown).

Figure 4-7: Time series of chloride measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

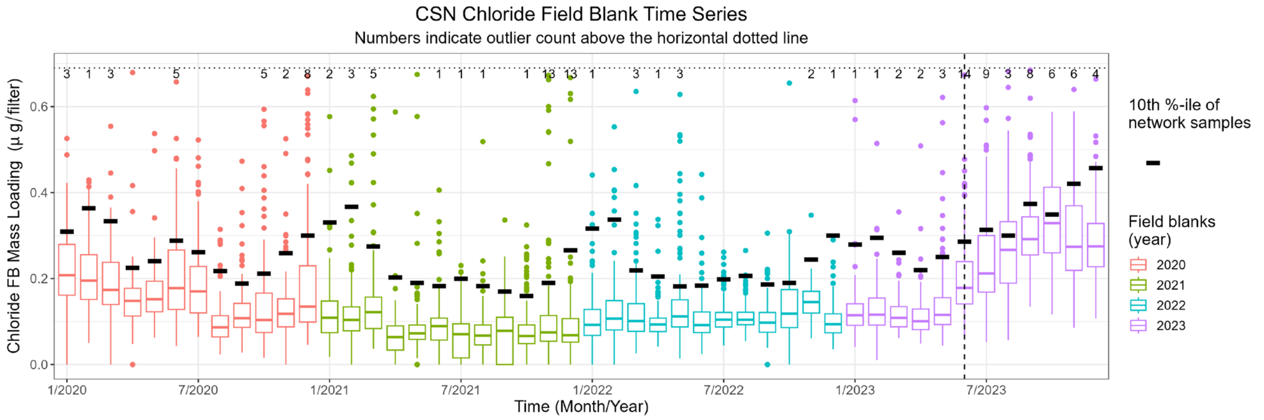


Figure 4-8: Time series of nitrate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

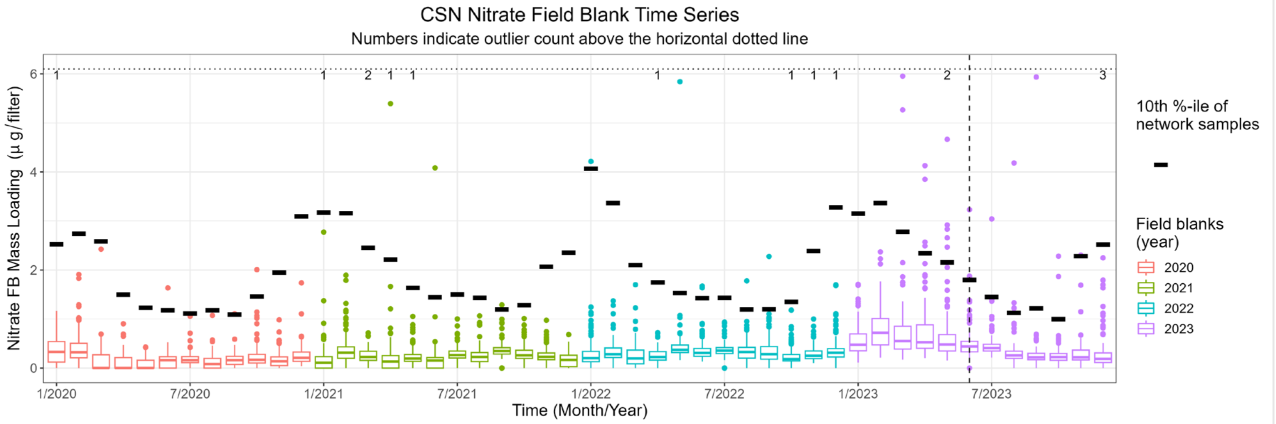


Figure 4-9: Time series of potassium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

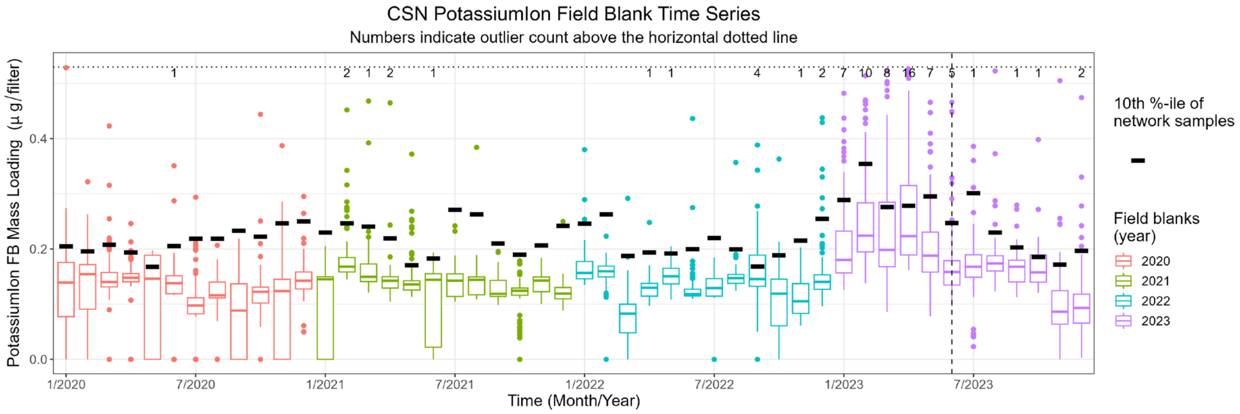


Figure 4-10: Time series of sodium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

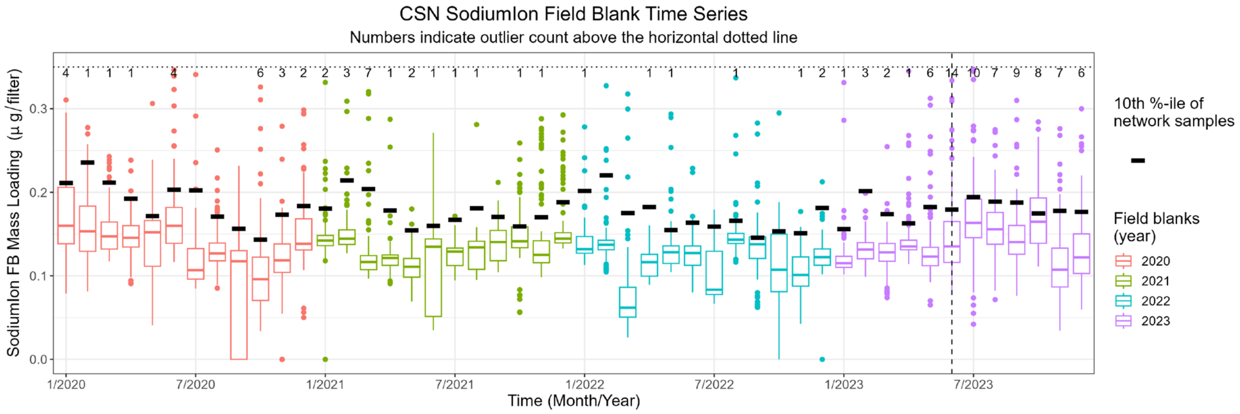
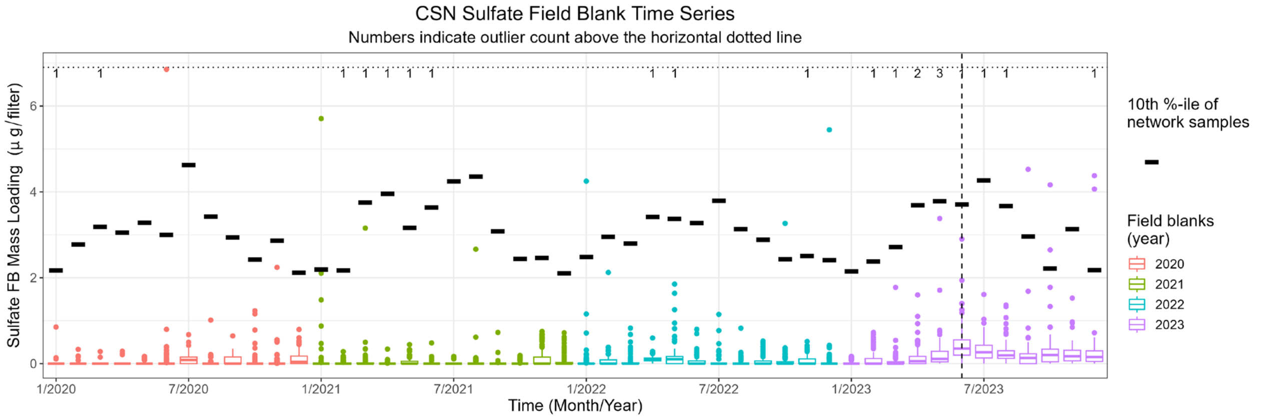


Figure 4-11: Time series of sulfate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.



4.1.3.3 Carbon Species Field Blanks

Field blank mass loadings for organic carbon (Figure 4-12) and elemental carbon (Figure 4-13) are examined in an effort to identify possible contamination that may be occurring in the field or in the lab.

The plots for OCTR and ECTR 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 + 1.5×IQR boundary shown by the horizontal dotted line. The vertical dotted line indicates the sample-handling lab transition from WSP to RTI. All of the data plotted (starting 2020) is from UCD.

Figure 4-12: Time series of organic carbon by reflectance (OCTR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

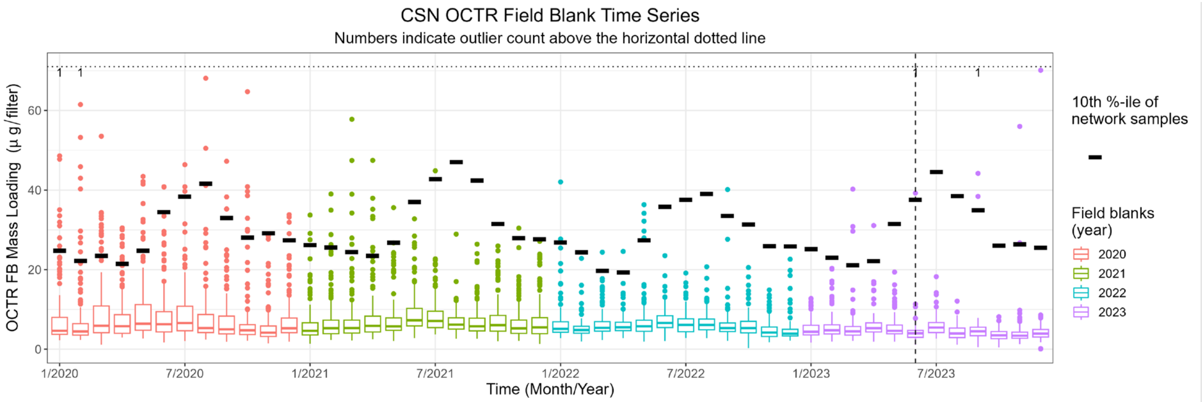
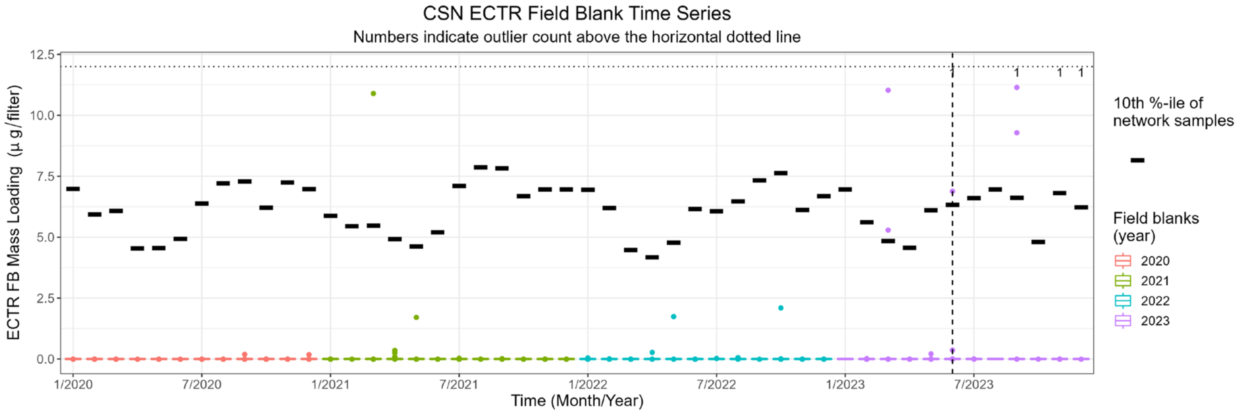


Figure 4-13: Time series of elemental carbon by reflectance (ECTR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.



4.1.3.4 *Elemental Species Field Blanks*

Time series of monthly median mass loading of field blanks are shown in Figures 4-14 through 4-23 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 4-5).

- Silicon (Si; Figure 4-17) 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 4-18) monthly median field blank mass loadings are very lightly loaded and starting in September 2021, very little sulfur is detected.
- Potassium (K; Figure 4-19) monthly median field blank mass loadings are showing more variability since August 2020.
- 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 4-20), titanium (Ti; Figure 4-21), iron (Fe; Figure 4-22), or zinc (Zn; Figure 4-23).

For the following figures: 4-14 to 4-23; 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. The vertical dotted line indicates the sample-handling lab transition from WSP to RTI

Figure 4-14 shows Cr. Chromium is showing an increase due to suspected stainless steel contamination.

Figure 4-14: Time series of chromium (Cr) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

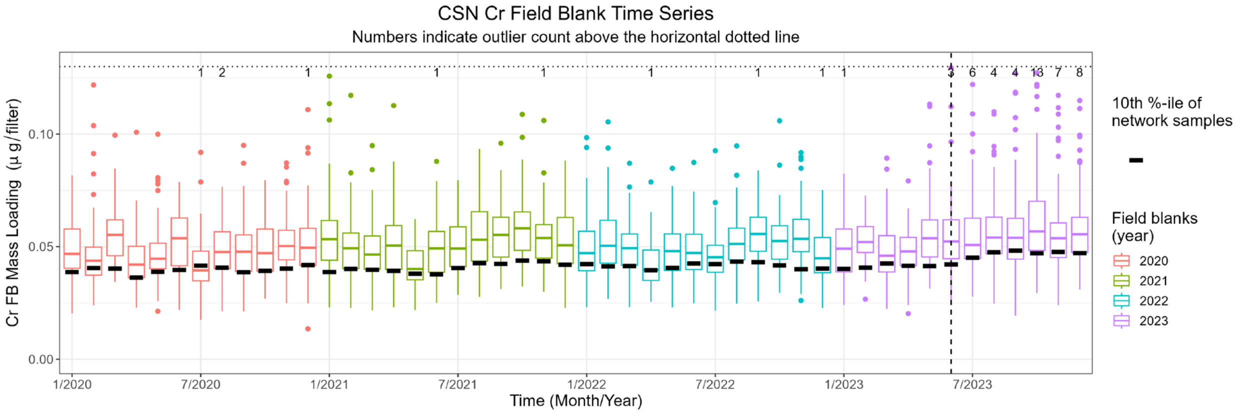


Figure 4-15 shows Cl. Chlorine is not showing the same elevation that chloride is on Nylon filters by IC.

Figure 4-15: Time series of chlorine (Cl) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

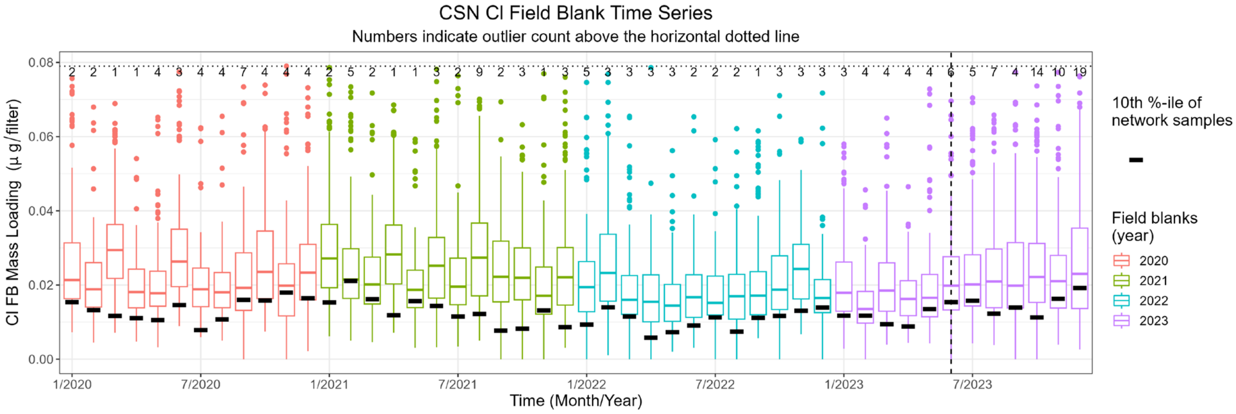


Figure 4-16 below plots Na field blanks. There is a change in 2021 when the XRF CaF target was removed from operation for time.

Figure 4-16: Time series of sodium (Na) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

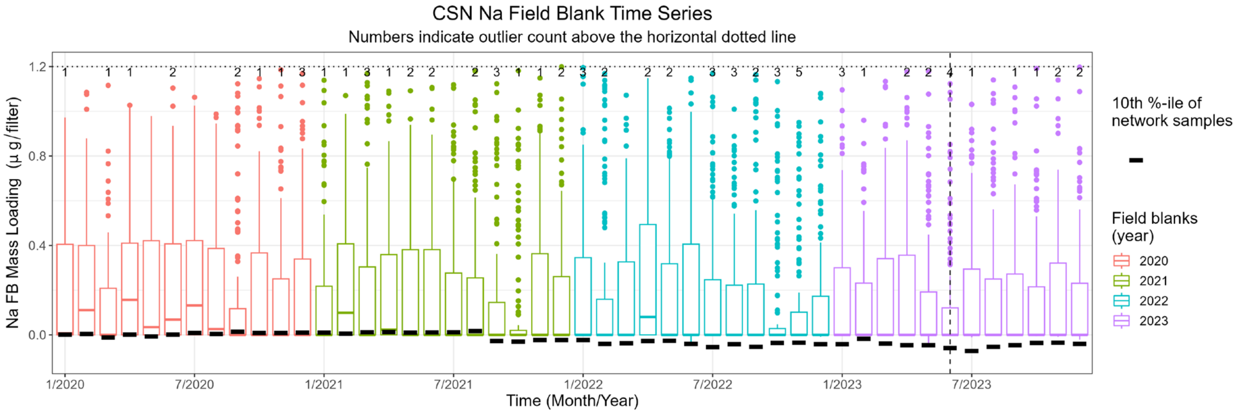


Figure 4-17: Time series of silicon (Si) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

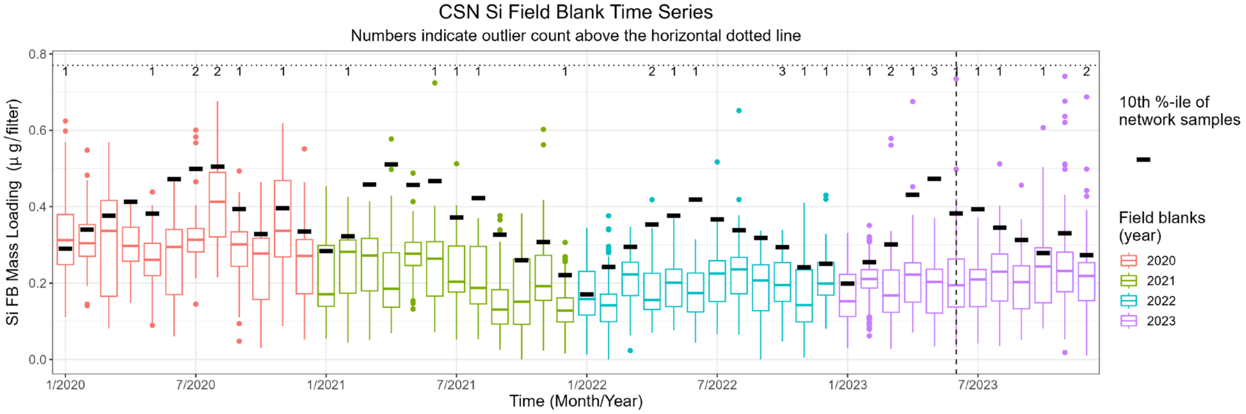


Figure 4-18: Time series of sulfur (S) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

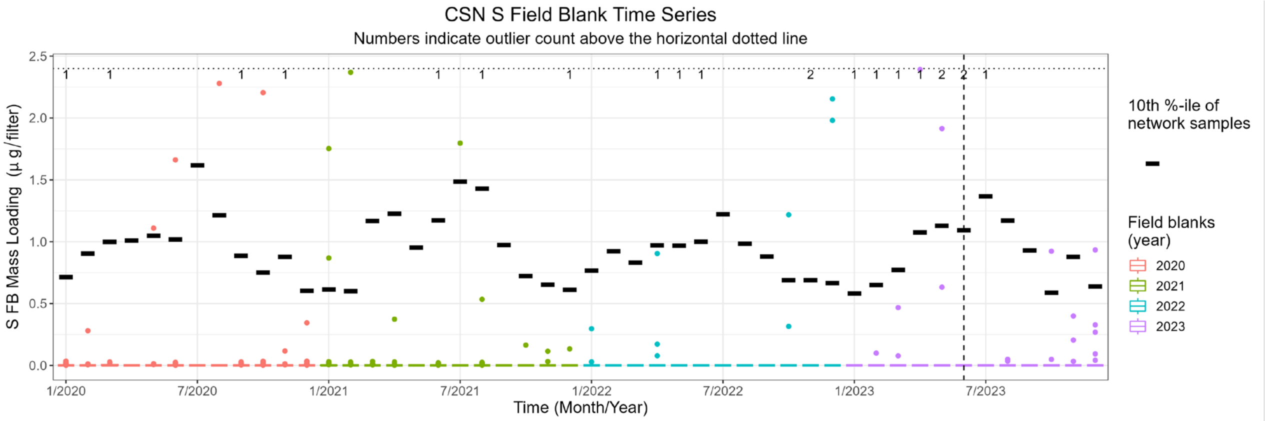


Figure 4-19: Time series of potassium (K) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

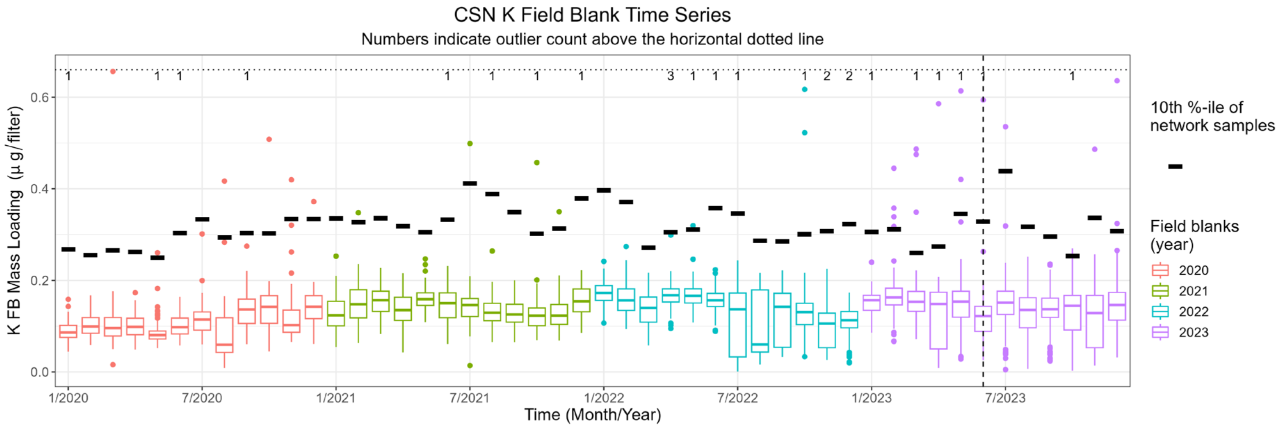


Figure 4-20: Time series of calcium (Ca) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

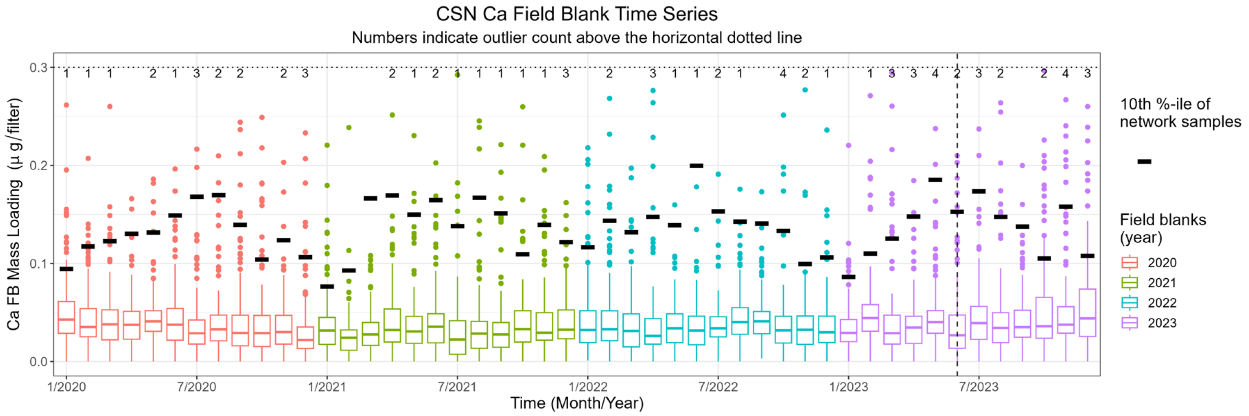


Figure 4-21: Time series of titanium (Ti) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

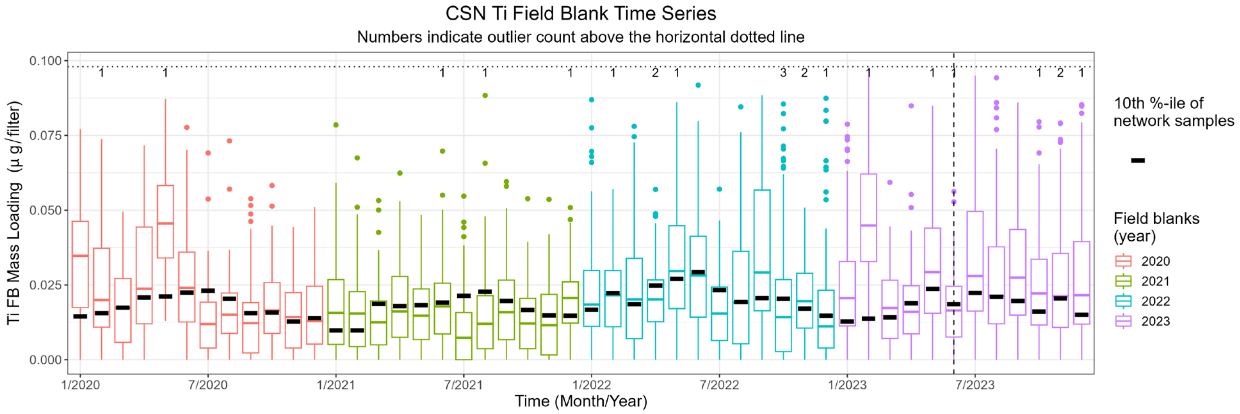


Figure 4-22: Time series of iron (Fe) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.

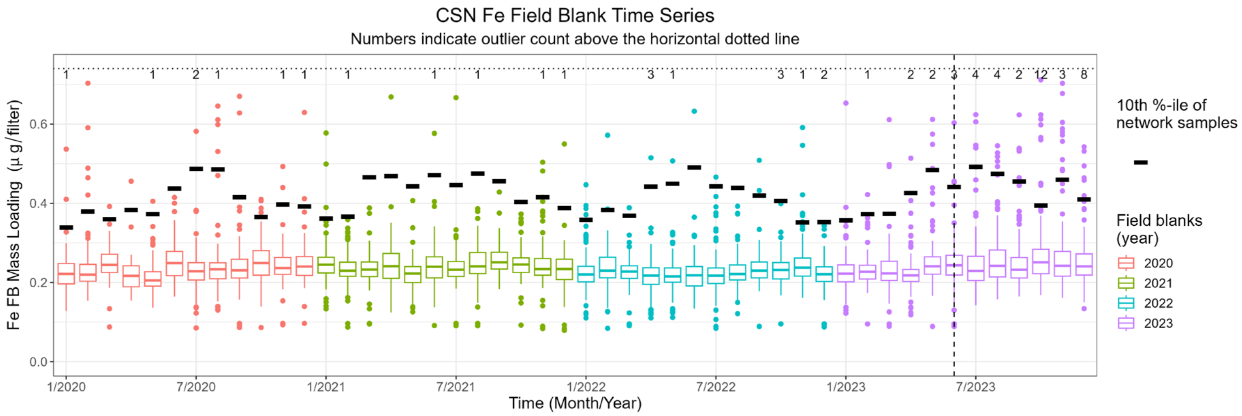
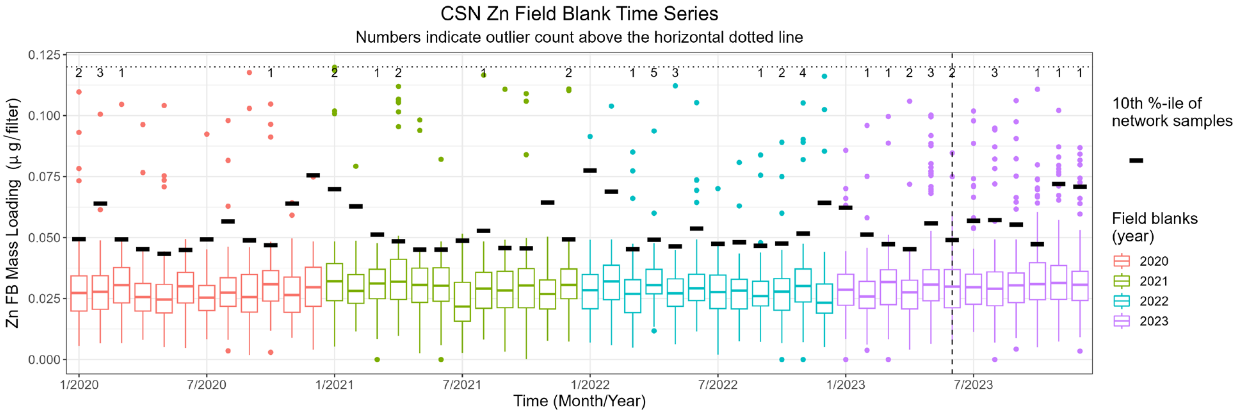


Figure 4-23: Time series of zinc (Zn) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2020 through December 31, 2023.



4.1.3.5 Optical Absorption Field Blanks

Field blank mass loadings for tau_633 (Figure 4-24) are examined 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 get units of Mm^{-1} and 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. More details are contained in the document *UCD CSN SOP #277: Optical Absorption Analysis*.

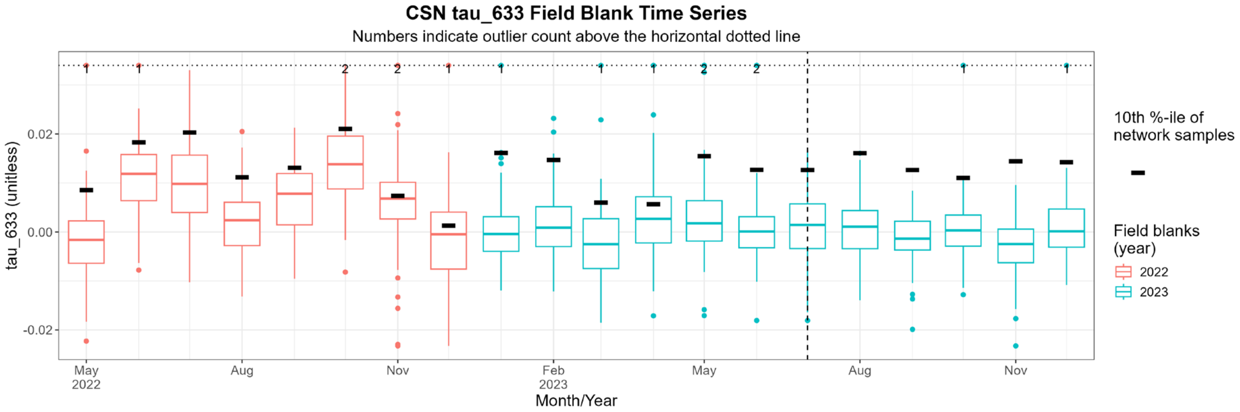
$$\tau_{abs} = \ln\left(\frac{1-r}{t}\right)$$

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

CSN data was collected for several years but delivery to AQS started May 2022. An effort to validate and deliver past data is underway. The start date for data will be August 2020.

In Figure 4-24, 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 4-24: Time series of tau_633 measured on PTFE filter field blanks (FB), for valid field blanks collected Aug 1, 2020 through December 31, 2023.



4.1.3.6 Laboratory Blanks for UCD Analysis

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. RTI also does this as the current SHL. A total of 65 PTFE laboratory blanks, 65 Nylon laboratory blanks, and 60 Quartz laboratory blanks were analyzed during the current reporting period. Summaries of the analyses are in section 4.3.1 (quartz), section 4.3.2 (nylon), and section 4.3.3 (PTFE).

4.1.3.7 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.

4.1.3.8 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 except gravimetry, calculated as 95th percentile minus median of field blanks, using 50 field blanks collected in or closest to the sampling month for each respective filter type. Gravimetric Mass MDL is calculated as 95th percentile of field blanks, using 50 field blanks collected in or closest to the sampling month. Since less gravimetry is performed on less than 50 field blanks per month, each MDL is calculated using field blanks collected in closest months to sampling month. 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; 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, 2023 through December 31, 2023) are compared to those calculated using the same method from the previous reporting period (samples collected January 1, 2022 through December 31, 2022) (Table 4-5). 2022 MDLs are updated from the 2022 QA Report following the identification and update where Analytical MDLs in XRF and Carbon were using incorrect units.

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 (2020) and the current reporting period (2023). Typical MDLs are from the CSN laboratory analysis contract's statement of work.

Table 4-5: Average MDLs and percentage of reported data above the MDLs for all species.

Species	EPA Attachment D	2022 (previous reporting period)		2023 (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	8.2	13	6.2
Al	25	24	51	30	45
As	2.7	1.2	0.1	1.2	0.0
Ba	59	35	8.7	33	11
Br	2.3	1.2	15	1.2	16
Ca	7.6	12	88	13	86
Cd	23	14	6.0	14	4.9
Ce	88	41	5.5	42	4.8
Cl	11	3.1	49	5.5	41
Co	2.0	1.7	4.0	1.5	4.6
Cr	2.6	2.0	28	2.5	26
Cs	46	28	7.4	27	5.4
Cu	2.5	5.5	18	4.9	15
Fe	3.3	12	95	19	90
In	33	15	9.1	15	5.8
K	11	6.1	99	6.6	97
Mg	19	48	17	48	15

Species	EPA Attachment D	2022 (previous reporting period)		2023 (current reporting period)	
	Typical MDL, ng/m^3	Average MDL, ng/m^3	% Above MDL	Average MDL, ng/m^3	% Above MDL
Mn	2.9	2.9	28	2.9	30
Na	55	96	24	91	24
Ni	1.9	1.3	20	1.4	24
P	16	2.7	7.9	3.7	5.3
Pb	6.4	7.0	21	7.4	16
Rb	2.6	3.2	7.9	3.3	6.7
S	9.9	3.7	100	3.7	100
Sb	52	18	6.2	18	5.3
Se	2.6	2.7	8.0	2.6	7.0
Si	19	12	88	14	86
Sn	36	17	7.7	17	6.2
Sr	3.5	2.9	14	2.9	11
Ti	5.3	3.8	46	4.0	40
V	3.9	1.2	2.6	1.2	3.0
Zn	3.5	7.3	57	7.3	59
Zr	23	14	7.1	14	7.4
Ammonium	25	13	93	13	91
Chloride	27	16	83	35	65
Nitrate	22	44	99	82	97
Potassium Ion	24	13	76	26	62
Sodium Ion	30	13	67	22	53
Sulfate	35	31	100	48	100
Elemental Carbon (EC1)	95	29	100	20	100
Elemental Carbon (EC2)	63	15	100	10	100
Elemental Carbon (EC3)	63	12	39	6.0	64
Elemental Carbon (ECR)	63	3.8	100	4.1	100
Elemental Carbon (ECT)	63	17	100	3.5	100
Organic Carbon (OC1)	63	13	62	22	54
Organic Carbon (OC2)	63	24	100	22	100
Organic Carbon (OC3)	95	117	96	70	98
Organic Carbon (OC4)	95	59	99	36	99
Organic Carbon (OCR)	63	226	99	142	100
Organic Carbon (OCT)	63	228	99	142	100
Organic Pyrolyzed (OPR)	95	43	90	29	93
Organic Pyrolyzed (OPT)	63	42	94	29	97
Soil	NA	78	96	104	93
Reconstructed Mass	NA	402	100	466	100
fAbs	NA	2.1	85	1.8	87
PM2.5 (88502)	7500	---	---	3710	87

The differences from 2022 to 2023 are not unexpected from previous year changes. There are often changes due to filter lots, handling changes, improved methods, or atmospheric changes. For the carbon elements, most have been decreasing since peaks in 2019/2020. OC1 may be increasing because it is the fraction where most OC and VOCs are burned. For the ions, it could be related to the Nylon filter lots or handling. We will need to monitor 2024. In XRF, Cr, Fe, and Soil are possibly linked to the ongoing stainless steel contamination. Wildfire smoke on the East Coast may be contributing to Al, Cl, and P. We continue to monitor MDLs for changes, sources, and improvements to be made.

4.2 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 2023.

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.

4.2.1 Sample Shipping and Handling

With the commencement of work as part of the contract transition, several issues were identified over the course of the contract year for shipping and handling. These issues included:

1. Several filters went missing during the WSP to RTI transition.
    - 3 PTFE filters from the field that receive gravimetric analysis (have mass data, but no XRF data). The three filters measured for gravimetric mass were not delivered to UC Davis for XRF or HIPS analysis, therefore results for these filters are missing. One group of filters (6 total) from Chicago Com Ed, IL, which originated from WSP were not received by RTI, and therefore have no analytical data reported.
    - From Chicago Com Ed, IL, 2 quartz, 2 PTFE, and 2 nylon were not received from the last 2 dates WSP prepared.
    - The lab blanks in month 103 for Nylon and PTFE were also not received by UC Davis (5 each).
2. Several sites noted the modules received for sampling of the PTFE and Nylon filters had loose or missing screws. In instances where the site was able to tighten the modules adequately, they were instructed to do so, and a qualifier flag was applied to the data. In instances where the screws could not be applied or tightened, the filter was flagged as an invalid sampling event.
    - This was the result of some staff not being adequately trained at the startup of the project. Each of the issues were most prevalent in the June, July, August timeframe. Additional training was performed for staff with performance issues, additional checks were added to the cooler checklist, and meetings were scheduled to re-review necessary processes and procedures. The frequency of

negative observations for these issues dramatically dropped over the course of the year and are expected to remain low with these additional steps taken.

3. For a brief period, quartz filters were loaded in caps at some sites instead of in the filter holding compartment. In each instance of this occurrence, the filters were unsampled and invalidated with an “AR” code.
    - This was the result of some staff not being adequately trained at the startup of the project. Each of the issues were most prevalent in the June, July, August timeframe. Additional training was performed for staff with performance issues, additional checks were added to the cooler checklist, and meetings were scheduled to re-review necessary processes and procedures. The frequency of negative observations for these issues dramatically dropped over the course of the year and are expected to remain low with these additional steps taken.
4. Periodically throughout the year, some filters were mistakenly not loaded into their holders prior to being sent to sites for sampling. All instances of missing filters were flagged as invalid sampling events with an “AR” code.
    - This was the result of some staff not being adequately trained at the startup of the project. Each of the issues were most prevalent in the June, July, August timeframe. Additional training was performed for staff with performance issues, additional checks were added to the cooler checklist, and meetings were scheduled to re-review necessary processes and procedures. The frequency of negative observations for these issues dramatically dropped over the course of the year and are expected to remain low with these additional steps taken.
    - This is still periodically seen, though infrequently. It is estimated this is observed approximately one to two times a month. Staff who make the error are made aware of the mistakes made and are instructed to pay more attention to detail for these critical processes. These issues are continually monitored with no more actionable items planned at this time. Should frequency of the issues increase, additional steps will be taken to ensure resolution.
5. In a few instances, filters were reloaded after collecting ambient sample, causing a filter to be double sampled with an accompanying unsampled filter. All instances of double sampling and non-sampling filters were flagged as invalid sampling events with an “AR” code.
    - This is still periodically seen, though infrequently. It is estimated this is observed approximately one to two times a month. Staff who make the error are made aware of the mistakes made and are instructed to pay more attention to detail for these critical processes. These issues are continually monitored with no more actionable items planned at this time. Should frequency of the issues increase, additional steps will be taken to ensure resolution.
6. During the 9/6 sampling events, shipping labels for five sites were swapped, causing some sites to receive coolers not intended for their sites. In each instance the site collected samples on unintended modules. In each case the information received back was edited to match the correct sampling location with filters and collection data. A

validity flag was applied to each of these data sets, and none of the events were invalidated due to this mistake.

   - This was an isolated incident where the stack of shipping labels was out of sequence in five instances. Additional steps have been taken to ensure shipping labels are appropriately assigned to the correct sites, and staff are expected to verify shipping labels are scheduled to the correct site prior to completing the assembly process.

7. There was a repeated instance for three events where the Hurst Road (North Pole) location did not have a denuder installed in their Nylon module and thus had an invalid sampling event.
   - This was a discreet issue, started at the transition, where new staff were not checking for the denuder in the module, and data review staff were not reviewing the data in a timely enough manner to issue the necessary correction. Both these issues have been resolved through additional training and additional staff routine reviews.
8. UC Davis noted nine PTFE filter swaps in May, fourteen in June, five in July, twenty in August, thirteen in September, sixteen in October, eight in November, and four in December. Each of the swaps was caused by a transcription error by the SHAL lab, exchange of filters between events, or a swap of filters post-gravimetric analysis. All the issues were resolved prior to additional laboratory analysis at UC Davis.
   - This was caused mainly by new staff and an unfamiliarity with the overall process. The issue was resolved through implementation of a dual check of filter ID in the database used to process shipment and receipt of samples. It is a requirement that the filter ID is entered before and after sampling and that if the ID's do not match management must intervene to determine the correct course of action.
   - The PTFE filter ID is recorded prior to collection in the field. This ID is carried through the remaining processes of the filter up to and through the archiving procedure. In these instances, the expected ID did not match the physical ID on the filter; in each case this error was caught prior to XRF analysis. All filter misidentifications were resolved prior to analysis (or reporting) and the correct filter was assigned to the correct sampling event.
9. There were occasional instances where Null codes were entered without associated comment to data entries.
   - These were typically caused by data reviewers not recording a necessary comment, or data entry missing the comment during data entry. It is infrequent and can be quickly resolved through a simple communication between UC Davis and RTI. RTI is also implementing steps, during data generation, to flag instances where a null code is assigned, and a comment field is empty to resolve these discrepancies more quickly.
10. There were occasional instances where Null codes which should have been applied were not recorded, this was corrected during data review and validation.

    - These were typically caused by data reviewers not recording a necessary comment, or data entry missing the comment during data entry. It is infrequent and can be quickly resolved through a simple communication between UC Davis and RTI. RTI is also implementing steps, during data generation, to flag instances where a null code is assigned, and a comment field is empty to resolve these discrepancies more quickly.

11. There were occasional instances of two or more filters mistakenly being loaded into a single cassette for sampling.
    - This is still periodically seen, though infrequently. It is estimated this is observed approximately one to two times a month. Staff who make the error are made aware of the mistakes made and are instructed to pay more attention to detail for these critical processes. These issues are continually monitored with no more actionable items planned at this time. Should frequency of the issues increase, additional steps will be taken to ensure resolution.
12. In the data file provided to UC Davis, a wrong batch ID was assigned to a group of PTFE filters.
    - This was being caused when the gravimetry ID used for a batch of filters was mistakenly getting carried over to the XRF batch; this was observed in the July PTFE batch. Additional review checks are implemented and this issue appears completely resolved.
13. Several typos on data entry, prior to implementation of database system during the transition period.
    - This was simply typographical errors at contract startup, isolated to the samples collected in May. With the implementation of the database system in June, and a double entry requirement, the frequency of typos has significantly diminished.
14. After a review of data, it was observed that sample volumes were being mistakenly truncated.
    - This was caused by a setting in the operating system which was not pulling the complete information from entry. Affected data included PTFE and Nylon information for the months of June, July, August, September, and October. This setting was changed after it was discovered, and the issue appears completely resolved. All affected data was resubmitted with the correct number of decimal places for the months listed.
15. The XRF lab at UC Davis noted several instances of receiving flipped PTFE filters which were analyzed facing the wrong direction by XRF. There have been 4-5 instances of this issue noted, which has caused Chloride and Bromine data to be invalidated due to the volatility of the metals and the need for re-analysis.
    - This is still periodically seen, though infrequently. It is estimated this is observed approximately one to two times a month. Staff who make the error are made aware of the mistakes made and are instructed to pay more attention to detail for these critical processes. These issues are continually monitored with no more

actionable items planned at this time. Should frequency of the issues increase, additional steps will be taken to ensure resolution.

16. Based on XRF data showing an elevation of stainless-steel based metals, a suspected over-tightening of modules may be occurring during the assembly process. This pattern has increased both in frequency and intensity over the months starting June to December. It is suspected the over-tightening of module screws may be causing shedding onto the PTFE filter during sample collection.
    - No clear resolution has been determined for this issue, but several experiments are in progress. Beginning in March 2024, a switch to torque wrenches to tighten the modules consistently was implemented. As of sampling date August 20, 2024, the screws on a subset of SASS modules are being replaced with specialized plastic (PEEK) screws. Another subset of modules is undergoing a special cleaning process in a sonicating bath beginning with sampling date September 15, 2024. The impact of these changes will become clear in late 2024 or early 2025.

4.2.2 Gravimetric Analysis

The gravimetry lab did not experience any quality issues affecting CSN data during the 2023 reporting period.

There were two instances from the Hurst Road (North Pole) site where filters were post-weighed outside their permissible window due to the temperature and timeliness of return of the filters to the lab. In both these instances the data was flagged with a TS code.

There was also an instance of a gravimetry filter from the Southerly WTP site which was mistakenly not post weighed prior to being delivered to UC Davis for the 9/27/23 sampling event. Additional steps have been taken at RTI to prevent this occurrence from happening again in the future.

4.2.3 Elemental Analysis

4.2.3.1 Wrong XRF Application for QC Blanks

On April 11, 2023 it was noticed from the lab's XRF QC page that XRF-3 was analyzing the daily QC blank on the incorrect XRF application. The application being used was from the previous calibration of the instrument. A quick investigation showed that this started on the afternoon of April 7, 2023. The incident occurred because a manufacturer's technician was troubleshooting an issue with the instrument and changed the analysis application for the daily QC blank. After the troubleshooting was complete and the instrument was released back to the lab for use, the daily QC blank and multi-element reference samples were run to confirm QC checks before analyzing network samples. Unfortunately, the technician did not change the XRF application back and the lab analyst did not notice it had been changed. The issue was caught a few days later due to the checks on the XRF QC webpage. The only sample analyses performed with the wrong XRF application were those of the QC blank. Due to the nature of the blank measurement, the minimal change in the last calibration of XRF-3, and the passing results before and after the incident, it was determined that there was no impact on any network sample results. During the period of the incident, from April 7 to 11, 2023, XRF-3 was analyzing CSN samples from the January 2023 sampling month. See NR-0021 for details.

4.2.3.2 Zn Contamination Issues on XRF-3 and XRF-4

Daily QC measurements on XRF-3 showed multiple Zn contamination events beginning 1/20/2023 on both the daily QC blank and the daily QC ME samples. An investigation determined the contamination was caused by the hinge of the XRF sample area lid. Due to the position of the QC samples in the XRF sample deck, they are positioned under one of the hinges and were therefore susceptible to contamination falling from the hinge. Sampled filters are not positioned under these hinges and were not affected by the contamination. Additionally, the daily QC samples were temporarily moved to a different location and no samples were loaded in the area under the 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 on 5/22/2023. This prevented any contamination issues from the hinge and no network sample data was affected.

Daily QC measurements on XRF-4 showed a contamination event beginning 11/4/2023. The event included Zn contamination on XRF-4's daily QC blank. The QC failure continued until 11/15/2023. This event was not caught by our QC system because it occurred directly after the annual calibration on this instrument and the QC results were not being calculated in real-time, so could not be monitored in real-time. This issue stems from the fact that all the XRF instruments begin analyzing samples as soon as the calibration standards are analyzed, but before the calibrations are finalized. After the calibrations are finalized, which can take two to three weeks, the sample results are processed with the final calibration and transmitted to the database along with the QC results. Therefore, during this period of a couple of weeks, the QC results are not visible in the normal QC tools because they are not being transmitted to the database and they do not have calibrated loadings to compare to acceptance criteria. There is risk in this procedure, but due to analysis timelines this risk is considered acceptable so that analysis does not fall too far behind. The remediation of any QC failures is handled once the calibrations are completed. In case of any real issues with the analysis, the samples can be reanalyzed.

In this case an investigation determined that the contamination was isolated to the QC blank sample. This zinc contamination of QC samples is normal due to the mechanical construction of the instrument, but under normal circumstances it is caught and remediated immediately. The ongoing calibration delayed the observation of the QC failure this time. It was determined that there was no risk of additional contamination to any network samples and no sample results were impacted by this event. Cleaning contaminants off XRF-4's QC blank returned elemental readings to acceptable blank levels. Please see non-conformance report NR-0024 for additional details of these QC failures.

4.2.3.3 X-ray Intensity Loss on XRF-1

On 11/29/2023, an upward shift in X-ray intensity was noticed in the daily QC ME sample on XRF-1. The QC results did not fail acceptance, but this shift was unusual, so a recalibration was determined appropriate. No samples were being analyzed at the time of the shift as the instrument was undergoing testing after a repair for a vacuum leak. After recalibration, sample analysis restarted. However, then on 12/16/2023, the X-ray intensity shifted back down to the previous level. Again, it did not fail QC criteria, but the intensity shift was obvious in the QC control charts. A new calibration was created for this X-ray intensity level and all samples analyzed after the intensity shifted back down, were reprocessed with this calibration to match the X-ray intensity.

On 1/16/2024 the monthly QC test failed low for potassium on the SRM 2783 reference sample. Upon investigation, it was determined that the intensity shifted down again on 1/3/2024. All sample analysis was stopped. This shift was less than 5% and it was determined the impact on sample results was negligible, the monthly QC failed because the SRM results were already near the lower limit of acceptance. No further action was taken for the sample results. The manufacturer was called out to check the instrument and determined that there was debris on the detector window. This was cleaned and further testing indicated the X-ray intensities were stable. Network samples analyzed during this incident were from August 2023 to November 2023 sampling dates. Appropriate measures were taken to protect sample results and there was no impact on the sample results. See investigation report IR-0020 for additional information.

4.2.4 Ion Analysis

During this reporting period there were two corrective action incidences reported by the ions laboratory regarding blank filter checks and low biased data.

The incident involving blank filter checks occurred when blank filters were extracted in the glove box and contamination was introduced during the extraction. Additional rinses were added to the method so that contamination would not occur when the pipette tip came into contact with any surface within the glove box. There was no impact to the data. This was documented on an RTI corrective action report for project number 0218993.

The incident involving a low bias to analytical results for August samples was identified by the IC laboratory during routine random reanalysis of samples. They identified samples from three analytical batches where there were differences between the reanalysis and original result and upon a subsequent reanalysis they suspected that the samples had become contaminated and reported the original results to UC Davis. UC Davis flagged all of the samples that the IC lab flagged for contamination as outliers for the sulfur/sulfate ratios plus an additional 5 samples that were not identified by the IC lab for suspected contamination. UC Davis provided the sulfur results to the IC lab to compare results against all of the reanalysis results and it was confirmed that reanalysis results all compared well to the sulfur values measured at UC Davis by XRF. The IC lab requested edits and provided reanalysis data for all samples impacted. The IC lab determined that issue was likely due to an injection error. In the future the IC laboratory will reanalyze the entire batch of samples if samples are flagged during reanalysis for suspected contamination or sample injection errors. There was no impact to the data as all results were edited before data were reported to the AQS database.

4.2.5 Carbon Analysis

The quartz refrigerator did not have the temperature recorded on April 11 and 12, 2023. The temperatures recorded on the dates before and after April 11-12 were both under 4 degrees C. Moving forward, a designated lab staff will be responsible for each set of refrigerators, with supervising lab staff overseeing the log completions daily. See NR-0022 for more details.

In the document *UCD CSN SOP #402: Thermal/Optical Reflectance Carbon Analysis Using a Sunset Carbon Analyzer*, section 10.3.8 requires that the lab reviews each sample's thermogram (a timeseries of analyzer parameters and carbon signal) daily. However, it was discovered that the lab had not been doing this, due to a combination of some new automated QC checks in place and a lack of resources, since April 2022. Thermogram checks were being performed as needed when other QC issues were detected. Unfortunately, there were some thermogram checks that could be helpful to determine analysis issues that may not be caught by other QC checks. These issues would be of a one-off nature and not affect a group of sample analyses. After a thorough review of the thermogram checks it was determined that thermogram checks could be automated to look for issues that the QC checks will not catch, such as Unstable Laser Signal, Low Detector Baseline, and Fluctuating System Pressure. Software was developed in the form of an app and interface for the lab staff to use. See NR-0026 for details.

A small dip in the first EC heating stage (EC1) FID signal on the daily QC instrument blank (IB) test was found on all TOR analyzers after the He/O_2 gas was changed on 10/19/2023. This small dip in the FID signal translates to approximately -0.07 $\mu g/cm^2$ in carbon areal density, which is within the QC criteria for the daily IB check (TC within +/-0.3 $\mu g/cm^2$). This issue was only noticeable on the instrument blank (carbon free filter punch) measurements and would have insignificant impact on network sample results. However, this was a new issue and an investigation was conducted to resolve it. After confirming that the FID dip in EC1 occurred on all instruments directly after a new He/O_2 gas cylinder was installed and put into use, it was removed and a new He/O2 cylinder was installed on 11/7/2023. After the change, the IB EC1 issue was resolved. The compressed gas supplier was notified of the He/O_2 gas issue. See IR-0018 for details.

4.2.6 Optical Absorption

On January 9, 2024 while analyzing October 2023 CSN samples, closing QC was not performed on the HIPS optical instrument. That day sample analysis was suspended because of required software and computer updates for the HIPS instrument. This disruption to routine operation caused the analyst to miss the end of day QC tests. Morning QC that day and the following day passed QC tests, so there is low risk to the sample data. Procedures for these interruptions will be reviewed to minimize the risk of this happening in the future. See non-conformance report NR-0025 for details.

4.2.7 Data Processing

4.2.7.1 Data Flagging Modifications

Data are flagged as part of the CSN data validation process as detailed in the *UCD CSN TI #801C* and the *Data Validation for the Chemical Speciation Network* guide. Flags are applied throughout the sampling, filter handling, analysis, and validation processes, using automated checks and on a case-by-case basis. The use and application of flags evolves as problems are identified and remedied, and also in response to process improvements that are implemented to improve the quality and consistency of data for the end user.

4.2.7.2 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.

4.2.7.3 MDLs units for Elements and Carbon

In January 2023, AQRC discovered that some of the units used for analytical MDL calculations were incorrect for elements and carbon in years 2020, 2021, and 2022. At the time, the database did not have a column for tracking units and the analysis labs were delivering data in units different than the calculation method was set-up for. The result is that the delivered MDL for some elements and carbon species were lower than should have been. The most impacted species were As, Br, V, Zn, and EC3. The impact is minor since analytical MDL is not used in calculating the reported MDL and the correction in analytical MDL does not usually change the state of the data (above or below MDL). In most cases the field-blank-determined MDLs are larger than analytical, and the larger is reported.

To correct the issue, a unit field was added to the CSN database and SOPs were updated to include correct units. The affected data was redelivered on July 31, 2024.

4.2.8 Technical System Audit

The EPA did not conduct an audit of UC Davis or RTI during the time when 2023 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.

4.2.9 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.

At RTI, no internal audit took place in 2023. The next internal audit will likely take place in 2024.

4.3 Filter Acceptance Testing

Filter acceptance testing responsibilities have transitioned to UC Davis for quartz filter testing, to the RTI Ions lab for Nylon filter testing, and to the RTI gravimetry lab for PTFE filter testing.

4.3.1 Quartz Filter Testing

All filters provided to the test laboratory passed the $\leq 1.5\mu g/cm^2$ TCTC testing criteria. Results are provided in Table 4-6.

Table 4-6: Quartz Filter Acceptance Testing Results [ug/cm2].

Filter ID	OCTR [ug/cm2]	ECTR [ug/cm2]	TCTC [ug/cm2]
CSNQ0001FILTER1	-0.036	0.000	-0.035
CSNQ0001FILTER2	-0.001	0.000	-0.001
CSNQ0001FILTER3	0.170	0.000	0.170
CSNQ0001FILTER4	0.072	0.000	0.072
CSNQ0001FILTER5	0.187	0.000	0.187
CSNQ0001FILTER6	0.057	0.000	0.058
CSNQ0001FILTER7	-0.002	0.000	-0.002
CSNQ0001FILTER8	0.067	0.000	0.067
CSNQ0001FILTER9	0.301	0.000	0.302
CSNQ0001FILTER10	0.175	0.000	0.175
CSNQ0001FILTER11	-0.094	0.000	-0.094
CSNQ0001FILTER12	0.361	0.000	0.361
CSNQ0002FILTER1	0.300	0.000	0.300
CSNQ0002FILTER2	-0.048	0.000	-0.048
CSNQ0002FILTER3	-0.031	0.000	-0.030
CSNQ0002FILTER4	-0.015	0.000	-0.014
CSNQ0002FILTER5	0.137	0.000	0.137
CSNQ0002FILTER6	0.096	0.000	0.096
CSNQ0002FILTER7	0.084	0.000	0.084
CSNQ0002FILTER8	-0.037	0.000	-0.037
CSNQ0002FILTER9	0.101	0.000	0.101
CSNQ0002FILTER10	0.171	0.000	0.171
CSNQ0002FILTER11	0.245	0.000	0.245
CSNQ0002FILTER12	-0.037	0.000	-0.037
CSNQ0003FILTER1	0.236	0.000	0.236
CSNQ0003FILTER2	-0.036	0.000	-0.036
CSNQ0003FILTER3	-0.028	0.000	-0.028
CSNQ0003FILTER4	0.587	0.000	0.587
CSNQ0003FILTER5	0.037	0.000	0.037
CSNQ0003FILTER6	0.062	0.000	0.062
CSNQ0003FILTER7	0.198	0.000	0.198

Filter ID	OCTR [ug/cm2]	ECTR [ug/cm2]	TCTC [ug/cm2]
CSNQ0003FILTER8	0.049	0.000	0.049
CSNQ0003FILTER9	0.047	0.000	0.047
CSNQ0003FILTER10	0.434	0.000	0.435
CSNQ0003FILTER11	-0.026	0.000	-0.026
CSNQ0003FILTER12	-0.097	0.000	-0.097
CSNQ0004FILTER1	0.039	0.000	0.039
CSNQ0004FILTER2	-0.041	0.000	-0.041
CSNQ0004FILTER3	0.021	0.000	0.021
CSNQ0004FILTER4	0.066	0.000	0.066
CSNQ0004FILTER5	-0.108	0.000	-0.108
CSNQ0004FILTER6	-0.020	0.000	-0.020
CSNQ0004FILTER7	0.246	0.000	0.246
CSNQ0004FILTER8	0.084	0.000	0.084
CSNQ0004FILTER9	0.092	0.000	0.092
CSNQ0004FILTER10	0.318	0.000	0.318
CSNQ0004FILTER11	0.009	0.000	0.009
CSNQ0004FILTER12	0.281	0.000	0.281
CSNQ0005FILTER1	0.121	0.000	0.121
CSNQ0005FILTER2	0.147	0.000	0.147
CSNQ0005FILTER3	0.869	0.000	0.869
CSNQ0005FILTER4	0.126	0.000	0.126
CSNQ0005FILTER5	0.342	0.000	0.342
CSNQ0005FILTER6	0.078	0.000	0.079
CSNQ0005FILTER7	0.284	0.000	0.284
CSNQ0005FILTER8	0.080	0.000	0.081
CSNQ0005FILTER9	0.119	0.000	0.119
CSNQ0005FILTER10	0.208	0.000	0.208
CSNQ0005FILTER11	0.534	0.000	0.534
CSNQ0005FILTER12	0.363	0.000	0.363
CSNQ0006Filter1	0.227	0.000	0.227
CSNQ0006Filter2	0.394	0.000	0.394
CSNQ0006Filter3	0.370	0.000	0.370

Filter ID	OCTR [ug/cm2]	ECTR [ug/cm2]	TCTC [ug/cm2]
CSNQ0006Filter4	0.218	0.000	0.218
CSNQ0006Filter5	0.286	0.000	0.286
CSNQ0006Filter6	0.117	0.001	0.118
CSNQ0006Filter7	0.264	0.000	0.264
CSNQ0006Filter8	0.391	0.000	0.391
CSNQ0006Filter9	0.298	0.000	0.298
CSNQ0006Filter10	0.394	0.000	0.394
CSNQ0006Filter11	0.094	0.001	0.095
CSNQ0006Filter12	0.144	0.000	0.144
CSNQ0007Filter1	0.196	0.000	0.196
CSNQ0007Filter2	0.240	0.000	0.240
CSNQ0007Filter3	0.581	0.000	0.581
CSNQ0007Filter4	0.184	0.000	0.184
CSNQ0007Filter5	0.162	0.000	0.162
CSNQ0007Filter6	0.886	0.000	0.886
CSNQ0007Filter7	0.072	0.000	0.073
CSNQ0007Filter8	0.157	0.000	0.157
CSNQ0007Filter9	0.190	0.000	0.190
CSNQ0007Filter10	0.208	0.000	0.208
CSNQ0007Filter11	0.344	0.000	0.344
CSNQ0007Filter12	0.060	0.001	0.061
CSNQ0008Filter1	0.149	0.000	0.149
CSNQ0008Filter2	0.249	0.000	0.249
CSNQ0008Filter3	0.312	0.000	0.312
CSNQ0008Filter4	0.291	-0.001	0.290
CSNQ0008Filter5	0.061	0.001	0.062
CSNQ0008Filter6	0.307	0.000	0.307
CSNQ0008Filter7	0.202	0.000	0.203
CSNQ0008Filter8	0.312	0.000	0.312
CSNQ0008Filter9	0.045	0.000	0.045
CSNQ0008Filter10	-0.082	0.001	-0.081
CSNQ0008Filter11	0.044	0.000	0.044

Filter ID	OCTR [ug/cm2]	ECTR [ug/cm2]	TCTC [ug/cm2]
CSNQ0008Filter12	0.197	0.000	0.197
CSNQC0009-1	-0.002	0.000	-0.002
CSNQC0009-2	0.148	0.000	0.148
CSNQC0009-3	0.118	0.000	0.118
CSNQC0009-4	0.019	0.000	0.019
CSNQC0009-5	0.012	0.000	0.013
CSNQC0009-6	0.117	0.000	0.118
CSNQC0009-7	0.743	0.000	0.743
CSNQC0009-8	0.092	0.000	0.093
CSNQC0009-9	0.560	0.000	0.560
CSNQC0009-10	0.161	0.001	0.162
CSNQC0009-11	0.661	0.000	0.660
CSNQC0009-12	0.191	0.000	0.191
CSNQ0010 Filter 1	-0.017	0.001	-0.016
CSNQ0010 Filter 2	0.034	0.000	0.034
CSNQ0010 Filter 3	0.014	0.000	0.014
CSNQ0010 Filter 4	0.245	0.000	0.244
CSNQ0010 Filter 5	0.123	0.000	0.122
CSNQ0010 Filter 6	-0.075	0.001	-0.074
CSNQ0010 Filter 7	0.016	0.000	0.016
CSNQ0010 Filter 8	0.149	0.000	0.149
CSNQ0010 Filter 9	0.248	0.000	0.248
CSNQ0010 Filter 10	0.041	0.000	0.042
CSNQ0010 Filter 11	-0.071	0.001	-0.071
CSNQ0010 Filter 12	0.075	0.000	0.075
CSNQ0011 Filter 1	0.368	0.001	0.368
CSNQ0011 Filter 2	0.087	0.000	0.087
CSNQ0011 Filter 3	0.383	0.000	0.383
CSNQ0011 Filter 4	-0.169	0.001	-0.168
CSNQ0011 Filter 5	-0.056	0.001	-0.056
CSNQ0011 Filter 6	-0.143	0.001	-0.143
CSNQ0011 Filter 7	0.697	0.000	0.697

Filter ID	OCTR [ug/cm2]	ECTR [ug/cm2]	TCTC [ug/cm2]
CSNQ0011 Filter 8	0.241	0.000	0.241
CSNQ0011 Filter 9	0.059	0.000	0.059
CSNQ0011 Filter 10	0.282	0.000	0.282
CSNQ0011 Filter 11	0.061	0.001	0.062
CSNQ0011 Filter 12	0.091	0.001	0.092
CSNQ0012 Filter 2	-0.123	0.000	-0.123
CSNQ0012 Filter 2	-0.039	0.000	-0.039
CSNQ0012 Filter 3	-0.015	0.000	-0.015
CSNQ0012 Filter 4	-0.016	0.001	-0.015
CSNQ0012 Filter 5	-0.113	0.000	-0.113
CSNQ0012 Filter 6	0.076	0.000	0.077
CSNQ0012 Filter 7	0.021	0.000	0.021
CSNQ0012 Filter 8	0.141	0.000	0.141
CSNQ0012 Filter 9	-0.055	0.001	-0.054
CSNQ0012 Filter 10	0.351	0.000	0.352
CSNQ0012 Filter 11	0.154	0.000	0.155
CSNQ0012 Filter 12	0.125	0.000	0.125
CSNQ0013 Filter 1	0.033	0.000	0.033
CSNQ0013 Filter 2	0.078	0.000	0.078
CSNQ0013 Filter 3	0.034	0.000	0.034
CSNQ0013 Filter 4	0.037	0.000	0.037
CSNQ0013 Filter 5	0.002	0.000	0.002
CSNQ0013 Filter 6	-0.063	0.000	-0.063
CSNQ0013 Filter 7	-0.115	0.000	-0.114
CSNQ0013 Filter 8	0.013	0.000	0.013
CSNQ0013 Filter 9	0.001	0.000	0.001
CSNQ0013 Filter 10	0.018	0.000	0.018
CSNQ0013 Filter 11	-0.220	0.001	-0.219
CSNQ0013 Filter 12	-0.039	0.000	-0.039
CSNQ0014 Filter 1	-0.104	0.000	-0.104
CSNQ0014 Filter 2	0.082	0.000	0.082
CSNQ0014 Filter 3	-0.062	0.000	-0.062

Filter ID	OCTR [ug/cm2]	ECTR [ug/cm2]	TCTC [ug/cm2]
CSNQ0014 Filter 4	0.131	0.000	0.131
CSNQ0014 Filter 5	0.052	0.000	0.051
CSNQ0014 Filter 6	0.078	0.000	0.078
CSNQ0014 Filter 7	-0.036	0.001	-0.035
CSNQ0014 Filter 8	-0.048	0.000	-0.048
CSNQ0014 Filter 9	0.862	-0.001	0.862
CSNQ0014 Filter 10	0.147	0.000	0.147
CSNQ0014 Filter 11	-0.121	0.000	-0.120
CSNQ0014 Filter 12	-0.115	0.000	-0.115
CSNQ0015 Filter 1	-0.050	0.000	-0.050
CSNQ0015 Filter 2	0.020	0.000	0.020
CSNQ0015 Filter 3	0.005	0.000	0.005
CSNQ0015 Filter 4	-0.134	0.001	-0.134
CSNQ0015 Filter 5	-0.156	0.000	-0.156
CSNQ0015 Filter 6	-0.035	0.000	-0.035
CSNQ0015 Filter 7	-0.105	0.000	-0.104
CSNQ0015 Filter 8	0.274	0.000	0.274
CSNQ0015 Filter 9	-0.120	0.000	-0.119
CSNQ0015 Filter 10	-0.070	0.000	-0.070
CSNQ0015 Filter 11	-0.077	0.000	-0.077
CSNQ0015 Filter 12	-0.147	0.000	-0.147
CSNQ0016 Filter 1	0.092	0.000	0.092
CSNQ0016 Filter 2	0.015	0.000	0.015
CSNQ0016 Filter 3	0.218	0.000	0.218
CSNQ0016 Filter 4	-0.071	0.000	-0.071
CSNQ0016 Filter 5	-0.084	0.000	-0.084
CSNQ0016 Filter 6	0.198	0.000	0.198
CSNQ0016 Filter 7	-0.131	0.000	-0.131
CSNQ0016 Filter 8	0.076	0.001	0.076
CSNQ0016 Filter 9	-0.134	0.000	-0.134
CSNQ0016 Filter 10	0.099	0.001	0.099
CSNQ0016 Filter 11	0.235	0.000	0.235

Filter ID	OCTR [ug/cm2]	ECTR [ug/cm2]	TCTC [ug/cm2]
CSNQ0016 Filter 12	-0.173	0.001	-0.173
Max Result	0.886	0.001	0.886

4.3.2 Nylon Acceptance Testing

All filters provided to the test laboratory passed the ≤1µg/filter testing criteria for each anion and cation. Results are provided in Table 4-7.

Table 4-7: Nylon Filter Acceptance Testing Results.

	chloride	**nitrate**	**sulfate**	**sodium**	**ammonium**	**potassium**
	µg/filter	**µg/filter**	**µg/filter**	**µg/filter**	**µg/filter**	**µg/filter**
CSNN0001Filter1	0.05	0.24	0.00	0.13	0.10	0.14
CSNN0001Filter2	0.06	0.23	0.00	0.13	0.10	0.13
CSNN0001Filter3	0.09	0.23	0.00	0.13	0.10	0.14
CSNN0001Filter4	0.08	0.27	0.00	0.13	0.10	0.14
CSNN0001Filter5	0.08	0.00	0.00	0.13	0.10	0.14
CSNN0001Filter6	0.09	0.00	0.00	0.13	0.10	0.14
CSNN0001Filter7	0.07	0.50	0.00	0.13	0.11	0.14
CSNN0001Filter8	0.07	0.32	0.00	0.13	0.11	0.14
CSNN0002Filter1	0.07	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter2	0.00	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter3	0.09	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter4	0.08	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter5	0.06	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter6	0.04	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter7	0.09	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter8	0.14	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter9	0.10	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter10	0.13	0.00	0.00	0.13	0.10	0.15
CSNN0002Filter11	0.09	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter12	0.09	0.00	0.00	0.14	0.10	0.14
CSNN0002Filter13	0.07	0.00	0.00	0.13	0.10	0.15
CSNN0002Filter14	0.05	0.00	0.00	0.13	0.10	0.14

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter15	0.04	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter16	0.04	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter17	0.05	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter18	0.00	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter19	0.00	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter20	0.06	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter21	0.22	0.00	0.00	0.15	0.10	0.14
CSNN0002Filter22	0.21	0.00	0.00	0.15	0.10	0.15
CSNN0002Filter23	0.12	0.00	0.00	0.14	0.10	0.14
CSNN0002Filter24	0.18	0.00	0.00	0.14	0.10	0.14
CSNN0002Filter25	0.00	0.00	0.00	0.13	0.11	0.14
CSNN0002Filter26	0.00	0.00	0.00	0.13	0.10	0.13
CSNN0002Filter27	0.04	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter28	0.00	0.00	0.00	0.13	0.10	0.13
CSNN0002Filter29	0.00	0.00	0.00	0.13	0.09	0.14
CSNN0002Filter30	0.08	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter31	0.09	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter32	0.11	0.00	0.00	0.13	0.10	0.13
CSNN0002Filter33	0.11	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter34	0.06	0.00	0.00	0.13	0.10	0.00
CSNN0002Filter35	0.07	0.00	0.00	0.13	0.10	0.00
CSNN0002Filter36	0.06	0.00	0.00	0.13	0.09	0.14
CSNN0002Filter37	0.05	0.00	0.00	0.13	0.10	0.00
CSNN0002Filter38	0.10	0.00	0.00	0.13	0.09	0.14
CSNN0002Filter39	0.08	0.00	0.00	0.14	0.09	0.15
CSNN0002Filter40	0.11	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter41	0.13	0.00	0.00	0.13	0.09	0.14
CSNN0002Filter42	0.09	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter43	0.12	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter44	0.00	0.00	0.00	0.13	0.10	0.00
CSNN0002Filter45	0.09	0.00	0.00	0.13	0.10	0.14

	chloride	**nitrate**	**sulfate**	**sodium**	**ammonium**	**potassium**
	µg/filter	**µg/filter**	**µg/filter**	**µg/filter**	**µg/filter**	**µg/filter**
CSNN0002Filter46	0.00	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter47	0.00	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter48	0.03	0.00	0.00	0.13	0.10	0.14
CSNN0002Filter49	0.09	0.00	0.00	0.14	0.10	0.16
CSNN0002Filter50	0.08	0.00	0.00	0.14	0.09	0.15
CSNN0002Filter51	0.06	0.00	0.00	0.13	0.09	0.14
CSNN0002Filter52	0.10	0.00	0.00	0.13	0.09	0.14
CSNN0002Filter53	0.41	0.29	0.61	0.16	0.20	0.18
CSNN0002Filter54	0.16	0.15	0.21	0.11	0.14	0.14
CSNN0002Filter55	0.20	0.14	0.00	0.10	0.12	0.13
CSNN0002Filter56	0.22	0.46	0.00	0.11	0.11	0.15
CSNN0002Filter57	0.27	0.30	0.00	0.11	0.11	0.15
CSNN0002Filter58	0.25	0.22	0.00	0.11	0.11	0.14
CSNN0002Filter59	0.29	0.36	0.00	0.11	0.11	0.17
CSNN0002Filter60	0.30	0.28	0.00	0.11	0.11	0.15
CSNN0002Filter61	0.15	0.00	0.00	0.00	0.10	0.00
CSNN0002Filter62	0.08	0.10	0.00	0.00	0.10	0.00
CSNN0002Filter63	0.45	0.23	0.70	0.14	0.21	0.15
CSNN0002Filter64	0.14	0.00	0.00	0.12	0.10	0.14
CSNN0002Filter65	0.11	0.10	0.00	0.00	0.00	0.00
CSNN0002Filter66	0.17	0.08	0.00	0.00	0.00	0.00
CSNN0002Filter67	0.11	0.00	0.00	0.00	0.10	0.00
CSNN0002Filter68	0.23	0.00	0.00	0.11	0.13	0.14
CSNN0002Filter69	0.19	0.00	0.00	0.11	0.13	0.14
CSNN0002Filter70	0.20	0.11	0.00	0.12	0.10	0.14
CSNN0002Filter71	0.16	0.00	0.00	0.10	0.11	0.00
CSNN0002Filter72	0.40	0.00	0.48	0.15	0.18	0.16
CSNN0002Filter73	0.13	0.00	0.00	0.00	0.10	0.00
CSNN0002Filter74	0.18	0.21	0.00	0.00	0.10	0.00
CSNN0002Filter75	0.15	0.25	0.00	0.10	0.10	0.00
CSNN0002Filter76	0.29	0.24	0.00	0.11	0.12	0.14

	chloride	**nitrate**	**sulfate**	**sodium**	**ammonium**	**potassium**
	µg/filter	**µg/filter**	**µg/filter**	**µg/filter**	**µg/filter**	**µg/filter**
CSNN0002Filter77	0.27	0.26	0.00	0.11	0.12	0.14
CSNN0002Filter78	0.21	0.25	0.00	0.00	0.10	0.00
CSNN0002Filter79	0.23	0.19	0.00	0.10	0.10	0.00
CSNN0002Filter80	0.21	0.21	0.00	0.11	0.10	0.14
CSNN0002Filter81	0.32	0.25	0.00	0.11	0.10	0.15
CSNN0002Filter82	0.17	0.16	0.00	0.00	0.00	0.00
CSNN0002Filter83	0.47	0.27	0.81	0.15	0.27	0.18
CSNN0002Filter84	0.13	0.00	0.00	0.10	0.10	0.00
CSNN0002Filter85	0.27	0.08	0.00	0.00	0.00	0.00
CSNN0002Filter86	0.18	0.00	0.00	0.00	0.10	0.00
CSNN0002Filter87	0.20	0.10	0.00	0.00	0.10	0.00
CSNN0002Filter88	0.18	0.08	0.00	0.10	0.10	0.00
CSNN0002Filter89	0.22	0.00	0.00	0.00	0.00	0.00
CSNN0002Filter90	0.35	0.00	0.00	0.10	0.10	0.00
CSNN0002Filter91	0.15	0.00	0.00	0.11	0.10	0.00
CSNN0002Filter92	0.05	0.08	0.00	0.00	0.10	0.00
CSNN0002Filter93	0.23	0.16	0.29	0.11	0.14	0.14
CSNN0002Filter94	0.23	0.23	0.40	0.12	0.15	0.14
CSNN0002Filter95	0.22	0.16	0.00	0.11	0.10	0.00
CSNN0002Filter96	0.30	0.29	0.00	0.12	0.13	0.15
CSNN0002Filter97	0.17	0.17	0.22	0.12	0.13	0.14
CSNN0002Filter98	0.17	0.00	0.00	0.00	0.10	0.00
CSNN0002Filter99	0.13	0.00	0.00	0.11	0.12	0.00
CSNN0002Filter100	0.11	0.18	0.18	0.11	0.12	0.14
CSNN0002Filter101	0.23	0.20	0.37	0.12	0.15	0.15
CSNN0002Filter102	0.19	0.12	0.00	0.11	0.11	0.00
CSNN0002Filter103	0.18	0.12	0.00	0.11	0.11	0.00
CSNN0002Filter104	0.16	0.18	0.00	0.11	0.10	0.00
CSNN0002Filter105	0.16	0.00	0.00	0.11	0.10	0.00
CSNN0002Filter106	0.24	0.23	0.00	0.00	0.00	0.00
CSNN0002Filter107	0.11	0.12	0.11	0.00	0.00	0.00

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter108	0.17	0.21	0.00	0.00	0.00	0.00
CSNN0002Filter109	0.11	0.46	0.01	0.18	0.00	0.00
CSNN0002Filter110	0.08	0.18	0.00	0.00	0.00	0.00
CSNN0002Filter111	0.07	0.19	0.00	0.14	0.00	0.00
CSNN0002Filter112	0.08	0.30	0.00	0.14	0.00	0.00
CSNN0002Filter113	0.24	0.29	0.00	0.13	0.13	0.16
CSNN0002Filter114	0.08	0.36	0.00	0.15	0.00	0.00
CSNN0002Filter115	0.00	0.00	0.00	0.26	0.13	0.17
CSNN0002Filter116	0.14	0.34	0.00	0.16	0.00	0.00
CSNN0002Filter117	0.13	0.22	0.00	0.00	0.00	0.00
CSNN0002Filter118	0.20	0.32	0.00	0.15	0.00	0.00
CSNN0002Filter119	0.21	0.21	0.00	0.00	0.00	0.00
CSNN0002Filter120	0.23	0.22	0.04	0.00	0.00	0.00
CSNN0002Filter121	0.24	0.18	0.00	0.00	0.00	0.00
CSNN0002Filter122	0.16	0.17	0.00	0.00	0.00	0.00
CSNN0002Filter123	0.20	0.40	0.00	0.15	0.00	0.00
CSNN0002Filter124	0.25	0.22	0.00	0.00	0.00	0.00
CSNN0002Filter125	0.23	0.25	0.00	0.00	0.00	0.00
CSNN0002Filter126	0.22	0.21	0.00	0.00	0.00	0.00
CSNN0002Filter127	0.26	0.31	0.00	0.00	0.00	0.00
CSNN0002Filter128	0.22	0.16	0.00	0.00	0.00	0.21
CSNN0002Filter129	0.19	0.23	0.00	0.00	0.00	0.22
CSNN0002Filter130	0.32	0.18	0.00	0.00	0.00	0.20
CSNN0002Filter131	0.30	0.00	0.00	0.00	0.00	0.19
CSNN0002Filter132	0.29	0.00	0.00	0.00	0.00	0.28
CSNN0002Filter133	0.30	0.00	0.00	0.00	0.00	0.30
CSNN0002Filter134	0.57	0.00	0.07	0.00	0.13	0.23
CSNN0002Filter135	0.03	0.00	0.31	0.00	0.00	0.23
CSNN0002Filter136	0.30	0.09	0.00	0.00	0.00	0.23
CSNN0002Filter137	0.36	0.19	0.09	0.00	0.00	0.23
CSNN0002Filter138	0.25	0.00	0.00	0.12	0.13	0.22

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter139	0.03	0.00	0.00	0.00	0.00	0.23
CSNN0002Filter140	0.28	0.00	0.00	0.12	0.13	0.21
CSNN0002Filter141	0.40	0.00	0.00	0.13	0.13	0.22
CSNN0002Filter142	0.26	0.00	0.00	0.12	0.13	0.18
CSNN0002Filter143	0.26	0.09	0.13	0.15	0.13	0.18
CSNN0002Filter144	0.34	0.00	0.00	0.13	0.13	0.18
CSNN0002Filter145	0.27	0.09	0.00	0.13	0.13	0.16
CSNN0002Filter146	0.31	0.09	0.00	0.13	0.13	0.16
CSNN0002Filter147	0.27	0.09	0.13	0.13	0.13	0.17
CSNN0002Filter148	0.25	0.00	0.10	0.12	0.13	0.16
CSNN0002Filter149	0.22	0.00	0.00	0.13	0.13	0.17
CSNN0002Filter150	0.25	0.00	0.00	0.12	0.13	0.15
CSNN0002Filter151	0.10	0.00	0.00	0.12	0.13	0.16
CSNN0002Filter152	0.37	0.09	0.00	0.13	0.13	0.15
CSNN0002Filter153	0.33	0.00	0.00	0.13	0.13	0.00
CSNN0002Filter154	0.33	0.00	0.00	0.13	0.13	0.16
CSNN0002Filter155	0.33	0.12	0.00	0.13	0.13	0.15
Max Result	0.57	0.50	0.81	0.26	0.27	0.30

4.3.3 PTFE Filter Inspection

PTFE filter inspection involved a visual inspection of filters prior to use in the CSN program. During the inspection two filters, out of 160 targeted for visual inspection were observed to have minor, disqualifying issues. Several more filters were observed to have minor issues over the course of the assembly process by staff. All filters which were deemed unsuitable for use were discarded and not used.

5. Laboratory Quality Control Summaries

5.1 RTI Shipping and Handling Laboratory

There is no data generated or captured as part of the shipping and handling process.

As a matter of completeness, the null code AR is used during times when an invalid event is the caused by the shipping and handling lab. For this contract period, AR codes were used in instances where filters were not loaded into appropriate cassettes before sampling, the wrong filter type was loaded into a filter cassette before sampling, a filter was severely damaged and unanalyzable after sampling occurred, or filters were improperly loaded - including when the modules were not completely tightened as detailed in section 4.2.1.

In 2023, Table 4-3 notes the AR code was used 14 times for PTFE, 19 times for Nylon, and 46 times for Quartz.

The TT qualifier flag is applied whenever the filter temperature rises above 4 degrees C during transport or storage before analysis. This applies for individual shipments from the field as well as batch shipments to the analysis labs.

Table 5-1: TT flags applied to filters sampled in 2023 (field blanks excluded).

Batch	PTFE	Nylon	Quartz	Total
2023-05	826	473	816	2,115
2023-06	766	178	443	1,387
2023-07	757	234	228	1,219
2023-08	696	188	184	1,068
2023-09	140	140	140	420
2023-10	64	64	64	192
2023-11	45	45	45	135
2023-12	31	31	31	93

Note, some filters originated at WSP and were returned to RTI where flags would have been applied. Starting with the 2023-09 batch, the coolers used for shipping between labs were replaced with better-insulated versions and the number of TT flags has dropped.

5.2 RTI Gravimetric Lab

The RTI gravimetry lab provides mass results on a select subset of filters in the CSN program. RTI performs all analyses in compliance with 40 CFR Part 50, Appendix L, Guidance Document 2.12, and applicable Laboratory’s SOPs. Table 5-2 contains a summary of all the internal laboratory QC checks and their acceptance criteria.

5.2.1 Summary of QC Requirements

RTI performs all analyses in compliance with 40 CFR Part 50, Appendix L, Guidance Document 2.12, and applicable Laboratory’s SOPs. Table 5-2 contains a summary of all the internal laboratory QC checks and their acceptance criteria. Table 5-3 contains a summary of additional specific quality requirements.

Table 5-2: Summary of Gravimetry Lab QC Activities and Acceptance Criteria.

Requirement	Frequency	Acceptance Criteria	QA Guidance Document 2.12 Reference	Information Provided
Blanks				
Lot Blanks	9 per lot	< 15 µg difference	Part 50, App. L Sec. 8.2	Filter stabilization/ equilibrium
Lab Blanks	Enough to ensure 1 per post weighing session as a single use blank	± 15 µg difference	2.12 Sec. 10.5	Laboratory contamination
Calibration / Verification				
Balance Calibration	1/year	Manufacturers spec.	2.12 Sec. 9.3	Verification of equipment operation
Temp. Calibration	1/year	± 2° C	2.12, Sec. 4.3.8	Verification of equipment operation
RH Calibration	1/year	± 2%	2.12, Sec. 4.3.8	Verification of equipment operation
Accuracy				
Balance Audit	1/year	<+ 0.003 mg or manufacturers specs, whichever is tighter	2.12 Sec. 11.2.7	Laboratory technician operation
Balance Check (50, 100, 300, and 500 mg) working standards	beginning, every 10th sample, end	< 3µg	2.12 Sec. 10.6	Balance accuracy/stability
Calibration standards				
Working Mass Stds.	1/year	25 µg	2.12 Sec. 4.3 and 9.7	Standards verification
Primary Mass Stds.	1/year	25 µg	2.12 Sec. 4.3 and 9.7	Primary standards verification

Requirement	Frequency	Acceptance Criteria	QA Guidance Document 2.12 Reference	Information Provided
Precision				
Duplicate filter weighings	Every 10th filter	± 15 µg difference	2.12 Sec. 10.6	Weighing repeatability/ filter stability

Table 5-3: Gravimetry Quality Requirements.

Requirement	Frequency	Acceptance Criteria	Results
Post Sample Weighing	All Filters	≤30 days if receipt temperature ≤4 ˚C; ≤30 days if receipt temperature >4 ˚C and ambient collection temperature ≤ receipt temperature (TT flag applied); ≤10 days if receipt temperature >4 ˚C and ambient collection temperature > receipt temperature (TS Null code applied)	Two filters were assigned a TS Null code due to not meeting these criteria in 2023
Filter Visual Defect Check (unexposed)	All Filters	Correct type & size and for pinholes, particles or imperfections*	No filters which did not meet acceptance criteria were used.
Equilibration	All Filters	24 hours minimum	Requirement met for all filters.
Temp. Range	All Filters	24-hr mean 20-23°C	Requirement met for all filters.
Temp. Control	All Filters	+/- 2°C SD** over 24 hr.	Requirement met for all filters.
Humidity Range	All Filters	24-hr mean 30% - 40% RH or <5% sampling RH but > 20%RH	Requirement met for all filters.
Humidity Control	All Filters	+ 5% SD** over 24 hr.	Requirement met for all filters.
Pre/post Sampling RH	All Filters	difference in 24-hr means < + 5% RH	Requirement met for all filters.
Balance	All Filters	located in filter conditioning environment	Requirement met for all filters.

5.2.2 Summary of QC Checks

Following the quality requirements listed in Table 5-3, a working standard bracketing the mass of the filter is weighed each weighing session at the start, end, and after every ten masses are recorded. Two sets of standard masses were utilized during the 2023 CSN project year, one set of 300-mg and 500-mg weighing sets were used between May 23, 2023 through December 6, 2023 and a second 300 mg and 500 mg weighing set was used from December 7, 2023 through December 31, 2023. Trend charts over time for each can be found in Figures 5-1 through 5-4.

Figure 5-1: 300 mg standard mass #1.

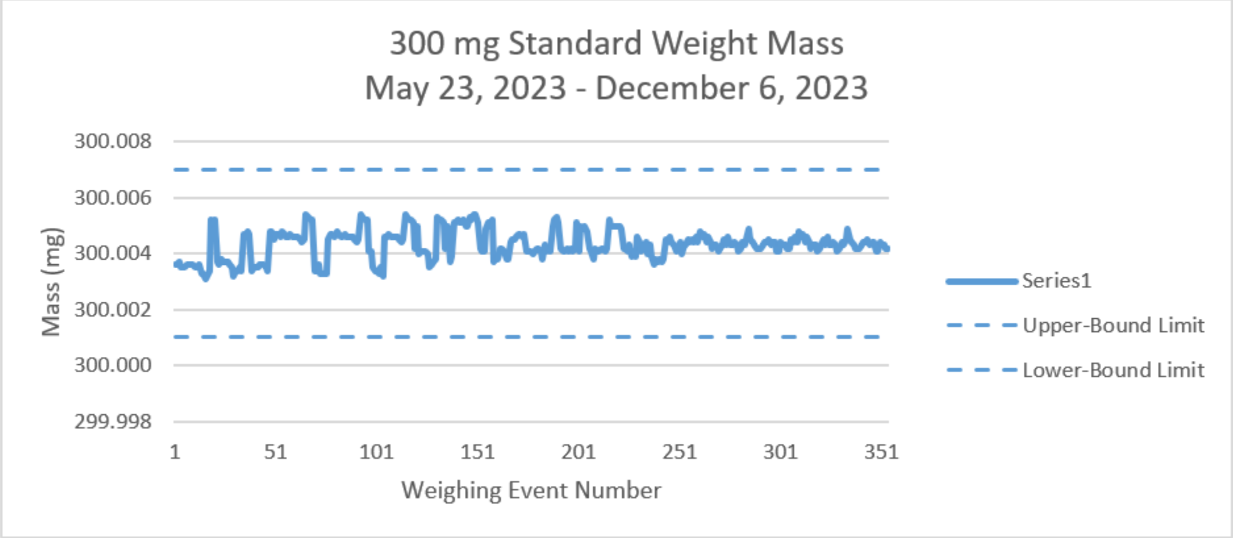


Figure 5-2: 500 mg standard mass #1.

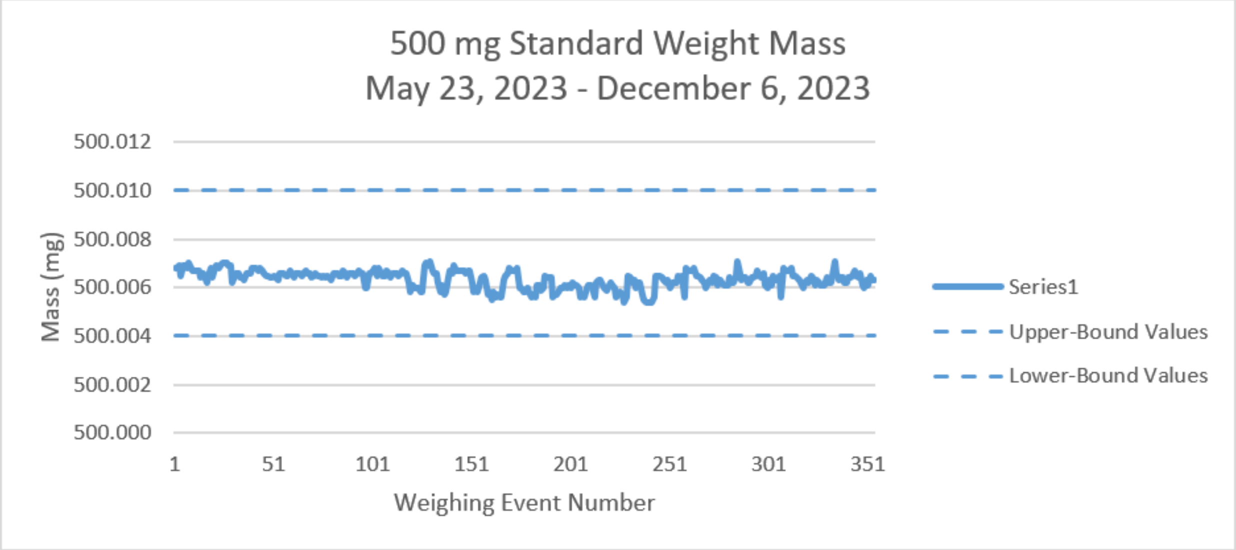


Figure 5-3: 300 mg standard mass #2.

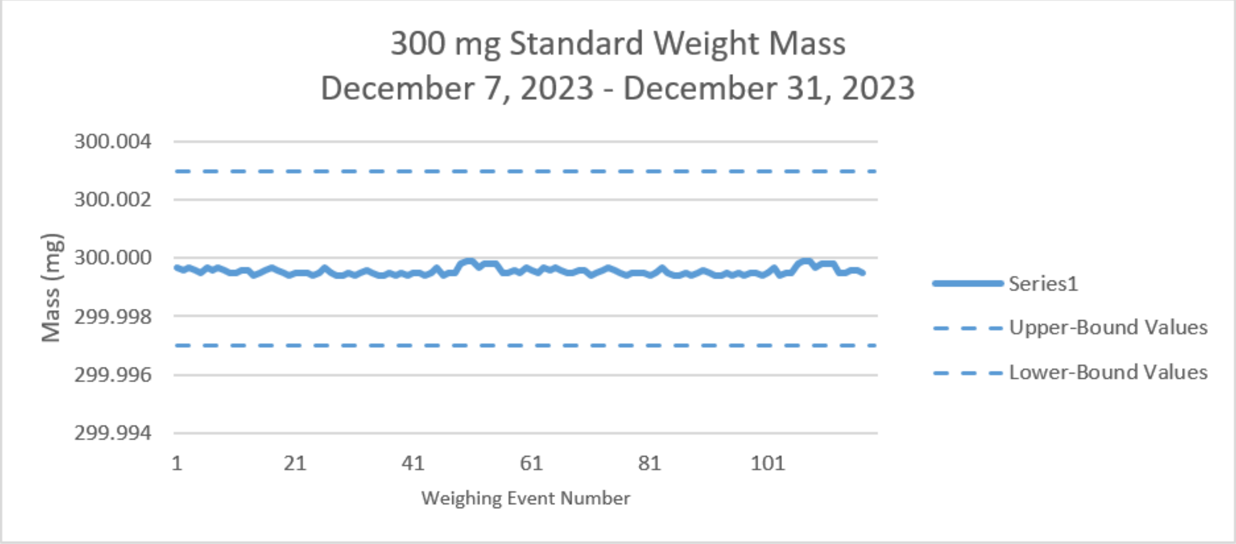
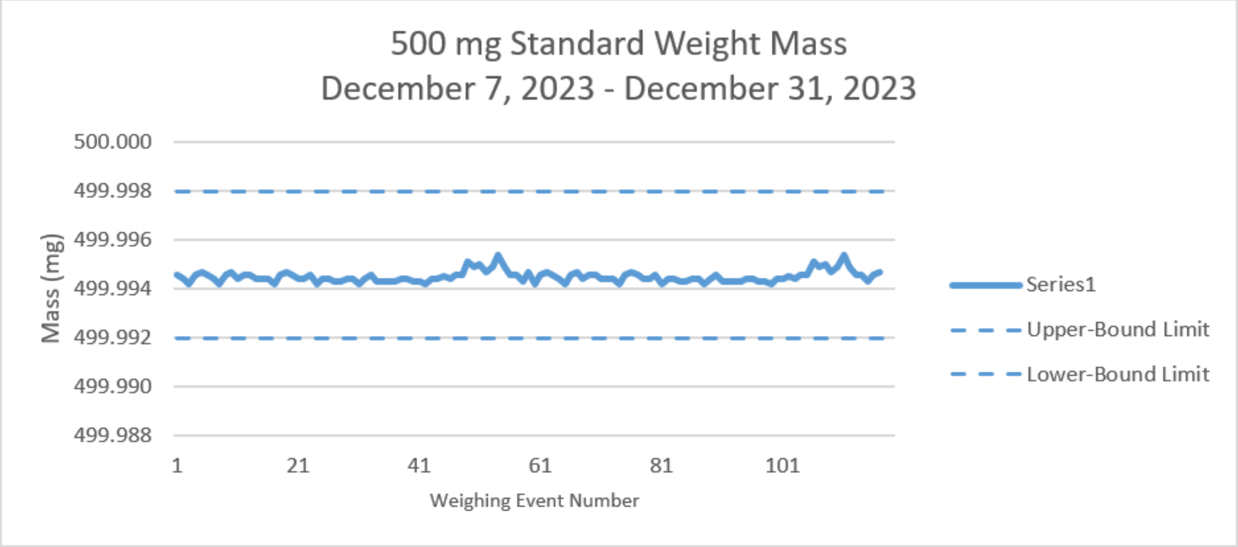


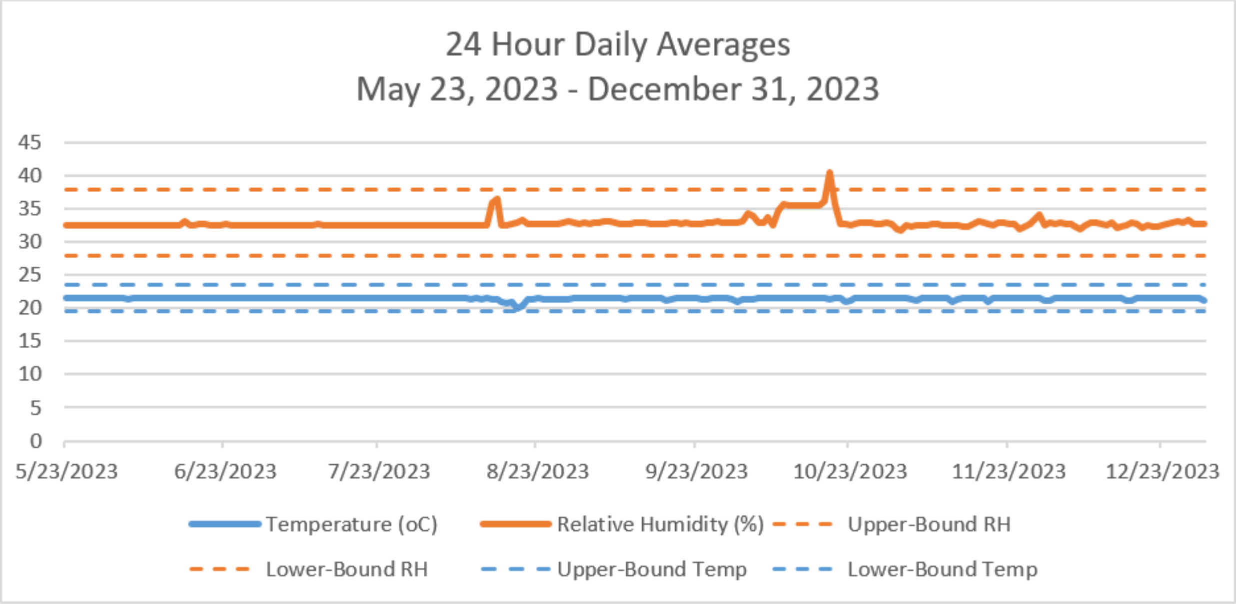
Figure 5-4: 500 mg standard mass #2.



5.2.3 Summary of Environmental Chamber Parameters

Following the quality requirements listed in Table 5-3, 24-hr averages for relative humidity and temperature, collected at 5-minute intervals is provided in Figure 5-5. In the displayed instances where chamber parameters exceeded permissible criteria, no weighing or filter equilibration was performed. Discreet chamber outlier events were primarily caused by planned maintenance and/or intentional chamber adjustment to meet project specific requirements.

Figure 5-5: 24 hr daily average of environmental chamber conditions.



5.2.4 Determination of Uncertainties and Method Detection Limits

For discussion of Method Detection Limits (MDLs) see Section 4.1.3.8.

For discussion of analytical uncertainty and total uncertainty see Section 4.1.2 and Section 7.5, respectively.

5.2.5 Audits, Performance Evaluations, Training, and Accreditations

5.2.5.1 System Audits

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

5.2.5.2 Performance Evaluations

UC Davis and RTI participated in the 2023 Mega PE interlaboratory comparison test for total mass by gravimetric weighing. Results were comparable to the other four laboratories that participated. The report can be accessed here, https://www.epa.gov/system/files/documents/2024-04/2023_megape_report_final.pdf.

5.2.5.3 Training

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

5.2.5.4 Accreditations

There are no accreditations for analysis of mass gain on aerosol filters by gravimetric measurement.

5.3 RTI Ion Chromatography Laboratory

The RTI Ion Chromatography Laboratory, as a subcontractor to UC Davis, received and analyzed extracts from nylon filters for batches 99 through 23-12, covering the sampling period January 1, 2023 through December 31, 2023. Routine analysis of these samples was performed March 17, 2023 through March 05, 2024. Both routine analysis and reanalysis was performed March 17, 2023 through April 11, 2024. 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 5-4 details the analysis dates for each batch of data, including both routine analysis and reanalysis.

Table 5-4: 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 (2023)	Analysis Batch #	IC Analysis Dates
January	99	3/17/2023 - 5/22/2023
February	100	4/14/2023 - 6/15/2023
March	101	5/19/2023 – 7/25/2023
April	102	6/23/2023 – 8/29/2023
May	103 / 23-05	7/19/2023 – 9/27/2023
June	104 / 23-06	8/24/2023 – 10/27/2023
July	23-07	9/25/2023 – 12-07-2023
August	23-08	10/16/2023 – 01/19/2024
September	23-09	11/09/2023 – 1/19/2024
October	23-10	12/14/2023 – 2/12/2024
November	23-11	1/12/2024 – 3/1106/2024
December	23-12	2/08/2024 – 4/11/2024

5.3.1 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 5-5. 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 5-5: RTI quality control measures for ion (anion and cation) analysis by ion chromatography.

Activity	Frequency	Acceptance Criteria	Corrective Action
Calibration regression	Daily	$R^2 \geq 0.999$	Investigate; repeat calibration
Continuing calibration verification (CCV) check standard; RTI dilution of a commercially prepared, NIST-traceable QC sample	Daily, immediately after calibration and at every 10 samples	Measured concentrations < 0.050 ppm: within 35% of known values. Measured concentrations >0.050 ppm: within 10% of known values.	Investigate; reanalyze samples
Duplicate sample	3 per set of 50 samples	Relative % Difference = 10% at 10x MDL Relative % Difference = 200% at MDL	Investigate; reanalyze
Spiked sample extract	2 per set of 50 samples	Recoveries within 90 to 110% of target values	Investigate; reanalyze
Reagent blanks	One reagent blank per reagent used (DI H_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

5.3.2 Summary of QC Results

RTI followed the acceptance criteria stated in Table 5-5. 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.

5.3.2.1 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.

5.3.2.2 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 5-6 and 5-7 lists the concentrations.

Table 5-6: Target concentrations of anion CCV check standards for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023).

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

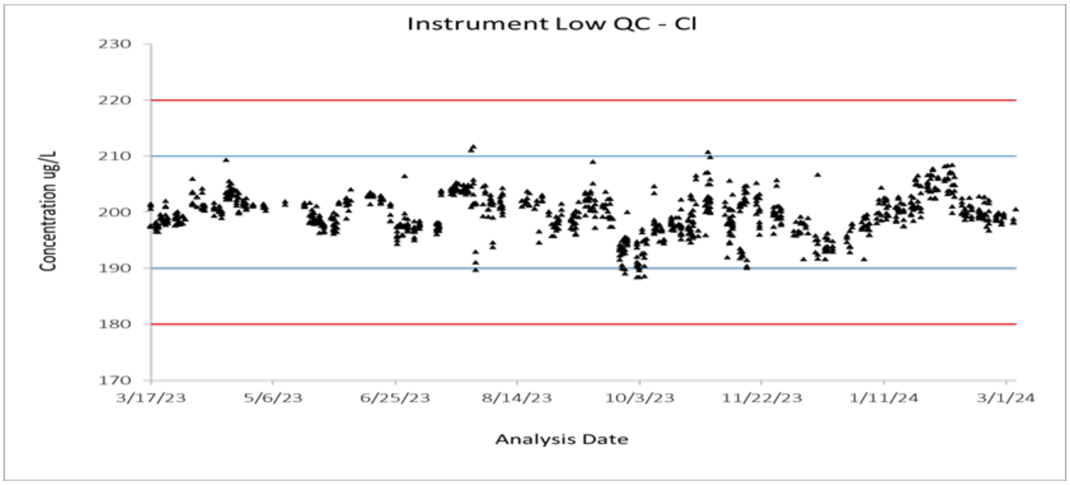
Table 5-7: Target concentrations of cation CCV check standards for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023).

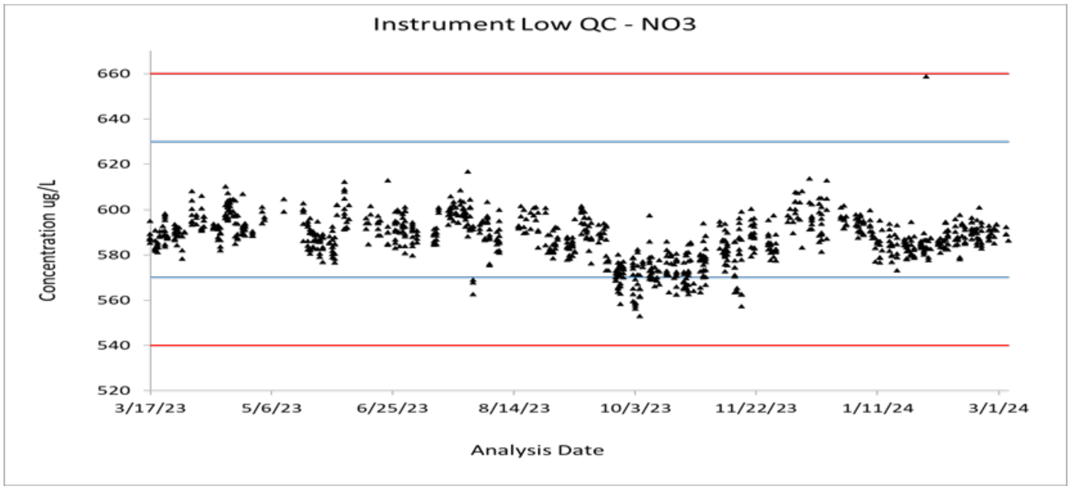
QC Sample	Na^+ (ppb)	NH_4^+ (ppb)	K^+ (ppb)
Instrument Low QC	20	20	20
Instrument Medium QC	250	250	250
Instrument Medium-High QC	750	750	750
Instrument High QC	2000	2000	2000

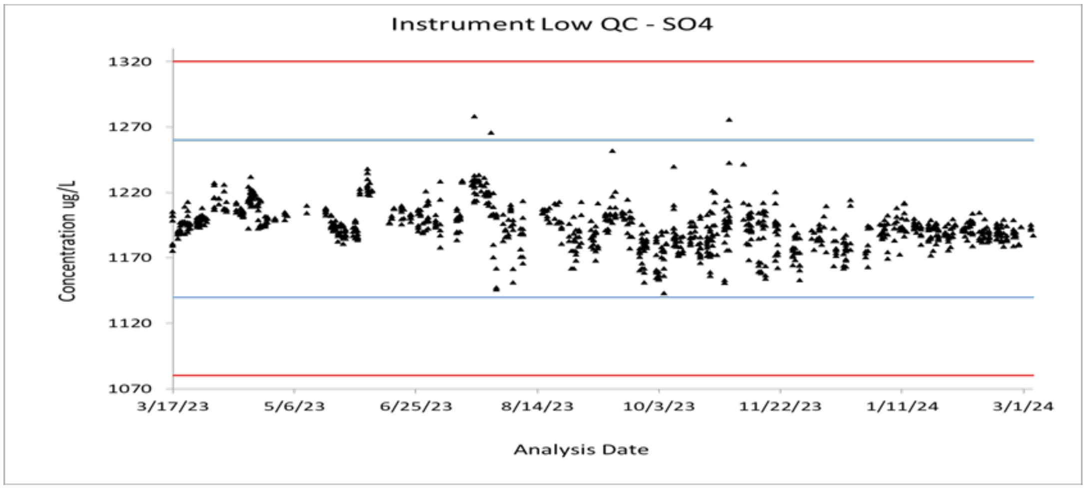
At least two CCV check standards are analyzed immediately after the calibration standards and a single CCV check standard is analyzed after every ten samples. When an instrument CCV check standard fails the acceptance criteria by falling outside of the control limits, impacted samples are reanalyzed. 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 5-6) and cation (Figure 5-7) 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.

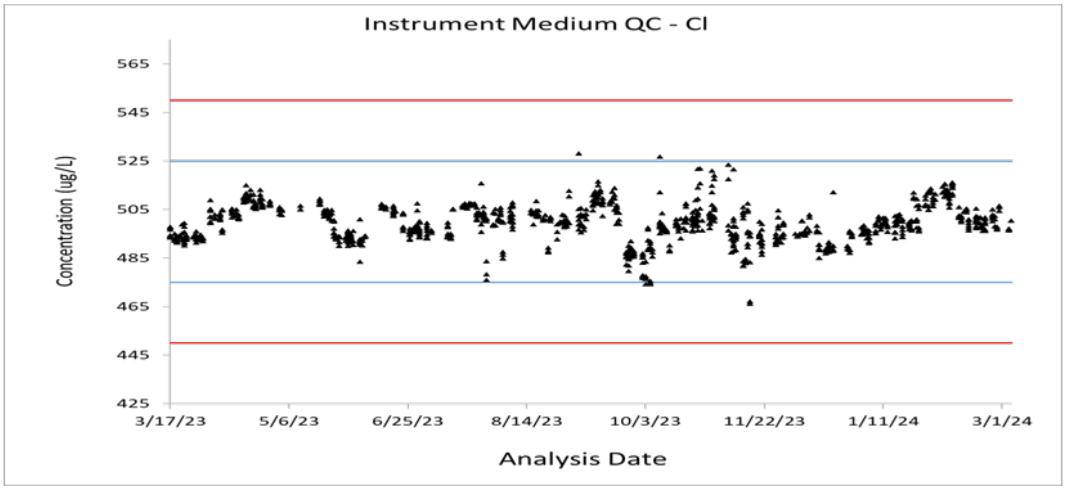
In the below control chart figures, red lines show upper and lower control limits set at ± 10% of the nominal concentrations for the low, medium, medium-high, and high standards. Blue lines show upper and lower warning limits.

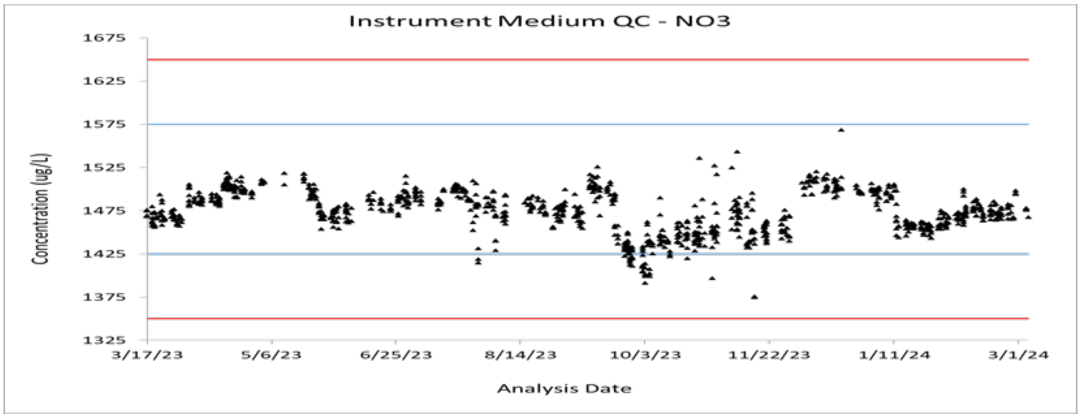
Figure 5-6: Control charts for anion CCV check standards at low, medium, medium-high, and high concentrations measured in units of µg/L (see Table 5-6) for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023).








Instrument Medium QC - Cl
Concentration (ug/L)
565
545
525
505
485
465
445
425
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Instrument Medium QC - NO3
Concentration (ug/L)
1675
1625
1575
1525
1475
1425
1375
1325
3/17/23
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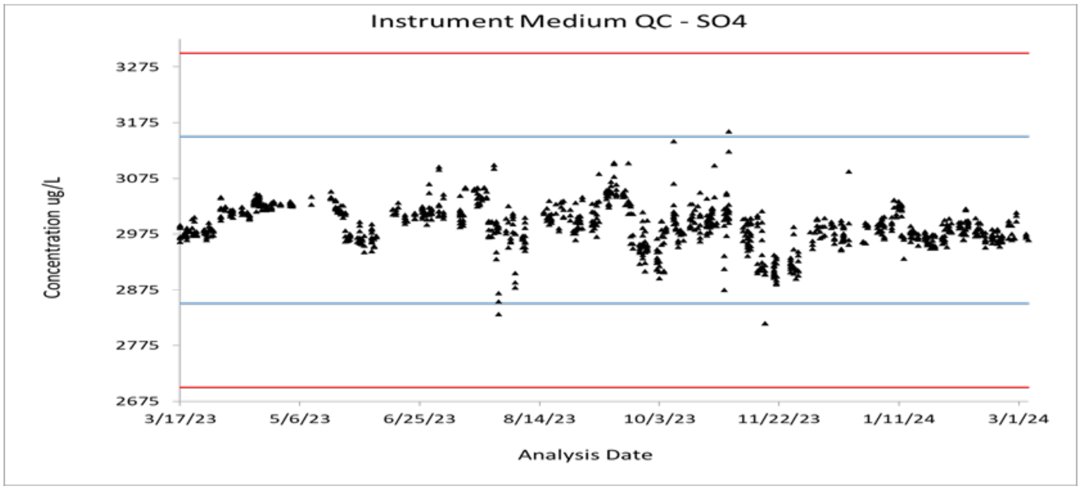
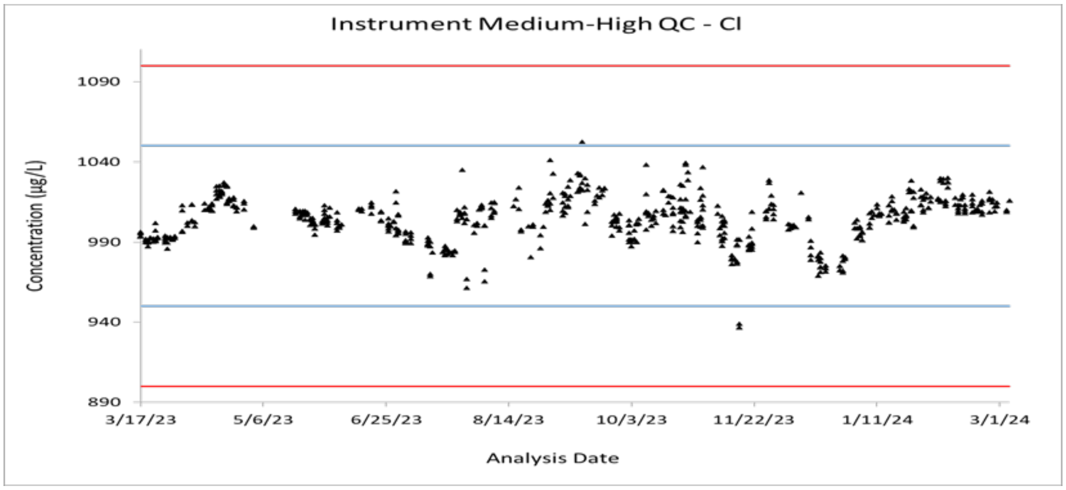
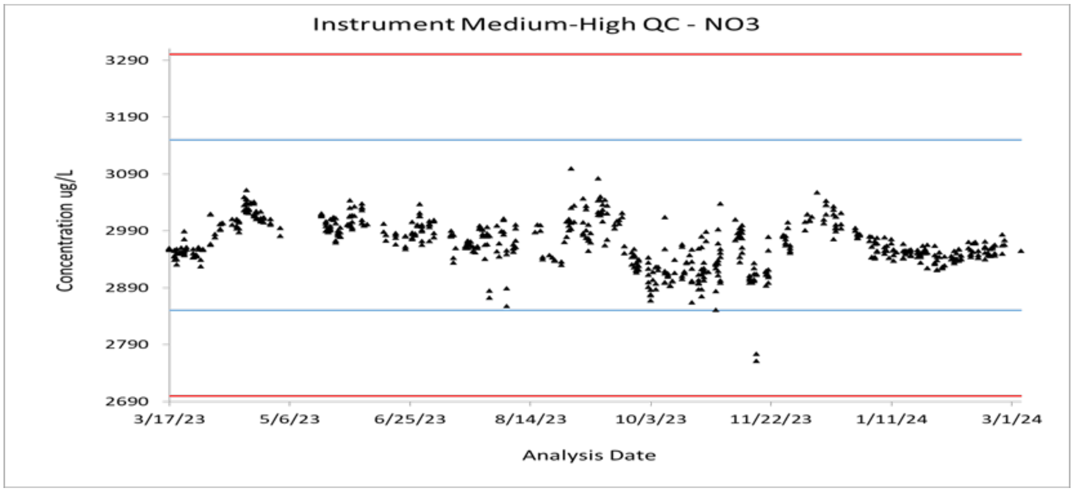
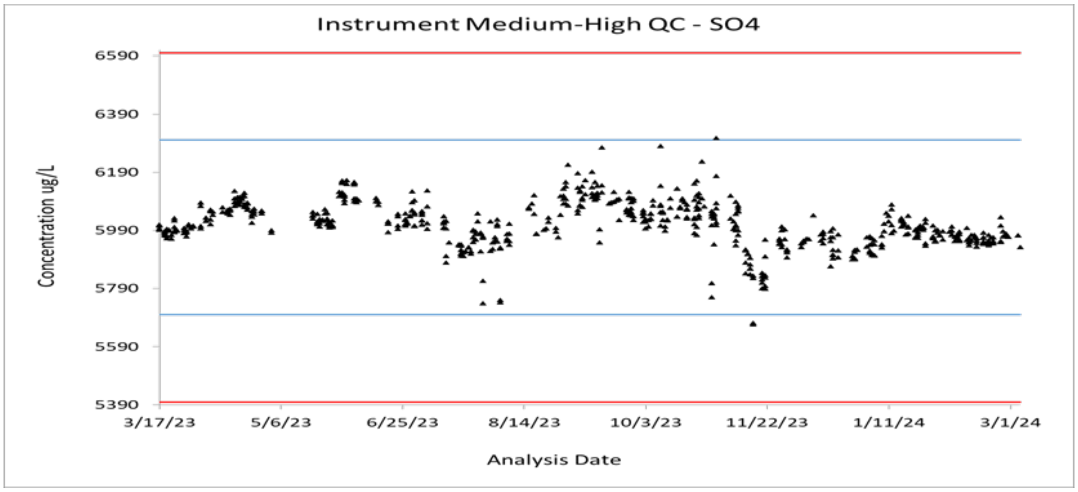
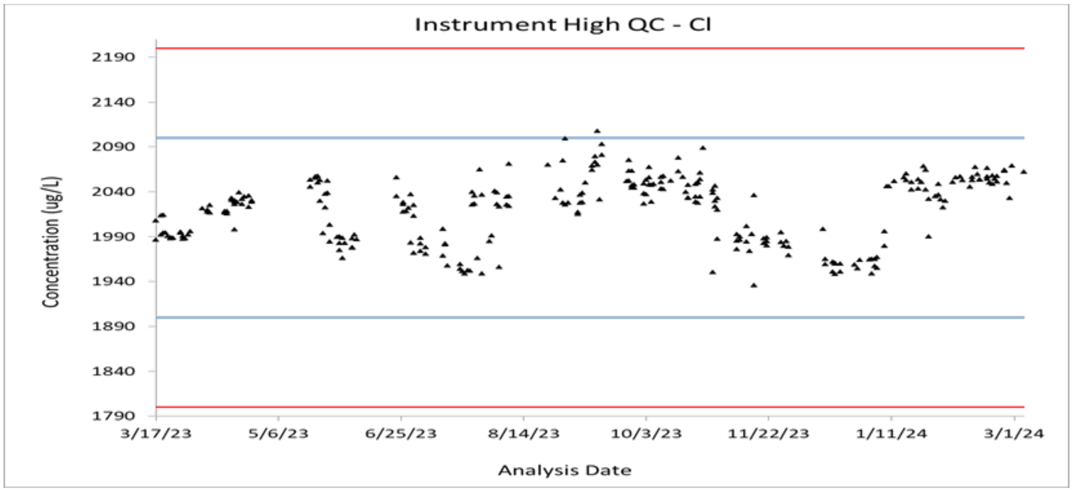
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

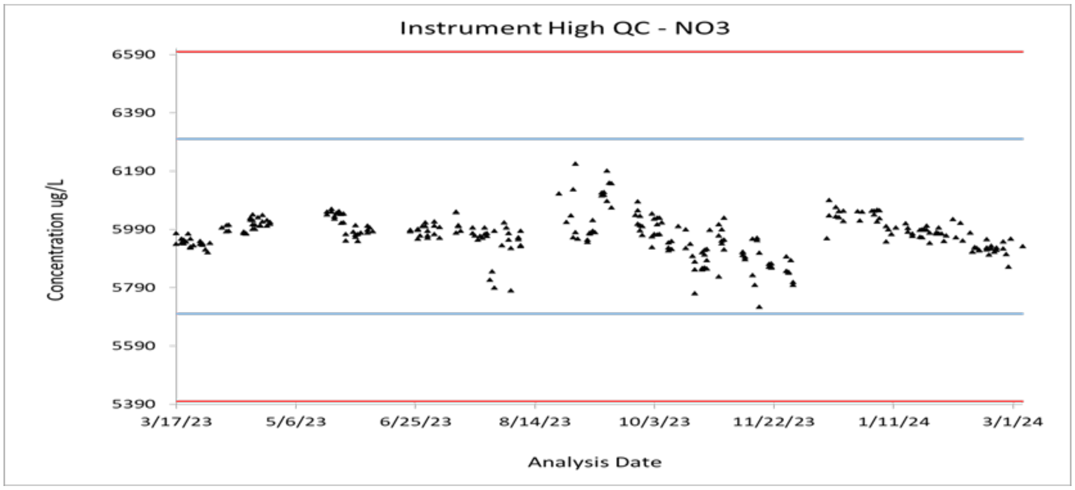

Instrument Medium QC - SO4
Concentration ug/L
3275
3175
3075
2975
2875
2775
2675
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

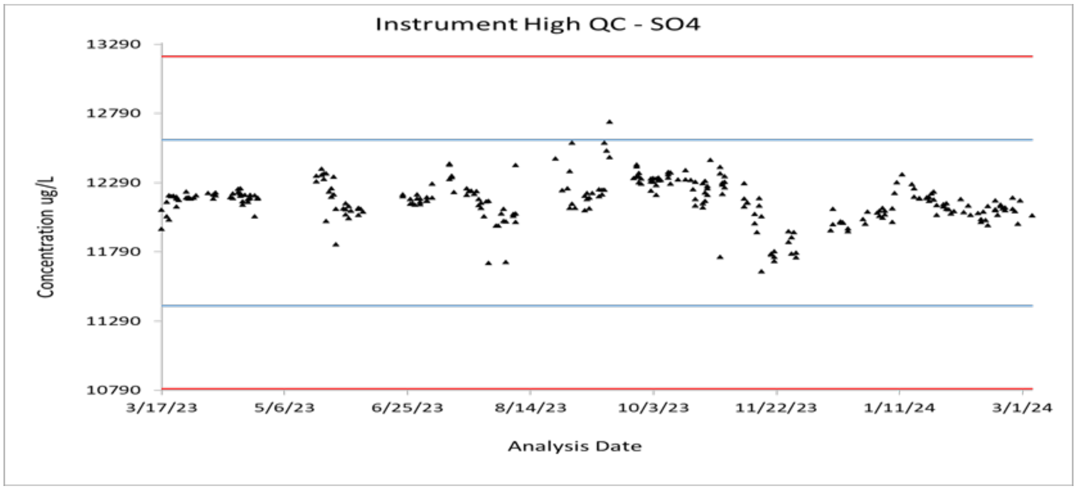

Instrument Medium-High QC - Cl
Concentration (µg/L)
1090
1040
990
940
890
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Instrument Medium-High QC - NO3
Concentration ug/L
3290
3190
3090
2990
2890
2790
2690
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Instrument Medium-High QC - SO4
Concentration ug/L
6590
6390
6190
5990
5790
5590
5390
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

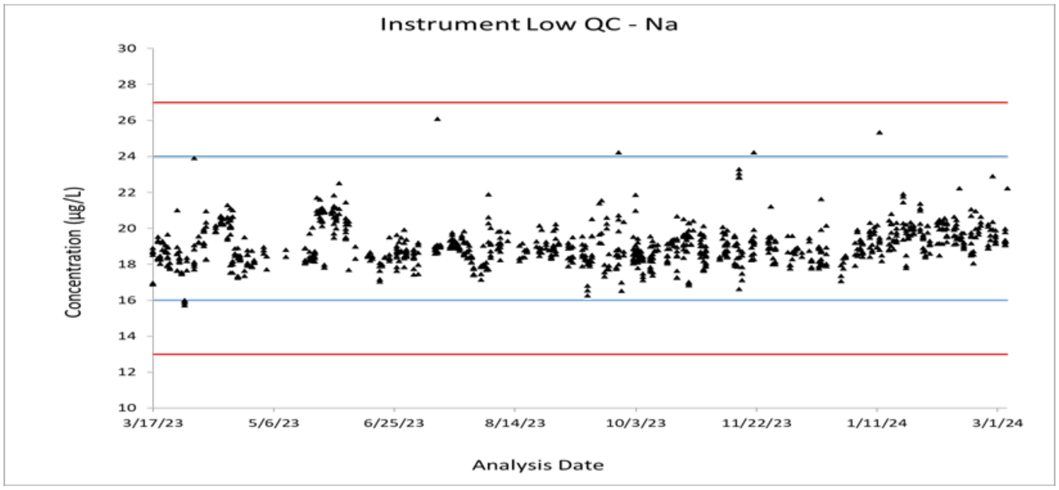


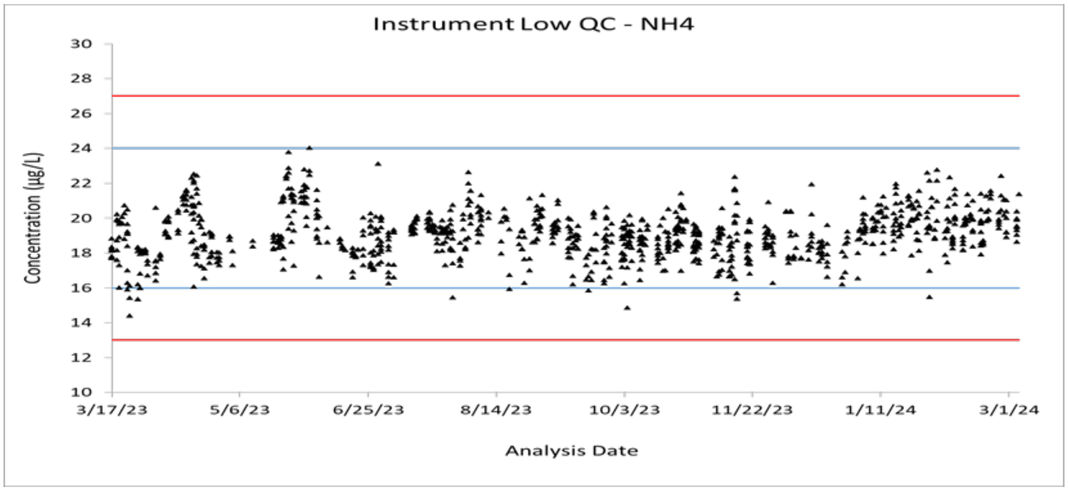


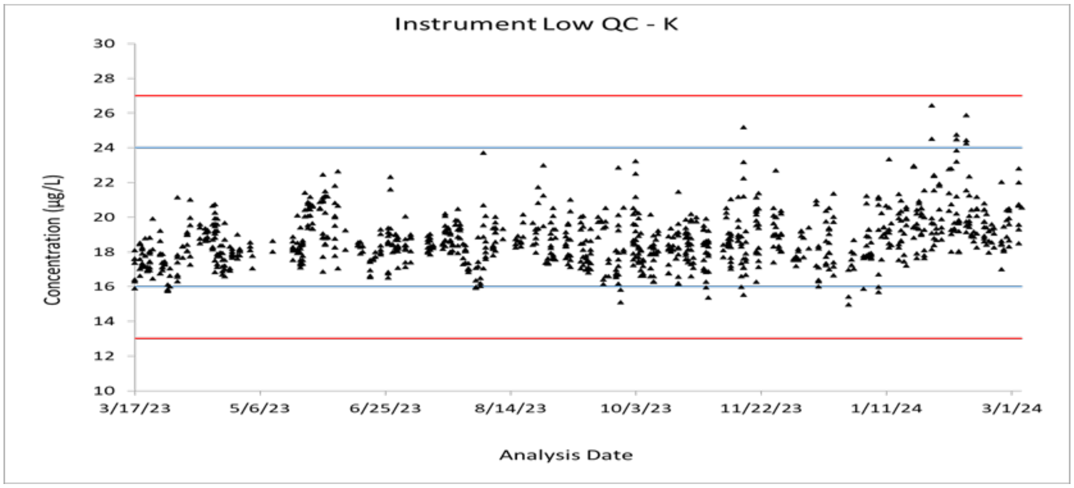


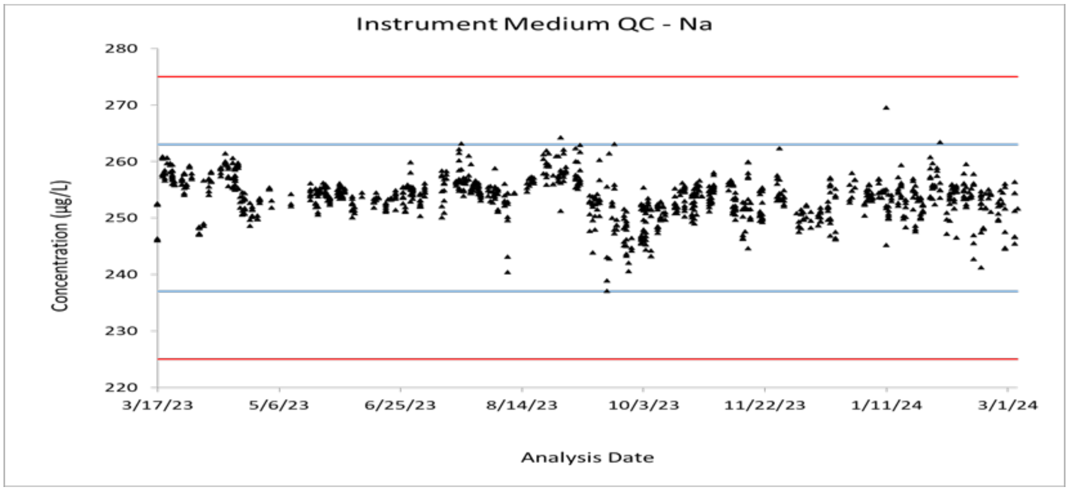
In the below control chart figures, red lines show upper and lower control limits set at ± 35% of the nominal concentrations for the low standards and ± 10% of the nominal concentrations for the medium, medium-high, and high standards. Blue lines show upper and lower warning limits.

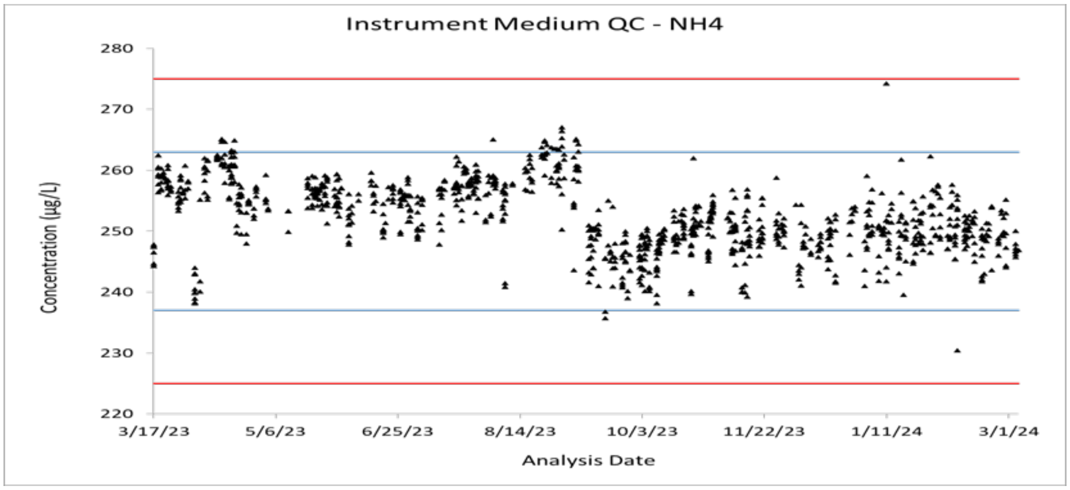
Figure 5-7: Control charts for cation CCV check standards at low, medium, medium-high, and high concentrations measured in units of µg/L (see Table 5-7) for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023).

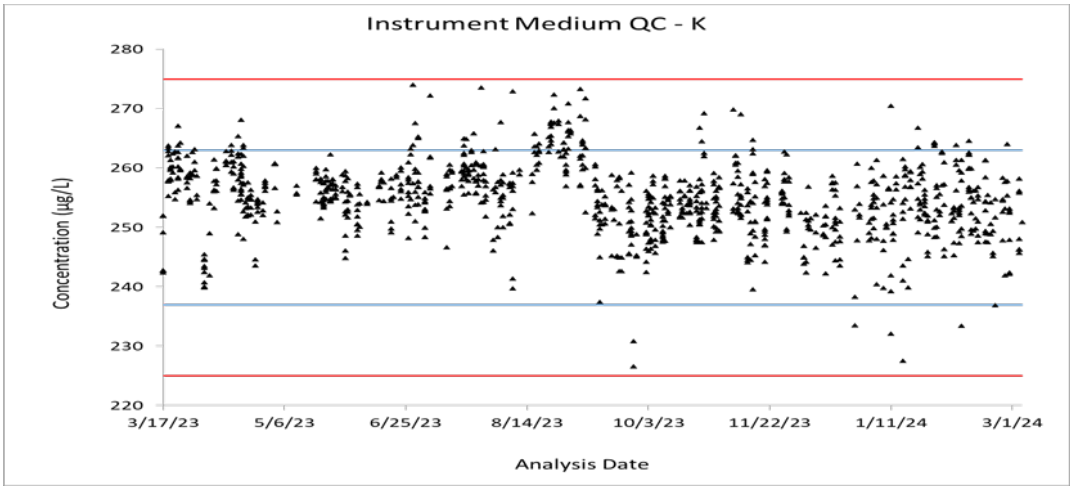







Instrument Medium QC - Na
280
270
260
250
240
230
220
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Concentration (µg/L)
Analysis Date


Instrument Medium QC - NH4
280
270
260
250
240
230
220
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Concentration (µg/L)
Analysis Date


Instrument Medium QC - K
280
270
260
250
240
230
220
3/17/23
5/6/23
6/25/23
8/14/23
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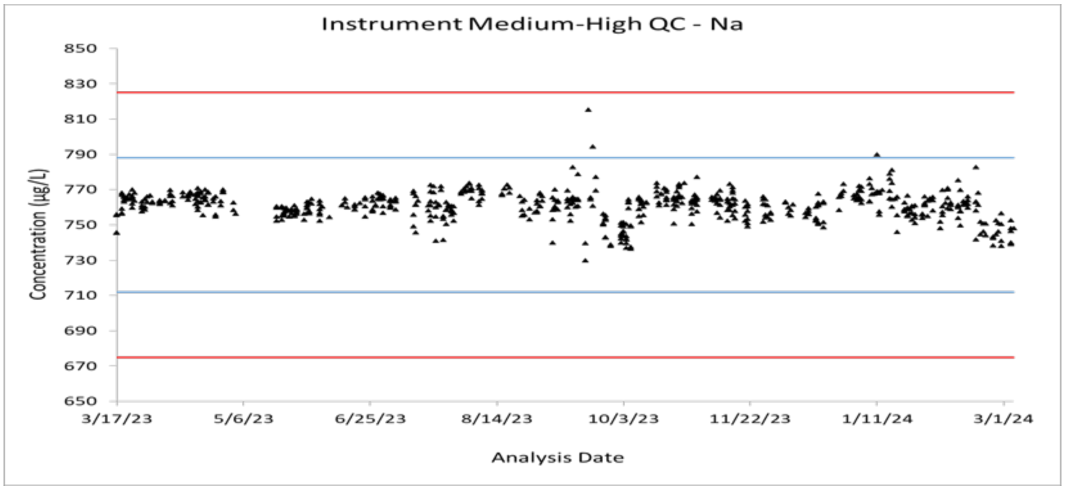
3/1/24
Concentration (µg/L)
Analysis Date


Instrument Medium-High QC - Na
Concentration (µg/L)
850
830
810
790
770
750
730
710
690
670
650
3/17/23
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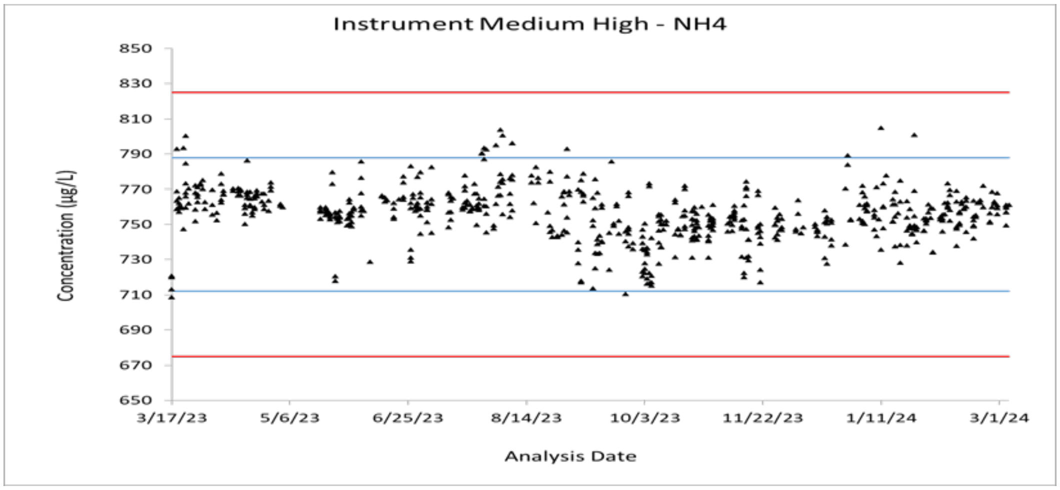
1/11/24
3/1/24
Analysis Date


Instrument Medium High - NH4
Concentration (µg/L)
850
830
810
790
770
750
730
710
690
670
650
3/17/23
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6/25/23
8/14/23
10/3/23
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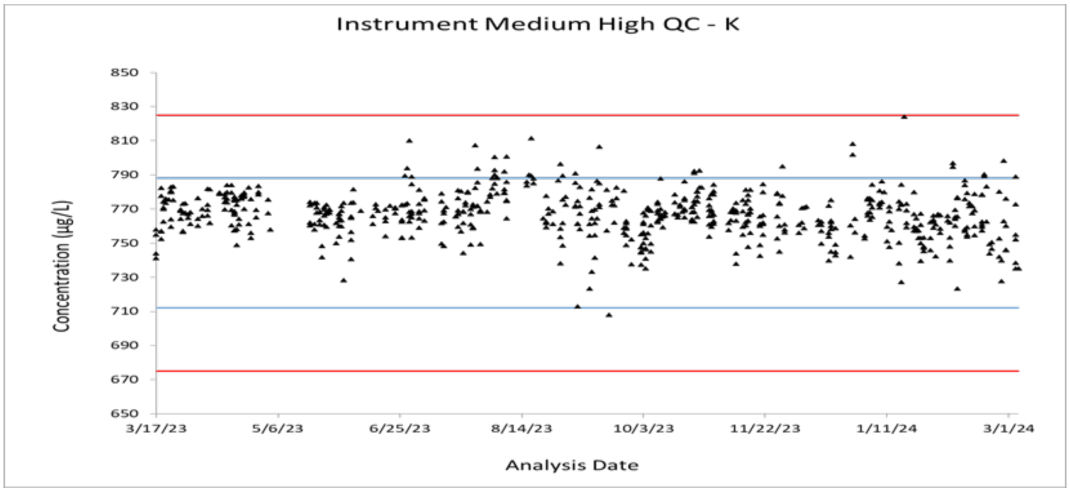
1/11/24
3/1/24
Analysis Date


Instrument Medium High QC - K
Concentration (µg/L)
850
830
810
790
770
750
730
710
690
670
650
3/17/23
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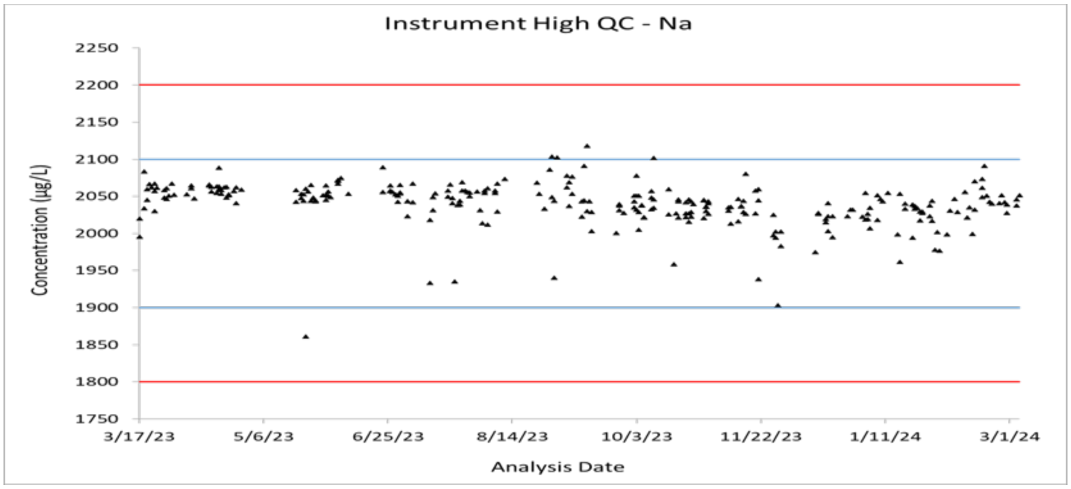
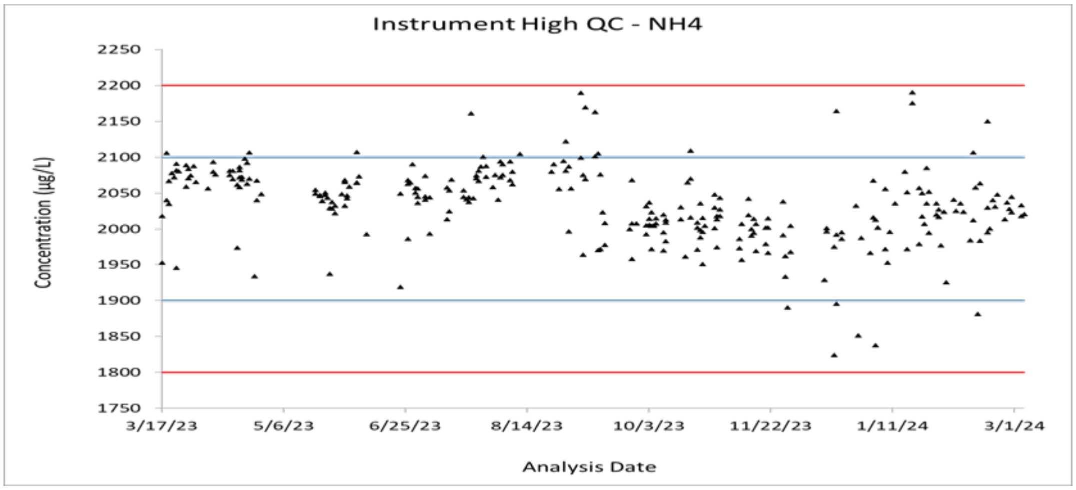
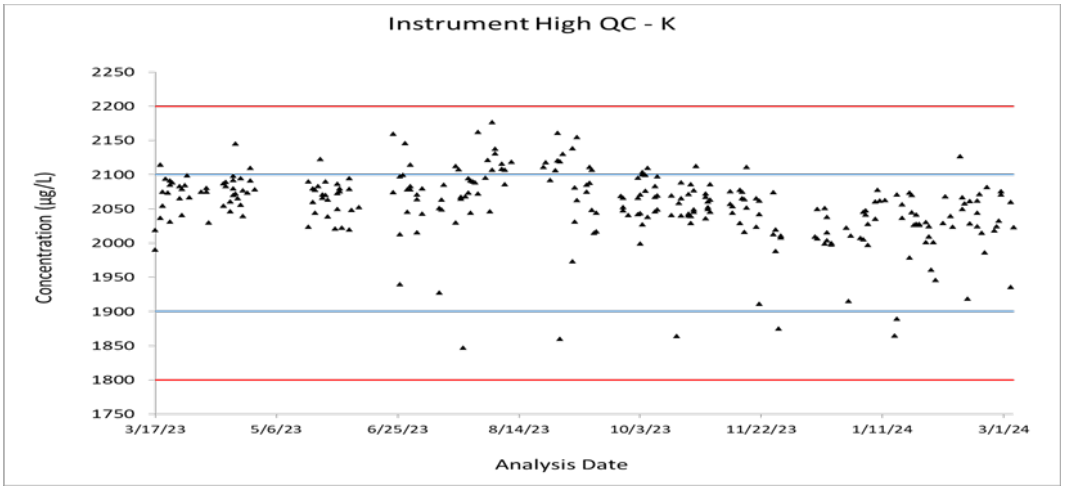
1/11/24
3/1/24
Analysis Date



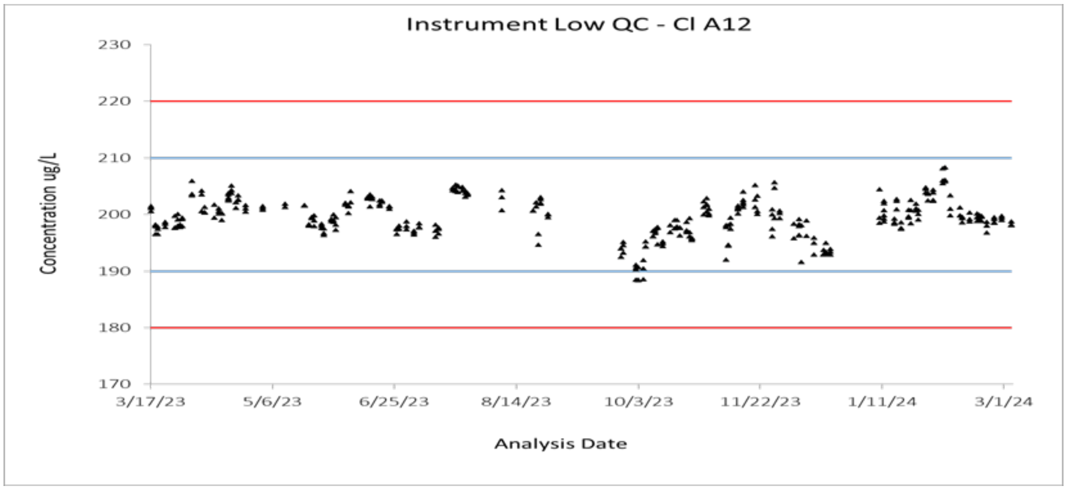


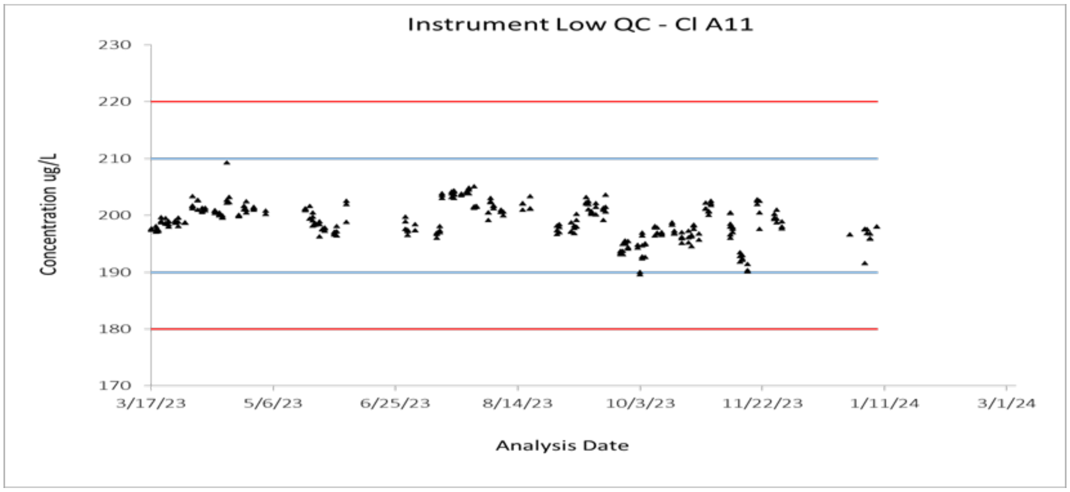


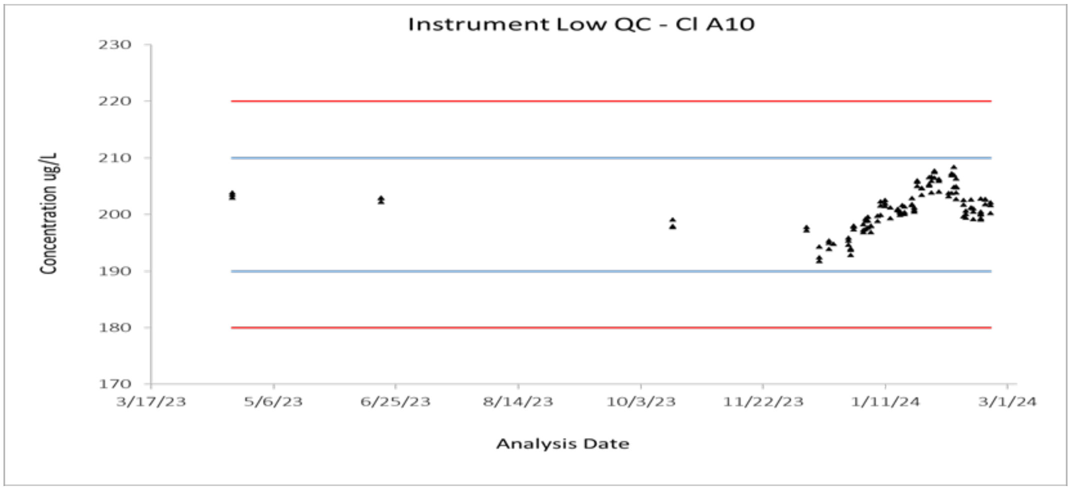
To demonstrate instrument-to-instrument performance, control charts for the lowest CCV check standards were generated where instruments A11, A12, A9, A10, and A8 are compared for anions (Figure 5-8) and instruments C9, C10, and C3 are compared for cations (Figure 5-9). The control charts illustrate consistent performance between instruments.

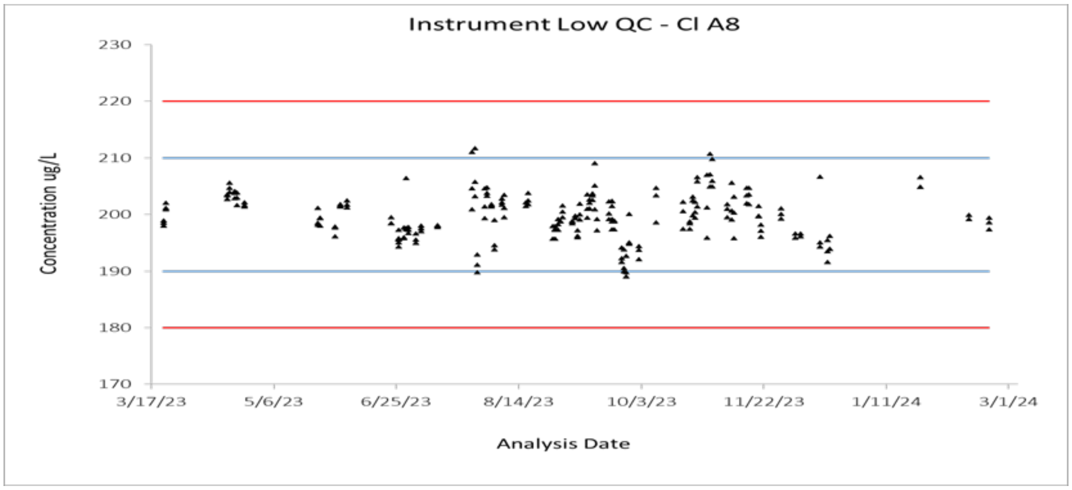
In the below control chart figures, red lines show upper and lower control limits set at ± 10% of the nominal concentrations. Blue lines show upper and lower warning limits.

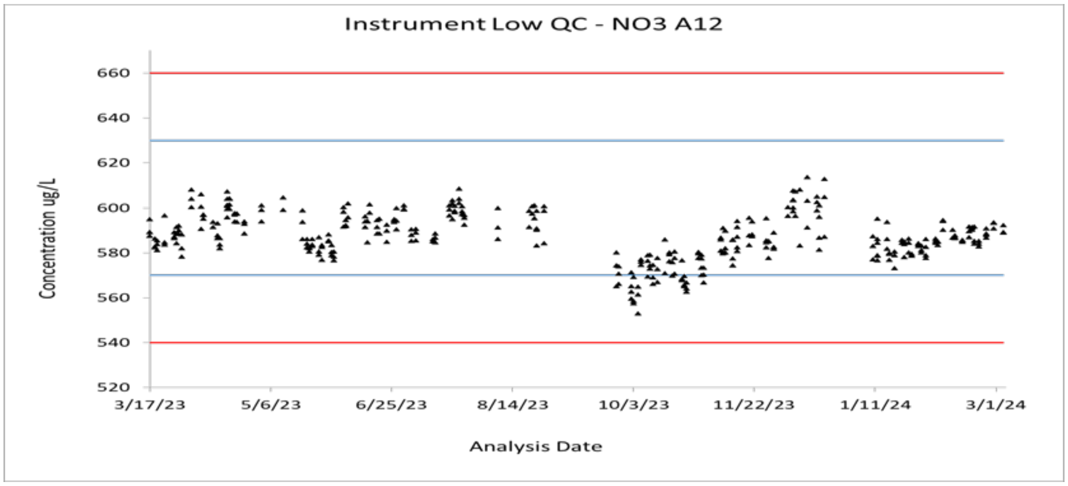
Figure 5-8: Control charts for anion CCV check standards showing comparability between instruments (A11 and A12, Thermo Dionex Aquion systems; A10, and A8 Thermo Dionex ICS-3000 systems) at low concentrations (see Table 4.1-3) for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023). Note that A10 was not utilized as often for CSN sample analysis as this system is part of a dual system configured for anion only analysis. It is more efficient to combine single anion/cation systems for CSN analysis.

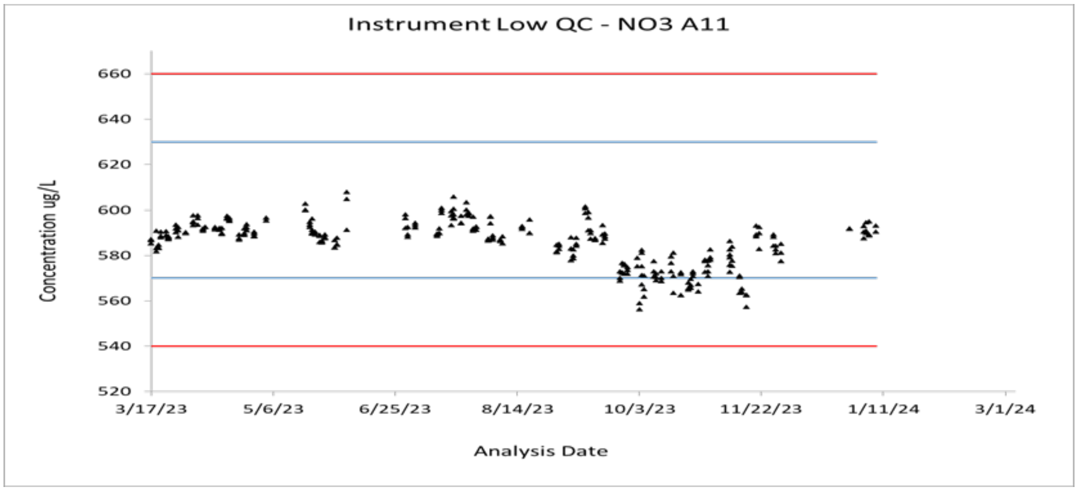


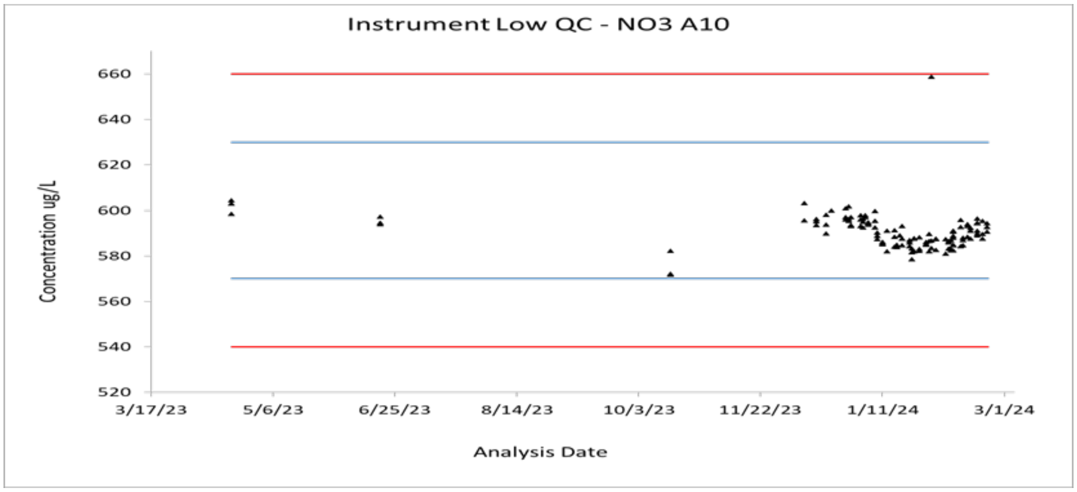


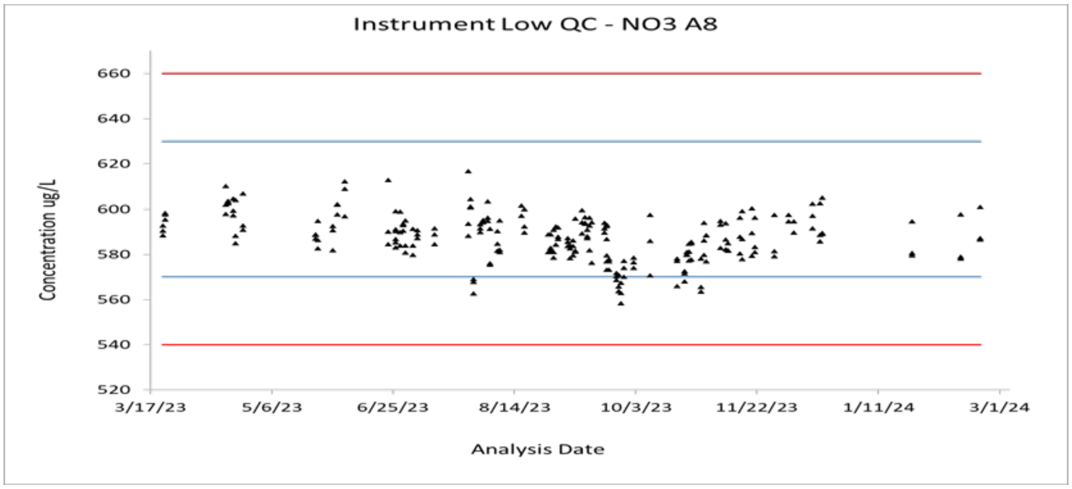

Instrument Low QC - Cl A10
Concentration ug/L
230
220
210
200
190
180
170
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

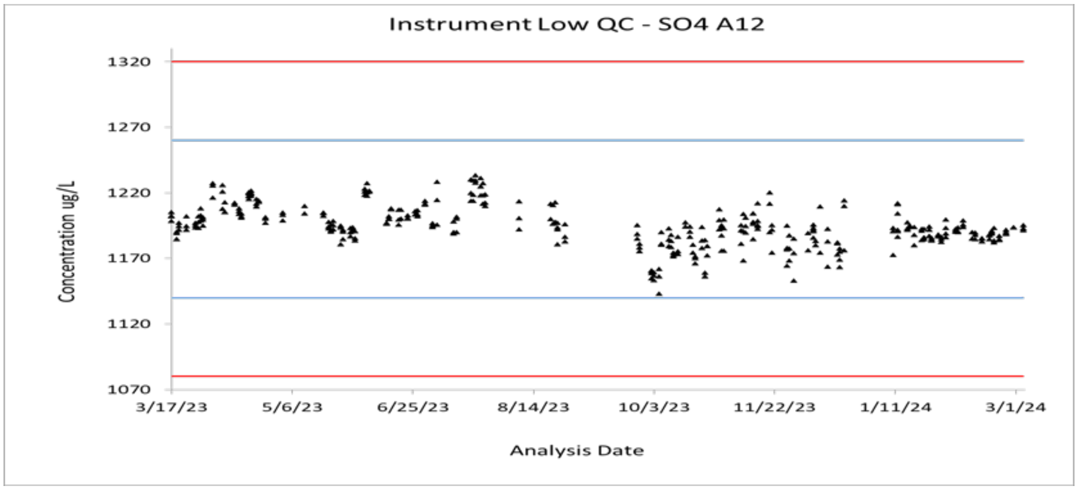

Instrument Low QC - Cl A8
Concentration ug/L
230
220
210
200
190
180
170
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

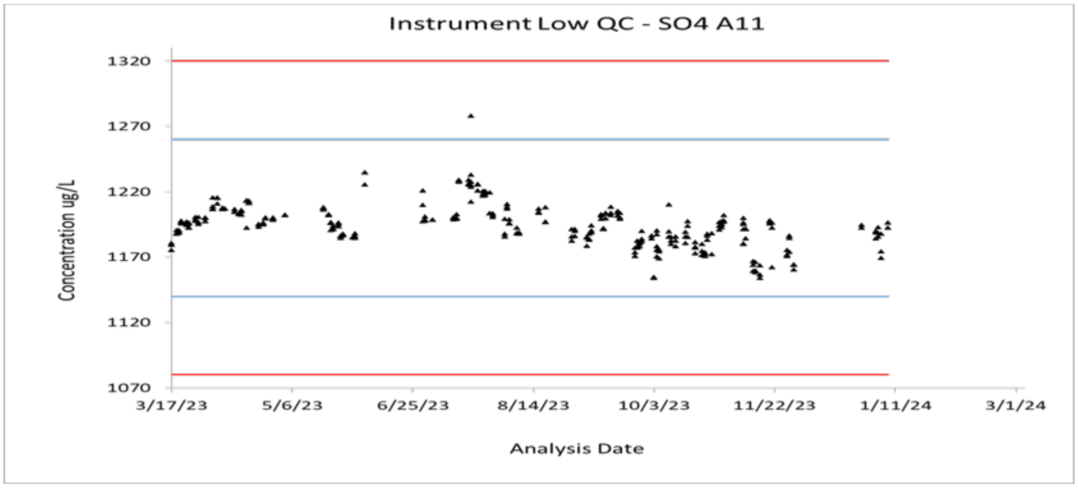

Instrument Low QC - NO3 A12
Concentration ug/L
660
640
620
600
580
560
540
520
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

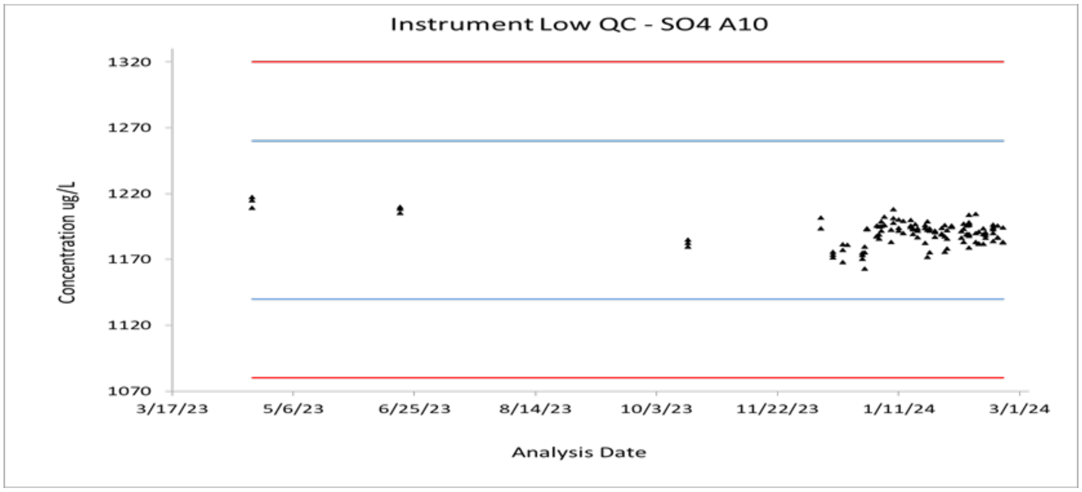

Instrument Low QC - NO3 A11
Concentration ug/L
660
640
620
600
580
560
540
520
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

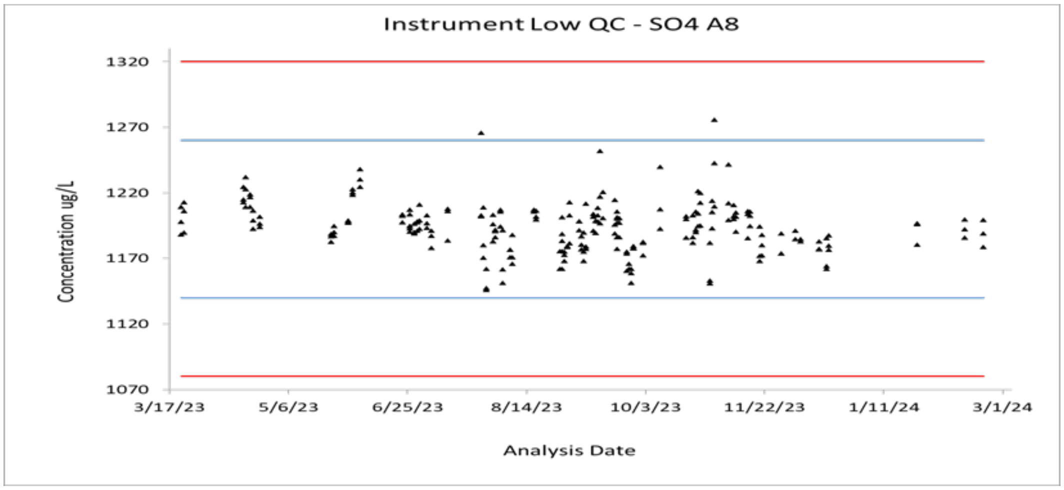

Instrument Low QC - NO3 A10
Concentration ug/L
660
640
620
600
580
560
540
520
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Instrument Low QC - NO3 A8
660
640
620
600
580
560
540
520
Concentration ug/L
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Instrument Low QC - SO4 A12
1320
1270
1220
1170
1120
1070
Concentration ug/L
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

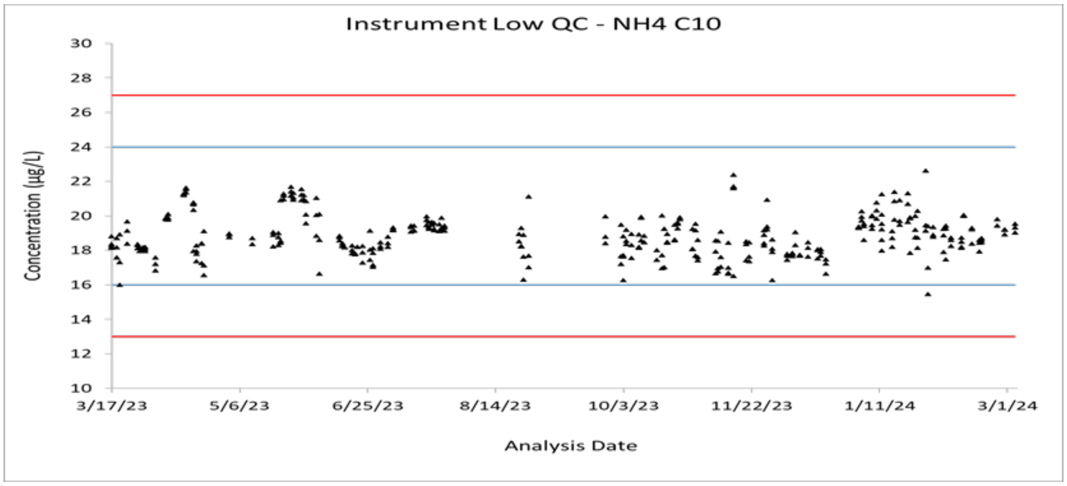

Instrument Low QC - SO4 A11
1320
1270
1220
1170
1120
1070
Concentration ug/L
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

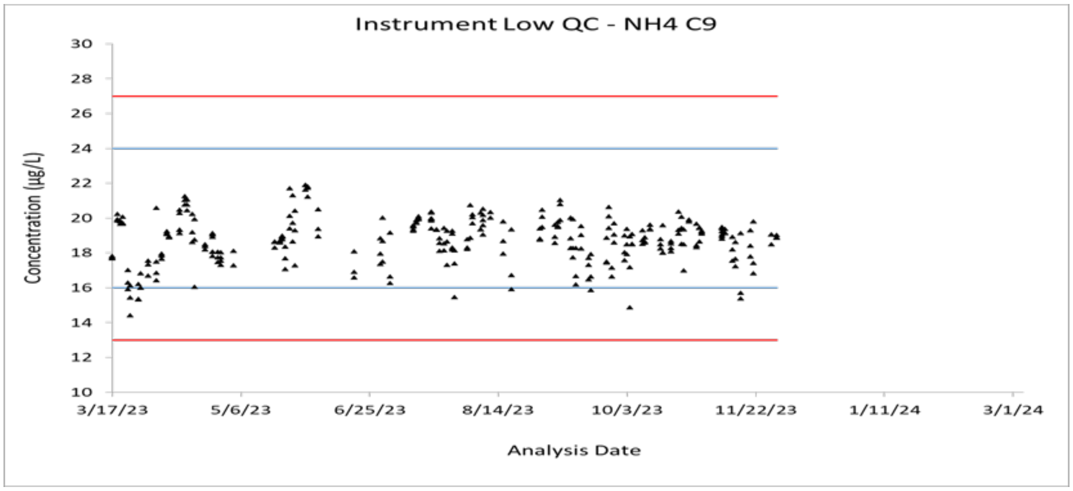


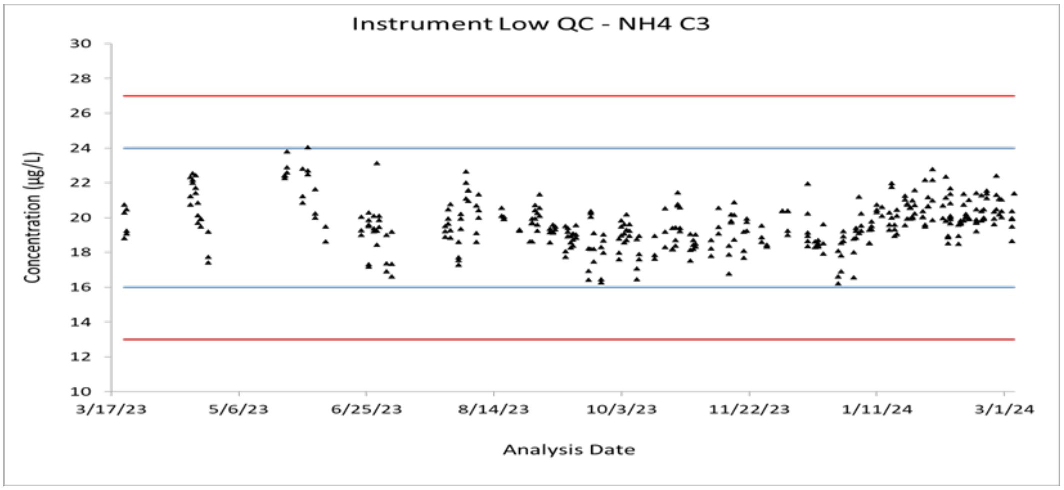


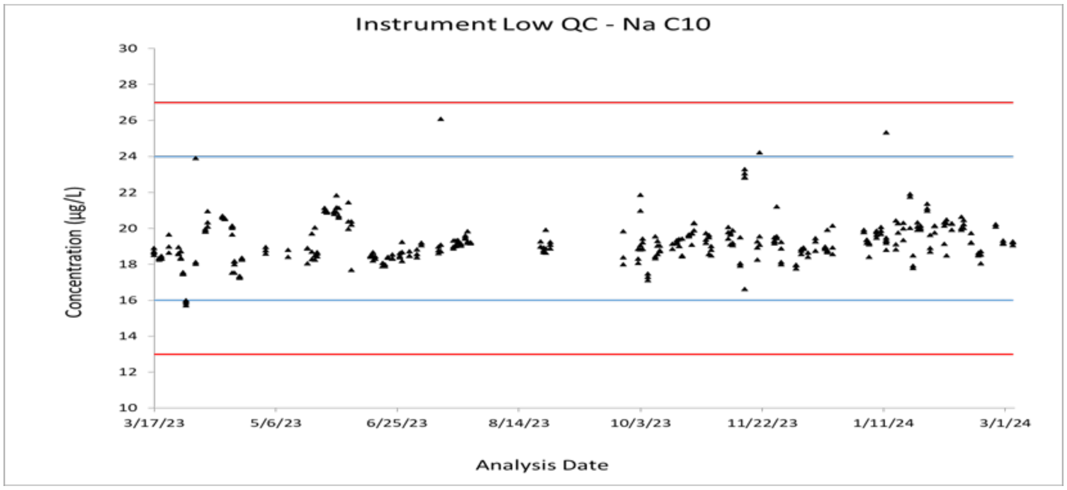
In the following control chart figures, red lines show upper and lower control limits set at ± 35% of the nominal concentrations. Blue lines show upper and lower warning limits.

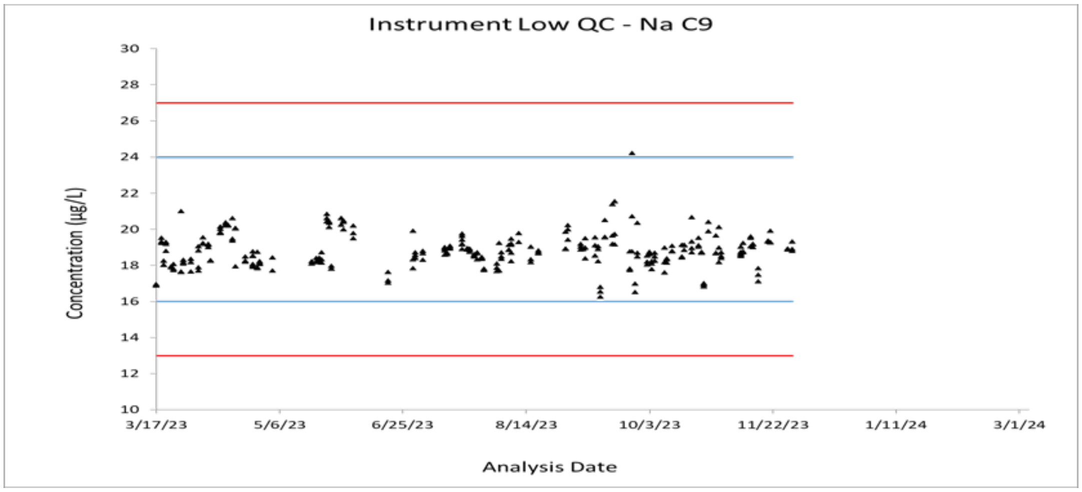
Figure 5-9: Control charts for cation CCV check standards showing comparability between instruments (C9 and C10, Thermo Dionex Aquion systems; C3 Thermo Dionex ICS-2000 systems) at low concentrations (see Table 5-4) for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023). Note that C9 was not utilized from early December through the new calendar year due to a maintenance issue and the unavailability of the spare part needed to repair the system.

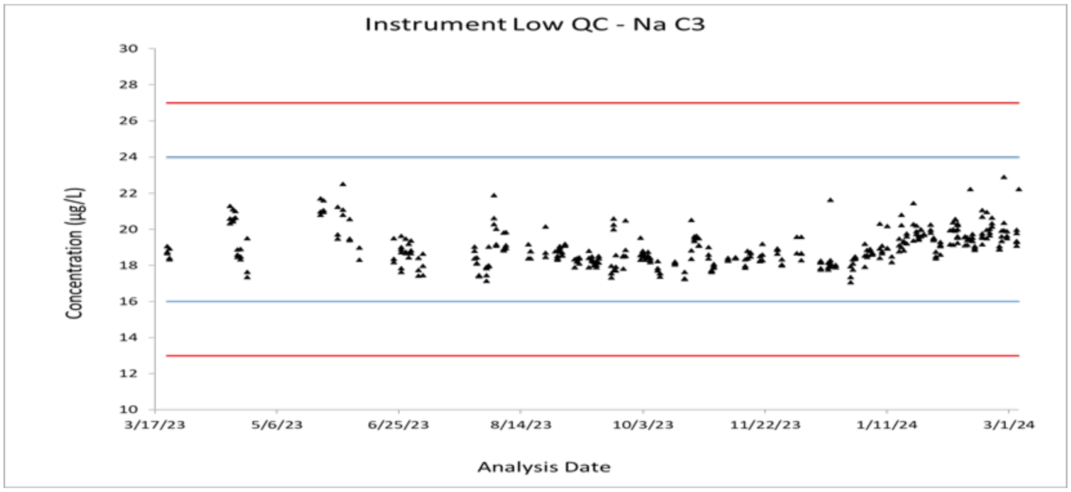


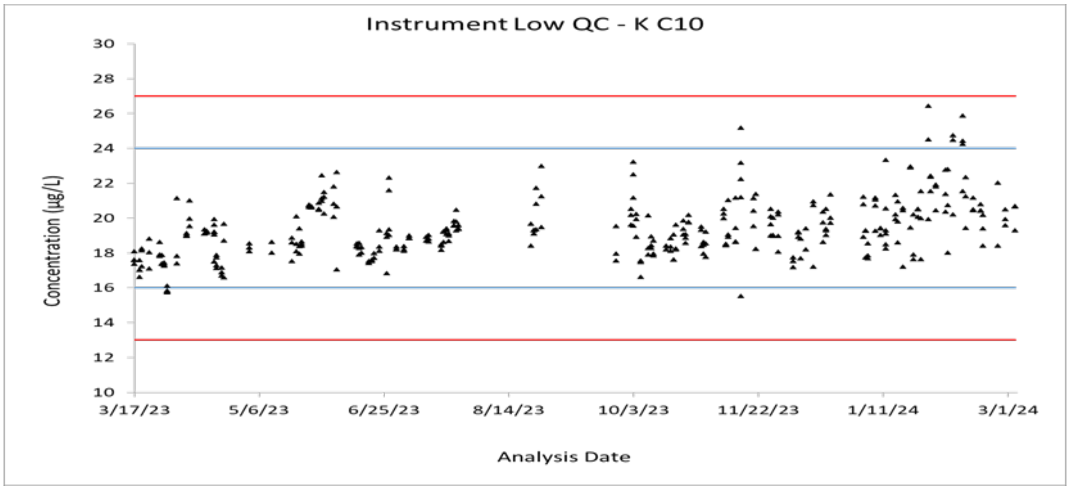


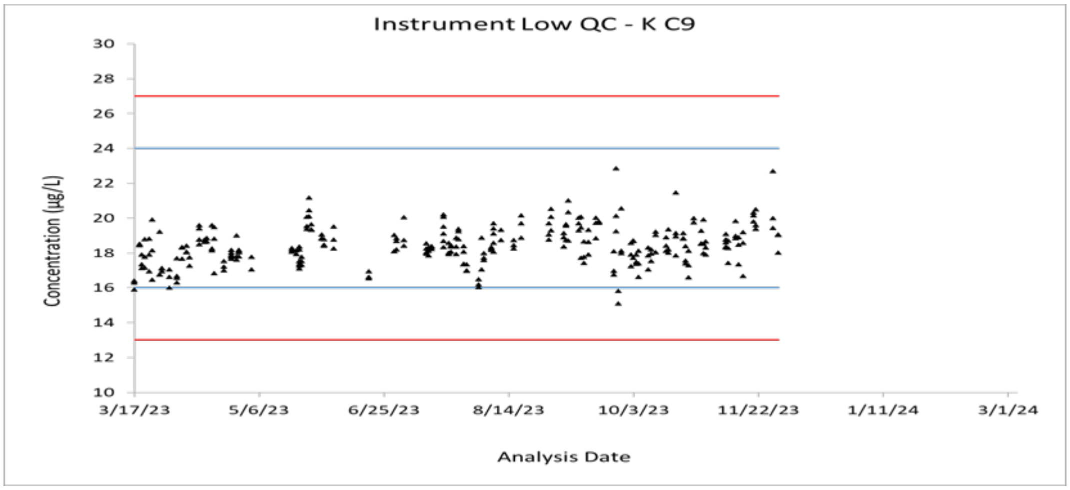


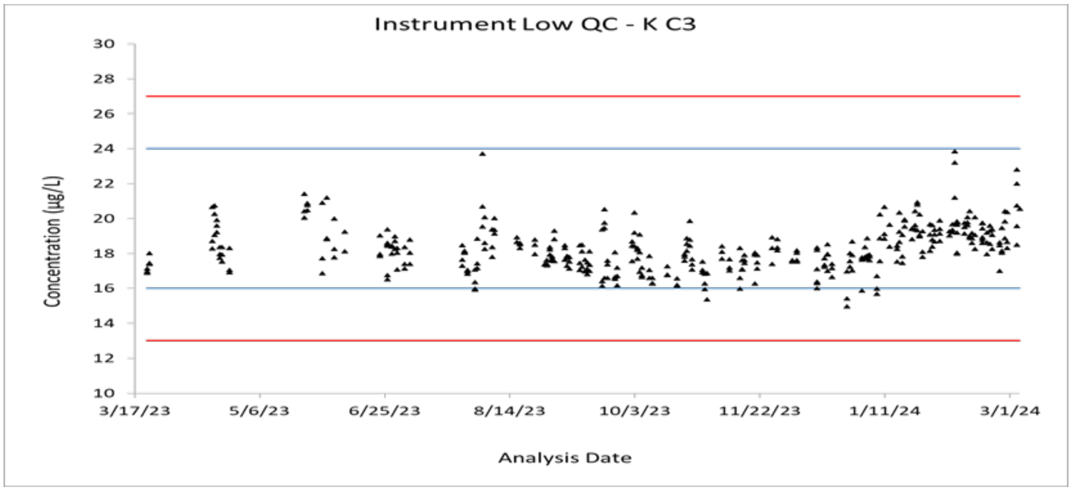

Instrument Low QC - Na C10
Concentration (µg/L)
30
28
26
24
22
20
18
16
14
12
10
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


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


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



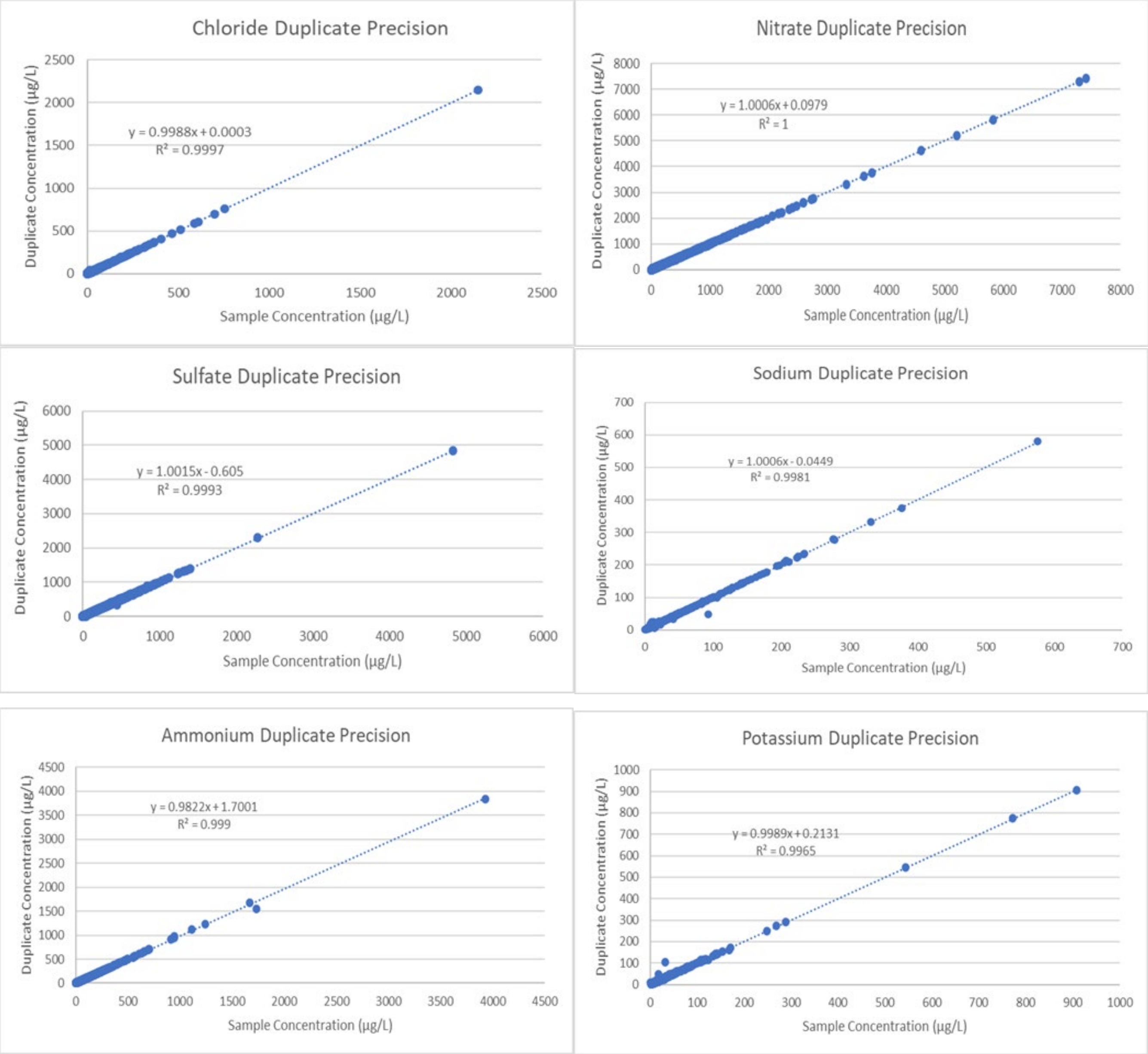




5.3.2.3 Duplicate Samples

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 ± 200% when sample concentrations are at or up to ten times the analytical MDL. During the analysis period when samples collected during 2023 were analyzed (March 17, 2023 through March 05, 2024), there were a total of 891 duplicate samples analyzed for anions (Figure 5-10), there were six cases where the RPD did not meet the acceptance criteria. Also during this analysis period, there were a total of 885 duplicate samples analyzed for cations (Figure 5-10), with four 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 5-10: Ion duplicate analysis results for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023). Cases that did not meet the acceptance criteria, as described in section 5.3.2.3, are included in these figures.

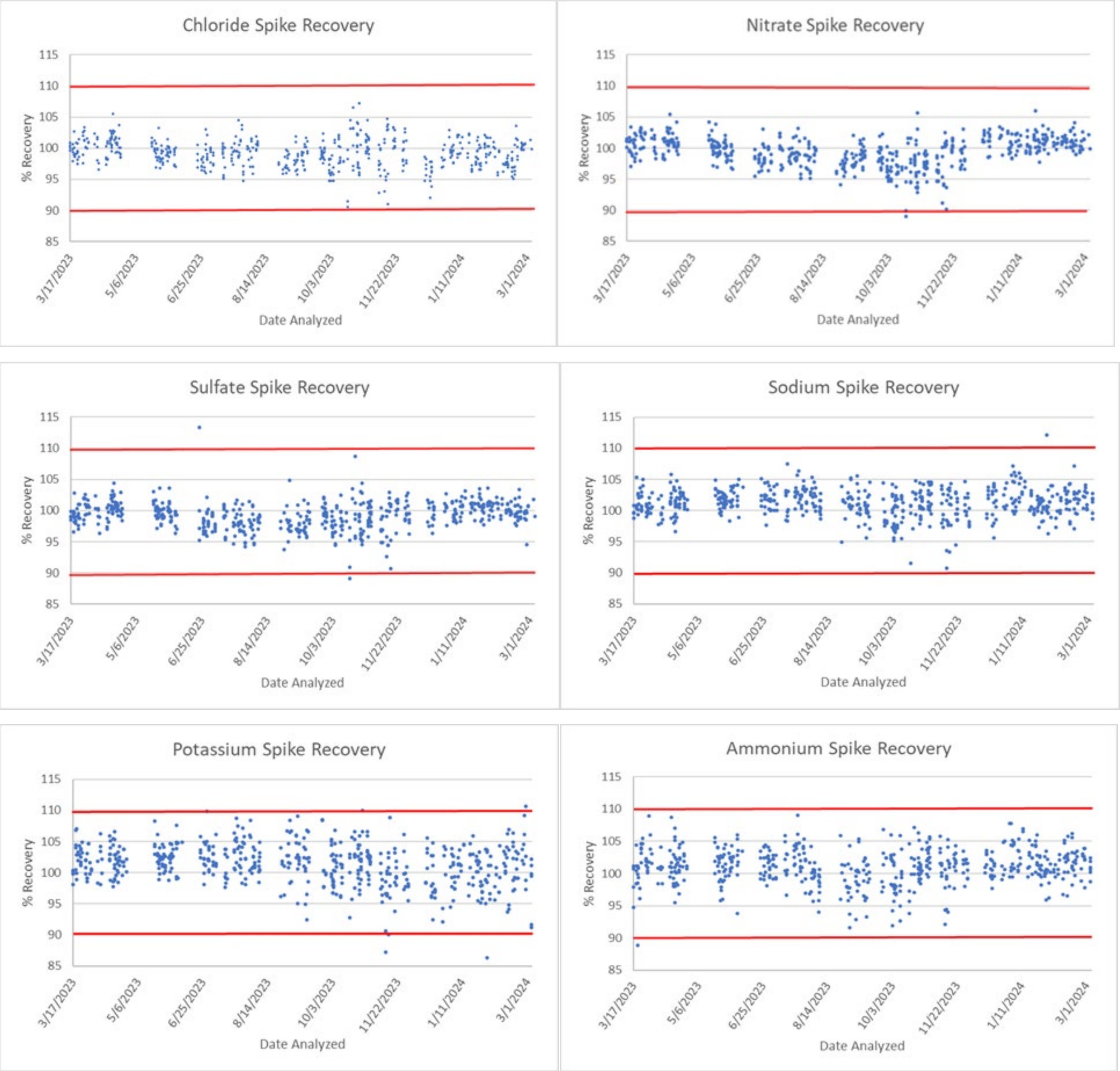


5.3.2.4 Spiked Sample Extracts

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 625 matrix spikes were analyzed for anions. There were seven cases where either chloride, nitrate, or sulfate failed spike recovery criteria (Figure 5-11); samples were reanalyzed for all cases. A total of 623 matrix spikes were analyzed for cations. There were eleven cases where spiked samples failed to meet recovery criteria of 90-100% for either sodium, ammonium, or potassium spiked samples (Figure

5-11); 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 5-11: Time series of recovery (%) for anion and cation of matrix spikes for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023).



5.3.2.5 *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 5-12: Concentrations of anions and cations in DI water blanks for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023). Black line indicates the analytical method detection limit.

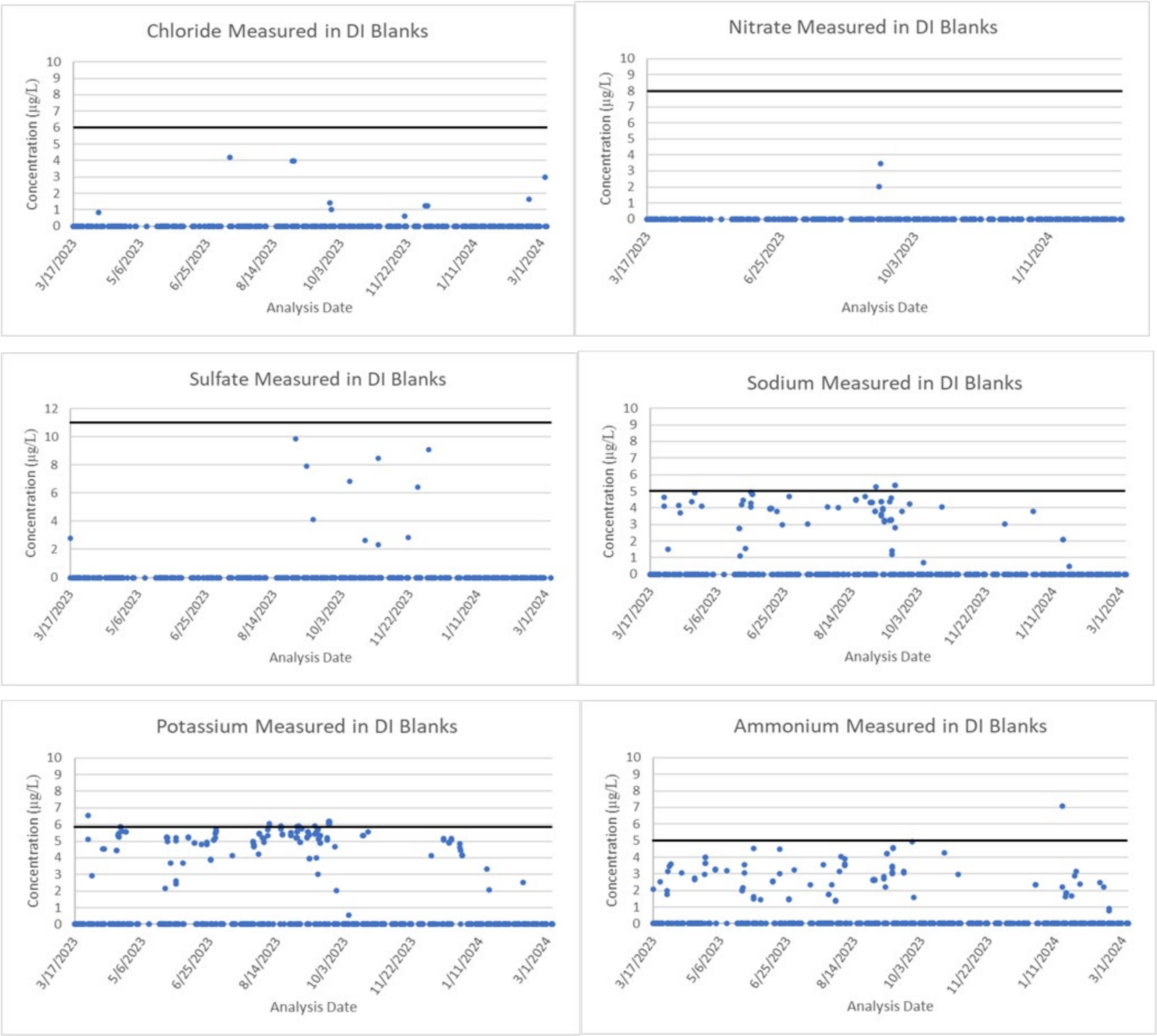
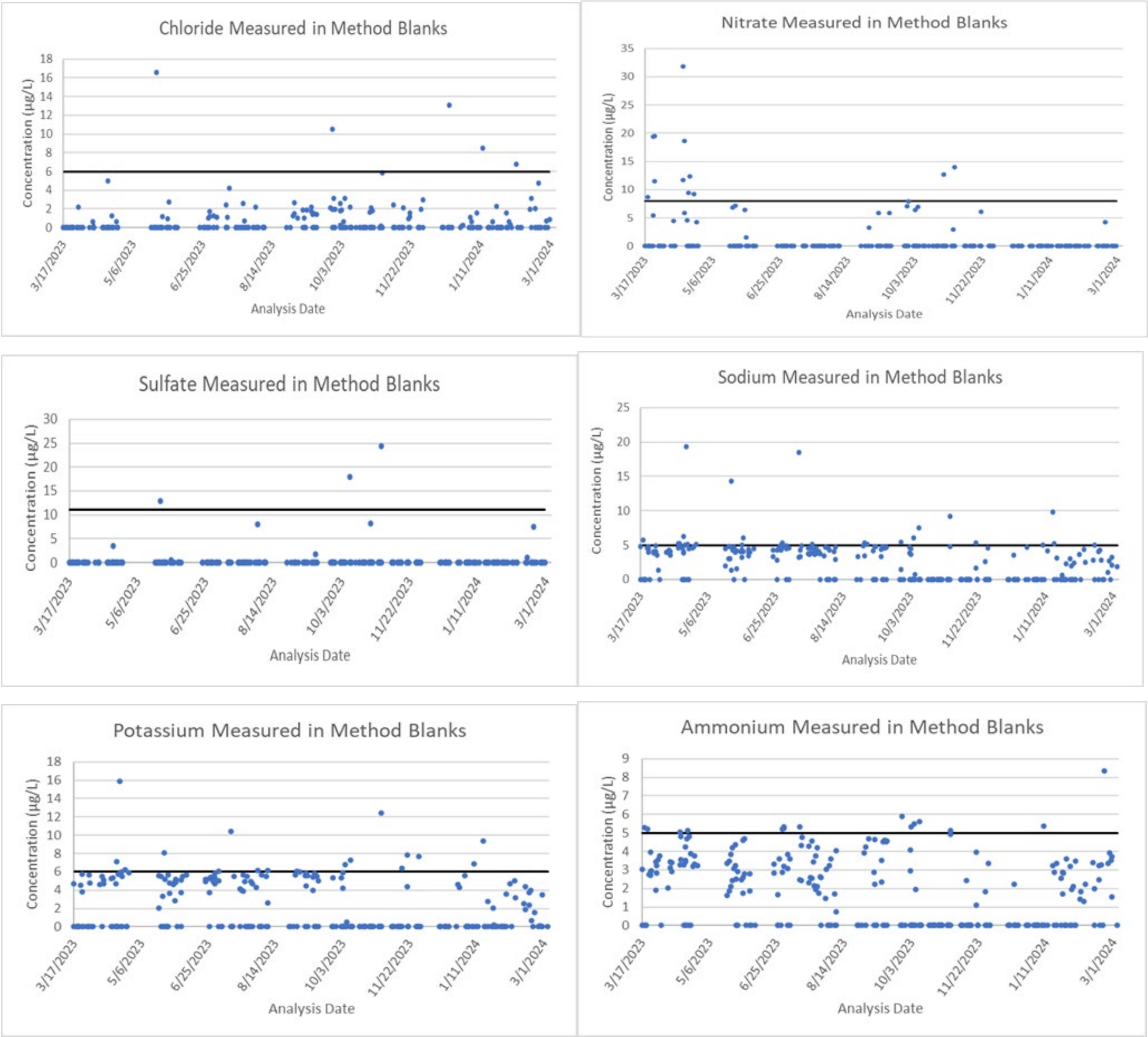


Figure 5-13: Concentrations of anions and cations in method blanks for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023). Black line indicates the analytical method detection limit.



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 5-2) there are no acceptance criteria associated with these measures. Because the concentrations in the LCS (Table 5-8 and Table 5-9) 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 5-14 and Figure 5-15) have more frequent outliers relative to the CCV check standards (Figure 5-6 and Figure 5-7), suggesting that background contamination may be introduced during the sample handling and processing of samples and is less likely to occur from instrumental issues. There were outliers noted for all cations in the LCS Low checks in March of 2023, this followed the preparation of a new LCS spiking solution. The LCS Low checks were within reasonable limits after the solution was discarded and prepared. 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 5-8: Target concentrations for anion LCS for the analysis period 03/17/2023 through 03/15/2024 (samples collected 1/1/2023 through 12/31/2023).

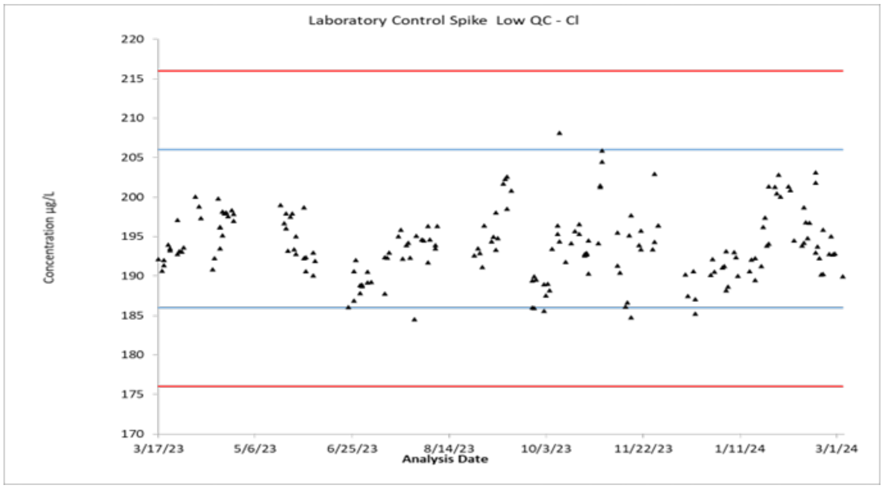
QC Sample	Cl^- (ppb)	NO_3^- (ppb)	SO_4^{2-} (ppb)
LCS Low	196	588	1180
LCS Medium	476	1430	2860
LCS High	2000	6000	12000

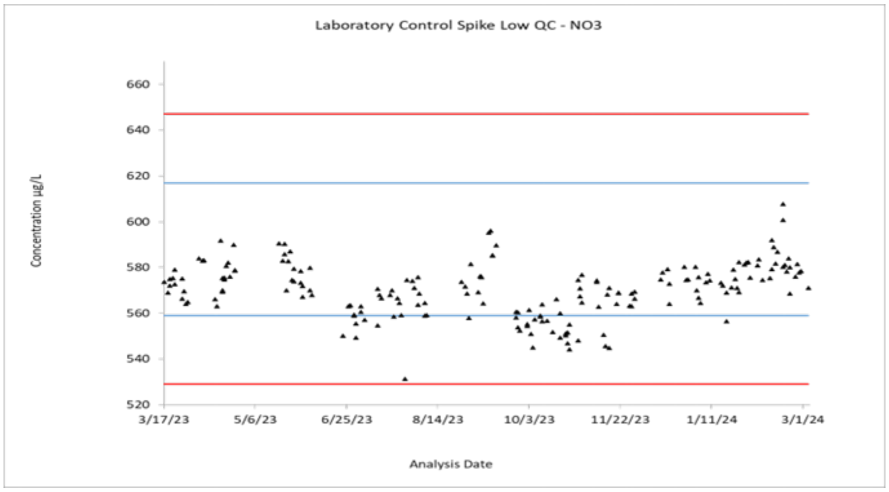
Table 5-9: Target concentrations for cation LCS for the analysis period 3/17/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).

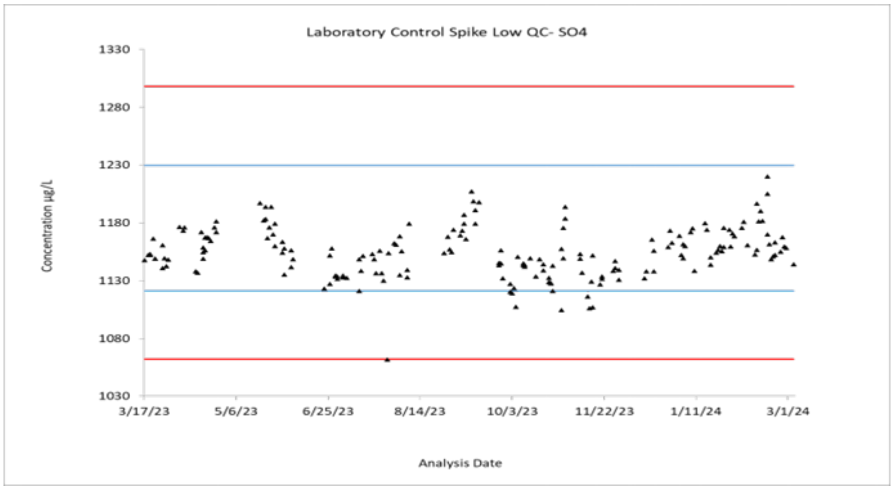
QC Sample	Na^+ (ppb)	NH_4^+ (ppb)	K^+ (ppb)
LCS Low	20	20	20
LCS Medium	276	276	276
LCS High	769	769	769

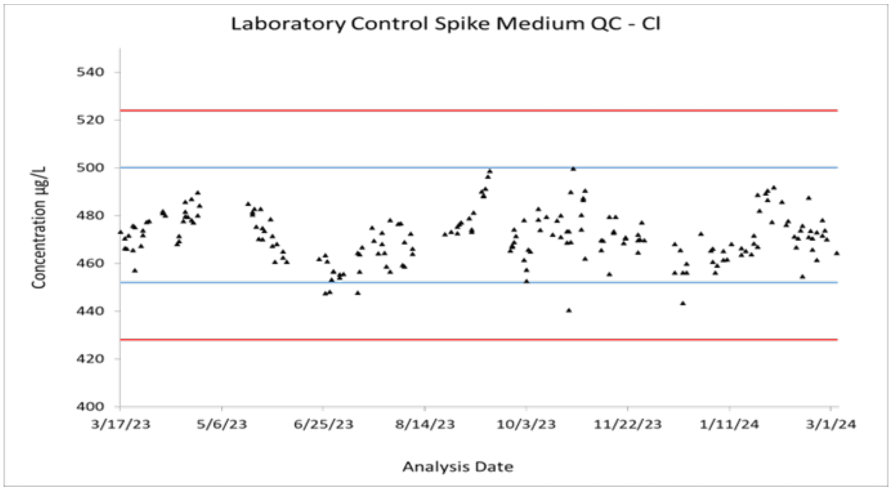
In figures 5-14 and 5-15 below, red lines show upper and lower control limits per the CCV check standard acceptance criteria. Blue lines show upper and lower warning limits.

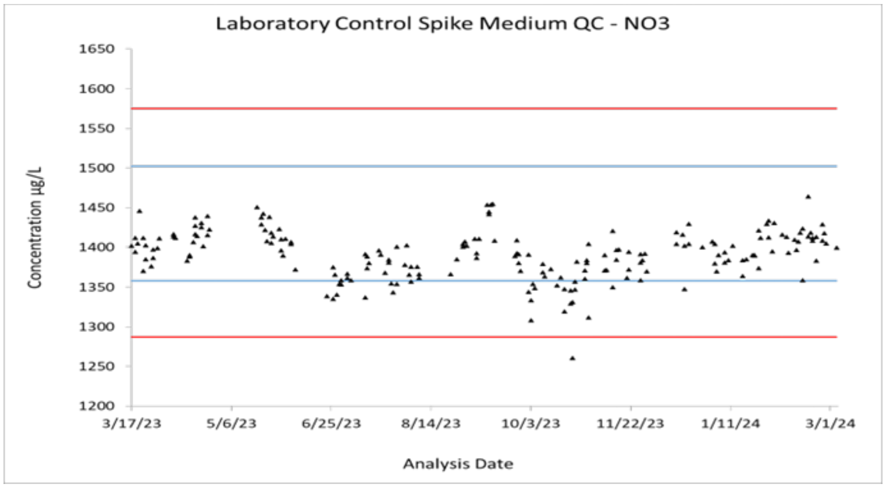
Figure 5-14: Control charts for anion LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023).

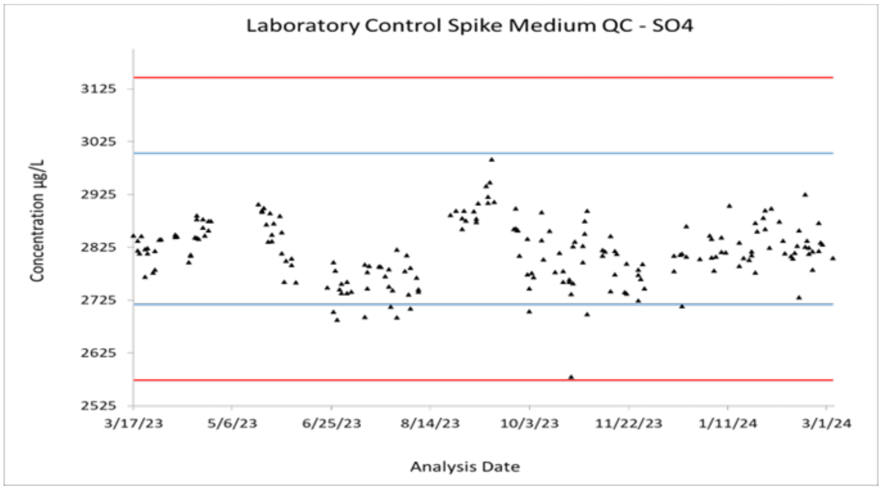


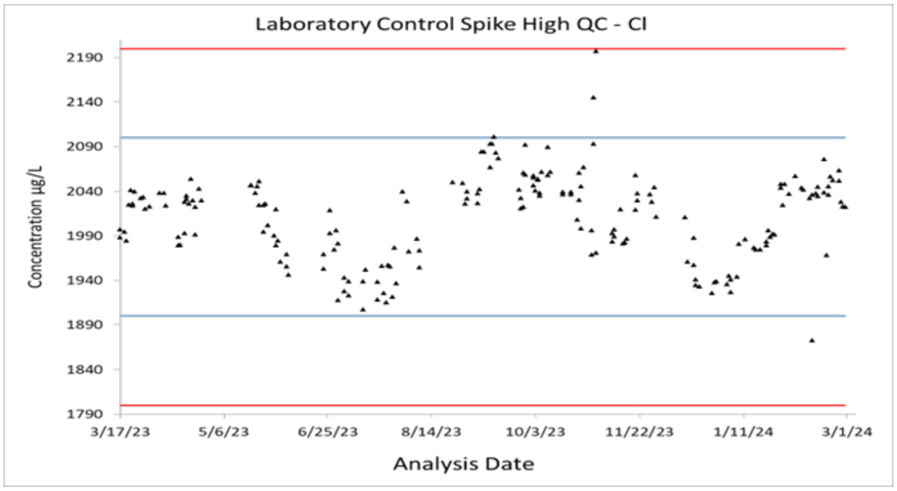

Laboratory Control Spike Low QC - NO3
Concentration µg/L
660
640
620
600
580
560
540
520
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

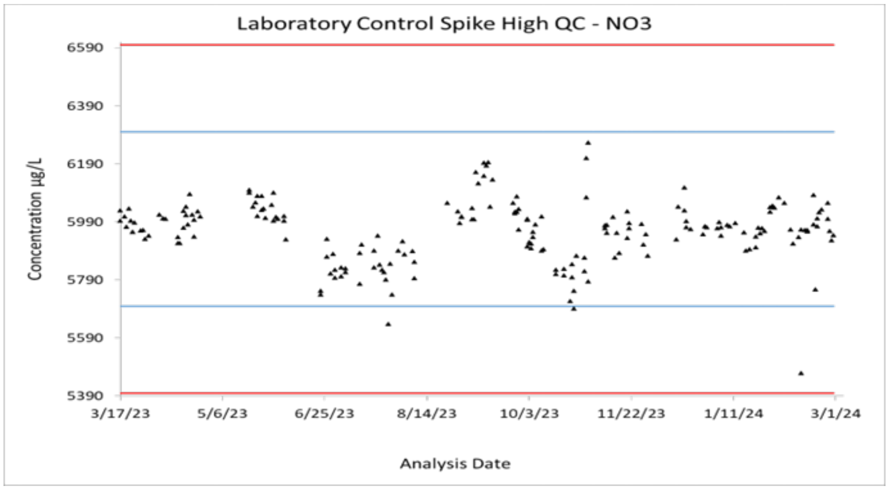

Laboratory Control Spike Low QC- SO4
Concentration µg/L
1330
1280
1230
1180
1130
1080
1030
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Laboratory Control Spike Medium QC - Cl
Concentration µg/L
540
520
500
480
460
440
420
400
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Laboratory Control Spike Medium QC - NO3
Concentration µg/L
1650
1600
1550
1500
1450
1400
1350
1300
1250
1200
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Laboratory Control Spike Medium QC - SO4
Concentration µg/L
3125
3025
2925
2825
2725
2625
2525
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Laboratory Control Spike High QC - Cl
Concentration µg/L
2190
2140
2090
2040
1990
1940
1890
1840
1790
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Laboratory Control Spike High QC - NO3
Concentration µg/L
6590
6390
6190
5990
5790
5590
5390
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

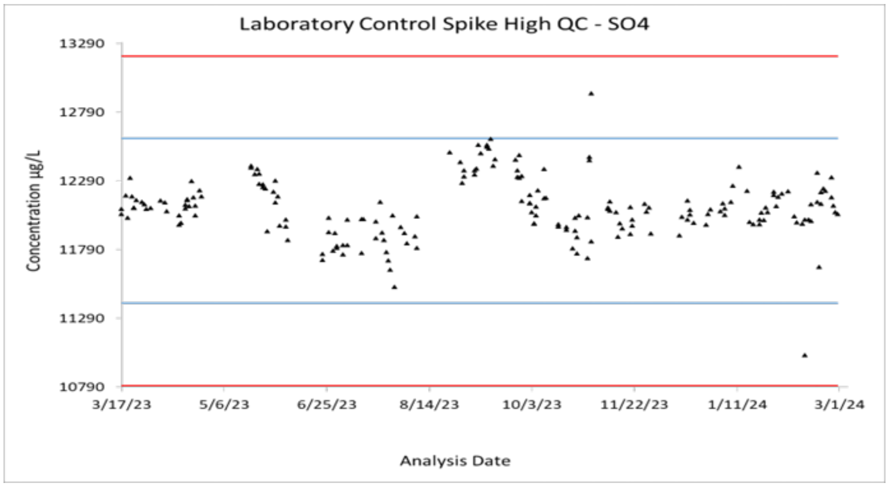
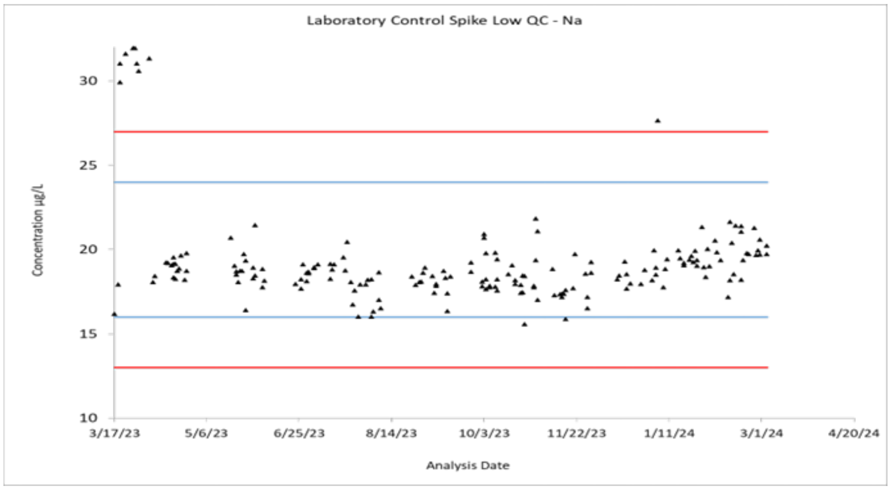
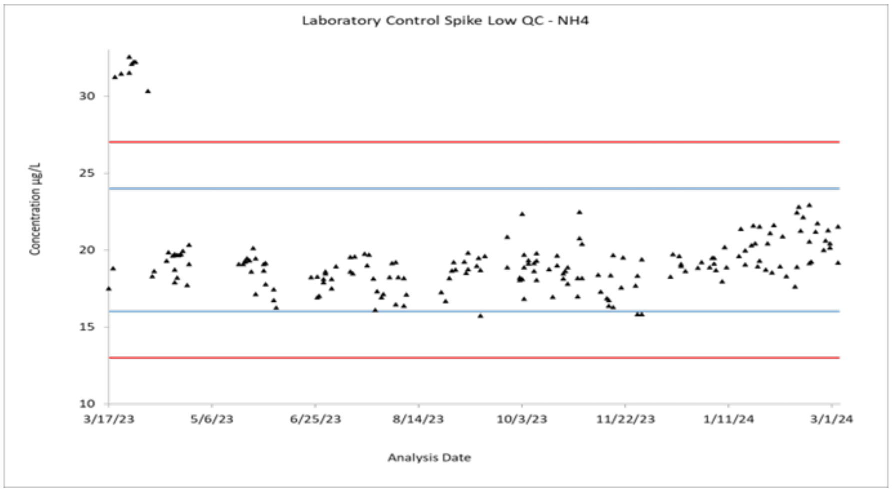
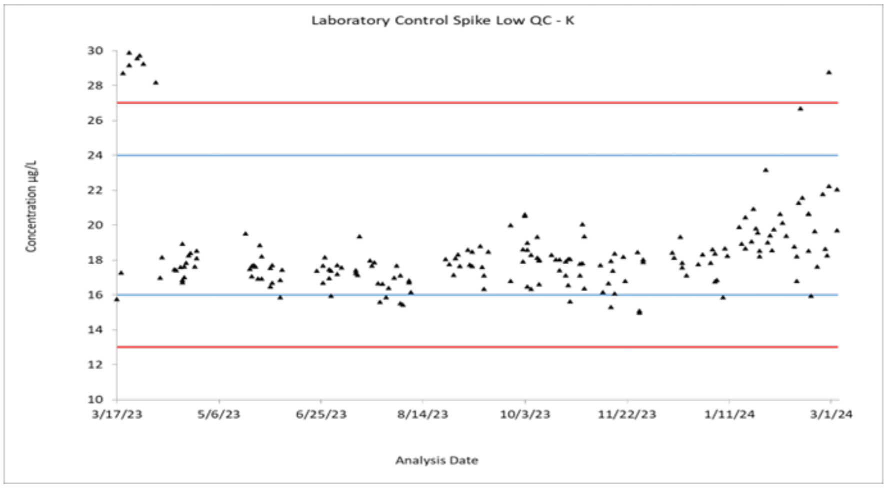
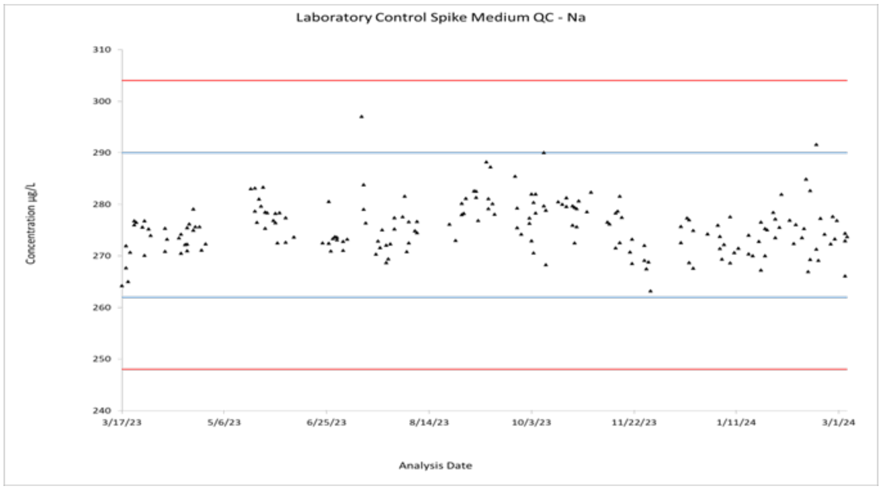

Laboratory Control Spike High QC - SO4
Concentration µg/L
13290
12790
12290
11790
11290
10790
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date

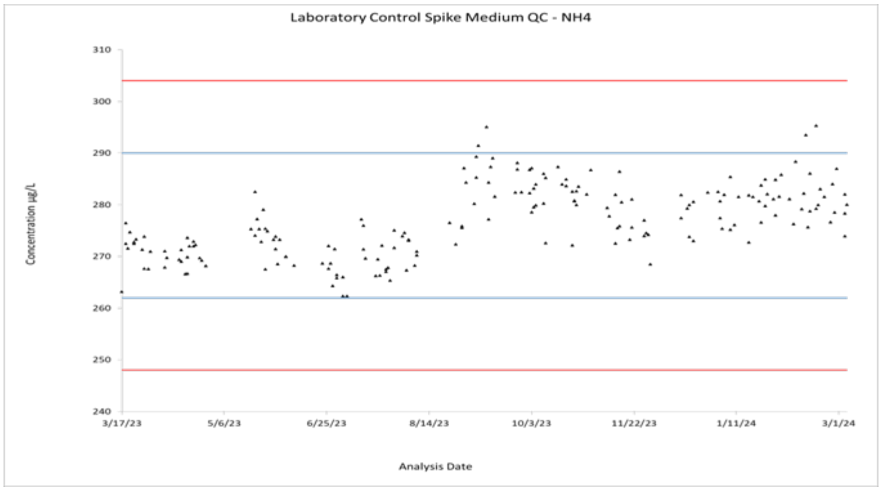
Figure 5-15: Control charts for cation LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023).

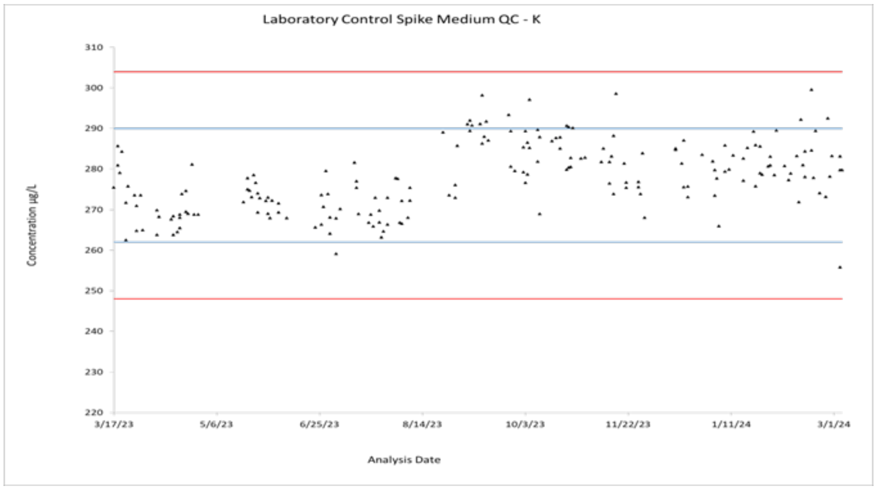


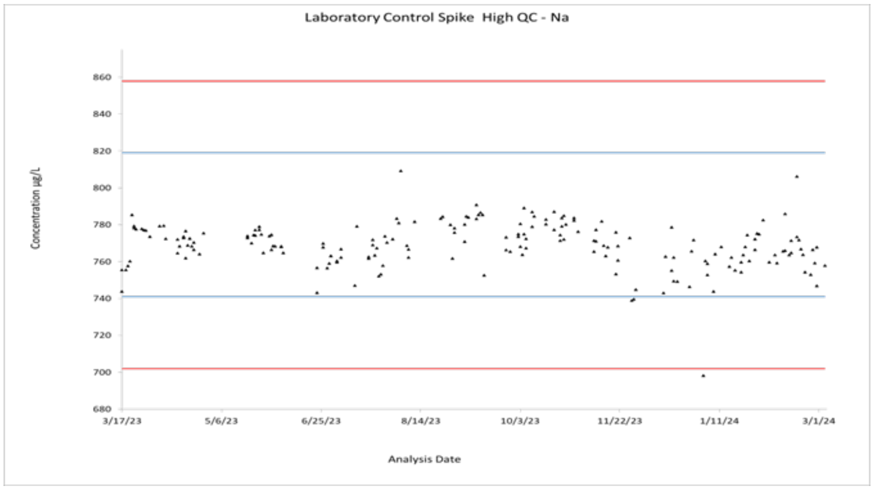


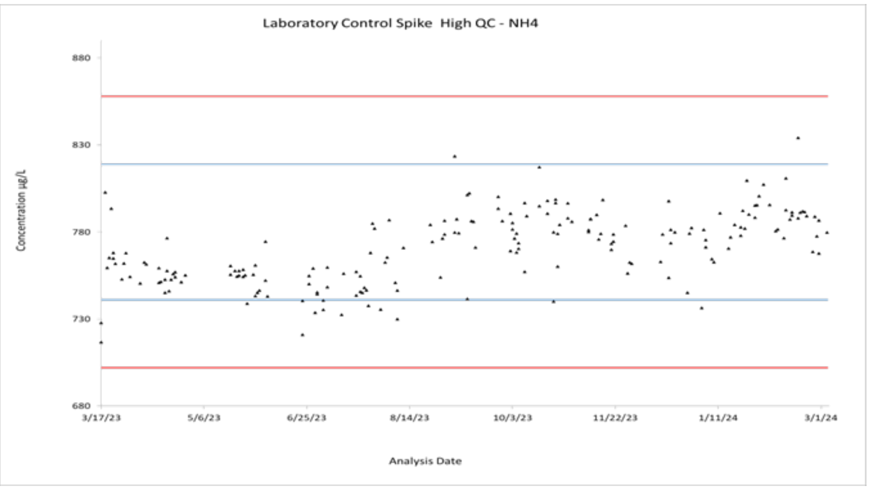


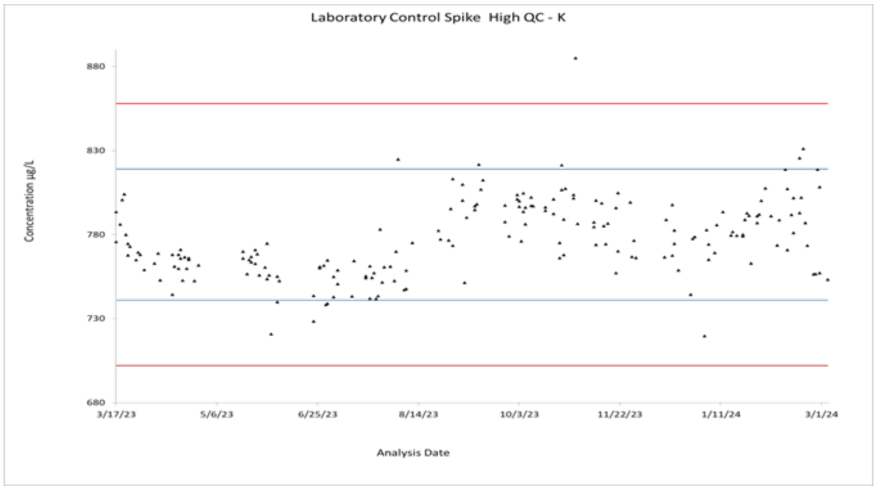

Laboratory Control Spike Medium QC - Na
Concentration µg/L
310
300
290
280
270
260
250
240
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Laboratory Control Spike Medium QC - NH4
Concentration µg/L
310
300
290
280
270
260
250
240
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Laboratory Control Spike Medium QC - K
Concentration µg/L
310
300
290
280
270
260
250
240
230
220
3/17/23
5/6/23
6/25/23
8/14/23
10/3/23
11/22/23
1/11/24
3/1/24
Analysis Date


Laboratory Control Spike High QC - Na


Laboratory Control Spike High QC - NH4


Laboratory Control Spike High QC - K

5.3.2.6 Round Robin (USGS)

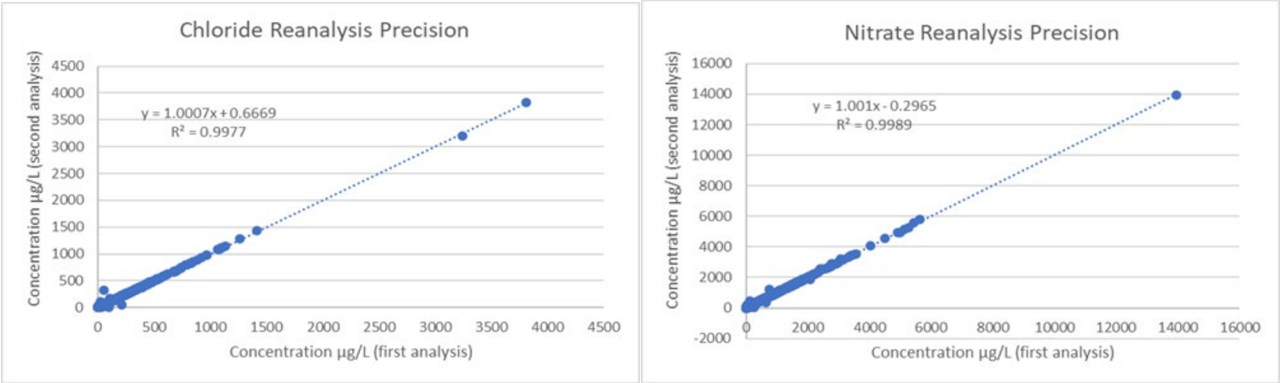
The RTI Ions Chromatography Laboratory participated in the National Atmospheric Deposition Program/Mercury Deposition Network Interlaboratory Comparison Program. The program is administered by the United States Geological Survey (USGS) Branch of Quality Systems. Four samples per month were sent to participating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

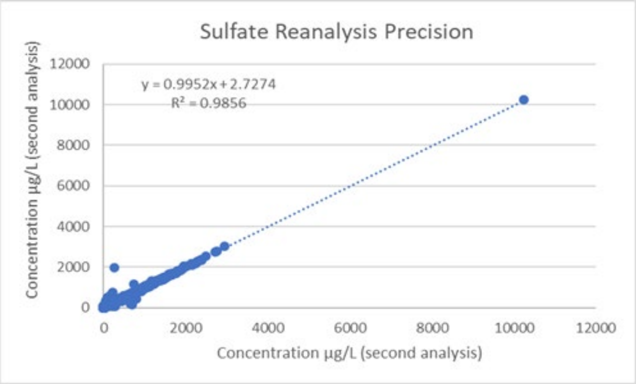
5.3.2.7 Reanalysis

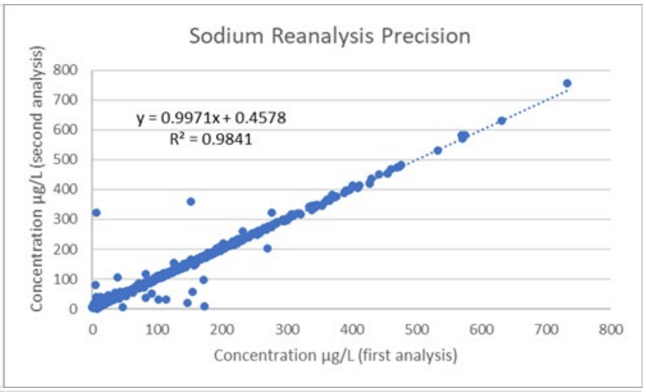
Replicate analyses are reanalyses where two analyses are performed on the same sample extract using different instruments. Five percent of all samples are randomly selected for reanalysis and are reanalyzed using different instruments and different calibration curves (these reanalyses are specific to the analytical acceptance criteria described in Table 5-5, distinct from additional reanalyses that may be requested later during the UC Davis Level 0 or Level 1 validation process described in section 7.3.1). Samples 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 5-5, 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.

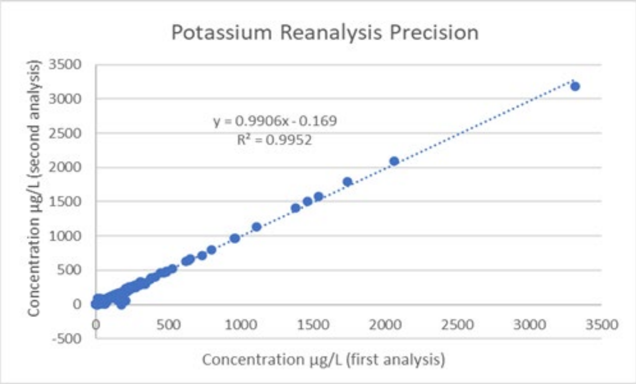
During this reporting period, there were 2,594 samples reanalyzed for anions and 2,673 samples reanalyzed for cations (Figure 5-16). Less than 1.1% of samples reanalyzed for anions and cations, failed to meet the acceptance criteria for precision between the original and reanalysis result. For cases 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.

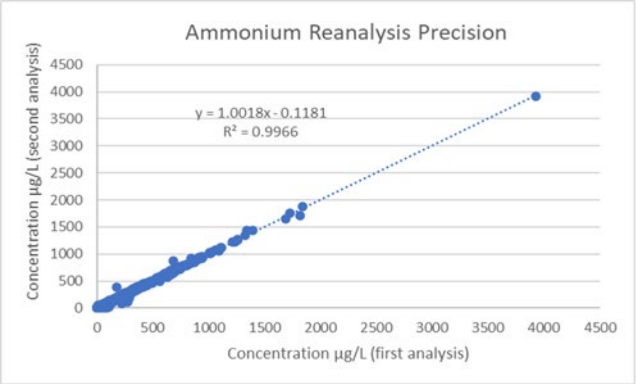
Figure 5-16: Ion reanalysis results for the analysis period 3/17/2023 through 3/05/2024 (samples collected 1/1/2023 through 12/31/2023).











5.3.3 Determination of Uncertainties and Method Detection Limits

For discussion of Method Detection Limits (MDLs) see Section 4.1.3.8.

For discussion of analytical uncertainty and total uncertainty see Section 4.1.2 and Section 7.5, respectively.

5.3.4 Audits, Performance Evaluations, Training, and Accreditations

5.3.4.1 System Audits

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

5.3.4.2 Performance Evaluations

UC Davis and RTI participated in the 2023 Mega PE interlaboratory comparison test for anion and cation analysis by Ion Chromatography. Results were comparable to the other four laboratories that participated. The report can be accessed here, https://www.epa.gov/system/files/documents/2024-04/2023_megape_report_final.pdf.

5.3.4.3 Training

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

5.3.4.4 Accreditations

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

5.3.5 Summary of Filter Blanks

5.3.5.1 Field Blanks

Over the sampling period (January 1, 2023 through December 31, 2023) there were 1,593 valid nylon filter field blanks. Table 5-10 and Table 5-11 summarize the field blank statistics.

Table 5-10: Nylon filter field blank statistics in µg/mL for the analysis period 3/24/2023 through 3/5/2024 (samples collected 1/1/2023 through 12/31/2023).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl^-	1593	0.008	0.011	0.000	0.376	0.018
NO_3^-	1593	0.015	0.022	0.000	1.156	0.040
SO_4^{2-}	1593	0.005	0.011	0.000	1.091	0.044
Na^+	1593	0.005	0.007	0.001	0.262	0.012
NH_4^+	1593	0.005	0.006	0.000	0.238	0.010
K^+	1593	0.007	0.008	0.000	0.067	0.006

Table 5-11: Nylon filter field blank statistics in µg/filter (extraction volume 25 mL) for the analysis period 3/2**4**/202**3** through 3/**5**/202**4** (samples collected 1/1/2023 through 12/31/2023).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl^-	1593	0.190	0.267	0.011	9.398	0.444
NO_3^-	1593	0.377	0.541	0.000	28.892	1.006
SO_4^{2-}	1593	0.118	0.280	0.000	27.270	1.106
Na^+	1593	0.135	0.178	0.034	6.541	0.292
NH_4^+	1593	0.130	0.145	0.000	5.955	0.245
K^+	1593	0.173	0.203	0.000	1.680	0.142

5.3.5.2 Laboratory Blanks

As described in Section 4.1.3.6 – 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 65 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 5-12 and Table 5-13 summarize the laboratory blank statistics.

Table 5-12: Nylon filter laboratory blank statistics in µg/mL for the analysis period 4/8/2023 through 3/5/2024 (samples collected 1/1/2023 through 12/31/2023).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl^-	65	0.005	0.013	0.001	0.471	0.058
NO_3^-	65	0.009	0.012	0.000	0.055	0.011
SO_4^{2-}	65	0.000	0.004	0.000	0.034	0.009
Na^+	65	0.005	0.009	0.002	0.313	0.038
NH_4^+	65	0.005	0.005	0.003	0.008	0.001
K^+	65	0.006	0.005	0.000	0.012	0.002

Table 5-13: Nylon filter laboratory blank statistics in µg/filter (extraction volume 25 mL) for the analysis period 4/8/2023 through 3/5/2024 (samples collected 1/1/2023 through 12/31/2023).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl^-	65	0.118	0.316	0.019	11.786	1.450
NO_3^-	65	0.217	0.306	0.000	1.368	0.275
SO_4^{2-}	65	0.000	0.104	0.000	0.842	0.216
Na^+	65	0.115	0.230	0.046	7.816	0.957
NH_4^+	65	0.122	0.122	0.069	0.205	0.033
K^+	65	0.139	0.129	0.000	0.286	0.050

5.4 UC Davis X-ray Fluorescence Laboratory

The UC Davis X-ray Fluorescence Laboratory received and analyzed PTFE filters from samples collected January 1, 2023 through December 31, 2023. 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 27, 2023 through April, 09, 2024 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 5-14 for details.

Table 5-14: Sampling months during 2023 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	99	2023-03-28 - 2023-05-24	2023-03-28 - 2023-04-10	2023-03-27 - 2023-04-10	2023-03-28 - 2023-04-10	2023-03-29 - 2023-04-10
February	100	2023-04-27 - 2023-05-10	2023-04-27 - 2023-05-10	NA	2023-04-27 - 2023-05-10	2023-04-27 - 2023-05-10
March	101	2023-05-25 - 2023-07-25	2023-05-25 - 2023-06-07	2023-05-24 - 2023-06-07	2023-05-25 - 2023-06-07	2023-05-25 - 2023-06-07
April	102	2023-07-04 - 2023-08-29	2023-07-03 - 2023-07-18	2023-07-04 - 2023-07-18	2023-07-04 - 2023-07-18	2023-07-13 - 2023-07-18
May	103 / 23-05	2023-07-31 - 2023-09-29	2023-07-31 - 2023-08-12	2023-08-01 - 2023-08-12	2023-07-31 - 2023-11-29	2023-07-31 - 2023-08-12
June	104 / 23-06	2023-08-26 - 2023-09-08	2023-08-26 - 2023-09-09	2023-08-25 - 2023-09-08	2023-08-26 - 2023-11-01	2023-08-12 - 2023-09-01
July	23-07	2023-09-22 - 2023-10-04	2023-09-21 - 2023-10-03	2023-09-22 - 2023-10-04	2023-09-21 - 2023-12-06	2023-09-21 - 2023-10-04
August	23-08	2023-10-26 - 2023-11-02	2023-10-24 - 2023-11-09	2023-10-25 - 2023-12-04	2023-10-24 - 2024-01-23	2023-10-25 - 2023-11-09
September	23-09	2023-11-22 - 2023-11-27	2023-11-22 - 2023-12-27	2023-11-22 - 2023-12-25	2023-11-03 - 2024-01-23	2023-11-22 - 2023-12-07
October	23-10	2023-12-22 - 2024-01-02	2023-12-06 - 2024-01-02	2023-12-20 - 2024-01-02	2023-12-07 - 2024-02-12	2023-12-06 - 2024-01-02
November	23-11	2024-01-26 - 2024-01-30	2024-01-16 - 2024-01-30	2024-01-16 - 2024-01-31	2024-01-16 - 2024-03-12	2024-01-16 - 2024-01-30
December	23-12	2024-02-26 - 2024-04-09	2024-02-27 - 2024-03-09	2024-02-27 - 2024-03-09	2024-02-26 - 2024-03-09	2024-02-27 - 2024-03-09
All Months	99 to 23-12	2023-03-28 – 2024-04-09	2023-03-28 – 2024-03-09	2023-03-27 – 2024-03-09	2023-03-28 – 2024-03-12	2023-03-29 – 2024-03-09

5.4.1 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 *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 5-15.

Table 5-15: 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	

* Deviation DV-0015 removed Zn as a QC check criteria element from the monthly SRM beginning on 10/13/2023 through the end of the analysis period for this report due to contamination of the irreplaceable SRM samples.

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.

5.4.2 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 4.2.3. 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.

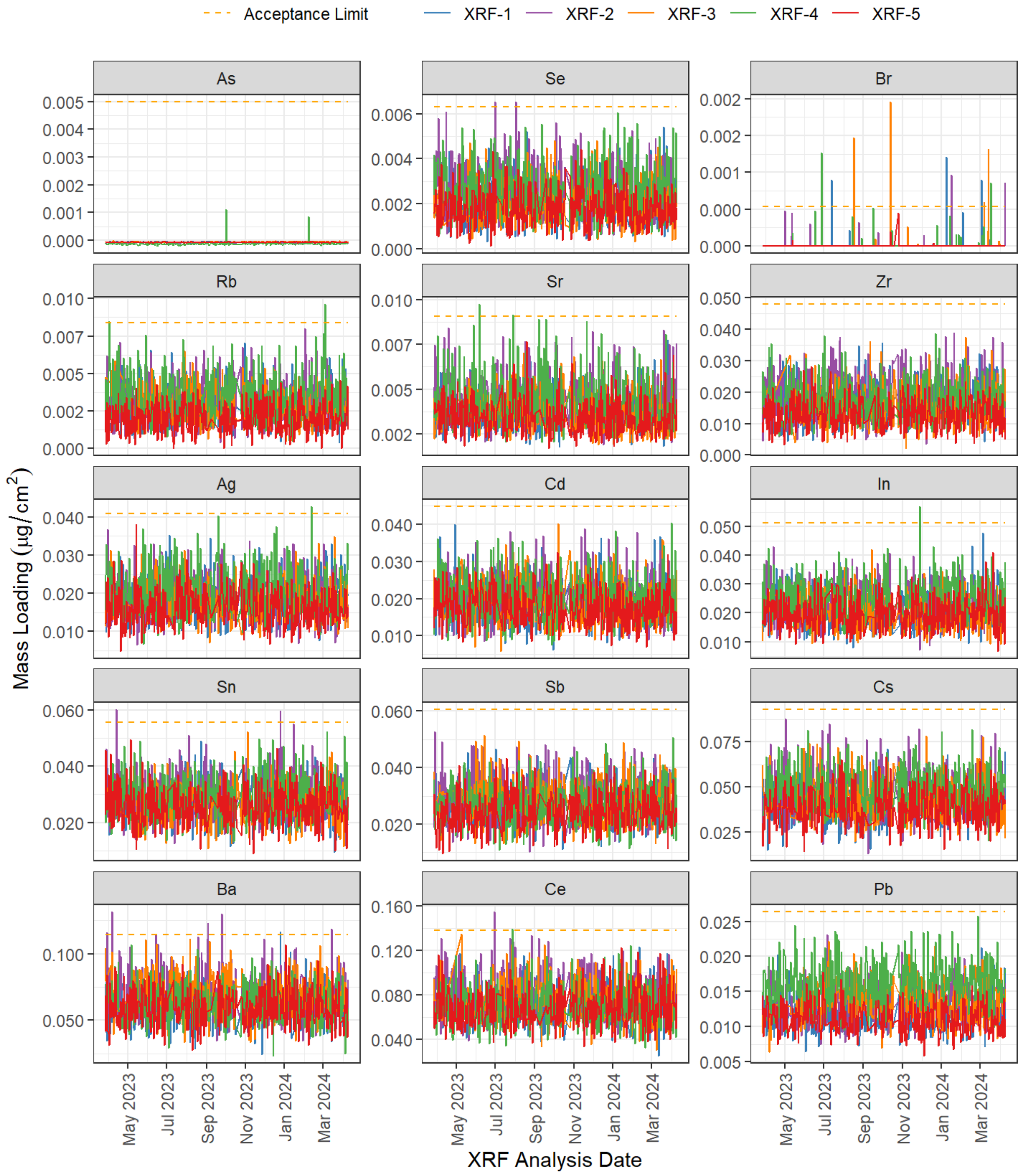
5.4.2.1 Results of Daily QC Checks

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 5-17 and Figure 5-18 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 seventeen samples from 2023 were reanalyzed for suspected zinc contamination. Of those, nine 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 moving parts of the instrument; zinc is a common contaminant in elemental analysis systems.

Figure 5-17: Analysis results from daily PTFE blanks for the analysis period 3/27/2023 through 4/09/2024 (see Table 5-14 for corresponding sampling dates). Elements Na through Zn shown.

Figure 5-18: Analysis results from daily PTFE blanks for the analysis period 3/27/2023 through 4/9/2024 (see Table 5-14 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 5-15. 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 5-16 through 5-20 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 5-15. XRF-2 and XRF-5 both failed the daily QC ME-RM acceptance for zinc during this analysis period. In both cases, the QC ME-RM on the instruments suffered from the occasional zinc contamination which comes from the gas piston and the hinge of the XRF lid. Since these samples stay loaded on the sample deck and are positioned directly under the gas piston and hinge, they are susceptible to this contamination. Attempts were made to remove the contamination, but it was not removable. In the case of XRF-2 the QC ME-RM sample was analyzed on another instrument which confirmed the high zinc contamination of the QC sample. Since the contamination could not be removed from the QC ME-RM samples, they were replaced with new ones. Because the contamination was limited to the QC samples, no network sample results were impacted.

Table 5-16: Descriptive statistics of XRF-1 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/27/2023 through 4/9/2024 (see Table 5-14 for corresponding sampling dates), N = 273.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.802	1.502	2.110	0	0	2.1
Si	0.724	0.635	0.949	0	0	2.1
S	14.588	13.482	16.478	0.4	0	0.8
K	2.057	1.902	2.325	0.4	0	1.0
Ca	2.031	1.830	2.237	0	0	1.0
Cr	0.859	0.780	0.953	0	0	0.6
Fe	2.441	2.165	2.646	0	0	0.7
Zn	0.320	0.278	0.340	2.2	0	2.7
As	0.588	0.532	0.650	0	0	0.9
Se	0.418	0.387	0.473	0	0	1.1
Rb	0.203	0.183	0.224	0	0	1.6
Sr	0.196	0.176	0.215	0	0	1.6
Cd	0.262	0.233	0.293	1.1	0	4.6
Sn	0.305	0.270	0.348	0.7	0	4.5
Pb	0.077	0.055	0.097	0	0	8.8

Table 5-17: Descriptive statistics of XRF-2 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/27/2023 through 4/9/2024 (see Table 5-14 for corresponding sampling dates), N = 201.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.477	1.188	1.697	0	0	1.7
Si	0.626	0.464	0.746	0	0	2.2
S	11.866	10.703	13.082	0	0	0.9
K	1.686	1.528	1.867	0	0	0.7
Ca	1.625	1.459	1.783	0	0	1.1
Cr	0.694	0.630	0.769	0	0	0.7
Fe	1.933	1.732	2.117	0	0	0.8
Zn	0.276	0.237	0.290	4.5	1.5	9.6
As	0.478	0.426	0.521	0	0	1.2
Se	0.350	0.315	0.385	0	0	1.1
Rb	0.166	0.149	0.182	0	0	2.0
Sr	0.160	0.144	0.176	0	0	2.1
Cd	0.217	0.185	0.241	0.5	0	4.9
Sn	0.253	0.214	0.286	1.0	0	5.5
Pb	0.063	0.042	0.083	0	0	10.6

Table 5-18: Descriptive statistics of XRF-3 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/27/2023 through 4/9/2024 (see Table 5-14 for corresponding sampling dates), N = 182.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.331	1.003	1.463	0	0	2.1
Si	0.934	0.750	1.034	0	0	2.0
S	10.261	9.533	11.652	1.6	0	1.1
K	1.448	1.316	1.608	0	0	0.4
Ca	1.384	1.242	1.518	0	0	1.2
Cr	0.580	0.520	0.635	0	0	0.9
Fe	1.641	1.448	1.770	0.5	0	1.7
Zn	0.338	0.291	0.356	0.5	0	1.1
As	0.405	0.363	0.444	0	0	1.3
Se	0.284	0.258	0.316	0	0	1.5
Rb	0.140	0.126	0.154	0	0	2.3
Sr	0.138	0.125	0.153	0	0	2.1
Cd	0.188	0.159	0.220	0.5	0	5.4
Sn	0.226	0.186	0.270	0	0	5.2
Pb	0.152	0.126	0.170	0.5	0	6.3

Table 5-19: Descriptive statistics of XRF-4 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/27/2023 through 4/9/2024 (see Table 5-14 for corresponding sampling dates), N = 286.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.693	1.585	2.143	0	0	2.1
Si	0.944	0.671	1.071	0	0	2.7
S	15.445	14.145	17.288	0	0	1.2
K	2.188	1.987	2.429	0	0	1.1
Ca	2.201	1.960	2.396	0	0	0.8
Cr	0.949	0.842	1.029	0	0	0.6
Fe	2.705	2.329	2.847	0.3	0	1.5
Zn	0.340	0.289	0.353	2.1	0	2.7
As	0.660	0.580	0.709	0	0	1.3
Se	0.465	0.422	0.516	0	0	1.1
Rb	0.221	0.198	0.242	0	0	1.5
Sr	0.214	0.191	0.233	0	0	1.6
Cd	0.285	0.244	0.316	0.3	0	4.3
Sn	0.334	0.290	0.367	0.7	0	4.1
Pb	0.082	0.062	0.104	0	0	8.0

Table 5-20: Descriptive statistics of XRF-5 results (µg/cm2) of the daily UC Davis ME-RM for the analysis period 3/27/2023 through 4/9/2024 (see Table 5-14 for corresponding sampling dates), N = 193.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.585	1.277	1.869	0	0	2.3
Si	1.500	1.315	1.779	0	0	1.6
S	11.614	10.546	12.889	0	0	1.0
K	1.763	1.607	1.964	0	0	0.8
Ca	1.645	1.496	1.828	0	0	1.0
Cr	0.491	0.440	0.538	0	0	1.2
Fe	1.892	1.704	2.083	0	0	0.9
Zn	0.214	0.180	0.220	5.2	1.6	10.8
As	0.596	0.535	0.654	0	0	1.0
Se	0.274	0.244	0.298	0	0	1.7
Rb	0.186	0.167	0.204	0	0	1.4
Sr	0.188	0.171	0.208	0	0	1.5
Cd	0.290	0.255	0.325	0	0	3.6
Sn	0.171	0.136	0.209	0	0	15.8
Pb	0.159	0.137	0.182	0.5	0	4.8

5.4.2.2 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 5-15. When more than two consecutive measurements exceed these limits, the results are marked unacceptable. Corrective actions for unacceptable results are described in section 5.4.2.1 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 5-15.

Tables 5-21 through 5-25 show the EDXRF statistics of the weekly UC Davis ME-RM through 4/20/2023.

Table 5-21: Descriptive statistics of XRF-1 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/29/2023 through 4/8/2024 (see Table 5-14 for corresponding sampling dates), N = 63.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.533	1.171	1.745	0	0	3.3
Si	2.413	2.160	2.659	0	0	2.3
S	8.760	7.877	9.627	0	0	1.6
K	1.507	1.344	1.642	0	0	0.9
Ca	1.336	1.188	1.452	0	0	1.2
Cr	0.104	0.094	0.115	0	0	2.0
Fe	1.404	1.256	1.535	0	0	1.3
Zn	0.105	0.093	0.114	0	0	2.3
As	0.618	0.557	0.681	0	0	1.1
Se	0.109	0.097	0.119	0	0	2.6
Rb	0.174	0.156	0.190	0	0	1.8
Sr	0.188	0.169	0.207	0	0	1.9
Cd	0.327	0.293	0.365	0	0	3.5
Pb	0.253	0.228	0.280	0	0	2.8

Table 5-22: Descriptive statistics of XRF-2 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/29/2023 through 4/8/2024 (see Table 5-14 for corresponding sampling dates), N = 61.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.543	1.171	1.745	0	0	2.0
Si	2.534	2.160	2.659	0	0	1.4
S	8.964	7.877	9.627	0	0	1.0
K	1.514	1.344	1.642	0	0	0.7
Ca	1.347	1.188	1.452	0	0	1.3
Cr	0.105	0.094	0.115	0	0	2.3
Fe	1.420	1.256	1.535	0	0	0.8
Zn	0.106	0.093	0.114	0	0	2.1
As	0.630	0.557	0.681	0	0	1.3
Se	0.110	0.097	0.119	0	0	2.5
Rb	0.176	0.156	0.190	0	0	1.7
Sr	0.190	0.169	0.207	0	0	1.7
Cd	0.333	0.293	0.365	0	0	2.9
Pb	0.254	0.228	0.280	0	0	3.0

Table 5-23: Descriptive statistics of XRF-3 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/29/2023 through 4/8/2024 (see Table 5-14 for corresponding sampling dates), N = 58.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.577	1.171	1.745	0	0	2.1
Si	2.538	2.160	2.659	0	0	1.2
S	8.853	7.877	9.627	0	0	1.2
K	1.490	1.344	1.642	0	0	0.8
Ca	1.339	1.188	1.452	0	0	1.5
Cr	0.105	0.094	0.115	0	0	1.9
Fe	1.402	1.256	1.535	0	0	1.1
Zn	0.105	0.093	0.114	0	0	2.2
As	0.628	0.557	0.681	0	0	1.4
Se	0.110	0.097	0.119	0	0	2.6
Rb	0.175	0.156	0.190	0	0	2.0
Sr	0.187	0.169	0.207	0	0	1.8
Cd	0.331	0.293	0.365	0	0	3.9
Pb	0.259	0.228	0.280	0	0	3.0

Table 5-24: Descriptive statistics of XRF-4 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/29/2023 through 4/8/2024 (see Table 5-14 for corresponding sampling dates), N = 62.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.329	1.171	1.745	0	0	2.9
Si	2.338	2.160	2.659	0	0	1.7
S	8.789	7.877	9.627	0	0	1.2
K	1.503	1.344	1.642	0	0	1.1
Ca	1.348	1.188	1.452	0	0	1.3
Cr	0.106	0.094	0.115	0	0	2.1
Fe	1.428	1.256	1.535	0	0	1.7
Zn	0.105	0.093	0.114	0	0	2.2
As	0.635	0.557	0.681	0	0	1.6
Se	0.111	0.097	0.119	0	0	2.3
Rb	0.176	0.156	0.190	0	0	2.0
Sr	0.190	0.169	0.207	0	0	1.8
Cd	0.330	0.293	0.365	0	0	3.0
Pb	0.257	0.228	0.280	0	0	3.2

Table 5-25: Descriptive statistics of XRF-5 results (µg/cm2) of the weekly UC Davis ME-RM for the analysis period 3/29/2023 through 4/8/2024 (see Table 5-14 for corresponding sampling dates), N = 58.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.504	1.171	1.745	0	0	3.6
Si	2.386	2.160	2.659	0	0	1.4
S	8.852	7.877	9.627	0	0	1.3
K	1.505	1.344	1.642	0	0	1.0
Ca	1.320	1.188	1.452	0	0	1.4
Cr	0.105	0.094	0.115	0	0	2.1
Fe	1.408	1.256	1.535	0	0	1.1
Zn	0.104	0.093	0.114	0	0	2.0
As	0.621	0.557	0.681	0	0	1.3
Se	0.110	0.097	0.119	0	0	2.2
Rb	0.174	0.156	0.190	0	0	1.9
Sr	0.187	0.169	0.207	0	0	1.6
Cd	0.330	0.293	0.365	0	0	3.1
Pb	0.252	0.228	0.280	0	0	2.7

5.4.2.3 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:

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

where $XRF1_i$, $XRF2_i$, $XRF3_i$, $XRF4_i$, and $XRF5_i$ are the mass loadings of the i^{th} element measured by each instrument and N is the total number of results of all instruments.

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

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

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

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

The precision is estimated by,

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

The results from this analysis, for the elements listed for the weekly ME-RM in Table 5-15, averaged over the UC Davis ME-RM samples used during the analysis period, are presented in Table 5-26. Note the precision for Sn is poor because the Sn loading on the ME-RM was below the MDL for the XRFs. Boxplots of the mass loading results from the instruments are presented in Figure 5-19 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 5-26: Precision and bias of all EDXRF instruments from the weekly UC Davis ME-RM calculated for the analysis period 3/27/2023 through 4/9/2024 (see Table 5-14 for corresponding sampling dates). Only elements listed in Table 5-15 for the weekly UC ME-RM are evaluated.

Element	XRF-1 Bias %	XRF-2 Bias %	XRF-3 Bias %	XRF-4 Bias %	XRF-5 Bias %	XRF-1 Prec. %	XRF-2 Prec. %	XRF-3 Prec. %	XRF-4 Prec. %	XRF-5 Prec. %
Al	2.2	3.2	6.9	-11.1	0.1	2.9	2.2	2.8	2.0	2.9
Si	-2.7	3.4	4.9	-1.0	-3.5	1.7	1.6	1.3	2.3	1.3
S	-1.4	1.5	0.1	0.0	-0.1	1.2	0.9	1.0	0.9	1.2
K	0.1	0.8	-1.2	0.1	0.0	0.8	0.6	0.7	0.8	0.8
Ca	0.1	0.5	-0.3	1.1	-1.5	1.2	1.2	1.5	1.1	1.4
Cr	-0.8	-0.1	0.0	1.1	-0.2	1.4	1.7	1.6	1.5	1.5
Fe	-0.5	0.3	-1.3	2.0	-0.7	1.3	0.9	1.1	1.4	1.0
Zn	-0.3	0.7	-0.4	0.5	-0.5	1.6	1.5	1.4	1.6	1.5
As	-1.3	0.6	0.1	1.6	-0.9	1.3	1.2	1.9	1.6	1.4
Se	-1.1	0.9	-0.5	1.2	-0.5	2.3	1.9	2.1	2.1	1.8
Rb	-0.6	0.4	-0.7	1.5	-0.8	2.5	2.2	2.0	2.4	1.9
Sr	-0.6	1.1	-0.2	1.0	-1.2	2.0	2.5	2.0	1.9	1.9
Cd	-1.3	0.5	0.6	2.1	-1.7	4.8	4.2	4.0	5.3	3.1
Sn	-5.9	4.2	-1.8	4.7	-2.1	18.5	16.1	13.6	20.4	17.2
Pb	-0.2	-0.3	0.5	1.0	-1.2	3.5	3.1	3.2	2.6	3.1

Figure 5-19: Instrumental comparison using the weekly UC Davis ME-RM, QC|ME-47-W|MTL049.

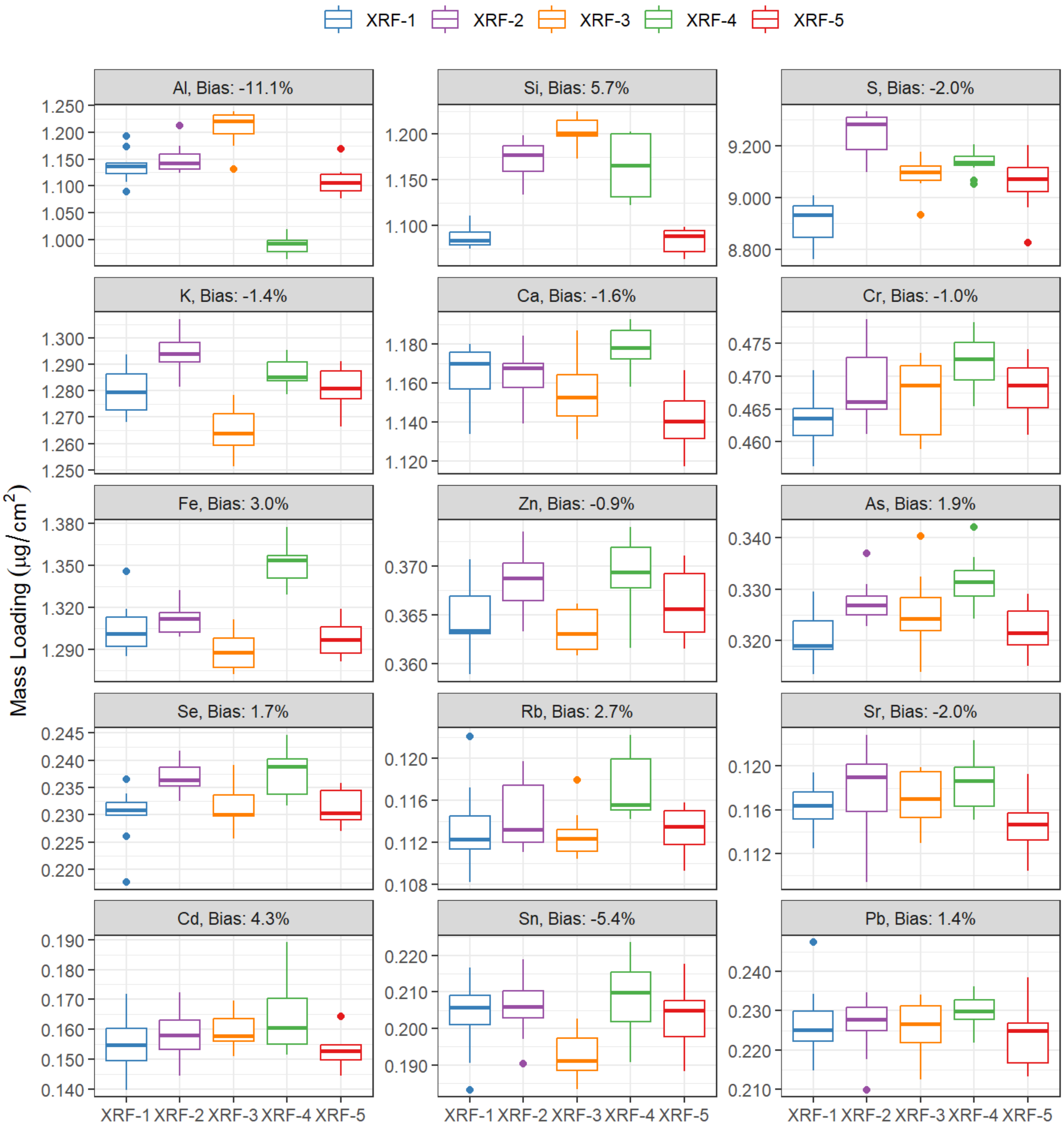
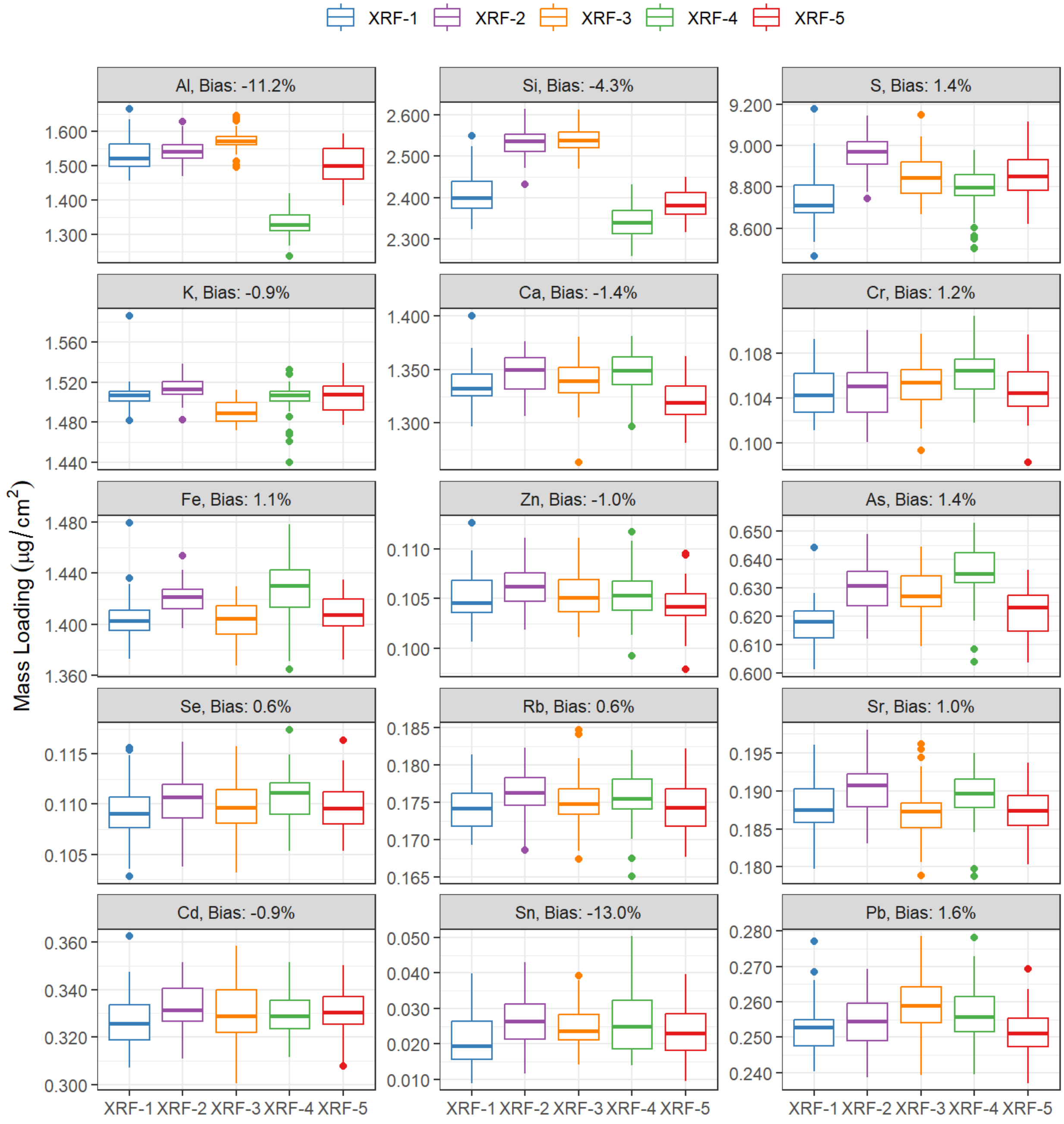


Figure 5-20: Instrumental comparison using the weekly UC Davis ME-RM, QC|ME-47-W|MTL5089.



5.4.2.4 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 5-21 shows the mean z-score plots during the analysis period. No issues were observed in the z-scores for this analysis period.

Figure 5-21: Inter-instrument comparison by z-score of monthly reanalysis sample set. The orange dashed lines indicate the mean z-score acceptance criteria of ±1.

5.4.2.5 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 (3/27/2023 through 4/9/2024) are shown in Figure 5-22, while Table 5-27 summarizes the calibrations performed during this analysis period. All EDXRF instruments underwent routine annual calibrations in October 2022 and October 2023. Additionally, XRF-1 had to be recalibrated in December 2023 because of an X-ray intensity loss, see section 4.2.3.3 for details. The results from the monthly NIST SRM 2783 analyses show failures for K on XRF-1 in January 2024. These failures are related to X-ray intensity loss issues on this instrument which are detailed in section 4.2.3.3. After the intensity issues were resolved, the SRM was reanalyzed later that month with passing results. Additionally, there were near failures for most instruments of Zn in September and October 2023. This Zn contamination has been discussed previously, but the ultimate result is that it cannot always be cleaned from the samples. SRM 2783 air filters are no longer available from NIST, so they can no longer be replaced when Zn contamination cannot be removed. Therefore, it was decided that Zn would no longer be monitored as a QC check with the monthly SRM sample. Deviation, DV-0015, was created to remove Zn from the monthly SRM QC check beginning in October 2023 which corresponds to the CSN August 2023 sampling month. Zn will continue to be monitored as part of the daily QC blank and ME-RM, weekly ME-RM, and monthly Reanalysis QC checks. There were no other issues with monthly SRM QC results indicating the calibrations for all instruments were stable over the calibration periods.

Figure 5-22: Error of each EDXRF instrument from the NIST SRM 2783 standard run monthly for the analysis period 3/27/2023 through 4/9/2024.

Table 5-27: Dates for calibrations performed on each EDXRF instrument during this analysis period (3/27/2023 through 4/9/2024).

EDXRF Instrument	Calibration Date	Reason for Calibration	Range of Sample Dates Analyzed
XRF-1	2022-10-19	Annual Calibration	2023-01-03 – 2023-07-29
XRF-2	2022-10-19	Annual Calibration	2023-01-12 – 2023-07-29
XRF-3	2022-10-20	Annual Calibration	2023-01-06 – 2023-07-29
XRF-4	2022-10-21	Annual Calibration	2023-01-06 – 2023-07-29
XRF-5	2022-10-24	Annual Calibration	2023-01-01 – 2023-07-29
XRF-2	2023-10-24	Annual Calibration	2023-08-04 – 2023-12-29
XRF-4	2023-10-24	Annual Calibration	2023-05-01 – 2023-12-29
XRF-3	2023-10-25	Annual Calibration	2023-08-04 – 2023-12-29
XRF-5	2023-10-25	Annual Calibration	2023-08-01 – 2023-12-26
XRF-1	2023-10-26	Annual Calibration	2023-08-04 – 2023-09-30
XRF-1	2023-12-22	Recalibration due to x-ray intensity change	2023-10-03 – 2023-12-29

5.4.3 Determination of Uncertainties and Method Detection Limits

For discussion of Method Detection Limits (MDLs) see Section 4.1.3.8.

For discussion of analytical uncertainty and total uncertainty see Section 4.1.2 and Section 7.5, respectively.

5.4.4 Audits, Performance Evaluations, Training, and Accreditations

5.4.4.1 System Audits

No system audits were performed during this analysis period.

5.4.4.2 Performance Evaluations

UC Davis participated in the 2023 Mega PE interlaboratory comparison test for elements by XRF. UC Davis results were comparable to the other four laboratories that participated. The report can be accessed here, https://www.epa.gov/system/files/documents/2024-04/2023_megape_report_final.pdf.

5.4.4.3 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.

5.4.4.4 Accreditations

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

5.4.5 Summary of Filter Blanks

5.4.5.1 Field Blanks

Over the sampling period (January 1, 2023 through December 31, 2023) there were 1,596 valid PTFE filter field blanks. Table 5-28 summarizes the field blank statistics.

Table 5-28: PTFE filter field blank statistics for the 2023 sampling analysis period 3/27/2023 through 4/9/2024 (samples collected 1/1/2023 through 12/31/2023).

Species	Count	Median (μg/cm^2)	Average (μg/cm^2)	Min (μg/cm^2)	Max (μg/cm^2)	St. Dev. (μg/cm^2)
Ag	1596	0.018	0.019	0.006	0.039	0.006
Al	1596	0.079	0.079	0.041	0.414	0.019
As	1596	0.000	0.000	0.000	0.001	0
Ba	1596	0.063	0.064	0.026	0.114	0.015
Br	1596	0	0	0	0.010	0.000
Ca	1596	0.003	0.006	0	1.184	0.032
Cd	1596	0.019	0.020	0.006	0.049	0.006
Ce	1596	0.072	0.073	0.028	0.133	0.018
Cl	1596	0.002	0.003	0	0.547	0.014
Co	1596	0.001	0.001	0	0.004	0.001
Cr	1596	0.005	0.005	0.002	0.152	0.006
Cs	1596	0.043	0.044	0.015	0.102	0.012
Cu	1596	0.009	0.008	0.003	0.021	0.003
Fe	1596	0.020	0.024	0.008	0.557	0.027
In	1596	0.021	0.022	0.008	0.047	0.007
K	1596	0.012	0.012	0.000	0.351	0.011
Mg	1596	0.008	0.015	0	0.410	0.021
Mn	1596	0.006	0.006	0.002	0.021	0.002
Na	1596	0	0.015	-0.005	0.485	0.028
Ni	1596	0.001	0.001	0	0.038	0.002
P	1596	0	0.000	0	0.007	0.001
Pb	1596	0.013	0.013	0.007	0.030	0.003
Rb	1596	0.003	0.003	0	0.008	0.001
S	1596	0	0.003	0	1.030	0.037
Sb	1596	0.027	0.027	0.010	0.064	0.008
Se	1596	0.002	0.002	0.000	0.008	0.001
Si	1596	0.018	0.019	0.001	1.220	0.033
Sn	1596	0.027	0.028	0.010	0.058	0.007
Sr	1596	0.004	0.004	0.002	0.009	0.001
Ti	1596	0.002	0.002	0	0.048	0.002
V	1596	0	0.000	0	0.002	0.000
Zn	1596	0.003	0.003	0	0.041	0.002
Zr	1596	0.016	0.017	0.003	0.045	0.006

5.4.5.2 Laboratory Blanks

Five PTFE laboratory blanks are shipped with each batch of routine filters to the analysis laboratory and analyzed. A total of 65 PTFE laboratory blanks were analyzed during the current reporting period. Table 5-29 summarizes the laboratory blank statistics.

Table 5-29: PTFE filter laboratory blank statistics for the 2023 sampling analysis period 3/27/2023 through 4/9/2024 (samples collected 1/1/2023 through 12/31/2023).

Species	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)
Ag	65	0.018	0.019	0.008	0.037	0.006
Al	65	0.071	0.072	0.046	0.095	0.013
As	65	0.000	0.000	0.000	0.000	0.000
Ba	65	0.064	0.067	0.040	0.109	0.015
Br	65	0.000	0.000	0.000	0.000	0.000
Ca	65	0.002	0.002	0.000	0.012	0.002
Cd	65	0.018	0.018	0.007	0.032	0.005
Ce	65	0.072	0.074	0.040	0.120	0.018
Cl	65	0.002	0.002	0.000	0.004	0.001
Co	65	0.001	0.001	0.000	0.004	0.001
Cr	65	0.004	0.004	0.002	0.006	0.001
Cs	65	0.042	0.043	0.024	0.078	0.011
Cu	65	0.008	0.008	0.003	0.015	0.003
Fe	65	0.019	0.019	0.008	0.029	0.003
In	65	0.021	0.021	0.009	0.041	0.007
K	65	0.011	0.010	0.002	0.018	0.004
Mg	65	0.020	0.020	0.000	0.076	0.018
Mn	65	0.006	0.006	0.003	0.009	0.001
Na	65	0.000	0.014	0.000	0.088	0.024
Ni	65	0.001	0.001	0.000	0.002	0.000
P	65	0.000	0.000	0.000	0.002	0.000
Pb	65	0.013	0.014	0.008	0.023	0.004
Rb	65	0.003	0.003	0.000	0.007	0.001
S	65	0.000	0.000	0.000	0.000	0.000
Sb	65	0.028	0.028	0.014	0.044	0.007
Se	65	0.002	0.002	0.001	0.005	0.001
Si	65	0.017	0.016	0.002	0.033	0.006
Sn	65	0.029	0.029	0.012	0.044	0.006
Sr	65	0.004	0.004	0.002	0.009	0.001
Ti	65	0.002	0.002	0.000	0.007	0.002
V	65	0.000	0.000	0.000	0.001	0.000
Zn	65	0.003	0.002	0.001	0.007	0.001
Zr	65	0.017	0.017	0.006	0.030	0.006

5.5 UC Davis Thermal Optical Analysis Laboratory

The UC Davis Thermal Optical Analysis (TOA) Laboratory received and analyzed quartz filters from batches 99 through 23-12, covering the field sampling period beginning from January 1, 2023 through December 31, 2023. Analyses of these samples were performed March 27, 2023 through March 5, 2024. 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 5-30: Sampling months in 2023 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 (2023)	Analysis Batch #	TOA Analysis Dates
January	99	03/27/2023-04/18/2023
February	100	04/19/2023 - 05/09/2023
March	101	05/17/2023 - 06/16/2023
April	102	06/21/2023 - 07/19/2023
May	103 / 23-05	07/20/2023-08/23/2023
June	104 / 23-06	08/17/2023-09/13/2023
July	23-07	09/15/2023 - 12/05/2023
August	23-08	10/16/2023 - 01/19/2024
September	23-09	11/08/2023 - 01/19/2024
October	23-10	12/13/2023 - 02/13/2024
November	23-11	01/11/2024 - 03/08/2024
December	23-12	02/09/2024 - 03/05/2024
All months	99 to 23-12	03/27/2023 - 03/05/2024

5.5.1 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 #904A*. 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 CH_4/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 5-31.

Table 5-31: 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.

5.5.2 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. However, thermogram review had not been performed on every sample analysis but was instead performed on sample analysis that failed other QC or validation checks. More details about this lapse in thermogram review are discussed in Section 4.2.5 (Corrective Actions) and also documented in nonconformance report, NR-0026. Samples impacted by failure to meet QC acceptance criteria outlined in Table 5-31 are reanalyzed.

5.5.2.1 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 *UCD CSN SOP #402*. Results are reviewed immediately upon analysis completion and are compared against the acceptance criteria. Table 5-32 lists the number of blanks analyzed during the report period and their areal density statistics.

Table 5-32: Statistics of daily quartz filter laboratory blank and instrument blank total carbon (TC) analyses on all carbon analyzers for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).

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	1260	0.20	0.23	-6.25	11.08	0.66	35
Laboratory Blank - R*	57	-0.05	-0.03	-2.48	5.54	0.86	1
Instrument Blank	1276	-0.05	-0.06	-2.66	3.38	0.19	46
Instrument Blank - R*	80	-0.27	-0.28	-1.08	0.26	0.22	36

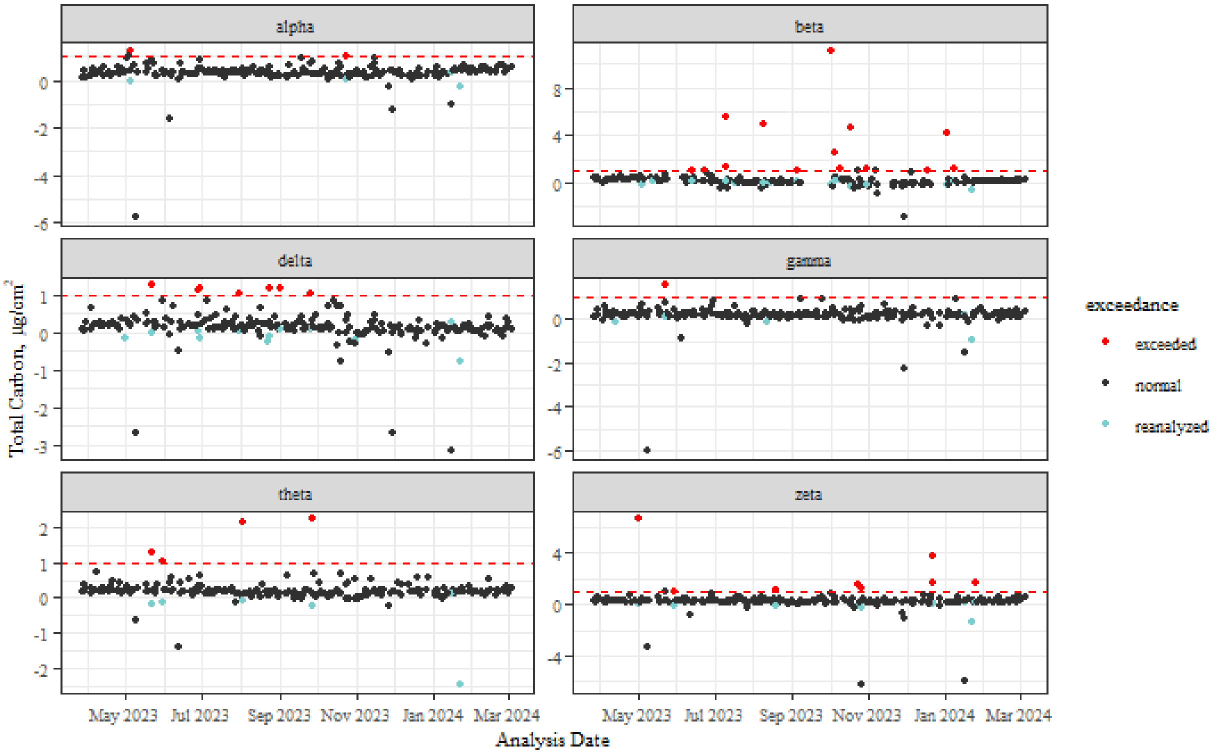
*Laboratory/Instrument Blank - R: Repeated laboratory/instrument blank when original analysis fails the acceptance criteria.

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 the abovementioned changes, the laboratory blanks were repeated multiple times on each analyzer to achieve an operable and stable baseline. Figure 5-23 and Figure 5-24 show the results of daily laboratory and instrument blanks, respectively, analyzed by each instrument during this reporting period.

Figure 5-23 shows the results of daily analyses of laboratory blanks by each instrument. In most cases, the repeated QB analysis is satisfactory. At the beginning of October 2023, Beta had a high QB TC result that exceeded acceptable limit due to a pressure peak issue at beginning of EC1 stage. This issue was resolved by adjusting the valve table and parameter file. Beta has an analysis gap in September 2023 because the autoloader attached to beta had a motor failure, causing an electric board shortage. This autoloader motor and electric board were replaced by an engineer from Sunset.

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 5-23: Total carbon results of daily quartz filter laboratory blanks from each analyzer for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).

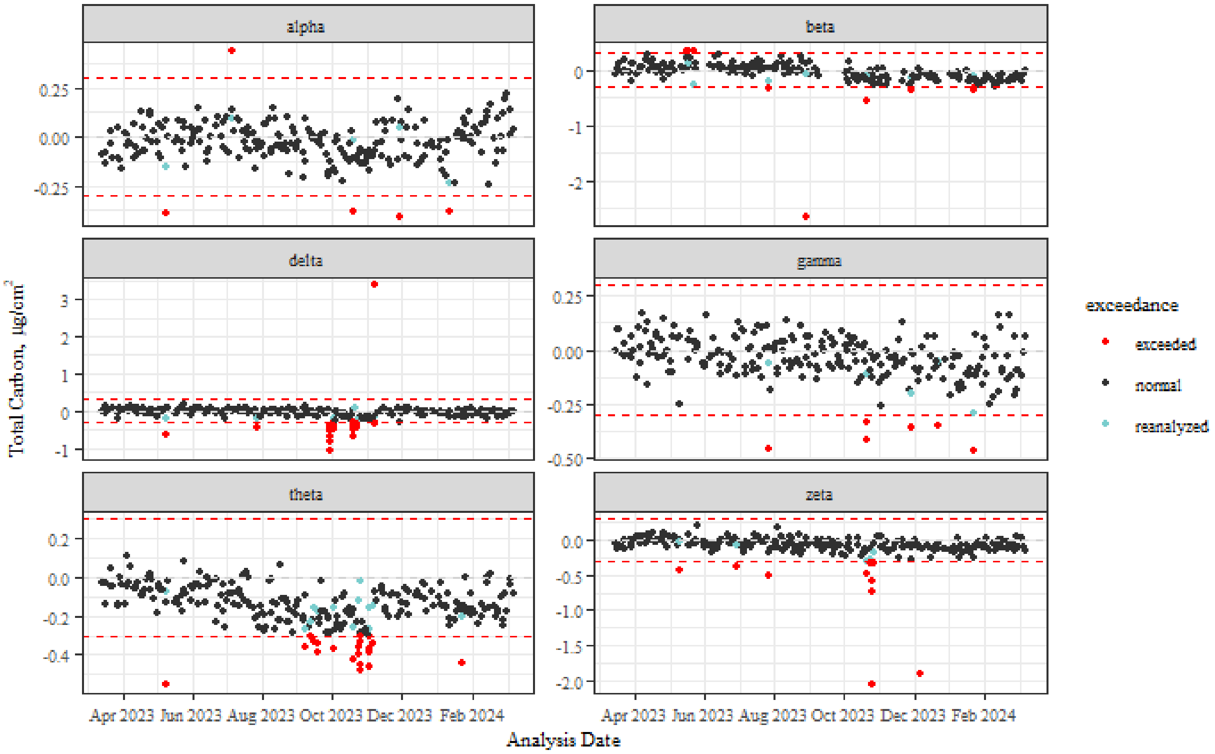


Instrument blank (IB) analysis is performed following the laboratory blank analysis by reusing the sample punch. The instrument blank acceptance criteria is TC (total carbon) within ± 0.3 µg/cm^2. When the instrument blank fails to meet the QC criteria (red points in Figure 5-24), analysis is repeated (blue points in Figure 5-24). If the Instrument Blank-R analysis still exceeds the acceptance limit (three cases during the report period; Table 5-32), 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.

The repeated IB analysis (IB-R) has higher failure rate than previous years for two reasons. First, blank tests that are usually performed after a methanator oven change were erroneously categorized as IB and counted towards IB-R failures. Moving forward, the blank tests after instrument maintenance will be given a unique Sample ID (e.g. blank test) to differentiate from the QC blanks. Second, as detailed in Section 4.2.5, the change of a new HeO_2 gas cylinder on 10-19-2023 introduced a small dip in the FID baseline at the EC1 stage on all instruments. The dip in FID signal is insignificant compared to network carbon concentrations but caused multiple IB failures. The issue was resolved after a new HeO_2 cylinder was installed.

Figure 5-24 shows the results of daily analyses of instrument blanks by each instrument. Horizontal dash lines in red color indicate the acceptance criteria of ± 0.3 µg C/cm^2 for total carbon areal density. For cases when the acceptance criteria were 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 5-24: Results of daily instrument blanks from each analyzer for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).



5.5.2.2 *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 5-33 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 5-33: 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*	17.5

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

Upon completion of the sucrose analysis, the measured TC is compared against the reference value (i.e. calculated TC) provided in Table 5-33. The % error between the measured and calculated TC is derived using Equation 5-1. 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 5-34 summarizes the statistics of the daily sucrose check. There were 72 exceedances out of the 1364 sucrose analyses during the report period. All repeat-analyses of the sucrose solution showed acceptable results (Figure 5-25).

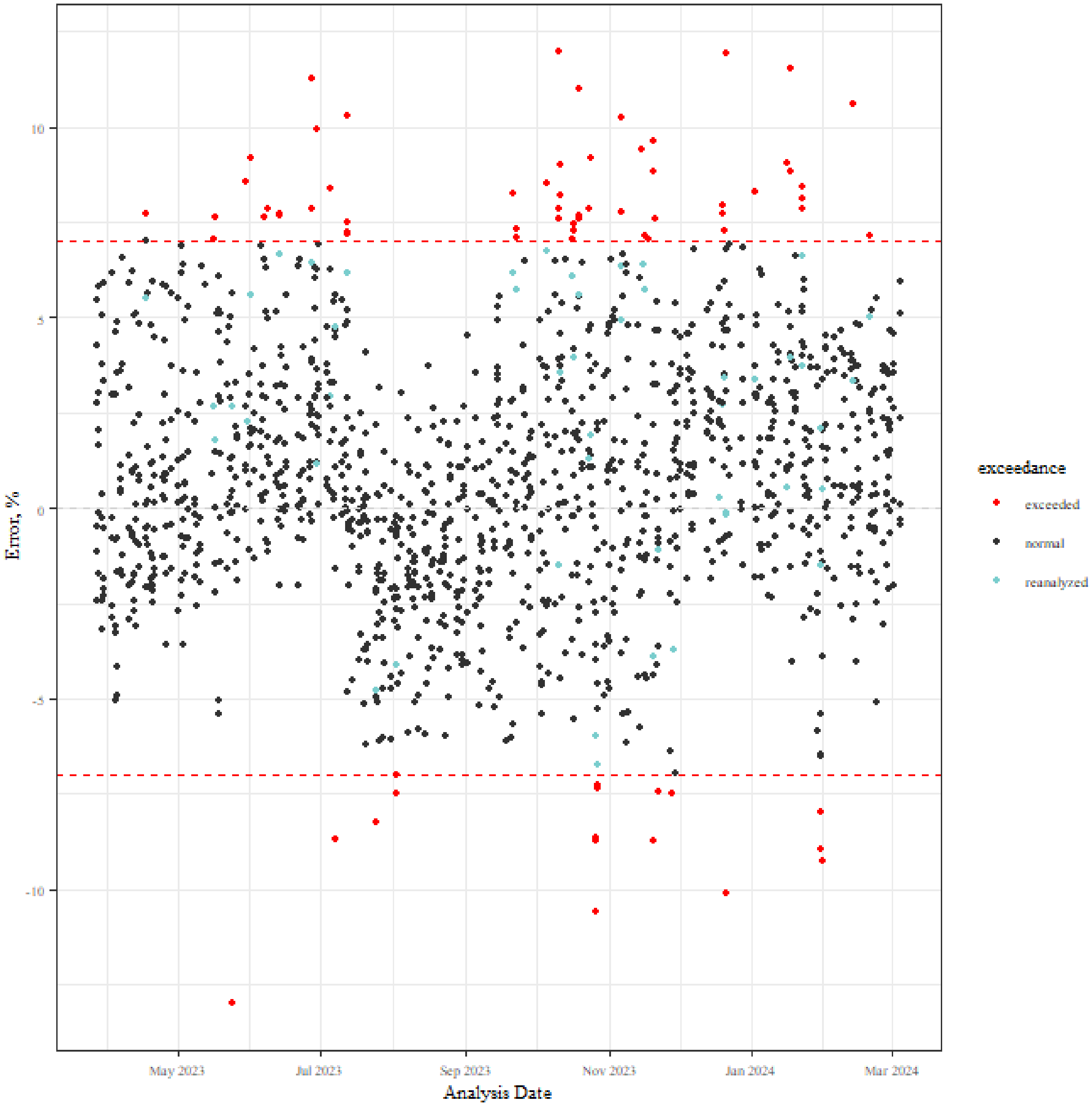
$$Error\ (\%) = \left(\frac{Measured\ TC - Calculated\ TC}{Calculated\ TC}\right) \times 100\% \tag{Eq. 5-1}$$

Table 5-34: Statistics of daily single-point sucrose standard total carbon analyses on all carbon analyzers for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).

Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
1364	0.7	0.9	-12.97	11.98	3.39	72

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 5-25: Results of daily single-point sucrose calibration standard check for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023) for all instruments.



5.5.2.3 *Calibration Peak Area Check*

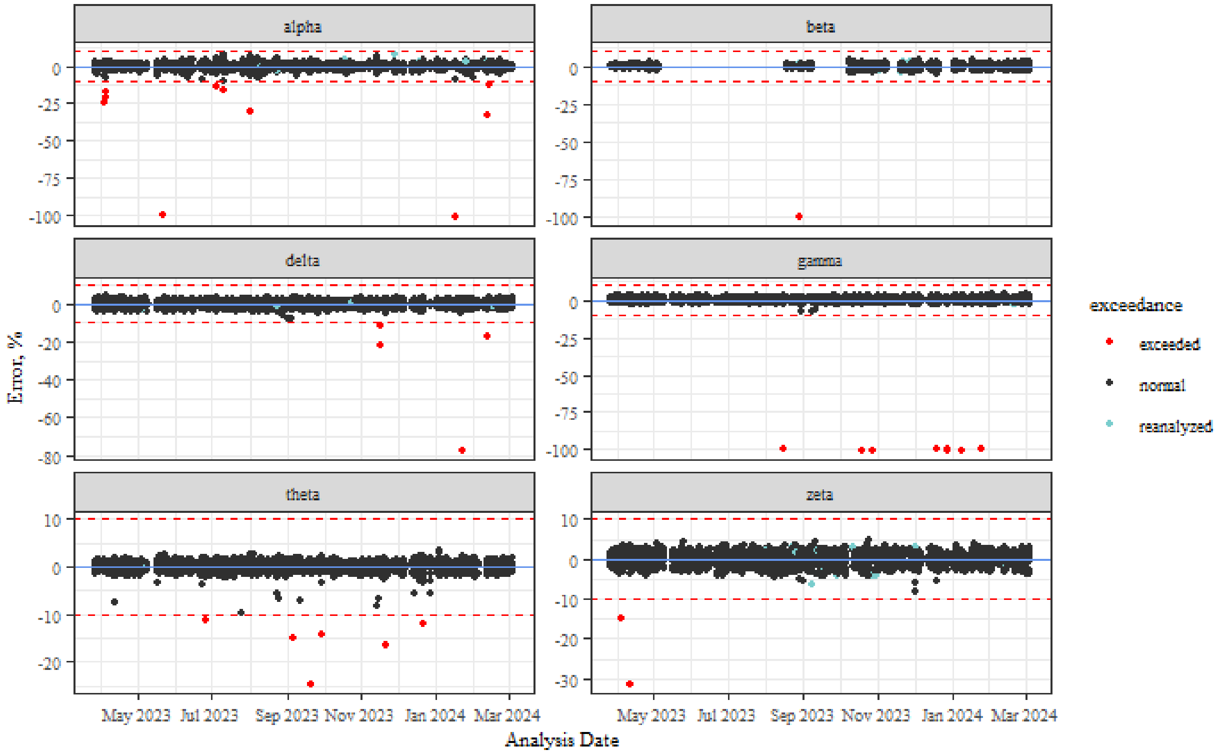
At the end of each analysis, a fixed amount of methane (CH_4) from a cylinder containing 5% CH_4 in helium is injected into the system as an internal gaseous standard. The CH_4 peak area is quantified and compared to the average peak area of all analyses performed on that instrument on that day. If the error (calculated using Equation 5-2) 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 5-35 summarizes the statistics of the calibration peak area checks. There were 31 exceedances during this reporting period. All affected samples were reanalyzed with acceptable results. Beta had analyzed significantly fewer samples compared to other analyzers because it was taken offline and used for testing the autoloader between 5/8 and 8/16/2023. Besides, no CSN network samples were analyzed on Beta between 9/8 and 10/6/2023 when autoloader was malfunctioning. Gamma's FID automatically turns off occasionally due to unstable gas flow, leading to zero calibration peak area. This issue was resolved after performing autozero (calibration of the gas valves) on Gamma.

$$Error\ (\%) = \left(\frac{Cal.Peak - Average\ Cal.Peak}{Average\ Cal.Peak}\right) \times 100\% \qquad \text{(Eq. 5-2)}$$

Table 5-35: Statistics of internal calibration peak area check on all carbon analyzers for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).

Analyzer	Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
Alpha	2591	0.12	-0.13	-100.8	7.86	3.45	10
Beta	1596	0.11	-0.06	-99.98	3.89	2.82	1
Delta	2515	0.13	-0.05	-77.75	4.66	2.29	4
Gamma	2646	-0.04	-0.31	-100.94	3.92	5.63	8
Theta	2530	0.03	-0.04	-24.84	3.24	1.23	6
Zeta	2522	0.12	-0.02	-31.56	4.76	1.72	2

Figure 5-26: Results of internal calibration area check for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023). 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).

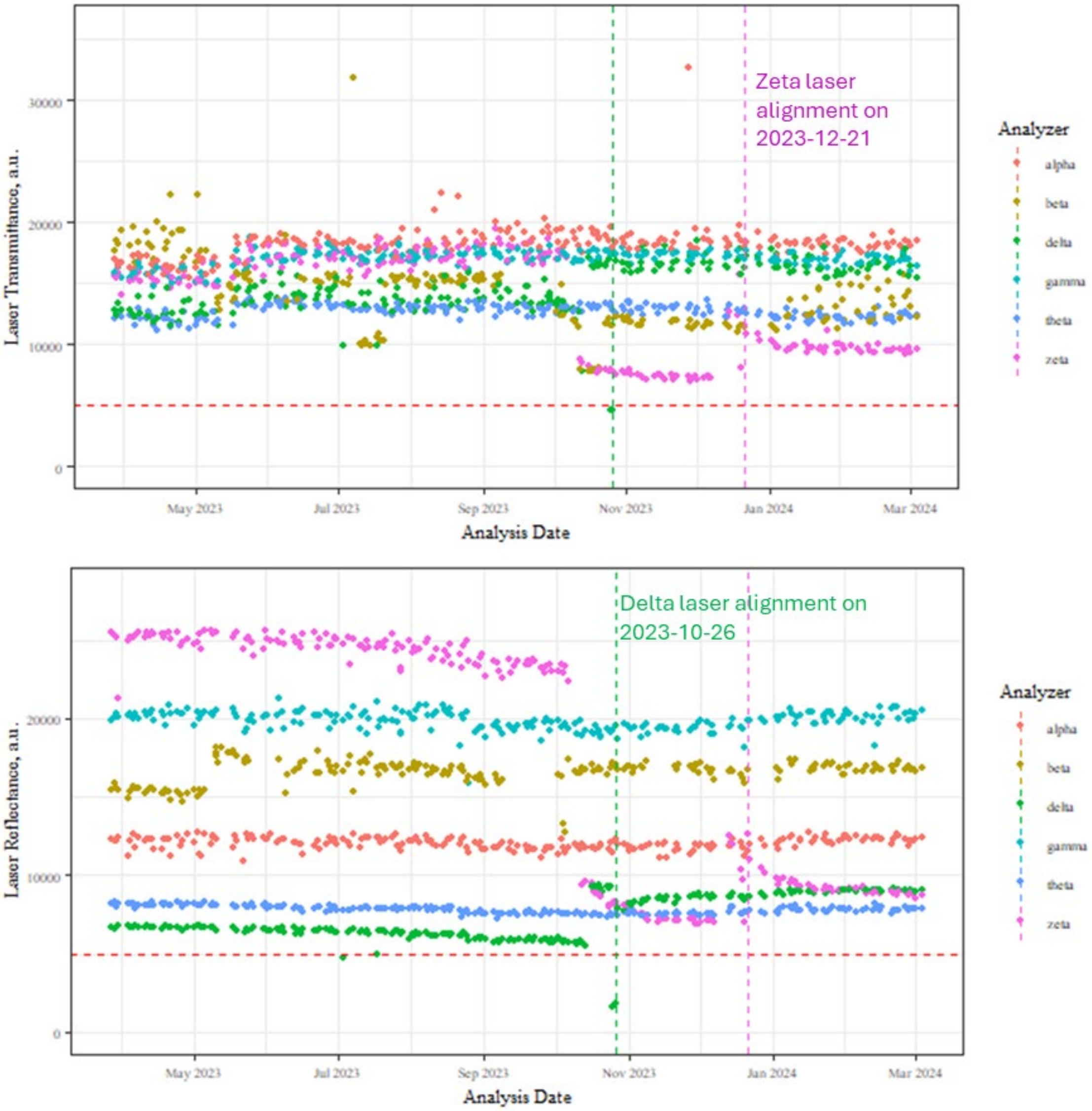


5.5.2.4 *Laser Performance Check*

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 5-27 shows the filter reflectance and transmittance initial readings for all instrument blank analyses during the report period. There were two exceedances of laser reflectance signal and two exceedances of laser transmittance signal. All exceedances occurred on Delta and are resolved after a laser realignment on 10/26/2023. A laser source alignment was performed on Zeta on 12/21/2023 to improve laser initial signal.

In the following figure, 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 5-27: Laser initial readings (top: Transmittance; bottom: Reflectance) of the instrumental blank analysis for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).



5.5.2.5 *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 5-36 lists the acceptance criteria for replicate analysis and the summary statistics from this reporting period. A total of 826 replicate analyses were performed out of the 14034samples 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. During this reporting period, there was a total of 50 TC exceedances and 61 ECR exceedances. A third punch from samples with exceedances were analyzed on a third analyzer. As noted in Table 5-36, all reanalysis of exceedances passed the QC criteria. Figure 4.3-6 shows the results of the replicate analyses. The original failed analyses are invalidated in the database and not plotted in this figure.

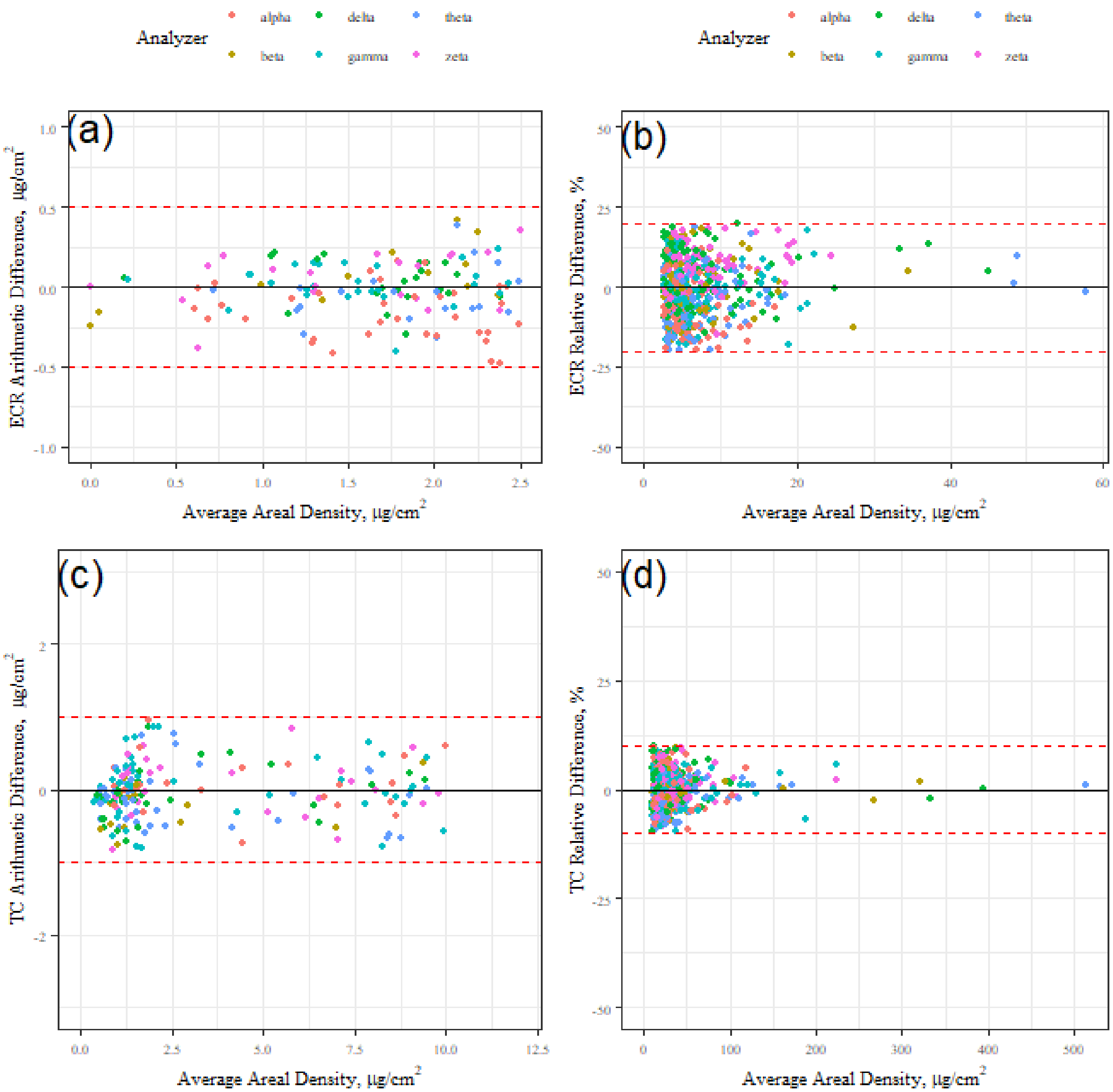
Table 5-36: Acceptance criteria and the summary statistics of the replicate analyses for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).

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	826	50	50
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	826	61	61

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

In the following figure, the red dashed lines in each panel represents the acceptance criteria. Note that arithmetic differences are plotted for low ECR and TC samples (Panel a and c), whereas relative differences are plotted for the rest of the samples (Panel b and d). The invalidated original results are not plotted.

Figure 5-28: Results of CSN replicate analysis for ECR (Panel a and b) and TC (Panel c and d) for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).



5.5.2.6 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 54 weekly PC samples were analyzed during this reporting period. Six punches were taken from the same PC sample, one analyzed by each instrument.

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:

$$Relative\ difference_i\ (\%) = \frac{(Measured_i - Average) \times 100}{Average}$$

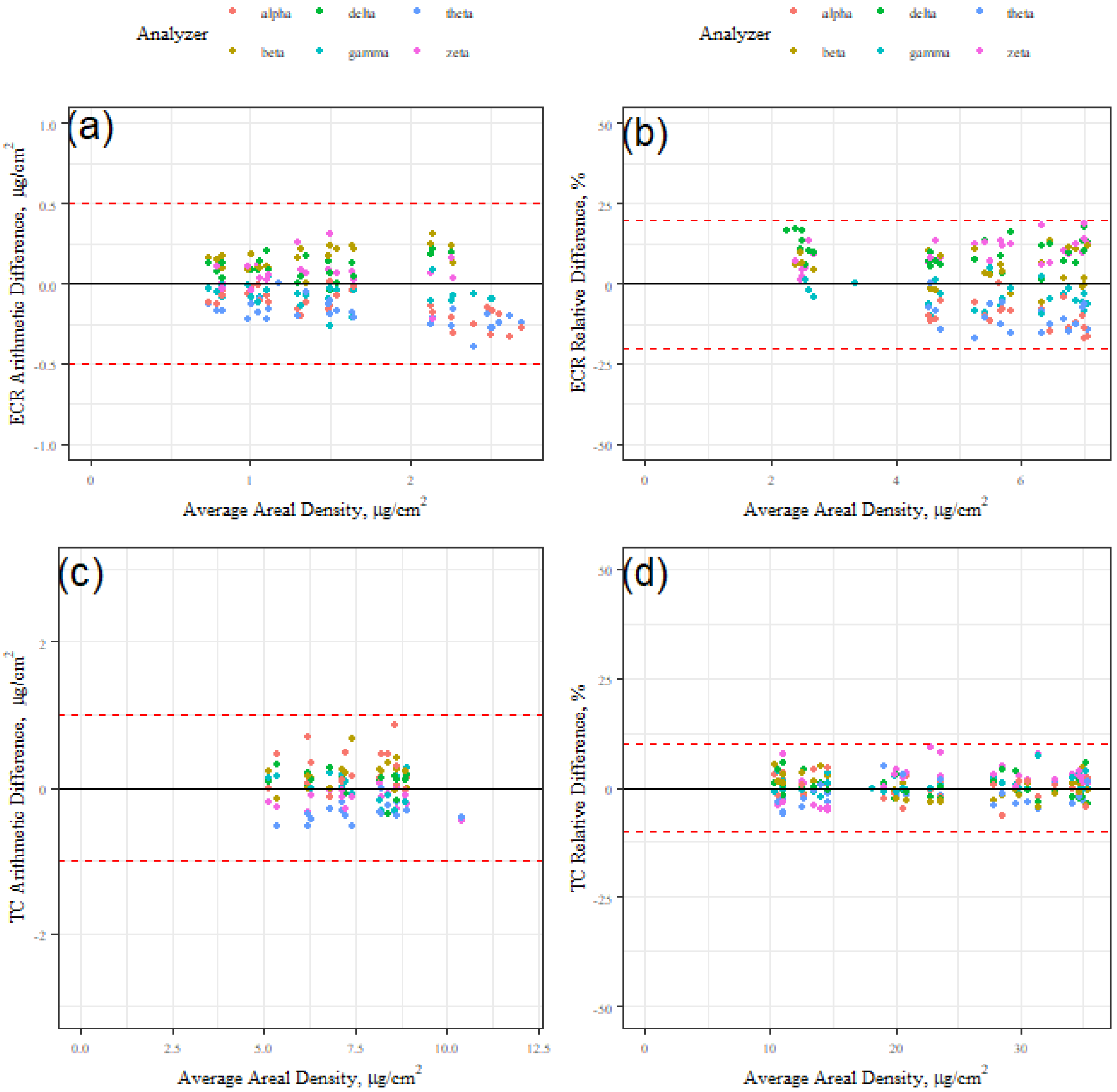
The acceptance criteria for inter-instrument comparison at low filter loadings (TC ≤ 10 µg C/cm^2 and ECR ≤ 2.5 µg C/cm^2) are based on the arithmetic difference between the measurement from a given analyzer and the average value for the same PC sample obtained from all analyzers used in each comparison. The acceptance criteria for inter-instrumental check is the same as that for the network sample replicates (See Table 5-31 for details). Exceeding the acceptance criteria results in further investigation of the instrument, and reanalysis of the performance check sample. Table 5-37 summarizes the statistics of the instrument bias for ECR and TC. There were no exceedances during this reporting period.

Table 5-37: 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 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).

	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	22	-9.58	-9.07	3.61	42	-1.51	-1.36	2.46
Beta	25	5.45	4.86	6.53	35	-0.12	0.03	2.64
Delta	27	1.22	1.74	4.99	41	0.28	0.58	2.46
Gamma	27	-0.49	-0.26	3.86	42	-0.21	-0.06	2.17
Theta	26	-5.41	-5.73	3.2	42	-1.68	-1.55	2.17
Zeta	30	10.76	10.64	4.69	41	2.52	2.55	2.72
	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	31	-0.15	-0.16	0.11	11	0.05	0.03	0.25
Beta	20	0.15	0.14	0.12	10	0.29	0.26	0.17
Delta	25	0.11	0.09	0.13	11	-0.05	0	0.19
Gamma	26	-0.09	-0.07	0.12	11	0.02	0.11	0.24
Theta	27	-0.18	-0.18	0.07	11	-0.32	-0.25	0.16
Zeta	22	0.11	0.14	0.1	11	-0.2	-0.17	0.12

Figure 5-29 shows the results of the weekly PC samples for each analyzer. The red dashed lines in each panel represent the acceptance criteria. Note that arithmetic differences are plotted for low ECR and TC samples (Panel a and c), whereas relative differences are plotted for the rest of the samples (Panel b and d).

Figure 5-29: 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 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).



5.5.2.7 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 5-33 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 5-38 summarizes the multi-point sucrose calibrations performed during this reporting period.

Table 5-38: Summary of multi-point sucrose calibration performed for the analysis period 03/27/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).

Analyzer	Calibration Date	Slope	r^2	Calibration Constant
Beta[2]	6/7/2023	1.05	1	21.27
Alpha[2]	7/13/2023	1.0529	0.9999	20.4871
Zeta[1]	9/14/2023	1.0482	0.9999	20.6831
Theta[1]	9/14/2023	1.0308	0.9998	20.0568
Alpha[1]	9/14/2023	1.0319	0.9999	19.8538
Gamma[1]	9/14/2023	1.0299	1	20.1753
Delta[1]	9/15/2023	1.03	1	20.28
Beta[1]	9/26/2023	1.0324	0.9999	20.6025
Delta[2]	10/20/2023	1.047	1	19.3696
Zeta[3]	10/27/2023	0.8993	0.9999	22.9991
Zeta[4]	11/20/2023	1.0563	0.9999	21.7733
Theta[3]	11/29/2023	0.964	0.9997	20.8058

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

[2] Daily sucrose reading is too high, and a consistent one-sided bias is observed with daily sucrose.

[3] Daily sucrose reading is too low, and a consistent one-sided bias is observed with daily sucrose.

[4] Zeta's previous sucrose calibration was done on 10/27/2023. However, a problematic HeOx gas cylinder was used at that time, which caused the calibration to be inaccurate and resulted in the sucrose measurements being too high after the HeOx cylinder was changed to a normal one.

5.5.2.8 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 5-39 summarizes the temperature calibrations performed on each analyzer during this reporting period.

Table 5-39: Summary of the temperature calibrations performed on each analyzer for the analysis period 03/27/2023 through 03/05/2024 (samples collected 01/1/2023 through 12/31/2023). Oven re-wrap refers to adjustment or replacement of heating coils that are wrapped around the sample oven.

			Temperature Offsets (°C)					
Analyzer	**Calibration Date**	**Oven Re-Wrapped?**	**140 °C**	**280 °C**	**480 °C**	**580 °C**	**740 °C**	**840 °C**
beta[1]	5/8/2023	no	-4	-4	-3	-4	-8	-21
alpha[1]	5/12/2023	no	-25	-45	-44	-48	-26	-35
zeta[1]	5/12/2023	no	-12	-15	0	2	16	5
delta[1]	6/20/2023	no	7	0	-24	-33	-28	-37
gamma[1]	6/20/2023	no	-15	-20	-4	-5	-6	-9.1
theta[1]	6/20/2023	no	10	17	33	28	11	4
zeta[1,2]	10/11/2023	yes	-25	-39	-26	-23	5	-3
alpha[1]	11/9/2023	no	-25	-43	-40	-42	-24	-32
beta[1]	11/16/2023	no	21	17	23	23	19	10
delta[1]	12/8/2023	no	13	13	-11	-21	-22	-31
gamma[1]	12/8/2023	no	-16	-23	-8	-9	-3	-9
theta[1]	12/8/2023	no	14	21	36	33	15	7

[1] Semi-annual temperature calibration

[2] Back oven thermocouple was replaced, and heating coil re-wrapped

5.5.3 Determination of Uncertainties and Method Detection Limits

For determination of Method Detection Limits (MDLs) see Section 4.1.3.8.

For uncertainty estimates see Section 7.5

5.5.4 Audits, Performance Evaluations, Training, and Accreditations

5.5.4.1 System Audits

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

5.5.4.2 Performance Evaluations

The UC Davis Thermal Optical Analysis Laboratory participated in the ERLAP 2024 OCEC Interlaboratory Comparison. Eight quartz filter samples were analyzed on Theta with the EUSAAR protocol at AQRC. Our results showed no bias in TC and OC, and a small positive bias for EC when compared to the other participating labs. Specifically, AQRC EC was on average 0.18 µg C/cm² (or 7.6%) higher than the reference value. See the references section of this report for more details (JRC138617). Possible causes for the minor deviation in EC include unverified EUSAAR temperature offsets and lack of lab QC using EUSAAR protocol. AQRC will implement similar QC measures with the EUSAAR protocol for the next ERLAP OCEC inter-laboratory study.

5.5.4.3 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 *UCD CSN SOP #402* and relevant Technical Information materials.

5.5.4.4 Accreditations

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

5.5.5 Summary of Filter Blanks

5.5.5.1 Field Blanks

Over the sampling period (January 1, 2023 through December 31, 2023) there were 1594 valid quartz filter field blanks. Table 5-40 summarizes the field blank statistics.

Table 5-40: Quartz filter field blank statistics for the analysis period 03/27/2023 through 03/05/2024 (samples collected 01/1/2023 through 12/31/2023). 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	1560	0.02	0.07	-0.11	12.21	0.43
EC2	1560	0.06	0.07	-0.05	1.68	0.09
EC3	1560	0.01	0.01	-0.07	0.21	0.02
ECR	1560	0	0.02	0.00	12.61	0.40
ECT	1560	0	0.02	0.00	9.90	0.31
OC1	1560	0.16	0.17	0.00	2.08	0.11
OC2	1560	0.31	0.35	0.02	10.20	0.38
OC3	1560	0.47	0.58	0.05	10.54	0.56
OC4	1560	0.15	0.20	-0.16	4.28	0.26
OCR	1560	1.23	1.43	-0.03	25.93	1.30
OCT	1560	1.23	1.43	-0.03	28.51	1.38
OPR	1560	0.09	0.13	-0.16	3.44	0.19
OPT	1560	0.09	0.13	-0.16	4.83	0.24

5.5.5.2 Laboratory Blanks Supplied by WSP and RTI

Five quartz laboratory blanks are shipped from the Sample Handling Laboratory (WSP or RTI) with each batch of routine filters to the analysis laboratory and analyzed. These filters are different from those used for daily QC as described in section 5.4.5.2, as the laboratory blanks are from the same filter lots as the CSN sample filters. The WSP filters were pre-fired by Desert Research Institute (Reno, NV) and delivered to WSP along with the quartz filters to be used for sampling, whereas the RTI filters are pre-fired by RTI. Both WSP and RTI laboratory blanks are analyzed by UCD carbon analysis lab. A total of 60 quartz laboratory blanks were analyzed during the current reporting period, with four analyses per filter (except for one lab blank on which 3 analyses were performed) on different analyzers. The laboratory blank statistics, summarized in Table 5-41, are based on 239 analyses. No specific QC criteria were established for the laboratory blanks, but the carbon contents on these filters are generally very low.

Table 5-41: Quartz filter laboratory blank statistics for the analysis period 03/27/2023 through 03/05/2024 (samples collected 01/1/2023 through 12/31/2023). 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	Filter Count*	Median (μg/cm^2)	Average (μg/cm^2)	Min (μg/cm^2)	Max (μg/cm^2)	St.Dev. (μg/cm^2)
EC1	60	-0.01	0	-0.09	0.38	0.05
EC2	60	0.01	0.02	-0.04	0.23	0.03
EC3	60	0.01	0.01	-0.03	0.15	0.02
ECR	60	0	0	0	0.01	0
ECT	60	0	0	-0.06	0	0
OC1	60	0.06	0.08	0	0.38	0.08
OC2	60	0.06	0.06	0.02	0.28	0.03
OC3	60	0.09	0.14	0.03	0.85	0.14
OC4	60	-0.02	-0.01	-0.23	0.33	0.07
OCR	60	0.23	0.28	-0.29	1.79	0.3
OCT	60	0.23	0.29	-0.29	1.79	0.3
OPR	60	0.01	0.02	-0.14	0.48	0.08
OPT	60	0.01	0.02	-0.14	0.48	0.08

*4 punches were taken out of each laboratory blank filter and analyzed on 4 different instruments

5.6 UC Davis Optical Absorption Laboratory

The UC Davis Optical Absorption Laboratory received and analyzed PTFE filters from batches 99 through 23-12, covering the field sampling period beginning from January 1, 2023 through December 31, 2023. Analyses of these samples were performed May 1, 2023 through April 10, 2024. 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 5-42: Sampling months in 2023 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 (2023)	Analysis Batch #	HIPS Analysis Dates
January	99	2023-05-01 - 2023-05-01
February	100	2023-05-11 - 2023-05-11
March	101	2023-06-13 - 2023-07-26
April	102	2023-07-26 - 2023-07-26
May	103 / 23-05	2023-08-16 - 2023-10-03
June	104 / 23-06	2023-09-12 - 2023-11-29
July	23-07	2023-10-05 - 2023-12-08
August	23-08	2023-11-14 - 2024-01-24
September	23-09	2023-11-14 - 2024-01-24
October	23-10	2024-01-09 - 2024-02-13
November	23-11	2024-02-01 - 2024-03-14
December	23-12	2024-03-07 - 2024-04-10
All months	99 to 23-12	2023-05-01 - 2024-04-10

5.6.1 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 5-43.

Table 5-43: 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 $r = -a_1 R/a_0$, 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.

5.6.2 Summary of QC Results

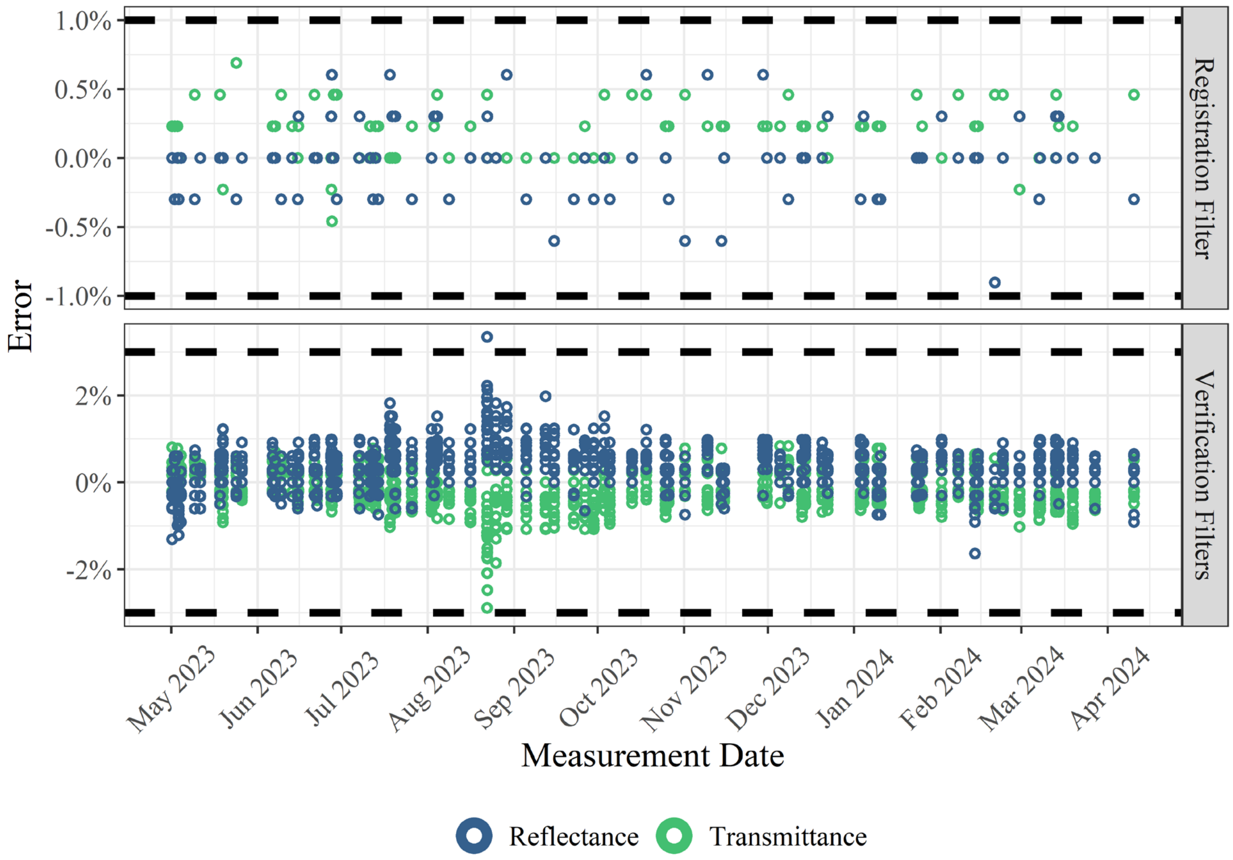
QC tests conducted over the course of the analysis period showed good overall control of the instrument and process. There were occasional acceptance criteria failures, which were investigated promptly and corrected with no impact on sample results. The following summarizes the QC issues which occurred during the analysis period reported here.

5.6.2.1 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 only failed one time during the period reported here. Figure 5-30 shows one failure for reflectance on verification filter number 11 which occurred the morning of 8/22/2023. The verification check was repeated a second time with passing results before any samples were analyzed.

Figure 5-30: HIPS detector response check of the Verification Filter set.

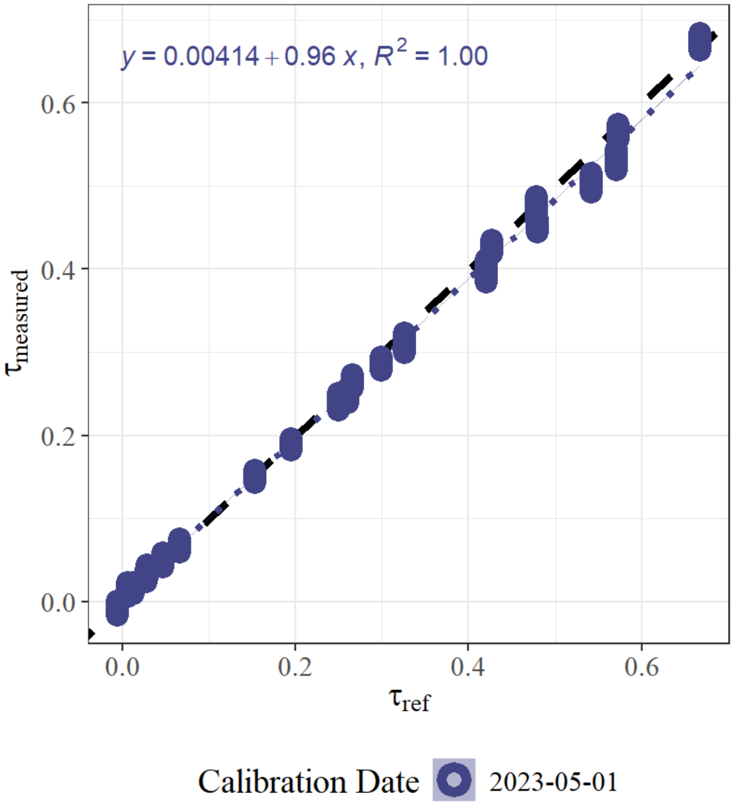


5.6.2.2 *Reanalysis Check*

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.

QC material comparison of τ_{abs} with reference values is shown in Figure 5-31.

Figure 5-31: HIPS linearity check of the Reanalysis Filter set.



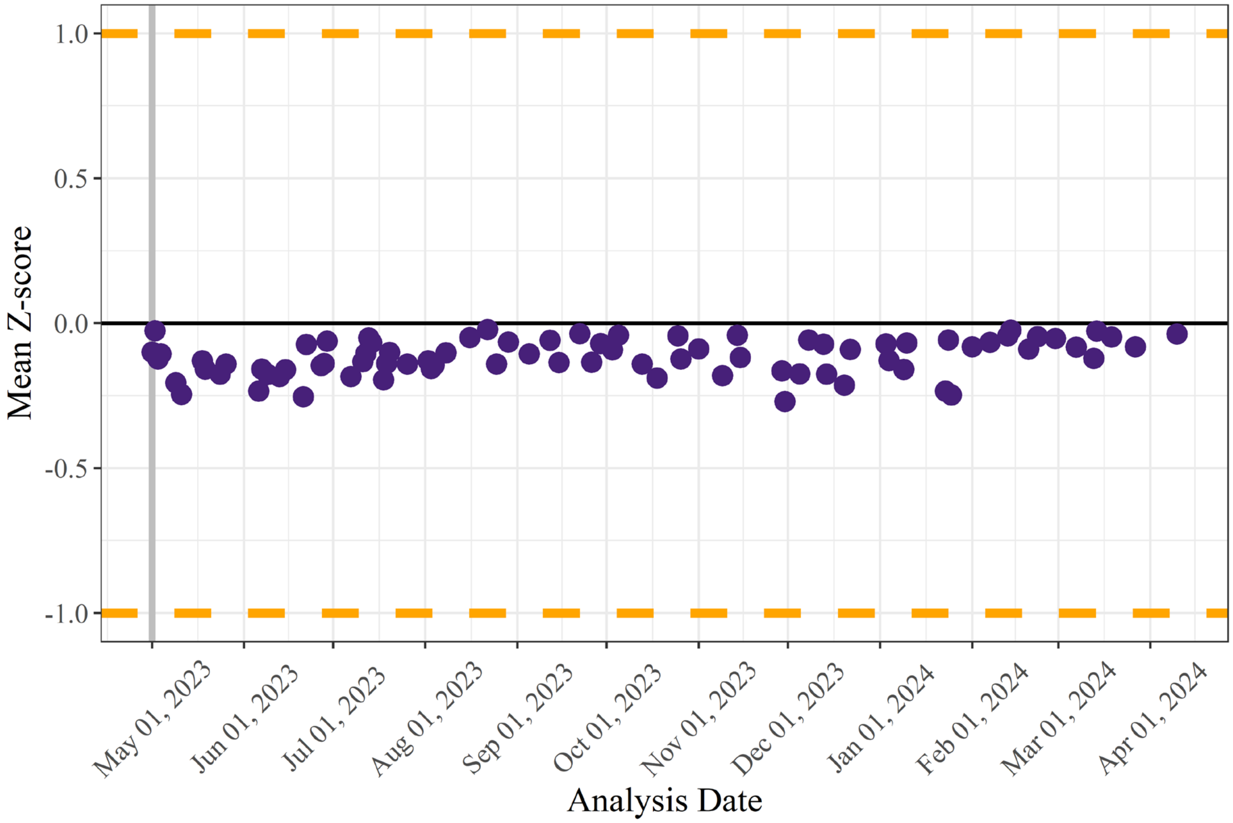
The linearity check passed for all calibrations of the Reanalysis Set. The HIPS instrument had a 100 % passing rate for the reanalysis set measurements within the uncertainty bounds, ± 2 X $U_{\tau_{abs}}$.

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 5-32.

Figure 5-32: HIPS reanalysis mean z-score. Vertical lines identify calibration dates. Horizontal lines demarcate the QC limits of the z-scores.



5.6.3 Determination of Uncertainties and Method Detection Limits

For determination of Method Detection Limits (MDLs) see Section 4.1.3.8.

For uncertainty estimates see Section 7.5

5.6.4 Audits, Performance Evaluations, Training, and Accreditations

5.6.4.1 System Audits

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

5.6.4.2 Performance Evaluations

No performance evaluations were conducted during this reporting period.

5.6.4.3 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.

5.6.4.4 Accreditations

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

5.6.5 Summary of Filter Blanks

5.6.5.1 Field Blanks

Over the sampling period (January 1, 2023 through December 31, 2023) there were 1596 valid PTFE filter field blanks. Table 5-44 summarizes the field blank statistics.

Table 5-44: PTFE filter field blank statistics for the 2023 sampling analysis period 5/1/2023 through 4/10/2024 (samples collected 1/1/2023 through 12/31/2023). Values are expressed as optical depth, which is unitless.

Species	Count	Median	Average	Min	Max	St. Dev.
fAbs	1596	0	0	-0.082	0.013	0.004

5.6.5.2 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 5-45 summarizes the laboratory blank statistics.

Table 5-45: PTFE filter laboratory blank statistics for the 2023 sampling analysis period 5/1/2023 through 4/10/2024 (samples collected 1/1/2023 through 12/31/2023). Values are expressed as optical depth, which is unitless.

Species	Count	Median	Average	Min	Max	St. Dev.
fAbs	65	-0.001	-0.001	-0.007	0.004	0.002

6. Data Management and Reporting

6.1 Sample Shipping and Handling

A data system for capturing shipping, field, and filter information was deployed starting with June 2023 sample collection; prior to this, filters and data originated at WSP. The data management system was developed and optimized to the support the CSN program. Revisions to the database were made to provide a better user experience and to optimize necessary processes. All database changes underwent testing prior to deployment to the staff.

The RTI SHAL provides UC Davis and the RTI Ions laboratory with monthly data files containing the requested field sampling information, filter ID's, and associated comments, flags, and receipt temperatures. These files are communicated between RTI and UC Davis monthly. UC Davis then reviews the files, and inquiries are communicated and resolved, as best as possible, prior to final data upload.

6.2 Denuder Refurbishment

There were no issues with denuder refurbishment activities in 2023 at RTI. A schedule, provided by WSP was followed to track the timeframe of when denuder refurbishment was required.

6.3 Number of Events Posted to AQS

Table 6-1 summarizes dates that data were delivered to AQS for samples collected January 1, 2023 through December 31, 2023. Data are expected to be delivered to AQS within 120 days of receipt of filters by the analytical laboratories. As of the June 2023 Sampling Month, with the new contract, data are expected to be delivered to AQS within 160 days after the end of the sampling month.

Deliveries were delayed because of the June 2023 SHAL transition. Beginning with the September 2023 sampling month, deliveries were delayed by an outage of the DART system used by SLT staff for data validation. The DART outage lasted from March 2024 to mid-May 2024 and impacted subsequent delivery timelines. September 2023 to December 2023 data deliveries were most impacted by the outage.

Table 6-1: Summary of data deliveries to AQS for samples collected January 1, 2023 through December 31, 2023.

Sampling Month (2023)	Analysis Batch #	Filter Receipt Date	AQS Delivery Date	Days
January	99	March 15, 2023	July 13, 2023	120
February	100	April 12, 2023	August 10, 2023	120
March	101	May 17, 2023	September 14, 2023	120
April	102	June 21, 2023	October 17, 2023	118
May	103 / 23-05	July 12, 2023 / July 19, 2023	November 16, 2023	120
June	104 / 23-06	July 12, 2023 / August 16, 2023	December 22, 2023	174*
July	23-07	September 13, 2023	February 13, 2024	196
August	23-08	October 12, 2023	March 14, 2024	195
September	23-09	November 8, 2023	April 4, 2024	186
October	23-10	December 13, 2023	May 15, 2024	197
November	23-11	January 11, 2024	June 5, 2024	187
December	23-12	February 9, 2024	June 21, 2024	172

* As of June 2023, Days are between first day of month following Sampling Month and AQS Delivery Date.

7. Quality Assurance and Data Validation

7.1 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 the January to May 2023 sampling. Filter Handling, Acceptance Testing, and Gravimetric Analysis was handled by WSP (formerly Wood) under their own QAPP and direct contract with EPA for those filters.

7.2 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.

7.2.1 UC Davis SOP Revisions

SOPs were delivered to EPA on 18 April, 2024. These final versions covered all UC Davis operations as well as the RTI versions. When the new contract was awarded and transitioned to UC Davis, we worked with RTI to review and update all necessary documents including QMP, QAPPs, SOPs, and TIs. The current QMP is v1.7 (dated May 31, 2023). The current UCD QAPP is v1.6 (dated November 20, 2023) and the current RTI QAPP is v0 (dated November 20, 2023). SOPs are updated when needed as procedures are added or modified. They are sent as a package to EPA on a regular basis.

Documents can be found at the following locations:

https://aqrc.ucdavis.edu/csn-documentation

https://www.epa.gov/amtic/chemical-speciation-network-quality-assurance

7.2.2 RTI SOP Revisions

During the initial contract year, no SOPs were finalized prior to December 31, 2023. All SOP’s for SHAL were utilized in draft format. All SOP’s will be finalized and approved in 2024 for use in the program. The gravimetry lab SOP was finalized and followed during 2023.

7.3 Summary of Internal QA Activities

7.3.1 UC Davis Data Processing 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.

7.3.2 RTI Data Processing QA Activities

Internal QA activities included:

- Review of the QAPP, incorporating comments from EPA and UC Davis.
- Review of all SOP’s listed in Section 7.3.
- Review of gravimetry data, gravimetry environmental chamber readings, gravimetry blanks, gravimetry mass standards, gravimetry holding times for filters, and review of acceptable parameters for weighing sessions.
- Review of datafiles prior to submission to UC Davis.

- Review of acceptance testing results.

7.4 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.

7.4.1 Sample Handling Reviews and Investigations (RTI)

7.4.1.1 Monthly Analysis Batch Review

Analysis batch review is performed through programmed database functions, and by personnel prior to submission to the laboratories.

Database checks are generally completion checks and are resolved before the data file is created. The database has a programmed feature which allows users to check and ensure all field data has fully been entered and issues resolved before data generation; if an issue persists, the individual measurement request ID matching the field data form for the sampling event is located and the information is accurately entered into the system to resolve the issue. The second database check involves checking to ensure all expected events have a corresponding filter and that the filter has been correctly logged in to the database system. If a filter is not present, and there is no record of why it should be missing, the filter is physically located and added to the set before the datafile generation is complete.

During the monthly datafile generation, several quality checks are run, and outliers are posted to a separate “Checks” file. This file is reviewed by personnel and all issues are resolved or flagged prior to submission to the analytical laboratories.

7.4.1.2 Post Shipment Investigations

As previously mentioned, the analytical laboratories perform a review of the data and inquire about suspected discrepancies or unclear anomalies in the data. The inquiry is reviewed and the notes and information captured as part of the sampling event is relayed to the laboratory reviewer to assist in resolving the issue. This periodic communication occurs approximately weekly through a shared document; emails and meetings are further used as necessary to resolve issues on an as needed basis.

7.4.1.3 Acceptance Data Review

Acceptance data is reviewed by the laboratories performing the analysis and by the SHAL project manager to ensure no results which would disqualify filters from being sampled are being used. For the year 2023 no filters or batches failed the acceptance criteria. Results from OCEC and Ions analysis were reported previously in this report.

7.4.2 Summary of Monthly Data Validation Review Results

7.4.2.1 Comparisons Across Years

Multi-year time series plots are used to examine large-scale trends and/or analytical problems. Comparisons to historical network data provide context for validation and review of more recent data.

Figures 7-1 and 7-2 show time series plots for the network-wide 90th percentile, median, and 10th percentile concentrations of organic carbon by reflectance (OCR) and elemental carbon by reflectance (ECR) respectively. Unusually high values were seen across the distribution for May, June, and July due to Canadian wildfires impacting a large portion of the network throughout the eastern United States.

Figure 7-1: Multi-year time series of network-wide organic carbon by reflectance concentrations (OCR).

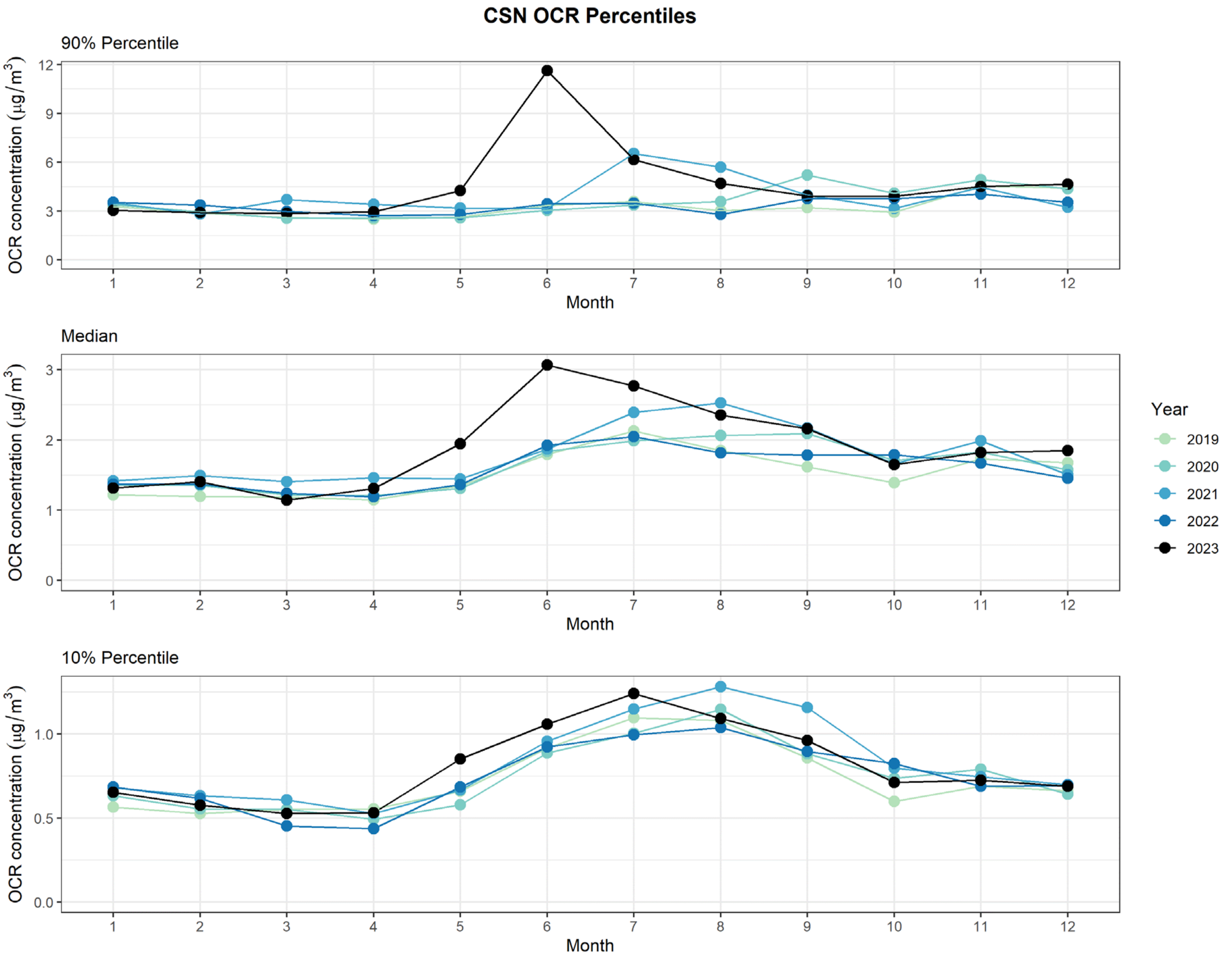
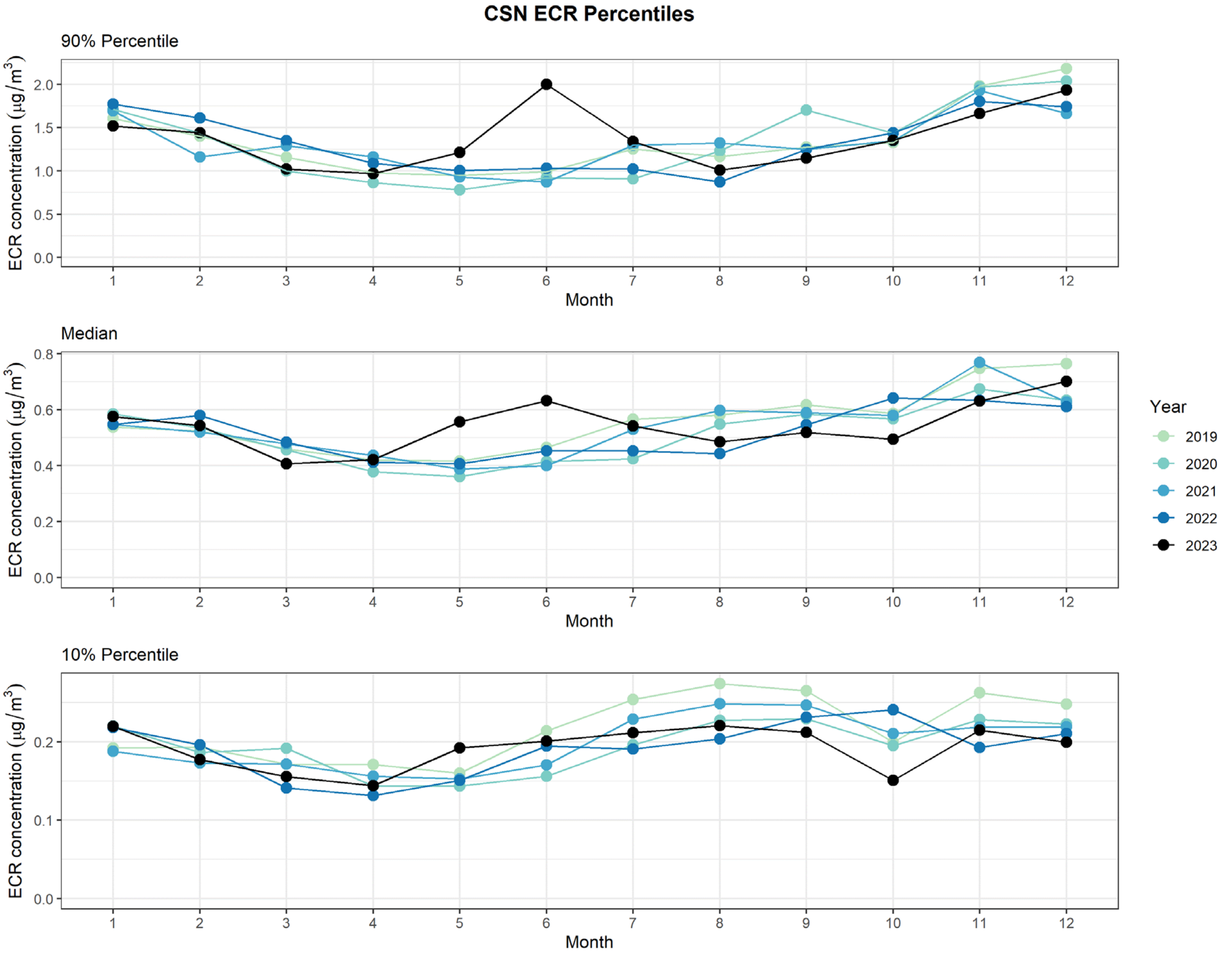
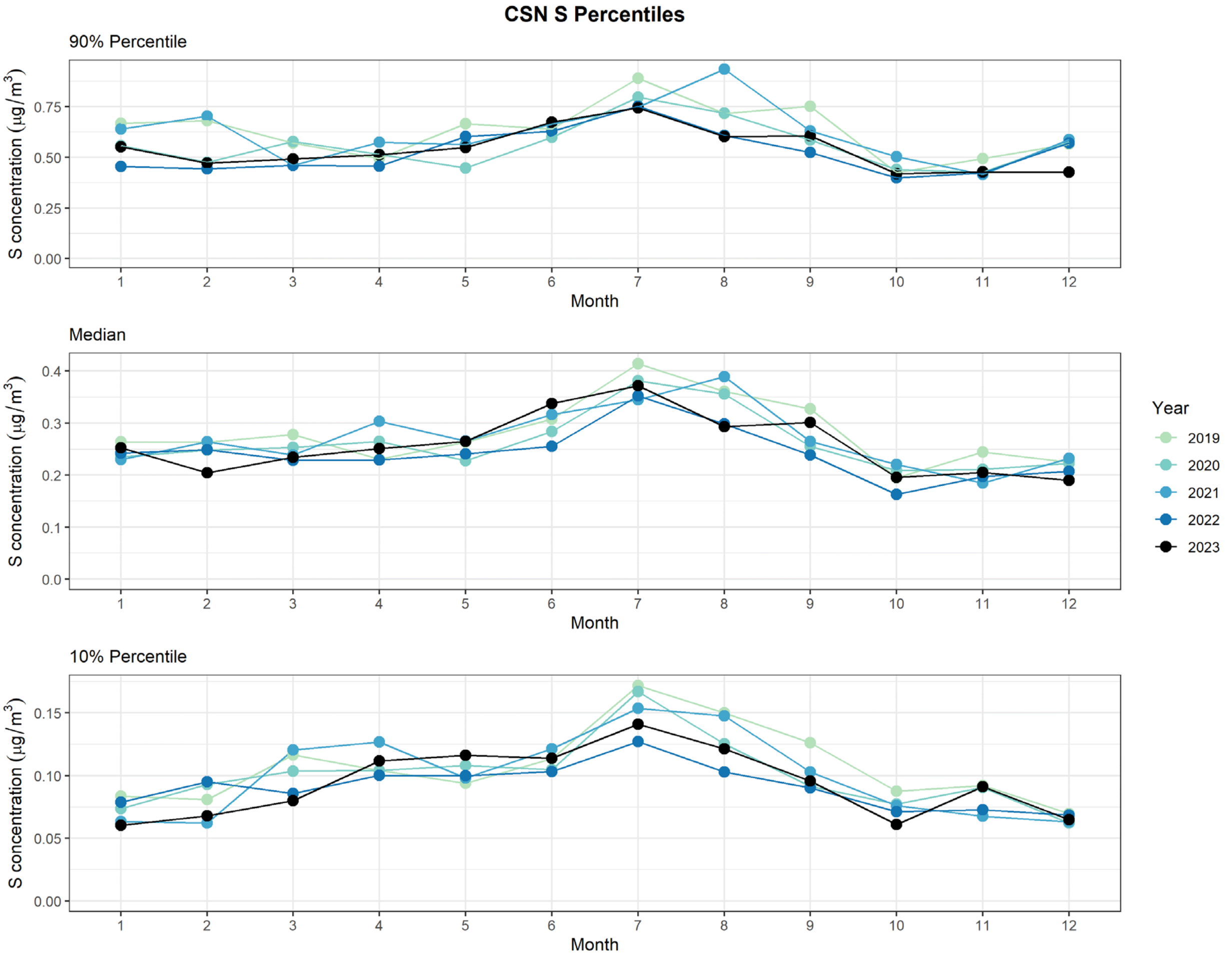


Figure 7-2: Multi-year time series of network-wide elemental carbon by reflectance concentrations (ECR).



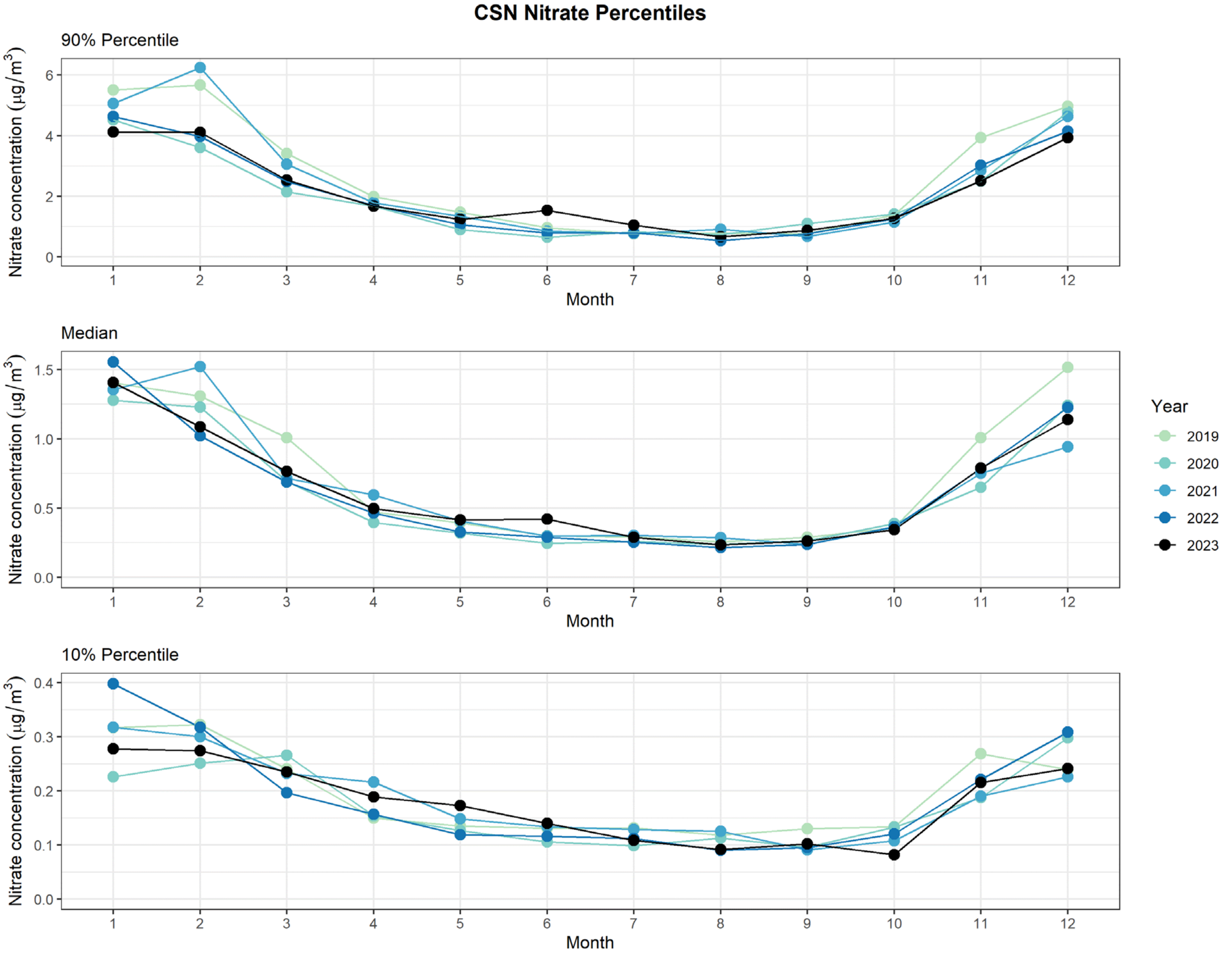
Similar to recent years, the 2022 sulfur concentrations generally continue to be low (Figure 7-3), with reduced seasonal variability.

Figure 7-3: Multi-year time series of network-wide sulfur (S) concentrations.



The 2022 nitrate concentrations continue to show strong seasonality with elevated winter concentrations (Figure 7-4).

Figure 7-4: Multi-year time series of network-wide nitrate concentrations.



UC Davis calculates and delivers composite variables for reconstructed mass (RCM) and soil. The 2019 through 2023 RCM and soil results are shown in Figure 7-5 and 7-6, respectively. High RCM in spring was driven by wildfire smoke.

Figure 7-5: Multi-year time series of network-wide composite variable reconstructed mass (RCM) concentrations.

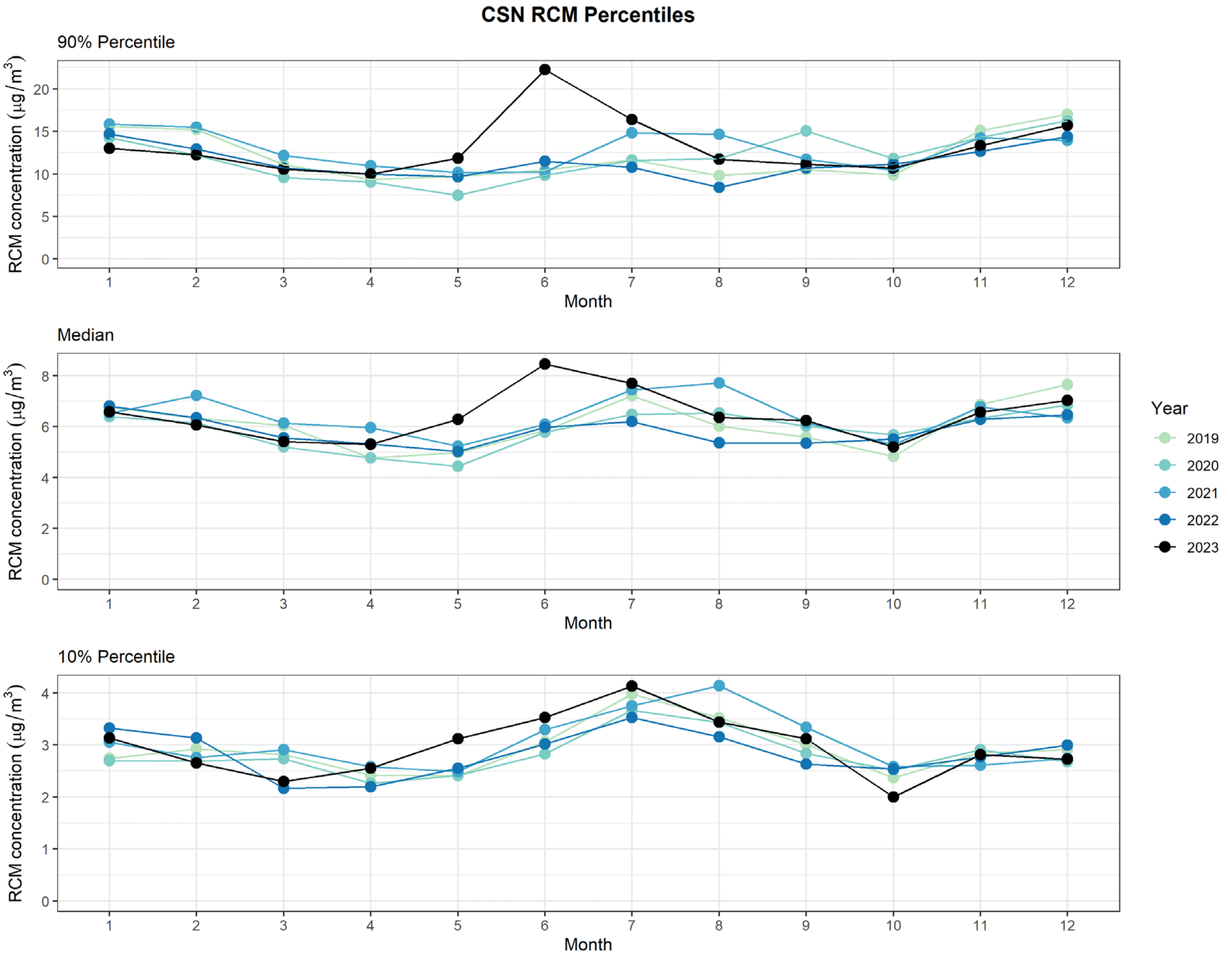
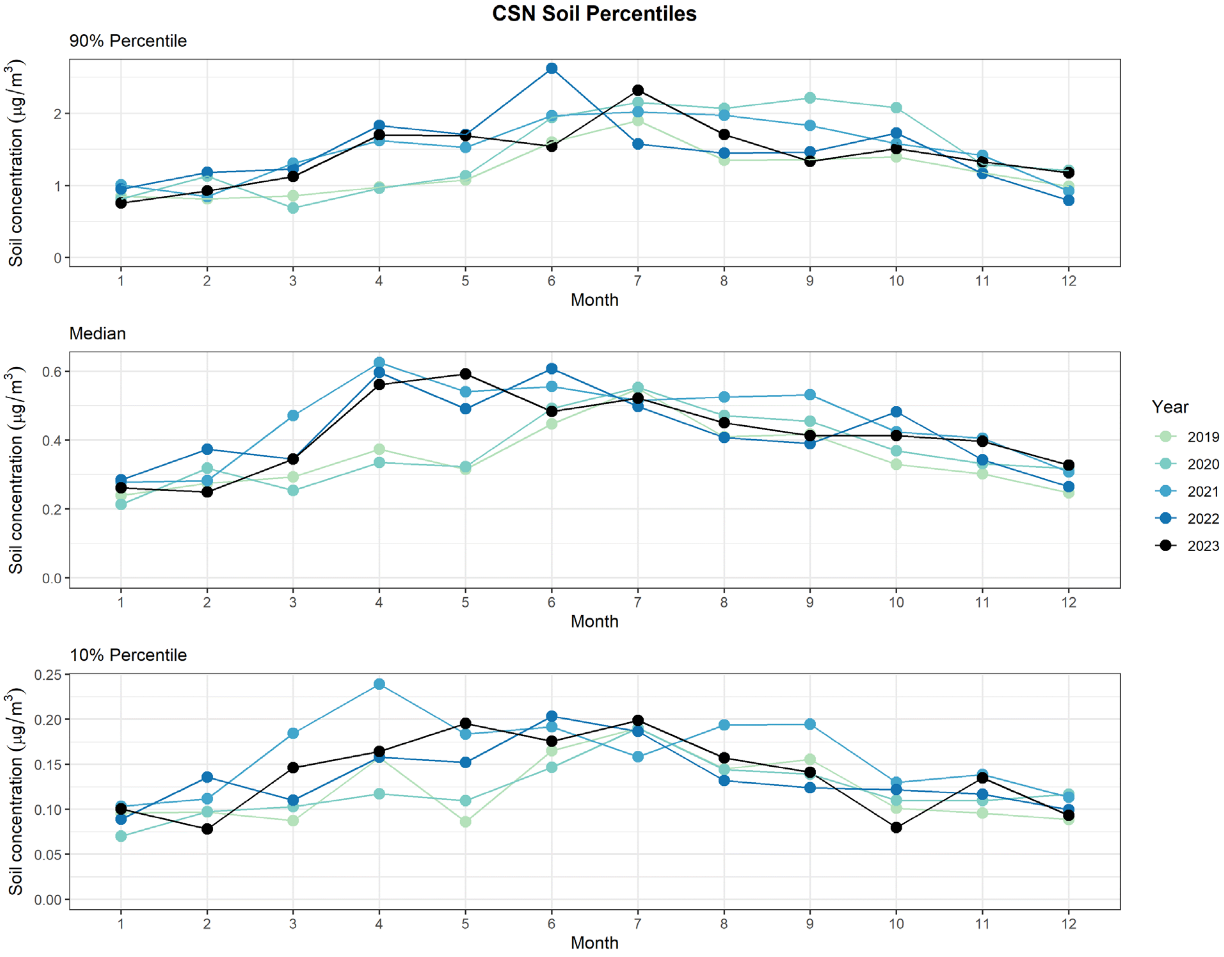
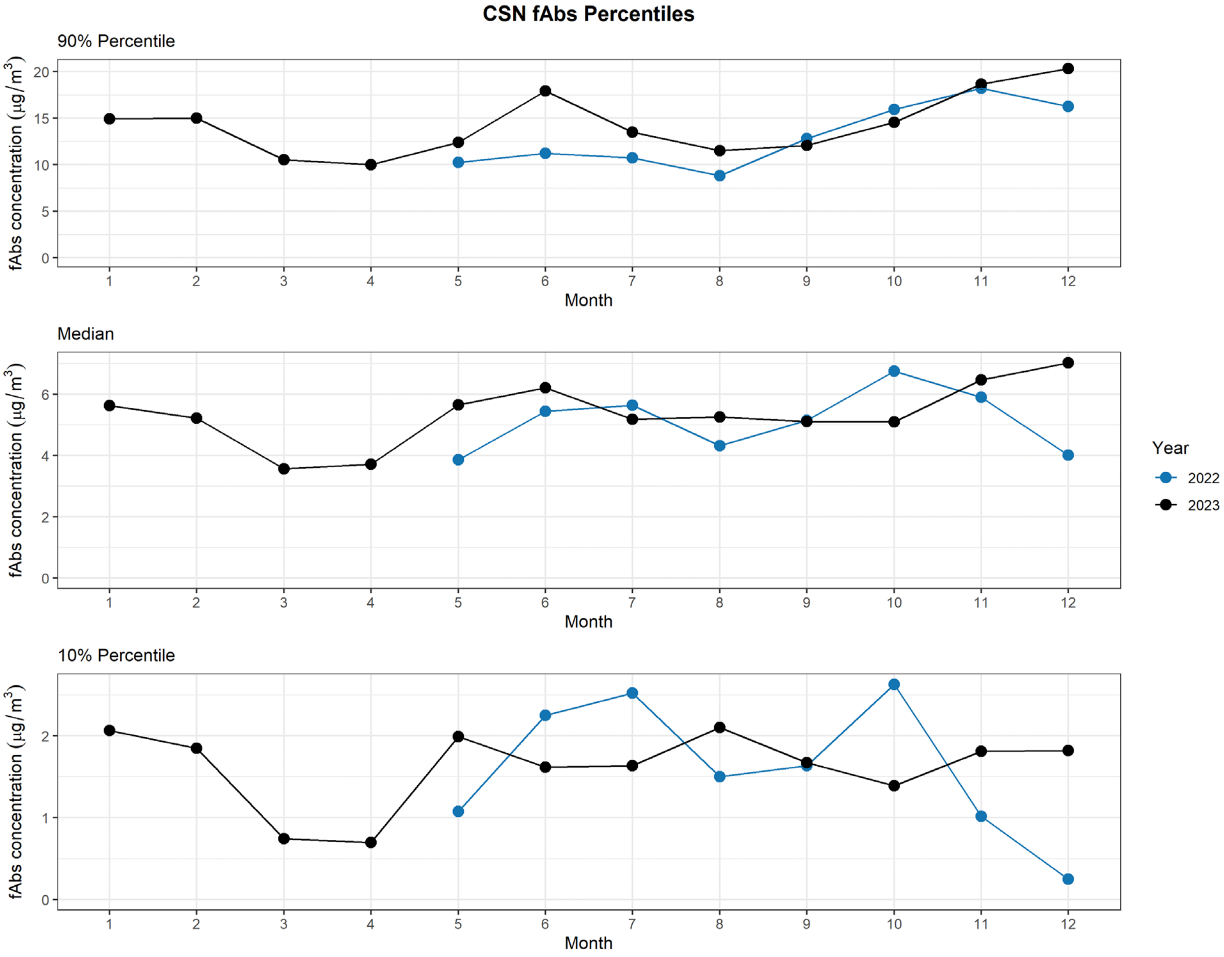


Figure 7-6: Multi-year time series of network-wide composite variable soil concentrations.



Starting in May 2022, AQRC began delivering fAbs measurements from 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 7-7 below has 2022-2023 data, which starts in May 2022 when we began delivering validate fAbs measurements. The delivery of available fAbs data from previous years is underway.

Figure 7-7: Single-year time series of network-wide fAbs concentrations.



After the contract transition from WSP to RTI, UCD has observed increased levels of what is assumed to be stainless steel contamination from the filter cannisters. This can be seen in the Cr and Ni timeseries below.

Figure 7-8: Single-year time series of network-wide Cr concentrations.

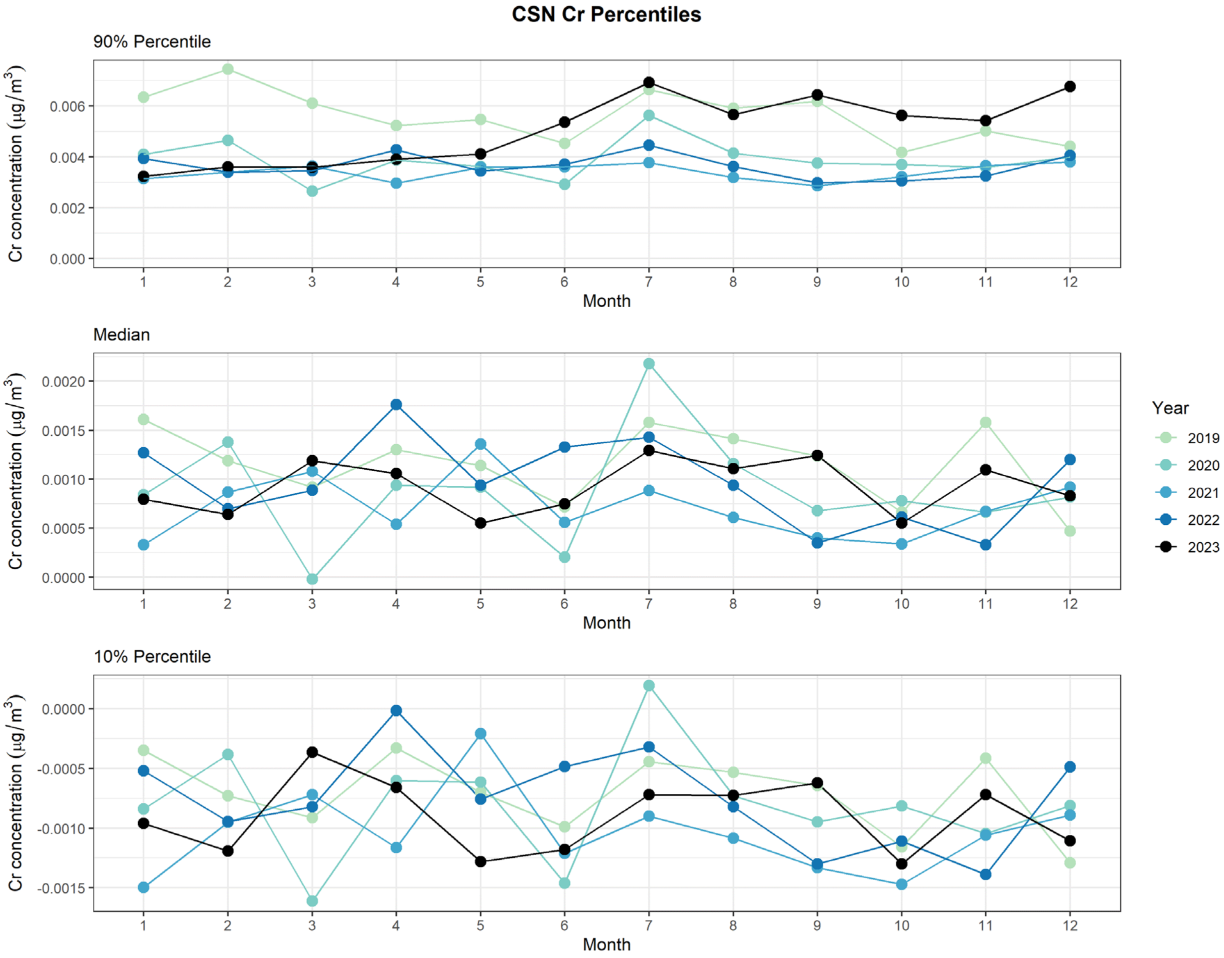
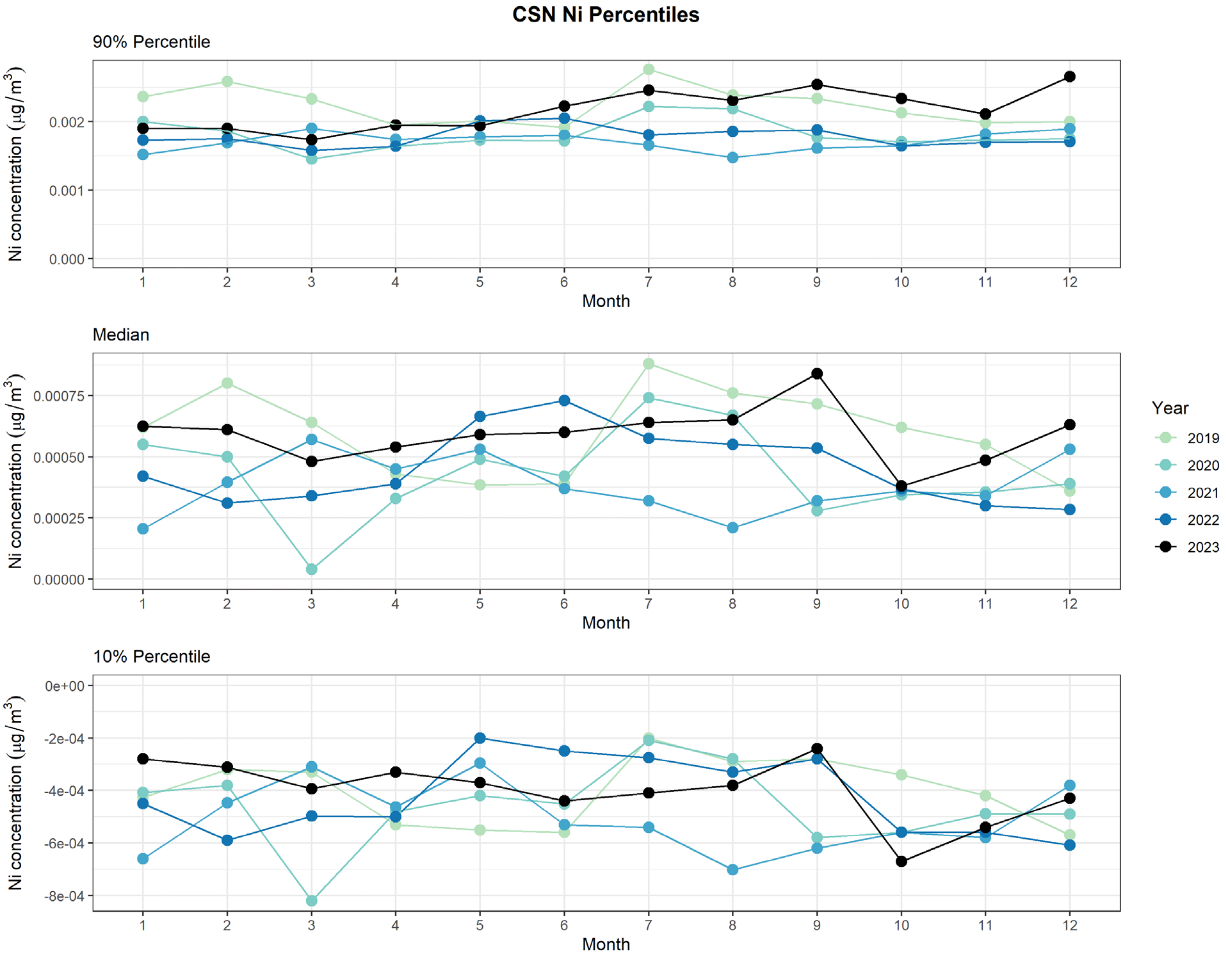
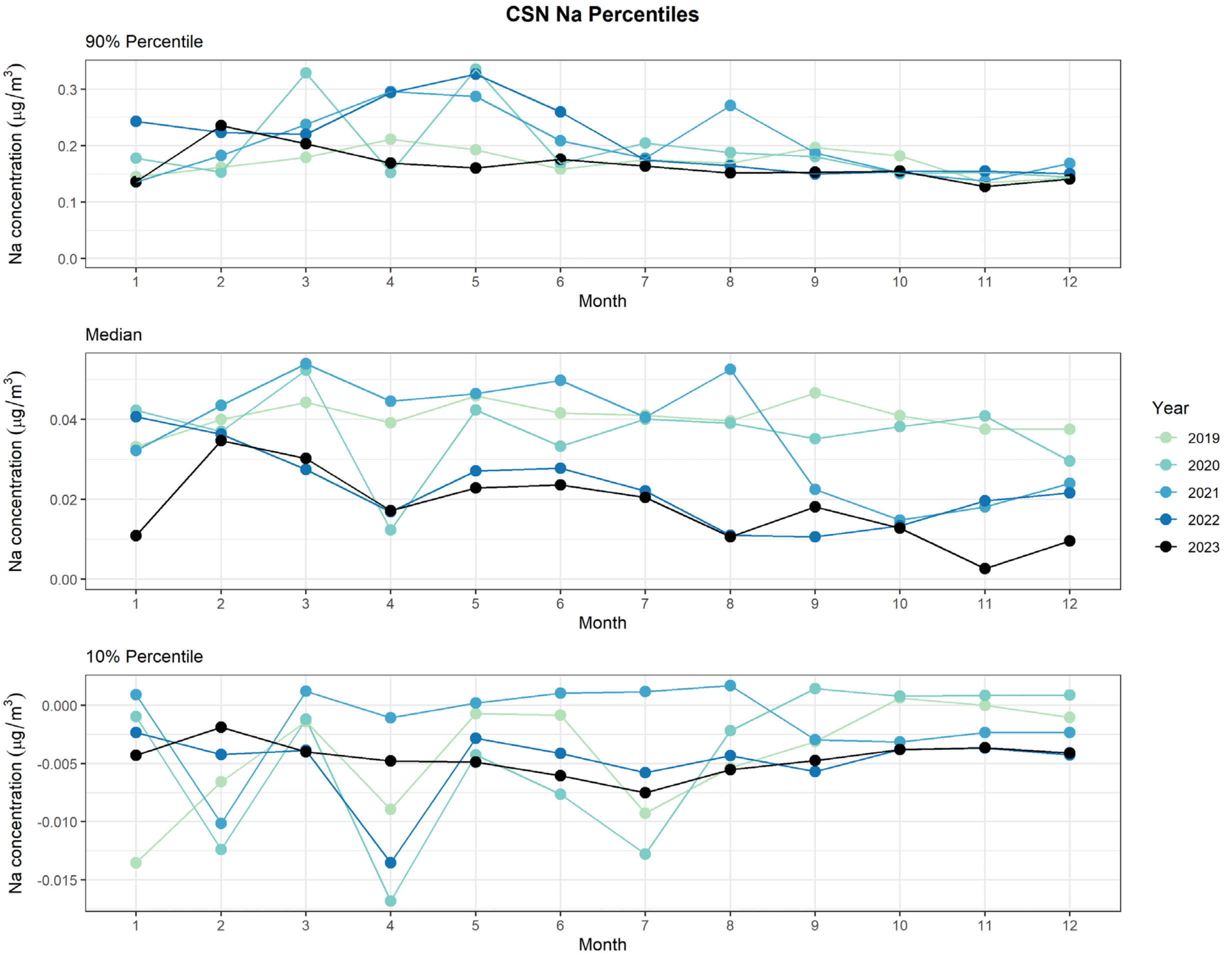


Figure 7-9: Single-year time series of network-wide Ni concentrations.



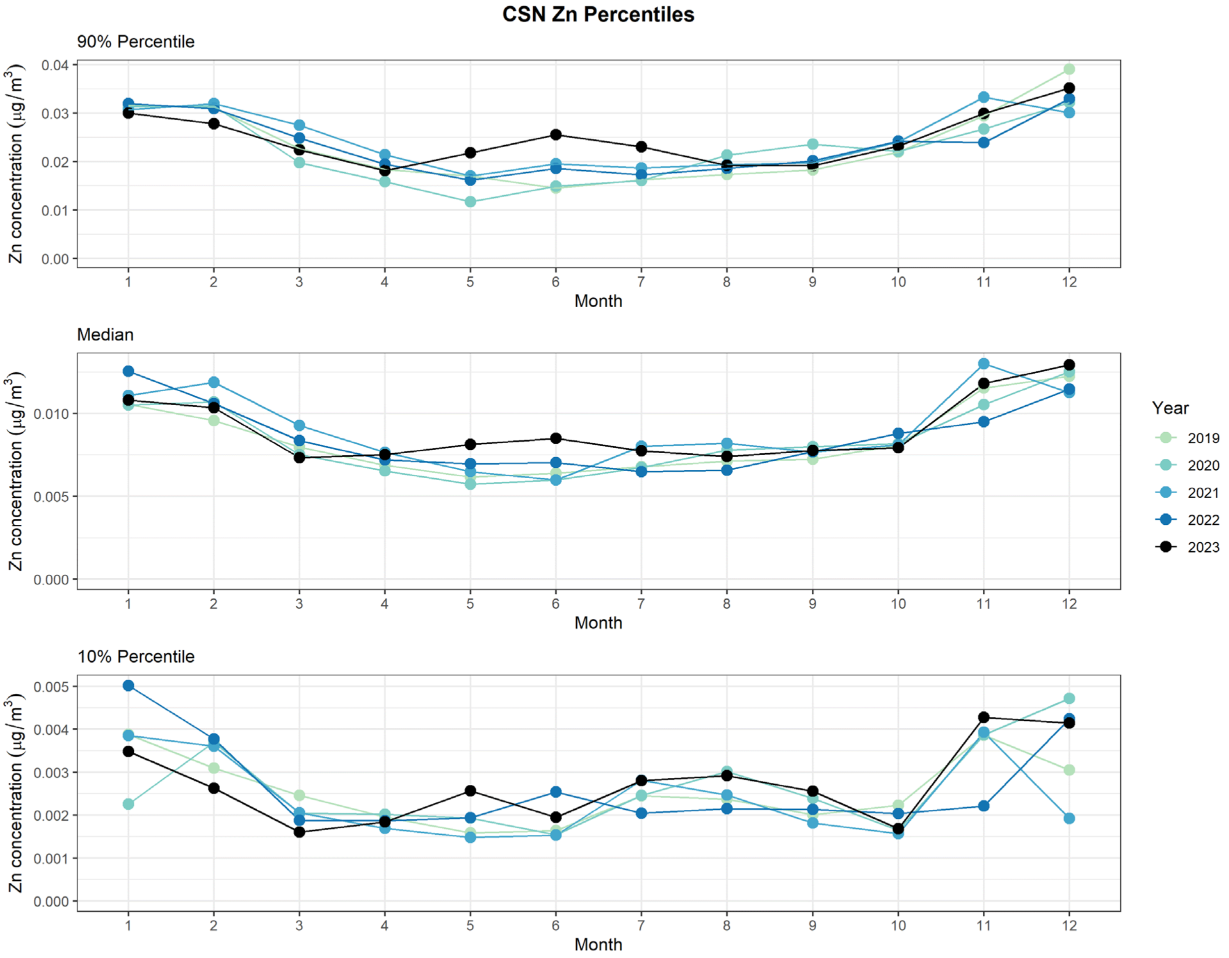
In the Na timeseries below, the medians for 2022 and 2023 are lower than previous years. This is also seen in the field blank plots.

Figure 7-10: Single-year time series of network-wide Na concentrations.



The Zinc timeseries is below. The May-July peaks may be tied to fire activity.

Figure 7-11: Single-year time series of network-wide Zn concentrations.



7.4.2.2 *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 events or analytical and sampling issues.

7.4.2.3 *Sulfur versus Sulfate*

PTFE filters are analyzed for elemental sulfur using EDXRF, and nylon filters are analyzed for sulfate (SO_4) using IC. The molecular weight of SO_4 (96 g/mol) is three times the atomic weight of S (32 g/mol), so the concentration ratio $(3\times S)/SO_4$ 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 7-12 shows that S and SO_4 are generally well correlated with a correlation coefficient of 0.93. Figure 7-13 shows that the ratio of $(3xS)/SO_4$ trended slightly down over previous years, with the median ratio below 1 toward the end of 2022. In 2023 the ratio moved a little higher compared to 2022.

Figure 7-12: Scatter plot of (3×S) versus SO_4, samples collected January 1, 2023 through December 31, 2023 (2021-2022 data are plotted in gray for comparison). Number of observations in 2023 (complete pairs) is 11,941. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.

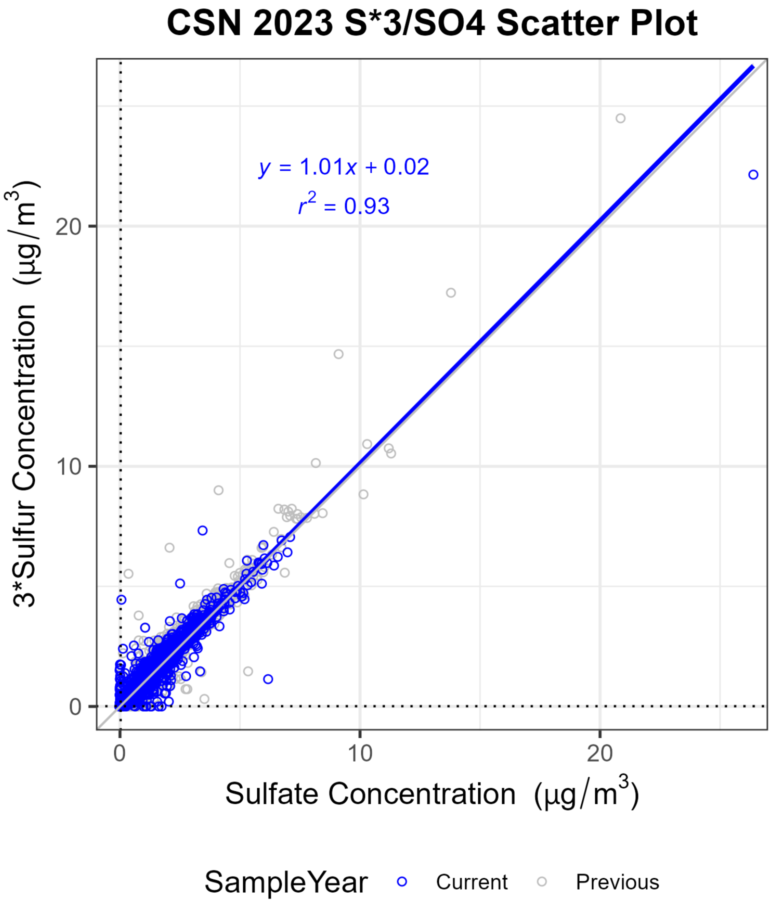
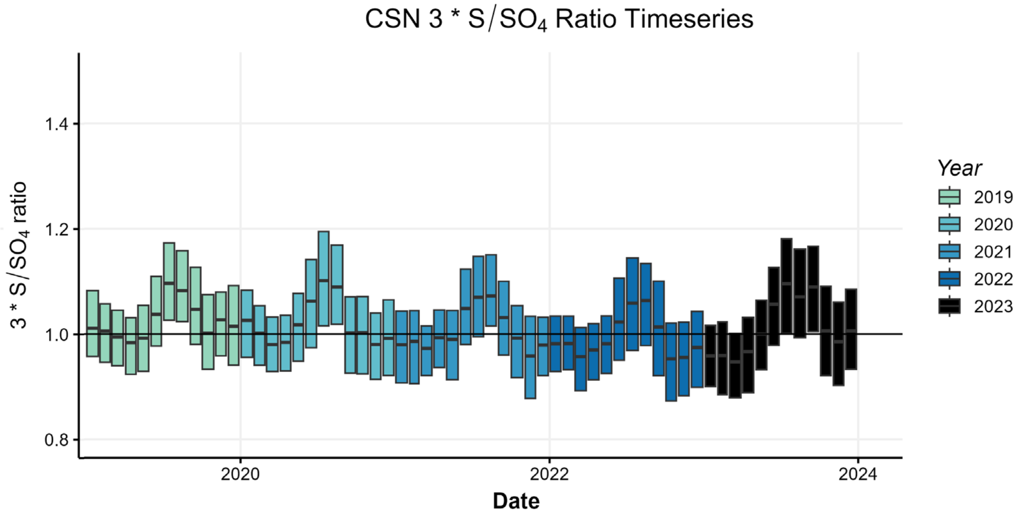


Figure 7-13: Timeseries of CSN monthly ratio of (3xS) versus SO_4, samples collected from 2019 to 2023.



7.4.2.4 *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 7-14).

Figure 7-14: Scatter plot of potassium versus potassium ion, samples collected January 1, 2023 through December 31, 2023 (2021-2022 data are plotted in gray for comparison). Number of observations in 2023 (complete pairs) is 11,941. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.

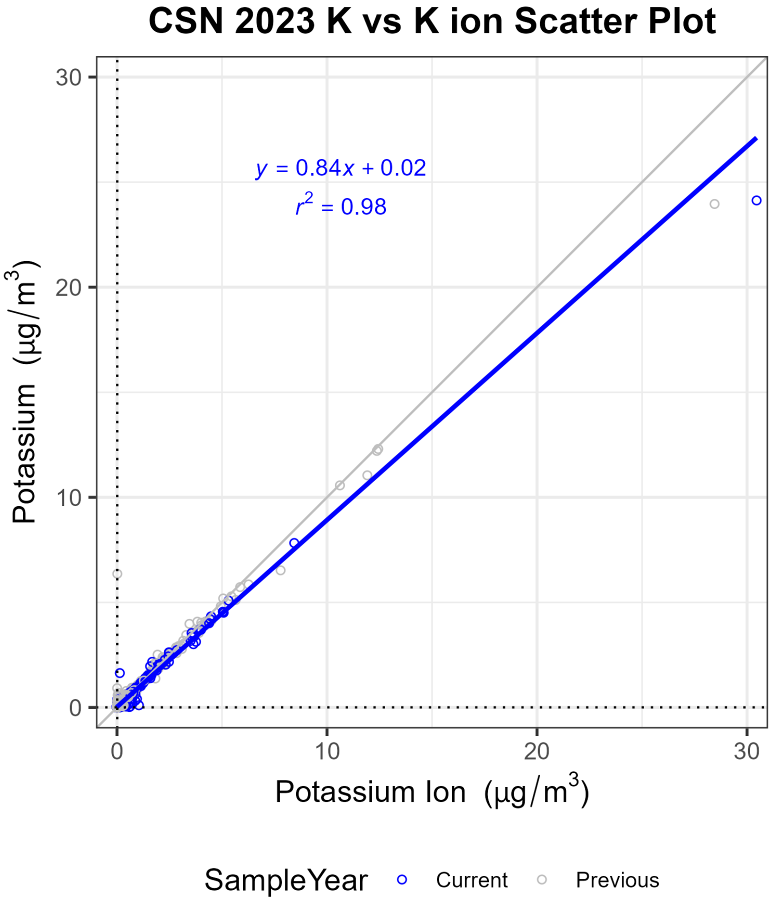
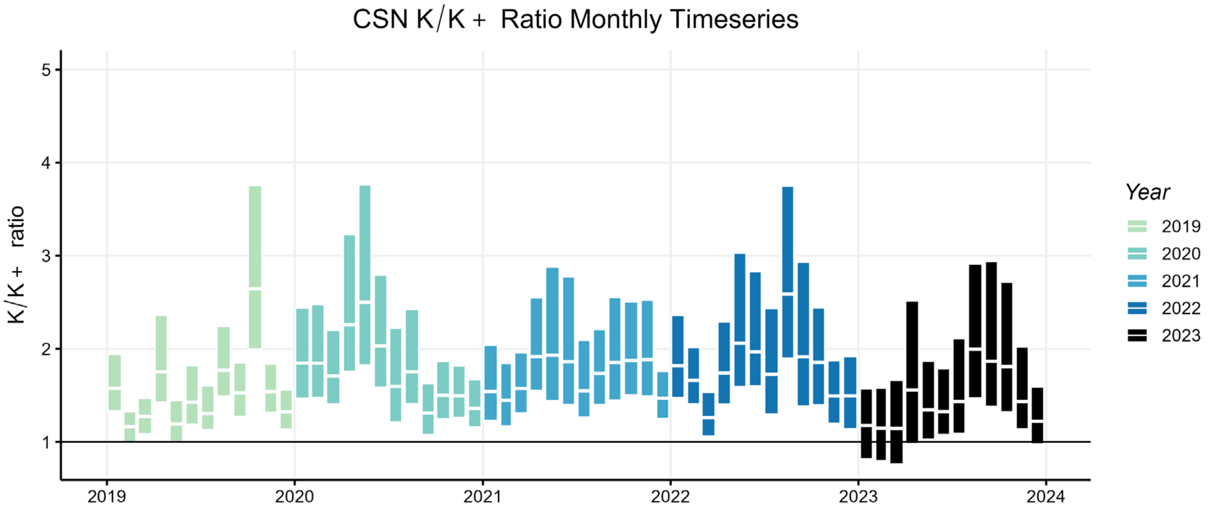


Figure 7-15 shows the multi-year timeseries of monthly ratio of K/K$^+$ over the past years.

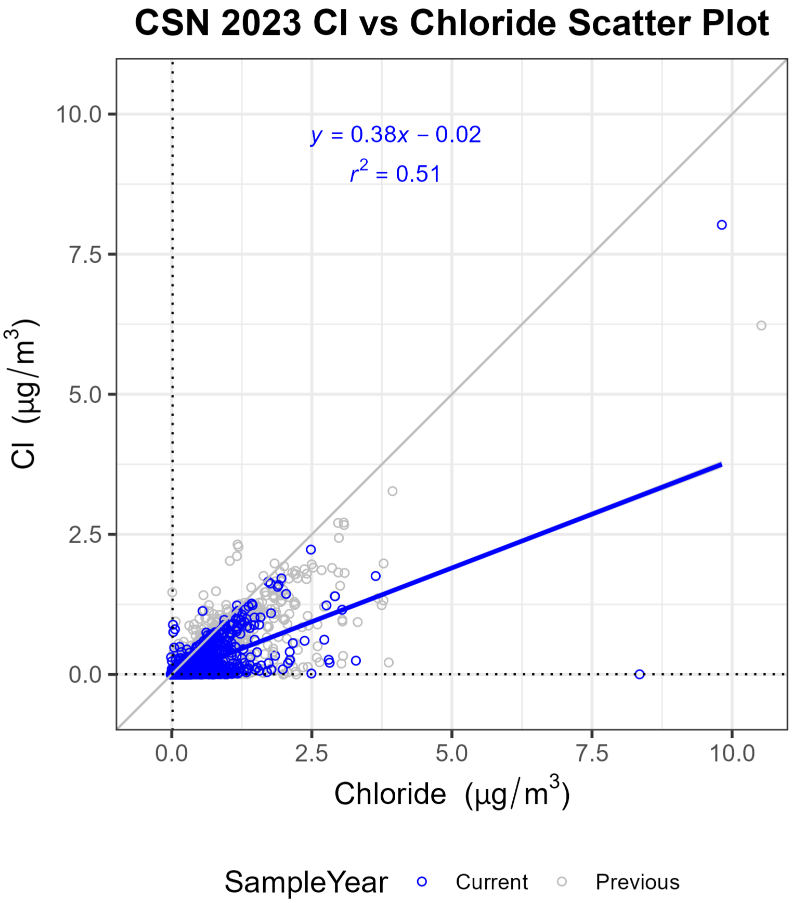
Figure 7-15: Timeseries of CSN monthly ratio of K versus K^+, samples collected from 2019 to 2023.



7.4.2.5 *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 7-16). In practice, chloride ion is often measured at higher concentrations than chlorine.

Figure 7-16: Scatter plot of chlorine versus chloride ion, samples collected January 1, 2023 through December 31, 20232 (2021-2022 data are plotted in gray for comparison). Number of observations in 2023 (complete pairs) is 11,904. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.



7.4.2.6 *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 PM$_{2.5}$ 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 7-17). 2023 RCM underestimated AirNow $PM_{2.5}$ more than in previous years, especially at high concentrations. The multi-year monthly ratio plot (Figure 7-18) shows historically low ratios in June 2023, when concentrations were highest and driven by Canadian wildfire smoke. When the organic mass is dominated by smoke, the mass fraction used to estimate organic mass from organic carbon is too low resulting in lower RCM/AirNow $PM_{2.5}$ ratios.

Figure 7-17: Scatter plot of reconstructed mass (RCM) versus AirNow $PM_{2.5}$ mass, samples collected January 1, 2023 through December 31, 2023 (2021-2022 data are plotted in gray for comparison). Number of observations in 2023 (complete pairs) is 9,428. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.

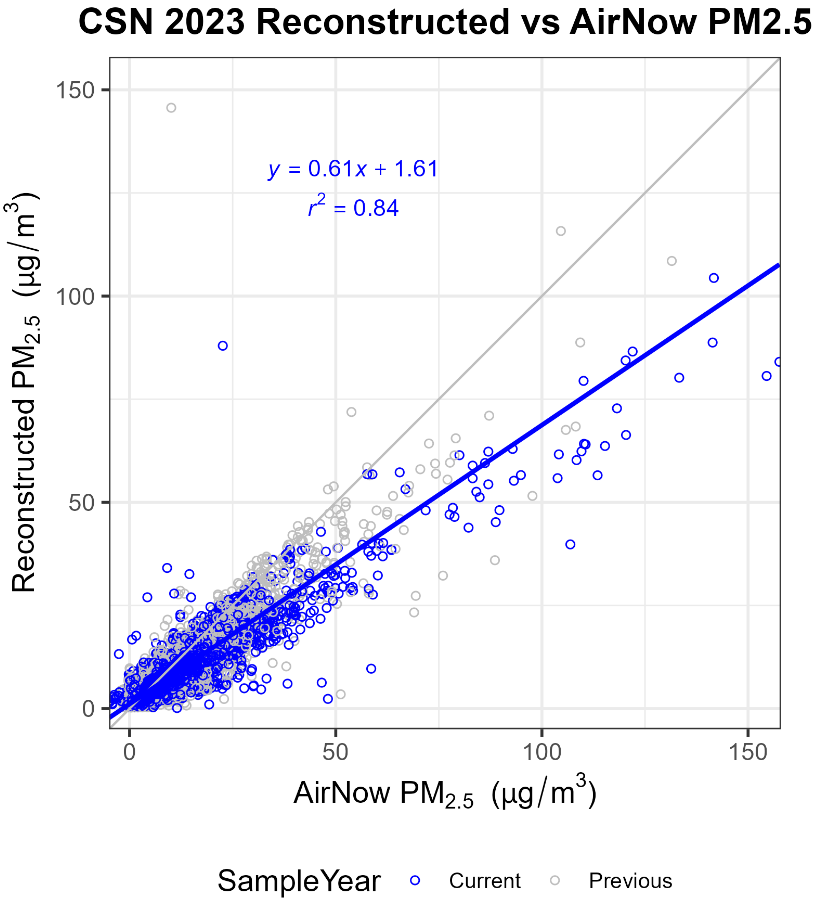
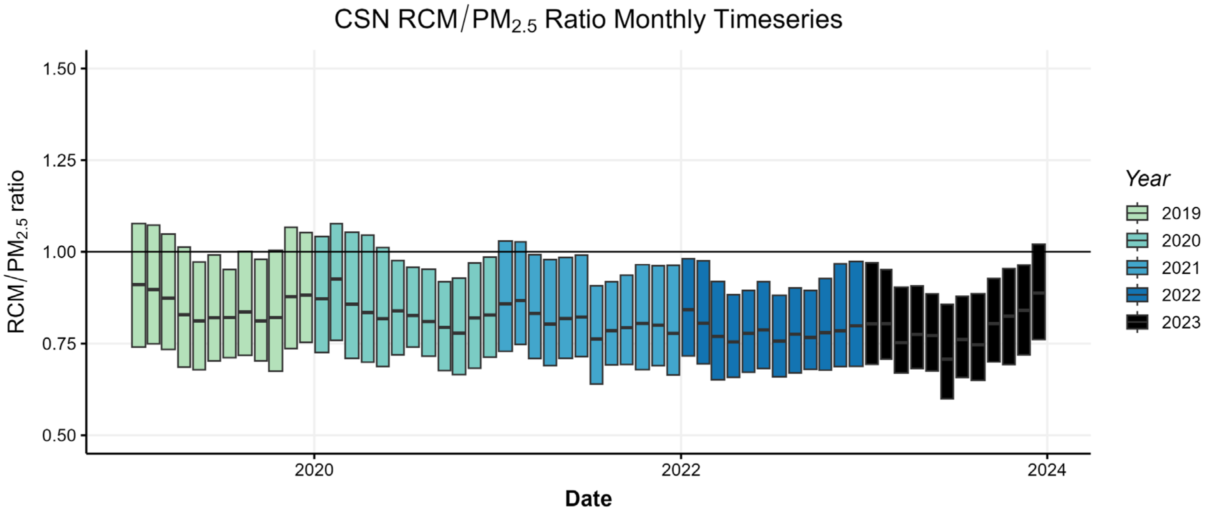


Figure 7-18: Multi-year monthly ratio plot.



7.4.2.7 *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 7-19: Timeseries of monthly ratio of fAbs versus ECR samples collected from 2020 to 2023

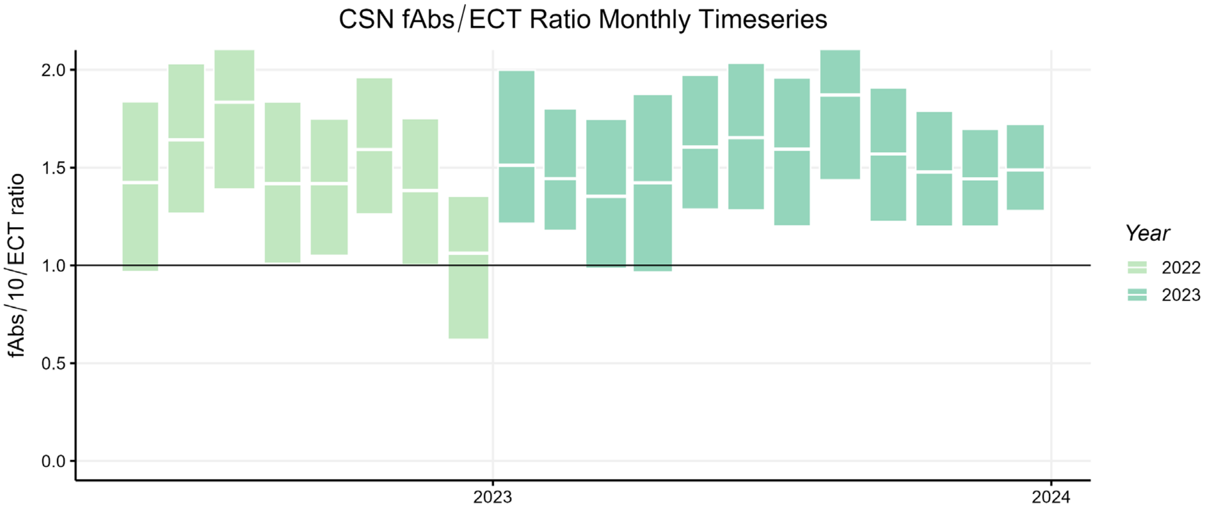
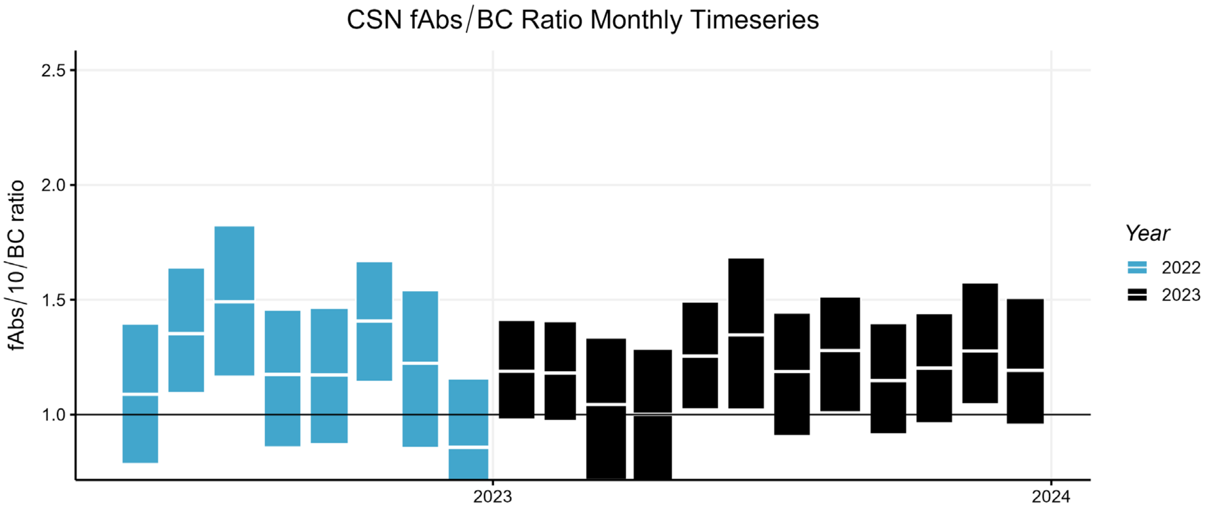


Figure 7-20: Timeseries of monthly ratio of fAbs versus BC samples collected from 2020 to 2023



7.5 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.

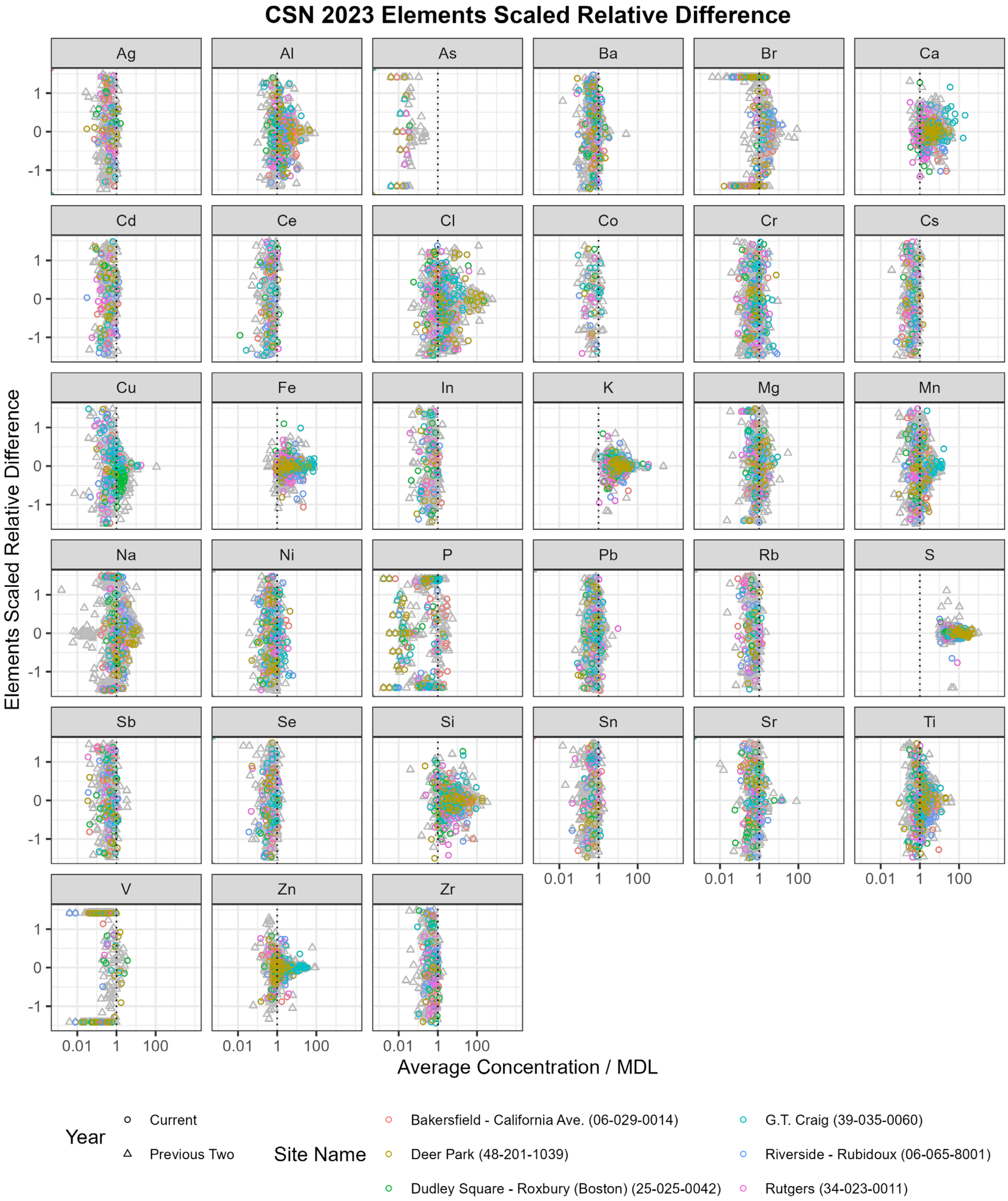
Scaled relative difference between sample pairs collected at CSN collocated sites is calculated as shown in Equation 7-1 and used to evaluate collocated precision (Figure 7-21, elements; Figure 7-22, ions; Figure 7-23, carbon). Data from the previous two years (2021-2022, gray triangles) are plotted together with the current year (2023) to allow for direct comparison.

$$Scaled\ Relative\ Difference\ (SRD) = \frac{(\text{collocated} - \text{routine})\ /\ \sqrt{2}}{(\text{collocated} + \text{routine})\ /\ 2} \qquad \text{(Eq. 7-1)}$$

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.

In the following Elements SRD plot, Ca at GT Craig may reflect Canadian wildfires in 2023.

Figure 7-21: Scaled relative differences for element measurements at sites with collocated samplers across the network (January 1, 2023 through December 31, 2023). Dotted vertical lines indicate MDL. Data from the previous two years (2021-2022) is plotted as grey triangles.



In the Ions SRD plots below, the Rutgers site noted debris on filters which may be seen in the Sulfate plot.

Figure 7-22: Scaled relative differences for ion measurements at sites with collocated samplers across the network (January 1, 2023 through December 31, 2023). Dotted vertical lines indicate MDL. Data from the previous two years (2021-2022) is plotted as grey triangles.

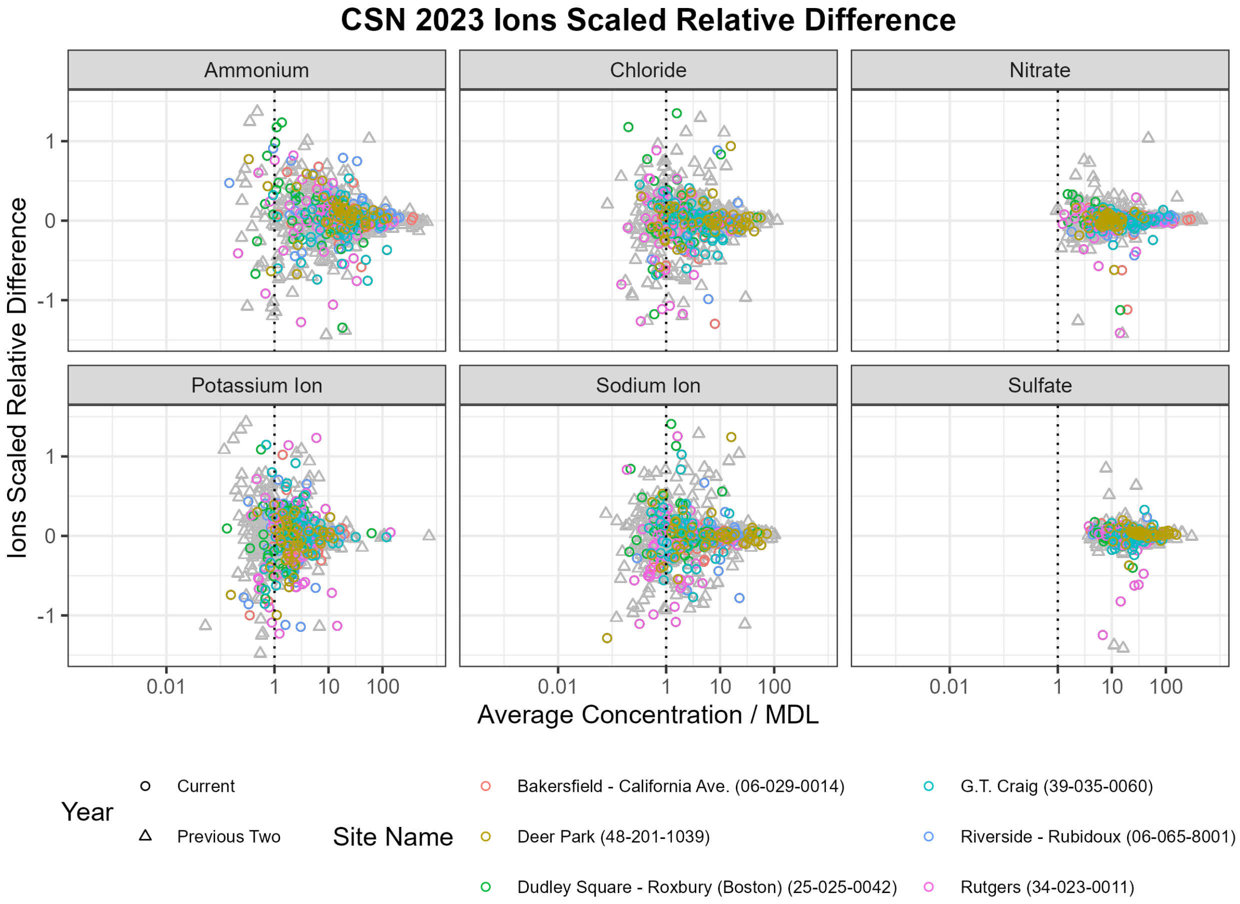
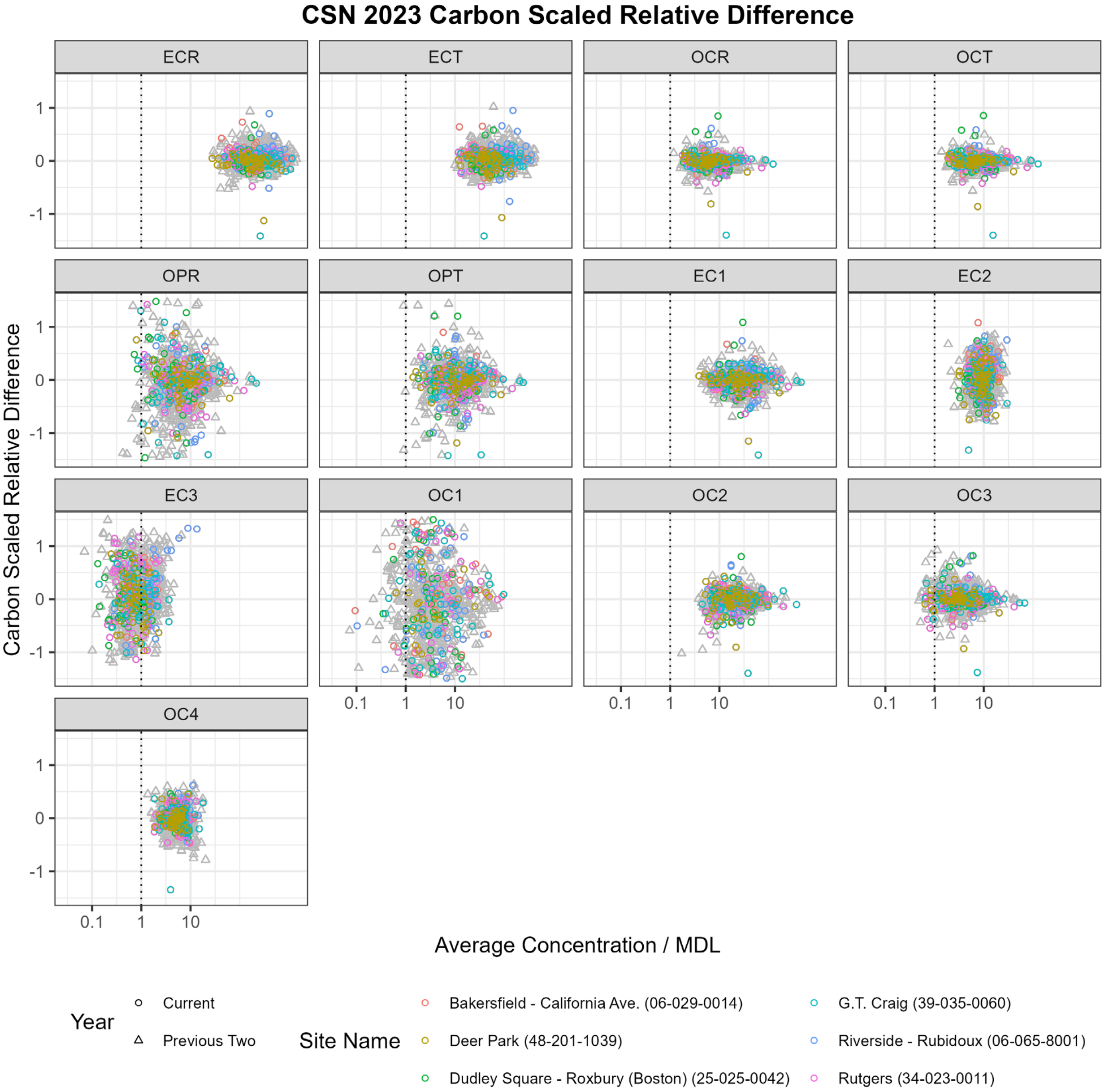


Figure 7-23: Scaled relative differences for carbon measurements at sites with collocated samplers across the network (January 1, 2023 through December 31, 2023). Dotted vertical lines indicate MDL. Data from the previous two years (2021-2022) is plotted as grey triangles. Elemental carbon (EC) fractions 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 7-1) 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, 2023 through December 31, 2023) 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 7-1 and Equation 7-2.

$$Fractional\ Uncertainty\ (\mathit{f}) = \frac{(84\text{th percentile of SRD}) - (16th\ percentile\ of\ SRD)}{2} \quad \text{(Eq. 7-2)}$$

Table 7-1 (elements), Table 7-2 (ions), and Table 7-3 (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 4.1.3.8) and additive uncertainty (Equation 7-3). Additive uncertainty includes both fractional uncertainty (Equation 7-2) 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.

$$Additive\ Uncertainty = \sqrt{(Analytical\ Uncertainty)^2 - (\mathit{f} \times C)^2} \quad \text{(Eq. 7-3)}$$

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 7-4 and Equation 7-5.

$$Relative\ Percent\ Difference\ (RPD_i) = \frac{X_i - Y_i}{X_i + Y_i/2} x100\% \quad \text{(Eq. 7-4)}$$

$$CV = P_{50th}\left(\frac{|RPD_i|}{\sqrt{2}}\right) \quad \text{(Eq. 7-5)}$$

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:

$$CV = \sqrt{\frac{n.\sum_{i=1}^{n} RPD_i^2 - (\sum_{i=1}^{n} RPD_i)^2}{2n(n-1)}} \times \sqrt{\frac{n-1}{X_{0.1,n-1}^2}} \qquad \text{(Eq. 7-6)}$$

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 7-1 (elements), Table 7-2 (optical), Table 7-3 (ions), and Table 7-4 (carbon) list median CV calculated using Equations 7-4 and 7-5 from collocated samples collected during 2023 (current reporting period) as well as 2022 (previous reporting period). The CFR CV calculated using Equations 7-4 and 7-6 from collocated samples collected during 2023 (current reporting period) and 2022 (previous reporting period) is also included.

In the below tables 7-1 to 7-4, 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, 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 the current reporting period, f is calculated from samples collected June 1, 2020 through May 31, 2022 and used in relevant calculations for samples between January 1, 2023 through December 31, 2023 and CV is calculated from samples collected January 1, 2023 through December 31, 2023.
- 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 7-1: Fractional uncertainty (f), median coefficient of variation (CV), and CFR coefficient of variation (CFR CV) for element species.

	f (%)		**f (%) Pairs**		**CV (%)**		**CV (%) Pairs**		**CFR CV (%)**		**CFR CV (%) Pairs**	
Species	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**
Ag	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Al	16.4	15.4	127	174	10.4	10.2	77	41	20.9	29.7	77	41
As	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Ba	25.0	25.0	0	0	---	15.5	4	2	15.5	10.9	4	2
Br	53.4	53.8	108	171	40.0	17.5	72	14	58.1	33.7	72	14
Ca	13.6	11.7	408	465	6.8	8.1	240	167	18.8	24.9	240	167
Cd	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Ce	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Cl	36.1	34.0	169	181	19.6	15.1	103	51	37.8	45.1	103	51

	f **(%)**		***f*** **(%) Pairs**		**CV (%)**		**CV (%) Pairs**		**CFR CV (%)**		**CFR CV (%) Pairs**	
Species	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**
Co	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Cr	25.0	25.0	0	0	---	2.6	1	3	---	110.7	1	3
Cs	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Cu	25.0	25.0	24	41	---	2.9	15	7	28.2	9.3	15	7
Fe	10.9	10.6	492	599	7.8	5.2	298	140	18.8	18.2	298	140
In	25.0	25.0	0	0	---	---	0	0	---	---	0	0
K	7.5	7.4	600	644	4.8	6.7	304	278	11.3	15.7	304	278
Mg	25.0	25.0	9	9	---	8.1	9	5	43.4	21.2	9	5
Mn	25.0	25.0	30	45	---	7.6	23	26	21.1	17.5	23	26
Na	17.9	19.5	64	65	---	16.1	38	22	19.9	24.8	38	22
Ni	25.0	25.0	1	1	---	---	0	0	---	---	0	0
P	25.0	25.0	16	28	---	---	5	0	31.5	---	5	0
Pb	25.0	25.0	1	1	---	12.1	0	1	---	---	0	1
Rb	25.0	25.0	0	0	---	---	0	0	---	---	0	0
S	5.2	5.3	640	679	3.5	3.9	341	318	11.9	9.5	341	318
Sb	25.0	25.0	1	2	---	---	0	0	---	---	0	0
Se	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Si	13.8	11.7	377	457	8.3	12.7	222	187	20.6	28.2	222	187
Sn	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Sr	25.0	25.0	1	1	---	0.8	4	3	8.6	2.8	4	3
Ti	16.6	16.3	125	180	---	10.8	52	28	16.7	23.6	52	28
V	25.0	25.0	2	8	---	18.5	6	1	64.1	---	6	1
Zn	11.2	12.5	387	508	7.9	3.8	240	45	16.9	10.2	240	45
Zr	25.0	25.0	0	0	---	---	0	0	---	---	0	0

For the previous reporting period of Table 7-2, 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 7-2: Fractional uncertainty (*f*), median coefficient of variation (CV), and CFR coefficient of variation for filter absorption (fAbs).

	f **(%)**		***f*** **(%) Pairs**		**CV (%)**		**CV (%) Pairs**		**CFR CV (%)**		**CFR CV (%) Pairs**	
Species	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**
fAbs	25.0	11.0	---	276	6.5	6.2	75	158	14.5	158	75	158

Table 7-3: Fractional uncertainty (*f*), median coefficient of variation (CV), and CFR coefficient of variation for ion species.

	f **(%)**		***f*** **(%) Pairs**		**CV (%)**		**CV (%) Pairs**		**CFR CV (%)**		**CFR CV (%) Pairs**	
Species	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**
Ammonium	8.2	8.5	582	600	7.2	8.3	288	260	20.6	22.8	288	260
Chloride	8.8	6.4	420	418	3.7	3.7	238	153	13.6	16.6	238	153
Nitrate	4.9	4.7	622	654	2.6	3.5	319	275	9.9	11.3	319	275
Potassium Ion	10.9	10.2	249	308	6.8	6.2	126	66	12.9	22.3	126	66
Sodium Ion	9.0	6.3	362	362	3.8	3.5	183	130	16.6	14.3	183	130
Sulfate	4.0	3.6	640	677	1.9	3.0	343	314	8.2	10.6	343	314

In the following Table 7-4, 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 7-4: Fractional uncertainty (*f*), median coefficient of variation (CV), and CFR coefficient of variation for carbon species.

	f **(%)**		***f*** **(%) Pairs**		**CV (%)**		**CV (%) Pairs**		**CFR CV (%)**		**CFR CV (%) Pairs**	
Species	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**
Elemental Carbon (EC1)	11.2	13.8	621	667	7.9	7.9	329	319	14.4	20.3	329	319
Elemental Carbon (EC2)	21.7	28.2	532	628	20.5	21.7	317	318	29.7	32.0	317	318
Elemental Carbon (EC3)	20.8	25.0	102	102	20.7	12.9	109	17	33.6	25.5	109	17
Elemental Carbon (ECR)	10.6	12.4	623	666	10.8	7.8	329	319	17.3	16.8	329	319
Elemental Carbon (ECT)	12.5	15.2	624	667	11.6	9.0	329	319	19.0	18.7	329	319
Organic Carbon (OC1)	31.9	33.8	268	269	23.6	17.7	91	59	44.8	39.1	91	59
Organic Carbon (OC2)	13.1	11.5	606	661	9.1	9.1	328	319	15.2	19.1	328	319
Organic Carbon (OC3)	10.8	10.3	141	238	8.1	5.5	245	272	14.9	16.4	245	272

	f (%)		*f* (%) Pairs		CV (%)		CV (%) Pairs		CFR CV (%)		CFR CV (%) Pairs	
Species	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**	**2022**	**2023**
Organic Carbon (OC4)	22.8	20.5	225	456	10.0	10.3	282	297	18.3	19.1	282	297
Organic Carbon (OCR)	6.8	7.0	361	486	5.7	4.6	302	314	11.4	13.5	302	314
Organic Carbon (OCT)	6.3	6.4	384	509	5.1	4.4	307	315	10.1	13.3	307	315
Organic Pyrolyzed (OPR)	18.6	22.0	382	431	15.9	15.0	215	251	26.6	31.1	215	251
Organic Pyrolyzed (OPT)	14.5	17.9	514	583	10.2	11.7	296	297	21.4	26.8	296	297

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