

Chemical Speciation Network (CSN)

Annual Quality Report

Samples Collected January 1, 2024 through December 31, 2024

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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 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, 2024 through December 31, 2024 (batches 24-01 to 24-12), 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 92.9% for PTFE filters, 92.9% for nylon filters, and 89.1% for quartz filters. Data from sites with non-standard sampler configurations are not included in the completeness calculations.

The EPA conducted a Technical Systems Audit (TSA) of the RTI laboratory from March 11 to March 12, 2025. RTI is a subcontractor to UC Davis on the CSN contract. Battelle was

contracted to perform the audit, with EPA and UC Davis representatives in attendance. RTI was processing December 2024 Ions samples at this time and UC Davis was validating October, November, and December data. The audit scope was limited to RTI processes. RTI processes included Sample Handling, Shipping, Gravimetry, and Ions analysis. The results of the audit included two findings and one concern for the CSN operations.

The first finding states, “Refrigerators used for filter storage upon receipt (pre-archive), do not have calibrated thermometers. Temperatures are not monitored nor on RTI’s RAM monitoring system.” The root cause was determined to be an oversight in cold chain where these refrigerators were a temporary holding area before the filters were sorted. RTI is in process of selecting, deploying, and qualifying thermometers for the temporary refrigerator(s) that will be consistent with other cold chain procedures at RTI for CSN filters. The final step involving the verification of the effectiveness of the corrective action was completed in early 2026.

The second finding states, “Criteria for environmental chamber relative humidity pre/post sample filter weighing ($\pm 5.1\%$) is not assessed.” The root cause was determined to be that staff failed to record relative humidity (RH) values in QC data sheets. The conditions were being monitored, but a training gap did not cover the necessity of documenting the RH for the session. The corrective action is to re-train staff and update the environmental log to record real-time RH and temperature readings to identify any sessions that fail to meet the requirement. This is currently being developed and will be evaluated at a future date.

The Concern states, “Gravimetric and environmental chamber records reviewed during audit of data quality did not provide for easy data tracking.” RTI is actively reviewing the feedback provided by TSA to identify opportunities for strengthening the data tracking process associated with pre- and post-weighing sessions.

The EPA did not conduct a Technical Systems Audit of the UC Davis laboratory during the 2024 data reporting period.

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 year-start (01/01/24) through the end of the calendar year (12/31/24) 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
1/1/24	Multiple	RTI requested updated information from sites in a letter provided with packages to start the new year. Thirty-three responses were received with contact information to use for more than fifty of the sites.	NA	NA	NA

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
1/1/24	Multiple	Starting using quartz filter lot 22039.	Completeness	All or partial	No
1/3/24	350010023 Del Norte, NM	Operator Donald Jaramillo requested information on a missing package to the site. After RTI provided the tracking number, Donald reached out to UPS and discovered the package was delivered to the wrong address. A replacement package was sent to the site, and after arriving the original package was delivered by UPS.	NA	NA	NA
1/4/24	180970078 Indianapolis – Washington Park, IN	Site emailed and indicated they were having equipment issues and were unable to collect quartz samples on their URG unit.	Completeness	All or partial	No
1/4/24	410510080 Portland - SE Lafayette, OR	Site started collection of samples for the CSN program.	Completeness	All or partial	No
1/19/24	481130069 Hinton, TX	Changed shipping location and addressee.	NA	NA	NA
1/26/24	500070014 Burlington - Main St, VT	Site emailed and informed RTI the site would be pausing shipments starting 1/31/24 for a few months. Site remained down for the remainder of 2024.	Completeness	All or partial	No
2/1/24	460990009 Sioux Falls- USD, SD	Changed shipping location and addressee.	NA	NA	NA
2/12/24	371830014 East Millbrook Middle School	New operator at site, changed addressee.	NA	NA	NA
2/20/24	Multiple	Site operator for Jasper Post Office emailed and indicated that the location for the URG cartridge and CF card on the FSCOC forms would swap locations causing confusion when entering the information to the URG sampler. RTI replied that the forms sort based on the lowest ID being printed in the third position and the higher ID being printed in the lower position. On 4/3/24, RTI made changes to the printout of the FSCOC forms to ensure the quartz cartridge was always listed first in order.	NA	NA	NA
2/26/24	20900035 Hurst Road – North Pole; AK	Changed shipping addressee.	NA	NA	NA

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
3/5/24	250130008 Chicopee, MA	Site operator emailed and informed the SHAL that due to sampler limitations, they were collecting 2Q, 4Q and 6Q samples on channels 3 and 4. RTI adjusted their data to reflect channels used.	Informational	Sampler collection position	Yes
3/6/24	421255001 East of Pittsburgh- Florence, PA	Changed shipping location and addressee.	NA	NA	NA
3/11/24	295100085 St. Louis - Blair Street, MO	Changed shipping location and addressee.	NA	NA	NA
3/22/24	530770009 Yakima – 4 th Ave, WA	Site had not returned five scheduled events. The site replied indicating the site was inaccessible from March 1 through March 23.	Completeness	All or partial	No
4/15/24	440071010 East Providence, RI	Site emailed and informed RTI the site would be pausing shipments starting 4/15/24 for a few months. Site remained down for the remainder of 2024.	Completeness	All or partial	No
4/27/24	180970078 Indianapolis – Washington Park, IN	Site emailed and indicated they were able to resume collection of quartz samples.	Completeness	All or partial	No
4/28/24	Multiple	RTI changed the field blank FSCOC form to remove temperature and BP sections. This change was done in response to a few sites who had asked the field blank forms to be differentiated from the routine events in some way beyond the header at the top of the form.	NA	NA	NA
5/14/24	Multiple	RTI merged the Null Forms for codes and flags received at the sites from two forms (one for URG samples, one for SASS samples) to one form. It was also decided to remove some flags not recorded by site operators.	NA	NA	NA
5/14/24	420010001 Arendtsville, PA	Changed shipping location and addressee.	NA	NA	NA
5/20/24	250250042 Roxbury (Boston) and Roxbury (Boston) Collocated sites, MA	Changed shipping addressee.	NA	NA	NA

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
5/24/24	Multiple	Starting using PTFE filter lot 256.	Completeness	All or partial	No
6/1/24	Multiple	At the request of UCD data validators, RTI starting using the "A1" flag code when an entry was edited or added by RTI data entry personnel. Previously, this information was captured only in the comments field.	NA	NA	Yes
6/3/24	250250042 Roxbury, MA	Site emailed indicating there was long-term construction occurring near the sampling site. The site had been using the AC null code for their sample collection, but after review the J flag was determined more appropriate. Data with the AC code was edited to a J flag and the J flag was applied by the site moving forward.	NA	NA	Yes
6/5/24	060658001 Rubidoux (collocated), CA	Site emailed and indicated the box they receive their samples in was contaminated, likely from a leaking icepack. A replacement package was sent.	NA	NA	NA
6/6/24	490494001, 490050007 Lindon and Cache Valley (Smithfield), UT	Sites requested RTI start providing scheduled pickups for their locations.	NA	NA	NA
6/11/24	470931017 Knoxville Rule High School, TN	Site emailed indicating their URG sampler was down, and requested RTI pause sending samples until it was operational again.	Completeness	All or partial	No
6/11/24	530770015 Toppenish, WA	Site emailed and indicated the box they receive their samples in was contaminated, likely from a leaking icepack. A replacement package was sent.	NA	NA	NA
6/23/24	340070002 Camden (NJ Fund), NJ	Site emailed and indicated they were moving locations and that sampling at this location should be stopped.	Completeness	All or partial	No
6/23/24	011130003 Phenix City S. Girard School, AL	Site emailed indicating their URG sampler was down, and requested RTI pause sending samples until it was operational again.	Completeness	All or partial	No
6/29/24	470931017 Knoxville Rule High School, TN	Site resumed quartz sample collection.	Completeness	All or partial	No
7/3/24	081230008 Platteville, CO	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
7/5/24	Multiple	Starting using quartz filter lot 22063.	Completeness	All or partial	No
7/10/24	132450091 Augusta, GA	Changed shipping location.	NA	NA	NA
7/11/24	420750101 Lebanon, PA	Changed shipping location.	NA	NA	NA
7/25/24	132150012 Columbus (Baker Middle), OH	Changed shipping location and addressee.	NA	NA	NA
7/26/24	202090021 JFK Center, KS	Site started collecting samples in CSN network after <1 year hiatus.	Completeness	All or partial	No
7/29/24	011130003 Phenix City S. Girard School, AL	Site resumed quartz sample collection.	Completeness	All or partial	No
8/22/24	280490020 Jackson NCore, MS	Changed shipping location and addressee.	NA	NA	NA
8/22/24	340070010 Camden South, NJ	Site started collection of samples. Previous site was Camden (NJ Fund), site moved to new location.	Completeness	All or partial	No
9/8/24	110010043 Washington DC - Station 43 PAMS, DC	Changed shipping addressee.	NA	NA	NA
9/12/24	202090021 JFK Center, KS	Site emailed indicating their URG sampler was down, and requested RTI pause sending samples until it was operational again.	Completeness	All or partial	No
9/18/24	202090021 JFK Center, KS	Site resumed quartz sample collection.	Completeness	All or partial	No
10/3/24	Multiple	Started collecting 25 mm PTFE filters at all collocated sites for analysis by XRF.	Completeness	All or partial	No
10/3/24	Multiple	Started using PTFE lot 249 filters for 25 mm study.	Completeness	All or partial	No

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
10/14/24	300490004 Seiben Flats, MT	Changed shipping addressee.	NA	NA	NA
10/21/24	360810124 Queens College, NY	Changed shipping location.	NA	NA	NA
10/21/24	420710007 Lancaster, PA	Changed shipping location and addressee.	NA	NA	NA
10/21/24	420710012 Lancaster Downwind, PA	Changed shipping location and addressee.	NA	NA	NA
10/27/24	181630021 Evansville Buena Vista Road, IN	Site emailed indicating their SASS sampler was down, and requested RTI pause sending PTFE and Nylon samples until it was operational again.	Completeness	All or partial	No
10/31/24	421290008 Greensburg, PA	Changed shipping location and addressee.	NA	NA	NA
11/14/24	340070010 Camden South, NJ	Site emailed indicating their URG sampler was down, and requested RTI pause sending samples until it was operational again.	Completeness	All or partial	No
12/6/24	295100085 St. Louis - Blair Street, MO	Changed shipping location and addressee.	NA	NA	NA
12/6/24	550790010 Milwaukee 16th St. Health Center, WI	Changed shipping location and addressee.	NA	NA	NA
12/20/24	421290008 Greensburg, PA	Changed shipping location and addressee.	NA	NA	NA
12/20/24	420210011 Johnstown, PA	Changed shipping location and addressee.	NA	NA	NA
12/11/24	Multiple	Starting using PTFE filter lot 261.	Completeness	All or partial	No

Date	AQS Site (Code, Name, State)	Description	Effect on Data	Type of Data Affected	Affected Data Flagged
12/26/24	391530017 Akron East High School, OH	Site started collection of samples. Previous site was Akron 5 Points, site moved to new location.	Completeness	All or partial	No

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 4.2 of the report.

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

3.1.1 Gravimetric Post-Weigh Holding Times Exceeded

There were six instances of invalidation of gravimetric data due to holding times being exceeded for post-weighing of filters. Additional steps and checks have been implemented to attempt to reduce this number.

3.1.2 Excessive Black Dust Accumulation on URG Quartz Filters.

On April 29, 2022 UC Davis first reported to EPA instances of many LJ flags being applied at some sites. An eventual site visit to Sacramento showed large amounts of black dust had accumulated on the filters and in the sampler. At this time, WSP was the contractor for sample handling and site communication. The black dust impacted quartz filter analysis results from Sacramento and other sites observing the accumulation. EPA, URG and UC Davis discussed best mitigation actions, and these will continue to be sent to sites experiencing this anomaly. The impact to data is significant in the analysis of Elemental Carbon (EC) and Pyrolyzed Carbon (OP) species and can be identified when OP is zero and EC concentration relates poorly to Filter Absorption (fAbs). When OP is zero, it is also an indication of poor Thermal Optical Analysis results (TOA). Beginning in 2024, EC, OP and all associated carbon fractions are reported invalid when OP is zero and is explained in the CSN EC Data Advisory

(https://www.epa.gov/system/files/documents/2024-06/f07-data-advisory_csn_ec_2024-05-23_508.pdf).

UC Davis tracks this issue on IR-0015.

3.1.3 Quartz Filter Flaking Edges

In 2024, both UC Davis and RTI observed a potential filter integrity issue involving flaking of the 25 mm quartz filters. Degradation of filters is not suspected; 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. Cytiva investigated and said that while there was no identifiable root cause and that the filters did not violate any quality parameter requirements during the manufacturing process, they would replace their dull dies with sharper ones. There is no available data to suggest the excess flaking from the filters is causing an adverse effect. RTI secured new lots of quartz filters from their supplier and have implemented a receiving check for flaking. UC Davis tracked this issue on IR-0021.

3.1.4 Suspected Stainless Steel Contamination

An issue of elevated stainless-steel components in PTFE filters was observed by the UC Davis XRF lab starting with 2023 sampling. Several discussions were held with RTI, UC Davis and EPA to discuss potential causes and more importantly, solutions to the issue, which was observed in some field blanks indicating it was not an ambient collection result. In previous years, with the previous shipping contractor, this contamination was observed and was resolved when the screws holding down the top of the collection module were tightened with less force. RTI's initial response was to attempt to tighten the modules prior to sampling with less force, this action did not resolve the issue satisfactorily. RTI's second response was to purchase torque dependent wrenches, which would only allow the SHAL technicians to tighten the screws to a specific torque starting in March; this action did not immediately resolve the issue satisfactorily. UC Davis recommended replacing some of the stainless-steel screws used in part of a single set of modules with nylon-based (PEEK) screws. This was deployed for a subset of 1Q modules in September; this action did not resolve the issue satisfactorily. UC Davis' second recommendation was a deeper cleaning of the modules using an ultrasonic water bath for a full set of modules. The 6a modules were cleaned by this method at RTI in September; this action did not resolve the issue satisfactorily. The stainless-steel issue continues to persist in 2025 sampling, though it has been noted that the amount of suspected contaminated filters has decreased significantly from its peak, no information available currently explains the drop in contaminated samples. UC Davis tracks this issue on IR-0026.

3.1.5 Sulfur Contamination in Denuder Coating

Following an evaluation of the Sulfur/Sulfate ratio between PTFE and nylon filters, UC Davis observed an elevated amount of sulfate on many nylon filters indicating potential contamination. The issue was first observed with samples collected in April 2024 at some sites. The following months had several more sets of denuders recoated and the number of Sulfur/Sulfate ratio outliers increased dramatically. RTI purchased new MgO powder and new ethanol (the two

components used to coat the denuders) and sent test samples to the UC Davis XRF lab. After testing it was discovered the original MgO powder had elevated levels of a sulfur-based compound. The contamination was most prevalent in the July to August time period, where the highest number of re-coatings were performed. RTI discarded the original contaminated MgO powder, and recoating of denuders was paused as the data was being further evaluated after additional sample collection. By the end of December 2024, it was decided the new MgO was considered clean and suitable for use, and recoating of denuders could resume. The last set collected in December 2024 was sampled using denuders coated with the new MgO powder. Additional information about the new MgO powder will be provided in the 2025 report once the data is available. This issue was tracked by UC Davis on IR-0027. There was only one set of coating which was missed on the schedule while determining the best course of action for resolution. This set was coated at the end of December, three months after its intended scheduled recoating.

3.1.6 Wood Debris in Filter Shipping Trays

UC Davis Sample Handling noted debris on the Petri trays and dishes from the RTI shipments. The observation was noticed most prominent in August 2024. This appears to be some wood fibers from a source in the handling area. Some fibers were found on filters and UC Davis did their best to carefully remove them. RTI had noticed some wood particles in the trays that hold the Petri slides. After it was brought to management's attention, the same contamination on some of the filters was also observed. RTI affixed a plastic cover on each table used in sample processing believed to be the source of the debris in the beginning of December 2024. Levels of observed particles have decreased with this change to a level that is nearly zero. UC Davis tracked this issue on IR-0028.

3.1.7 Increase in Number of PTFE Pinholes and Other Defects

UC Davis observed an increase in the number of pinholes reported on CSN 47 mm PTFE filters. This was first reported when UC Davis processed batch March 2025. The relevant lot is 261 and began sampling in December 2024. UC Davis has tracked the issue and reported back to RTI the findings. EPA has also been informed and periodically updated. Lot 261 has had a much higher instance of pinholes compared to previous lots reviewed. We are investigating several root causes that include an issue with the lot manufacturing, sample handling processes, sample handling components, sampler issues, and any other potential causes. MTL has also been engaged. A new lot, 263, was deployed into the CSN beginning in July 2025. The new lot had some pinholes reported at the beginning of deployment, but the reports dropped down to typical levels for most of the deployment. UC Davis tracks this issue on IR-0032.

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 qualified 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 underwent extensive testing and qualification to ensure they are fit for use before starting any network sample analysis. The instruments were deployed for the first time to analyze January 2025 CSN samples. All CSN samples in 2024 were analyzed on Panalytical Epsilon 5 instruments.

3.3.2 XRF-3 Operational Issues

AQRC has 5 Epsilon 5 (E5) instruments that run with the CSN and the IMPROVE network PTFE filters, performing XRF analysis. The analyzers run a high volume of filters year-round and have been in service for over a decade. As such, the electrical, mechanical, and other components require regular maintenance and replacement to keep the analyzer operational and within QC tolerances. Due to the age of the instruments, however, parts and service can be difficult to acquire. This is one of the reasons AQRC has pursued new instruments, as described in 3.3.1.

One of the analyzers, designated XRF-3 in CSN data, began to have hardware issues in March of 2024. A small subset of CSN filters, from Batch 2024-02, was running when one of these issues was discovered. As explained in more detail in section 4.2, these filters were re-run on a different analyzer so no delivered data is affected. However, XRF-3 has not been in use since the hardware issues began. We have attempted to resolve the problem in collaboration with Panalytical, however the root cause and correction have not yet been determined. For the CSN in 2024, most of the data was run on 4 instruments instead of the normal 5. For sample year 2025, the CSN filters were switched to the Bruker S2 Puma instruments. There is no plan to run CSN filters on the Panalytical E5s, including XRF-3, going forward.

3.4 UC Davis Thermal Optical Analysis Laboratory

3.4.1 TOA Lab Deviations

Deviation report DV-0017, which was started in January 2024, is still open. This deviation is for the use of a new auto-thermogram check which auto-flags any TOA sample analyses that fail thermogram check criteria. Prior to this the thermogram checks were performed manually, but there are not enough resources to continue to review every sample thermogram, so the automated check was instituted. The automated check system was reviewed and tested at the time of deployment. If ongoing review by the data validation team reports any data inconsistencies which may be due to issues which should be caught at thermogram review, the automated checks will be reviewed and updated as necessary. The automated checks have been in use during this reporting period and will become effective as soon as they can be added to document *UCD CSN SOP #402: TOR Carbon Analysis (Sunset 5L)*.

Deviation report DV-0019 was opened on August 13, 2024 to allow the use of the Sucrose 12 (add concentration) standard for transit time determination. This was implemented as the Sucrose 13 (add concentration), which is written into UCD CSN SOP 402, does not always provide a strong enough signal to effectively calculate the transit time. The higher concentration Sucrose 12 is more effective for this purpose, so this deviation was started to allow its use.

3.4.2 Sunset Autoloader Qualification Failed

During analysis year 2023, an autoloader manufactured by Sunset for the 5L analyzers was tested by AQRC. AQRC has a number of quality control measures, as well as operational and performance requirements that must be met, before the autoloader could 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.

In analysis year 2024, Sunset returned the autoloader. After testing, the autoloader failed to meet our production requirements. The instrument proved unreliable and broke down often. Other problems were operational. Our normal QC process has a daily: laboratory blank, instrument blank, and sucrose standard check. The autoloader could not be programmed to perform these tasks before network filters in an efficient way. The hardware and software issues are too large for us to invest more time. The autoloader has been retired and moved into a storage facility out of the lab.

3.5 UC Davis Optical Absorption Laboratory

3.5.1 Lab Moved to New Room

In May 2024 the optical absorption laboratory was moved from Room 132C to Room 138 at 1560 Drew Ave. The move was made to accommodate a new ICP-MS laboratory which will be installed in room 132C. This move was performed prior to the start of analysis of any 2024 samples. Testing and quality control after the move to the new room showed the instrument response did not change after the move. However, slightly higher variability in blank data was observed and attributed to different HVAC air flows in the room and in October 2024, solid sides were added to the optical table to block the air flow which returned variability to normal levels. All quality control checks continued to pass with no issues between the room move and the installation of the solid sides.

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 (1/1/2024 – 12/31/2024).

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	13,178	12,766	12,248	518	95.9	92.9
Nylon	13,178	12,766	12,243	523	95.9	92.9
Quartz	13,178	12,718	11,736	982	92.3	89.1

Across the network there were nine 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, 2024 through December 31, 2024.

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 (1/1/2024 – 12/31/2024).

AQS ID # / Location	Completeness			Null Codes		
	PTFE	Nylon	Quartz	PTFE	Nylon	Quartz
01-073-0023-5 North Birmingham, AL	93.4%	92.6%	68%	AH (50%) BJ (25%) Other (25%)	AH (55%) BJ (22%) Other (23%)	AN (87%) SV (5%) Other (8%)
06-037-1103-5 Los Angeles – North Main Street, CA	97.5%	97.5%	47.5%	AG (67%) AV (33%)	AG (67%) AV (33%)	AH (72%) AV (14%) Other (14%)
10-003-2004-5 Wilmington – MLK, DE	97.5%	97.5%	35.2%	AB (33%) AG (33%) AQ (33%)	AB (33%) AG (33%) AH (33%)	BA (71%) AH (23%) AN (6%)
12-073-0012-5 Tallahassee Community College, FL	91.8%	95.1%	70.5%	AD (20%) AH (20%) Other (60%)	AD (33%) AO (33%) SA (33%)	AN (56%) AH (17%) Other (27%)
13-245-0091-5 August, GA	96.7%	93.4%	67.2%	AO (100%)	AO (50%) DA (50%)	AH (85%) AO (10%) AB (5%)
18-163-0021-5 Evansville – Buena Visa Road, IN	42%	42%	93.4%	AN (93%) AI (3%) AL (3%)	AN (90%) AI (7%) AL (3%)	AH (50%) AN (50%)

AQS ID # / Location	Completeness			Null Codes		
	PTFE	Nylon	Quartz	PTFE	Nylon	Quartz
21-111-0067-6 Louisville – Cannon’s Lane, KY	98.4%	98.4%	52.5%	AU (100%)	AU (100%)	BA (47%) AS (17%) Other (36%)
39-135-1001-5 National Trail High School, OH	93.4%	94.3%	68%	AV (88%) AH (12%)	AV (86%) AH (14%)	AV (51%) AN (33%) Other (16%)
47-093-1017-5 Rule High School, TN	100%	100%	57.4%	---	---	AN (87%) BA (9%) AV (4%)

Samples can be invalidated for a variety of reasons, as detailed in the *UCD CSN TI #801C* and the *Data Validation for the Chemical Speciation Network* guide. Null codes indicate the reasons for invalidation (Table 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 1/1/2024 – 12/31/2024.

Null Code	SASS PTFE	SASS Nylon	URG Quartz	Total	Null Code Description
AN	149	148	220	517	Machine Malfunction
AH	87	66	261	414	Sample Flow Rate or CV out of Limits
AV	83	83	109	275	Power Failure
BA	4	4	112	120	Maintenance/Routine Repairs
AF	30	29	48	107	Scheduled but not Collected
BJ	38	40	25	103	Operator Error
AG	17	17	45	79	Sample Time out of Limits
AI	18	19	12	49	Insufficient Data (cannot calculate)
AB	15	15	15	45	Technician Unavailable
AQ	16	14	13	43	Collection Error
AO	13	14	11	38	Bad Weather
AR	3	13	21	37	Lab Error
SV	5	18	9	32	Sample Volume Out of Limits
AS	0	0	27	27	Poor Quality Assurance Results
BB	8	8	8	24	Unable to Reach Site
AK	1	1	13	15	Filter Leak
AL	4	6	5	15	Voided by Operator
AU	2	2	10	14	Monitoring Waived
DA	5	8	0	13	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)
BI	4	4	4	12	Lost or damaged in transit
SA	4	4	3	11	Storm Approaching

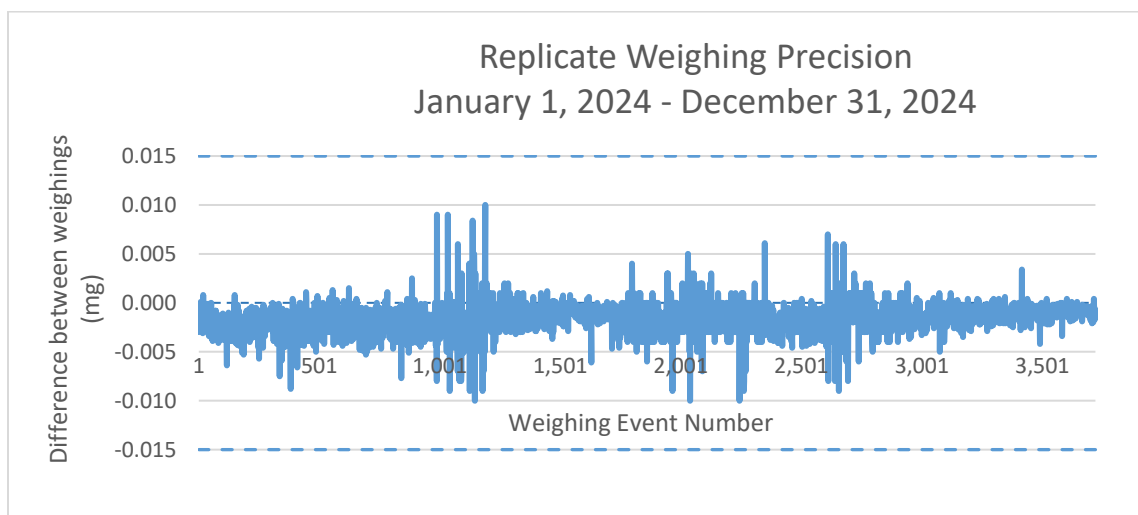
Null Code	SASS PTFE	SASS Nylon	URG Quartz	Total	Null Code Description
BE	3	3	3	9	Building/Site Repair
AJ	4	0	3	7	Filter Damage
AD	1	1	3	5	Shelter Storm Damage
AC	2	2	1	5	Construction/Repairs in Area
AW	1	3	0	4	Wildlife Damage
TS	1	1	1	3	Holding Time Or Transport Temperature Is Out Of Specs.

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 exceeding the permissible $\pm 15 \mu\text{g}$ 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, the Virgin Islands, and the state of Vermont.

Figure 4-1: Replicate weighing precision.



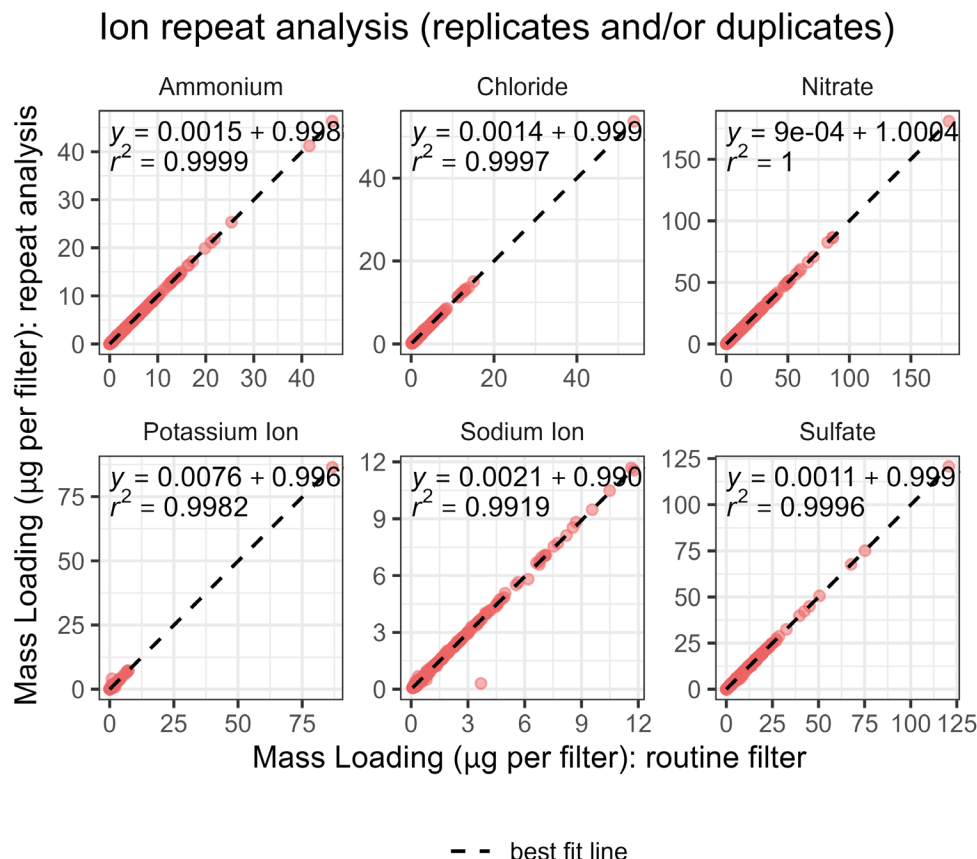
4.1.2.2 Ion Analysis

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 5- 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). Nine 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 1/1/24 – 12/31/24.



4.1.2.3 Elemental Analysis

Replicate EDXRF analyses of routine CSN samples were started on December 20, 2020. The data for 2024 is plotted in Figure 4-3 below. A legacy dataset is used to calculate a comparison RMS (Root Mean Squared) where both the routine and replicate measurement must be above $2 \times \text{MDL}_{\text{analytical}}$. In addition, a minimum of 10 pairs meeting that criteria is required.

Step 1: Replicate Precision Estimates Using Legacy Replicate Measurements

Each week, the XRF instruments take replicate measurements. To evaluate 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. AQRC has chosen to use at least 12 months of filter replicates (approximately 5% of all filters) as the historical dataset to calculate RMS. 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 $\geq 2x \text{MDL}_{\text{Analytical}}$ 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. Data collected with CSN filter sample dates from 2020 and 2021 were used as the legacy dataset, shown in Table 4-4.

Table 4-4: Pairs above $2x \text{MDL}_{\text{analytical}}$ 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.

Due to time and resource constraints, the AQRC 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 legacy RMS 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.

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

Once the expected precision for each element is calculated using the legacy data, the 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 legacy dataset (2020/2021).
- 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.

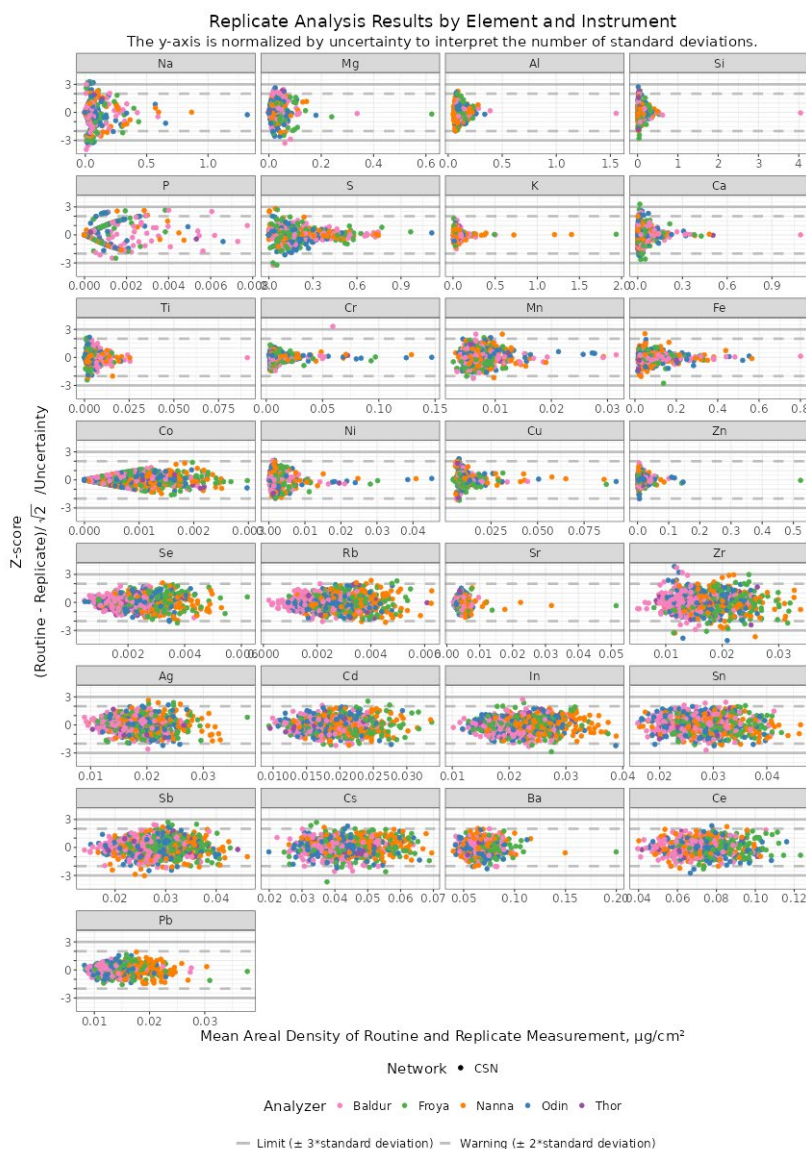
Using the statistical data for sample years 2020-2021, we set limits for each measured element. The dataset for sample year 2024 is as follows:

- 691 filters had replicate measurements for sample year 2024, out of 12,766 samples collected (Table 4.1-1), or 5.41 % 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 20,039 (639 x 29 elements) replicate measurements. There are a total of 50 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, 99.75% of points plotted, passed the criteria ((20,039-50)/20,039).
 - Most of the failures were in Na (33 failures) and Zr (10 failures).

- 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.

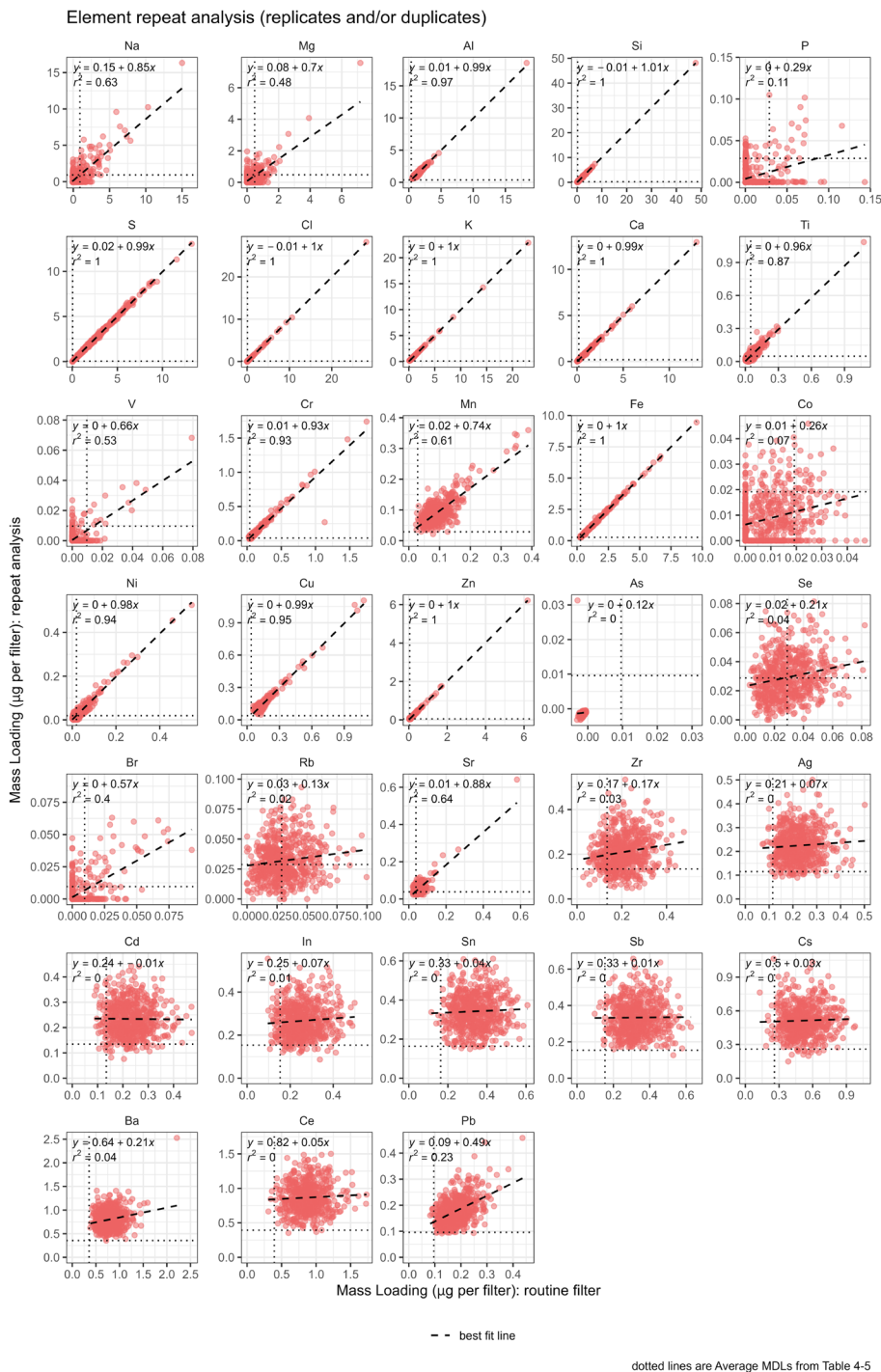
Figure 4-3: Replicate analysis results by element and instrument for sample year 2024.



Comparisons of element mass loadings from repeat analyses (replicates) on PTFE filters analyzed by EDXRF are shown below. Five different EDXRF instruments were used for routine and repeat analyses where both replicate and duplicate analyses are performed on the same instrument. The data here is the same dataset as used in Figure 4-3 above, however, Figure 4-3 does not check all elements due to volatility (Br, Cl) or lack of minimum pairs above 2x MDL in the legacy dataset. Figure 4-4 plots all element mass loadings for routine vs. replicate.

Seen below, many elements do not repeat well and are more likely reporting noise. Cl looks better than expected. Replicate measurements are taken within 24 hours of routine measurements, so there may not be enough time to volatilize off noticeably. Also, filters are analyzed approximately 2 months after sampling, giving plenty of time for volatile Cl to leave the filter before first analysis. The data of Figure 4-4 is from samples collected during January 1, 2024 through December 31, 2024.

Figure 4-4: EDXRF repeat analysis (replicates and/or duplicates) results.



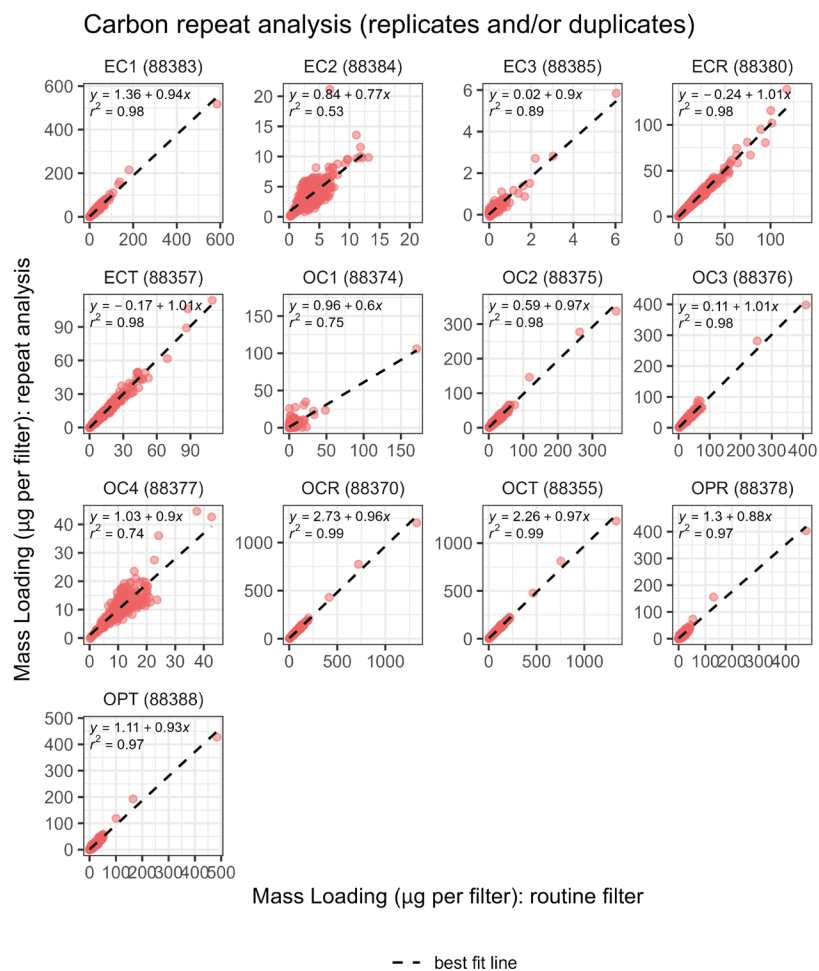
In addition to replicates on network filters, EDXRF precision was evaluated by analyzing the same set of samples, which are UCD-made multi-element reference materials (see Table 5-15). These are analyzed monthly to assess both the short- and long-term stability of the EDXRF measurements as described in *UCD CSN SOP #302* (see section 5.5.2.4).

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 4-5), 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 4-5 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 4-5: Carbon repeat analysis (replicates and/or duplicates) results; data from samples collected during January 1, 2024 through December 31, 2024.



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).

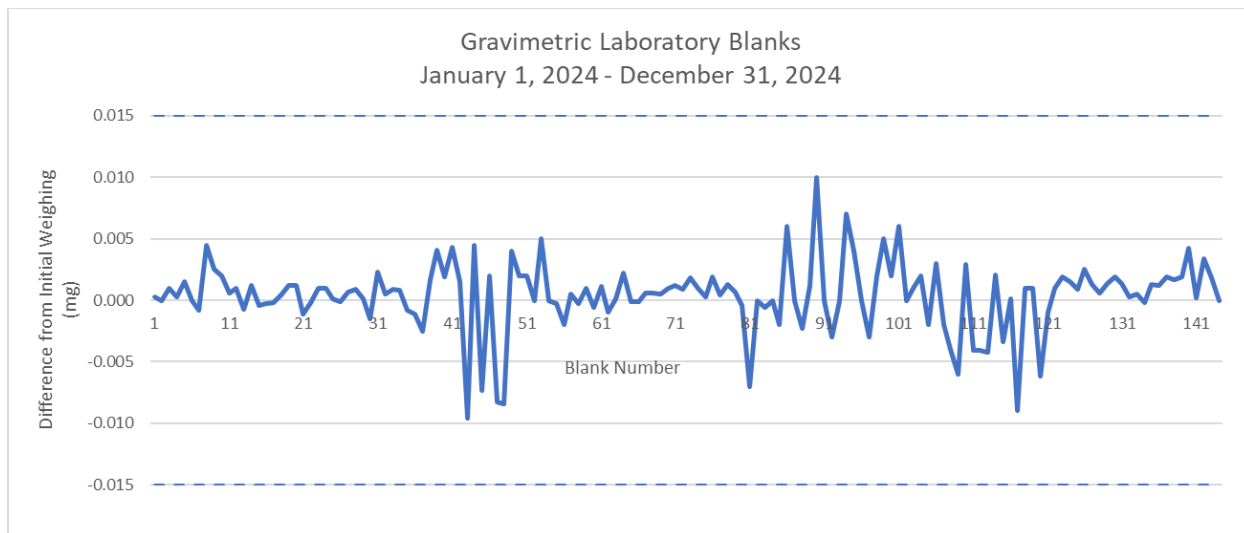
Beginning in May 2017, field blanks are collected once per month for each filter type per site; prior to May 2017 field blanks were collected less frequently.

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 $\pm 15\mu\text{g}$ difference between pre and post – weighing. Results are provided in Figure 4-6.

Figure 4-6: Gravimetric laboratory blanks.

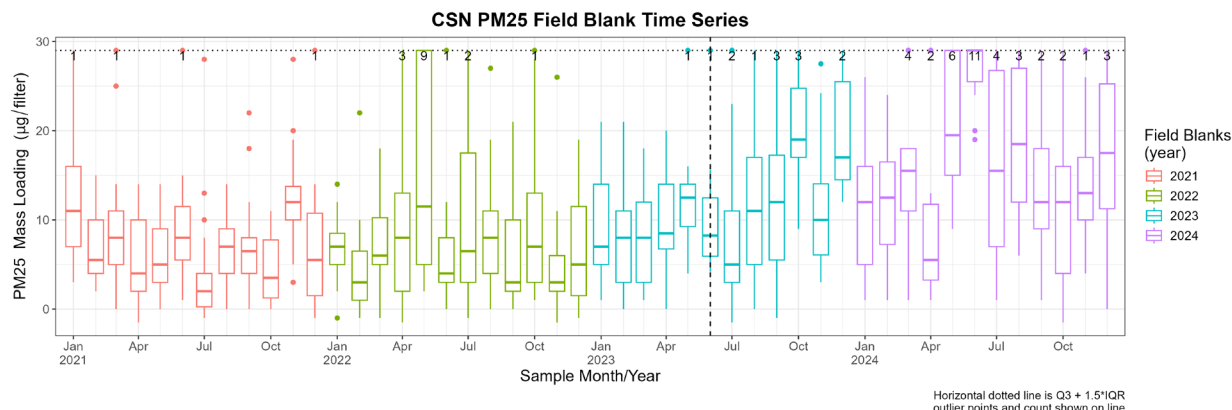


Time series of monthly median mass loading of field blanks are shown in Figures 4-7 for PM 2.5 (where at least 50% of the network sample concentrations are above the reported method detection limit, see Table 4-5).

For the following figure 4-7; 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 $1.5 \times \text{IQR}$ (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond $1.5 \times \text{IQR}$. Outlier points that are off scale are plotted at the $Q3 + 1.5 \times \text{IQR}$ boundary shown by the horizontal dotted line. The vertical dotted line indicates the sample-handling lab transition from WSP to RTI.

Figure 4-7: Time series of $\text{PM}_{2.5}$ gravimetric mass measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

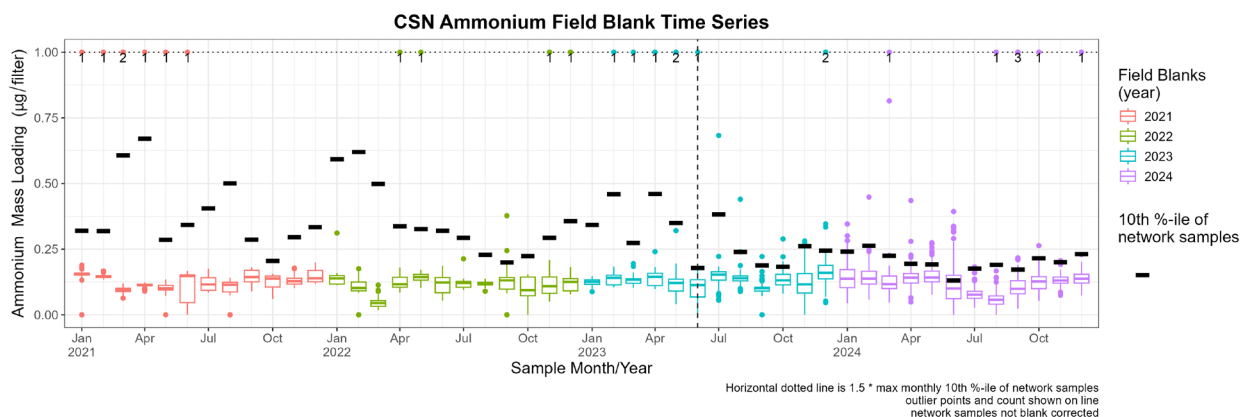


4.1.3.2 Ion Species Field Blanks

Field blank mass loadings for the ion species (Figure 4-8 through 4-13) are examined in an effort to identify changes that may be occurring in the ions measurement lab.

In the following Figures 4-8 to 4-13, 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 $1.5 \times \text{IQR}$ (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond $1.5 \times \text{IQR}$. Outlier points that are off scale are plotted at the $Q3 + 1.5 \times \text{IQR}$ boundary shown by the horizontal dotted line. The vertical dashed line indicates when the sample-handling transitioned from WSP to RTI.

Figure 4-8: Time series of ammonium measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.



In the figure below, chloride field blanks have been elevated since RTI took over sample-handling. Cl is not increasing. The cause for this increase is unknown, but chloride field blank loadings decreased in 2024.

Figure 4-9: Time series of chloride measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

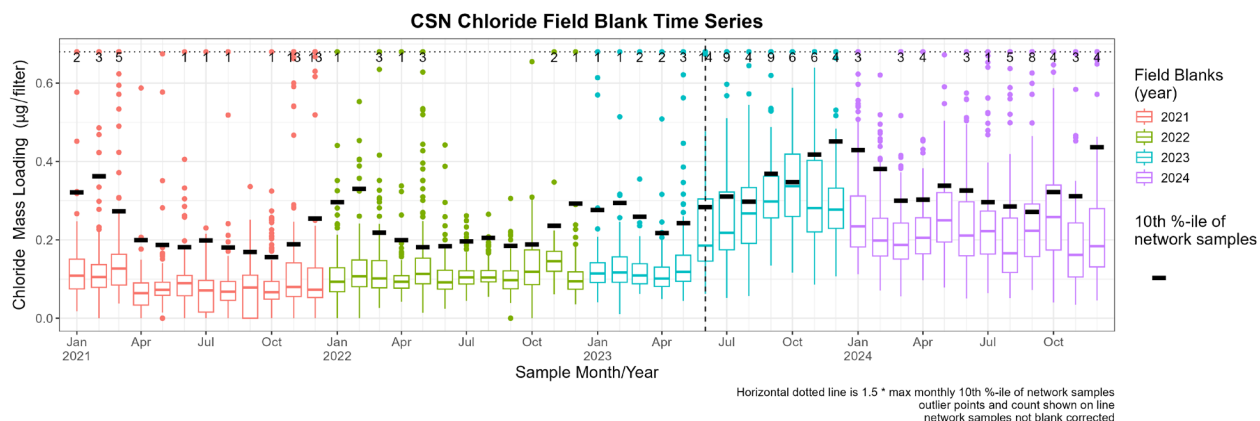


Figure 4-10: Time series of nitrate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

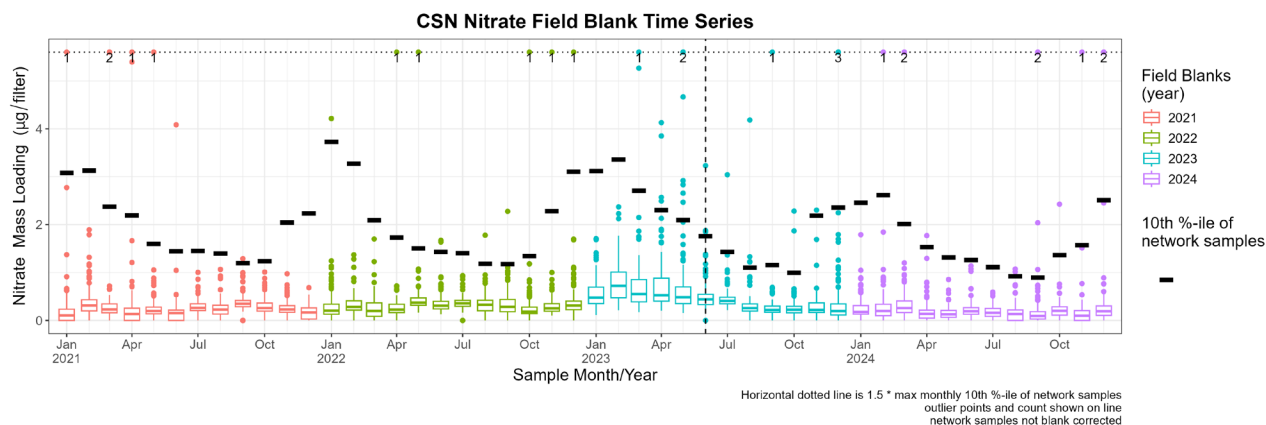


Figure 4-11: Time series of potassium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

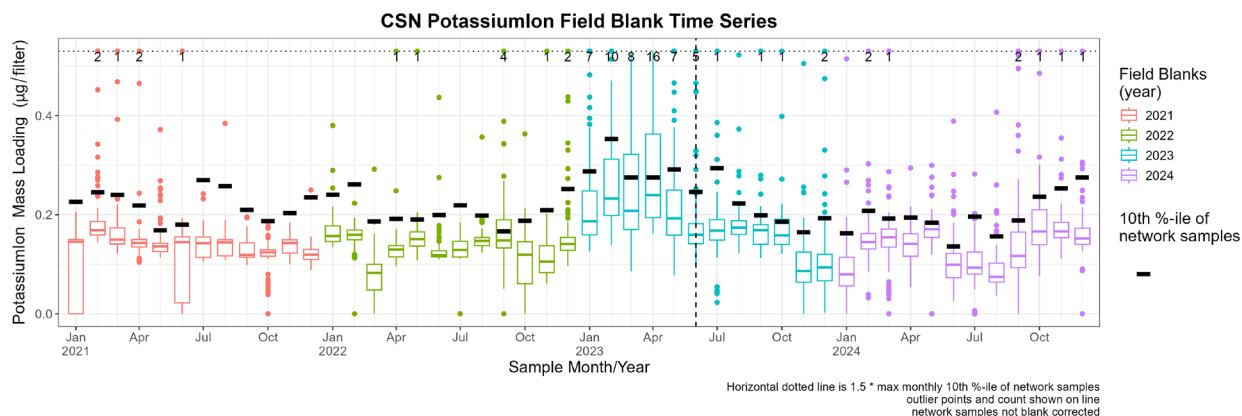


Figure 4-12: Time series of sodium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

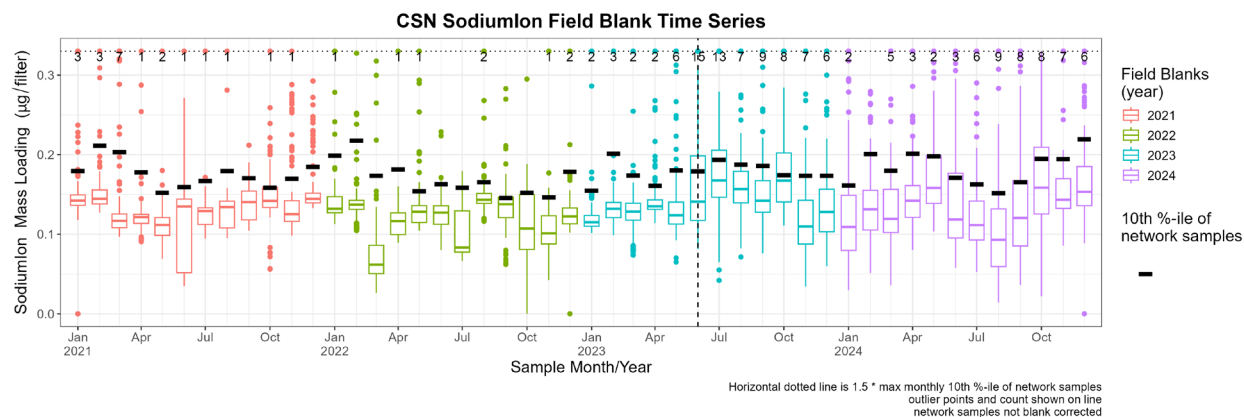
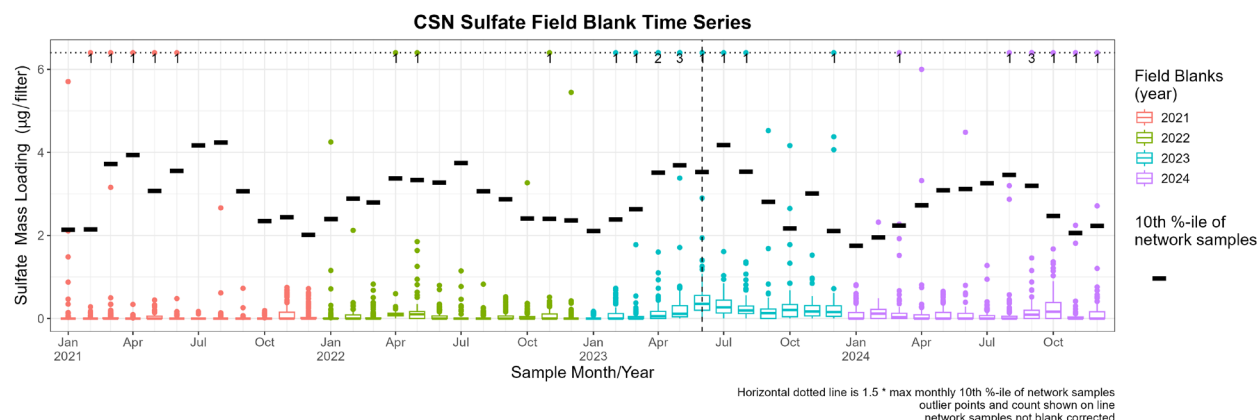


Figure 4-13: Time series of sulfate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.



4.1.3.3 Carbon Species Field Blanks

Field blank mass loadings for organic carbon (Figure 4-14) and elemental carbon (Figure 4-15) 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 $1.5 \times \text{IQR}$ (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond $1.5 \times \text{IQR}$. Outlier points that are off scale are plotted at the $Q3 + 1.5 \times \text{IQR}$ 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 2021) is from UCD.

Figure 4-14: Time series of organic carbon by reflectance (OCTR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

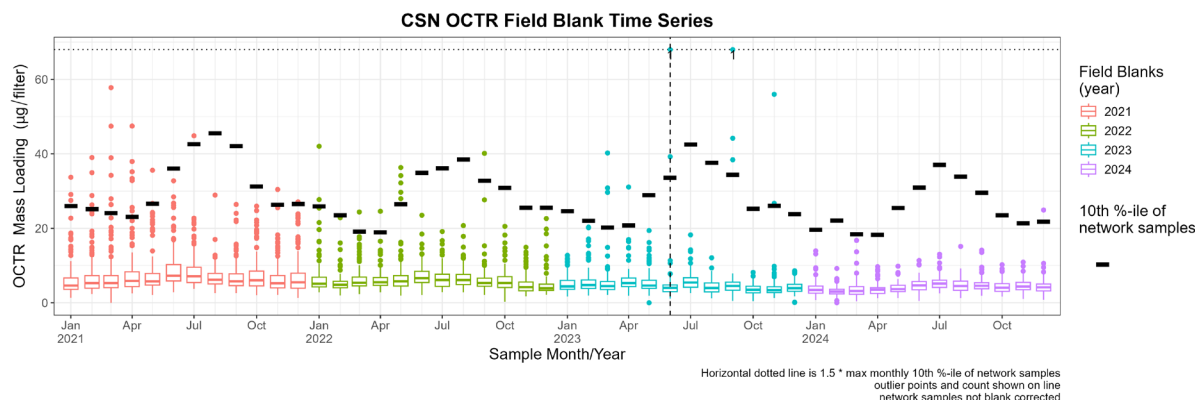
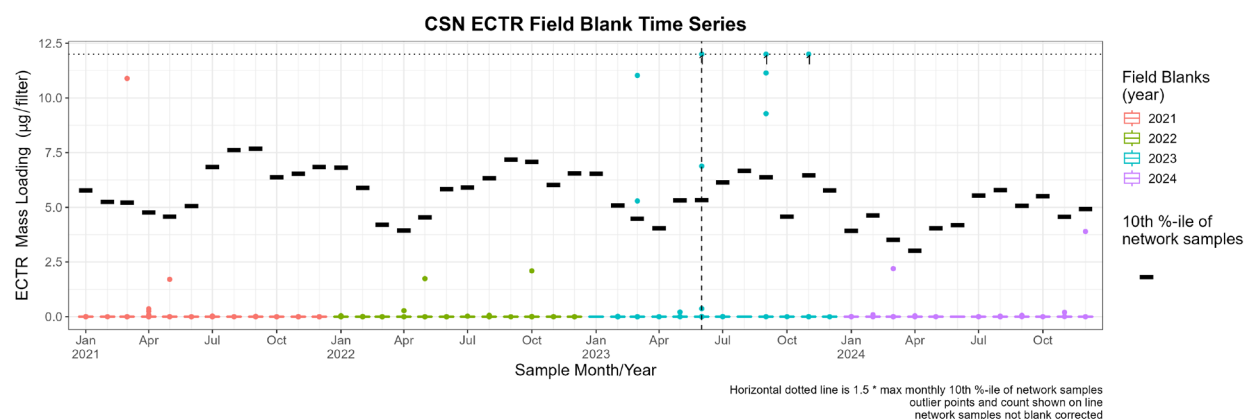


Figure 4-15: Time series of elemental carbon by reflectance (ECTR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.



4.1.3.4 Elemental Species Field Blanks

Time series of monthly median mass loading of field blanks are shown in Figures 4-16 through 4-25 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).

For the following figures: 4-16 to 4-25; 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 $1.5 \times \text{IQR}$ (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond $1.5 \times \text{IQR}$. Outlier points that are off scale are plotted at the $Q3 + 1.5 \times \text{IQR}$ boundary shown by the horizontal dotted line. The vertical dotted line indicates the sample-handling lab transition from WSP to RTI.

Chromium (Figure 4-16) field blanks are associated with stainless steel contamination that has been seen sporadically in CSN over many years. When RTI took over sample handling in June 2023, there was an increase in contamination found on field blanks. The root cause has not yet

been identified, however several mitigation techniques were implemented including torque drivers. Others tested but not widely implemented were increased sonication and plastic bolts.

Figure 4-16: Time series of chromium (Cr) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

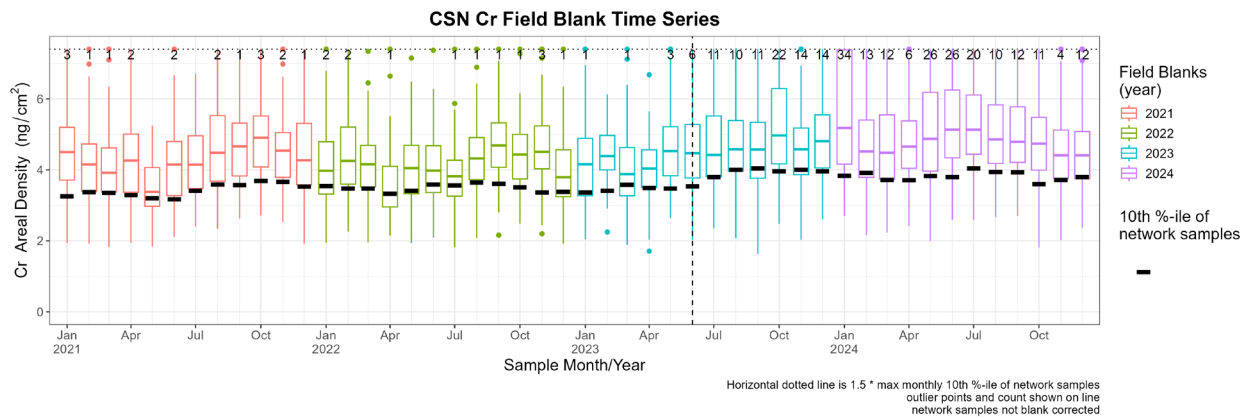


Figure 4-17 shows Cl. Chlorine does not show the same elevation that is seen on chloride from nylon filters by IC.

Figure 4-17: Time series of chlorine (Cl) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

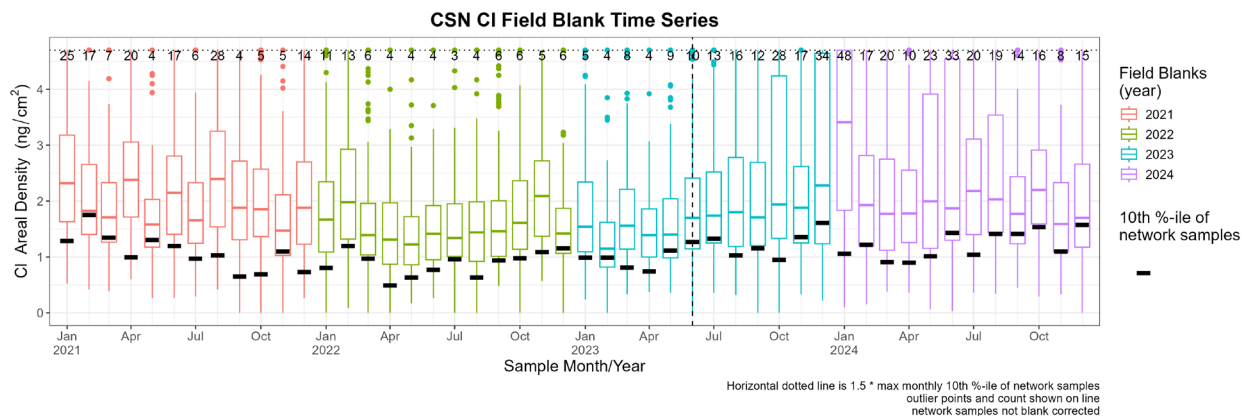
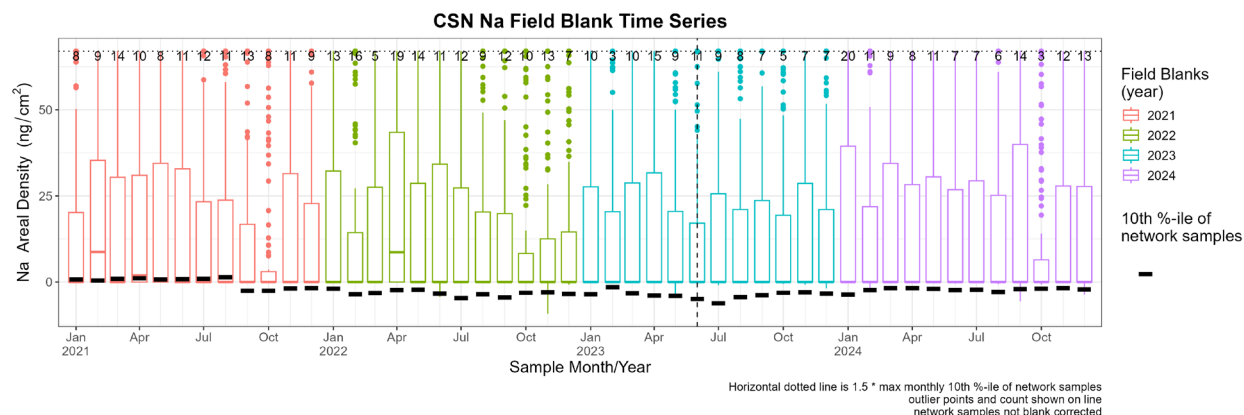


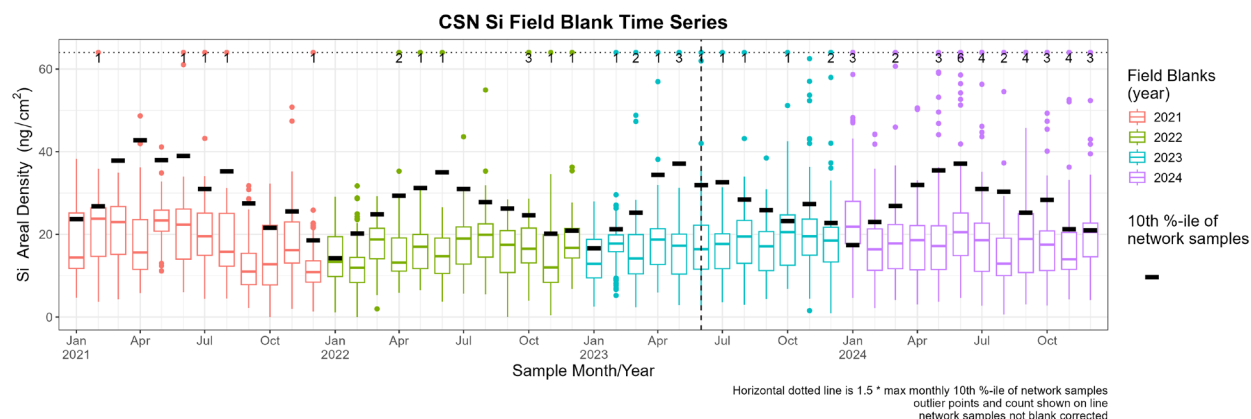
Figure 4-18 below plots Na field blanks. There is a change in 202 when the XRF CaF target was removed from operation to reduce analysis time.

Figure 4-18: Time series of sodium (Na) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.



Silicon (Si; Figure 4-19) monthly median field blank mass loadings continue to show variability.

Figure 4-19: Time series of silicon (Si) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.



Sulfur (S; Figure 4-20) monthly median field blank mass loadings are very lightly loaded.

Figure 4-20: Time series of sulfur (S) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

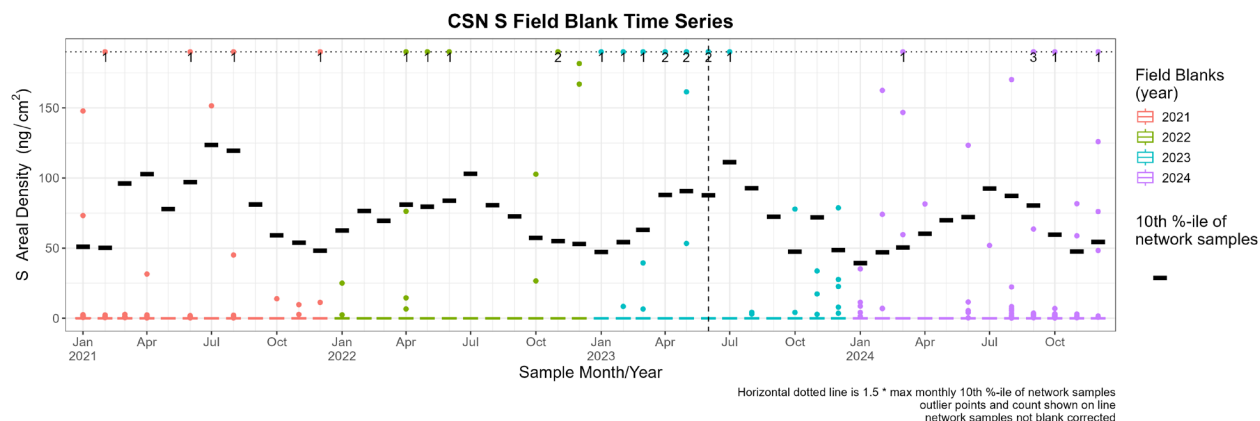


Figure 4-21: Time series of potassium (K) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

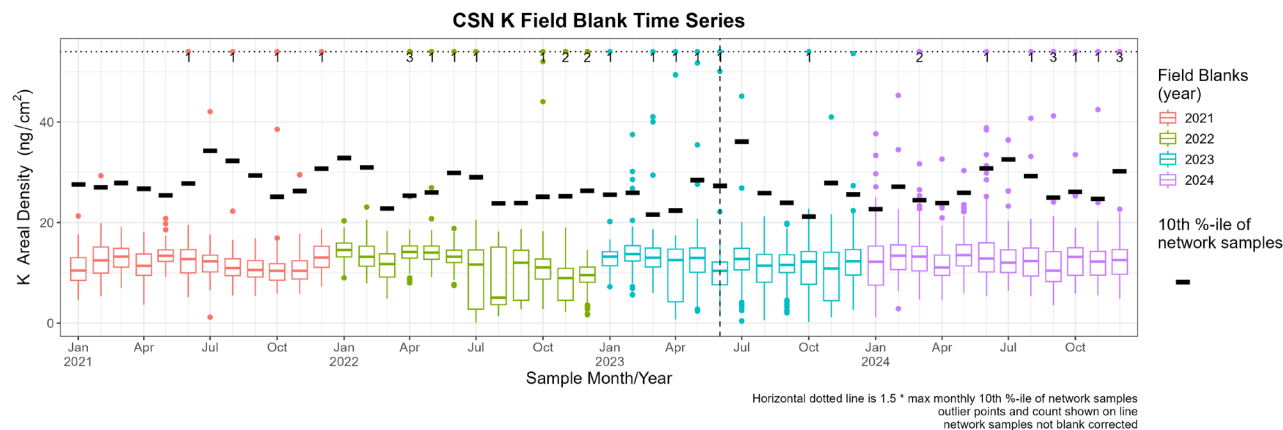


Figure 4-22: Time series of calcium (Ca) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

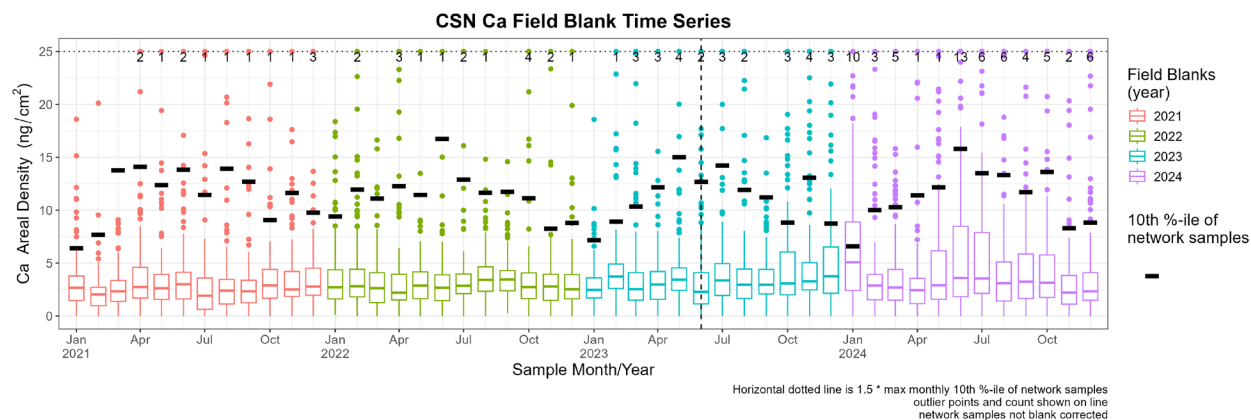


Figure 4-23: Time series of titanium (Ti) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

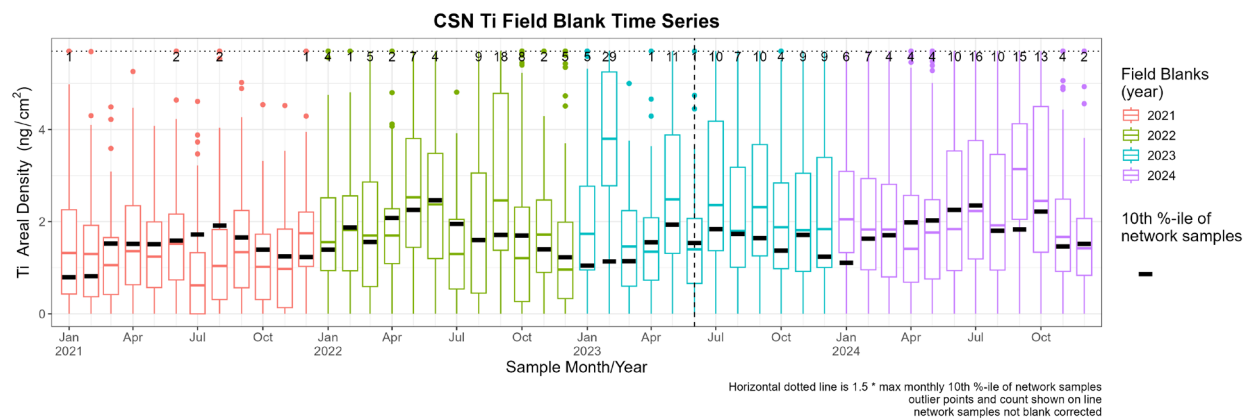


Figure 4-24: Time series of iron (Fe) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.

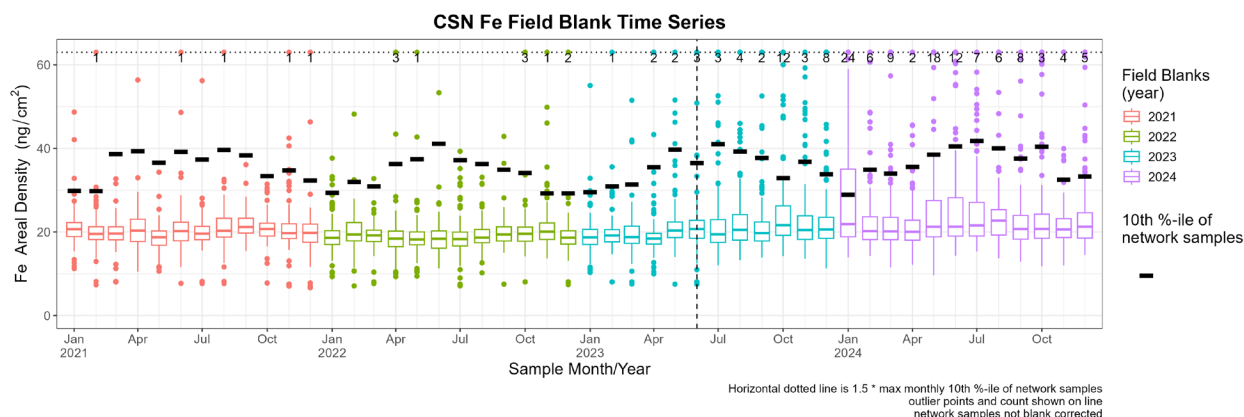
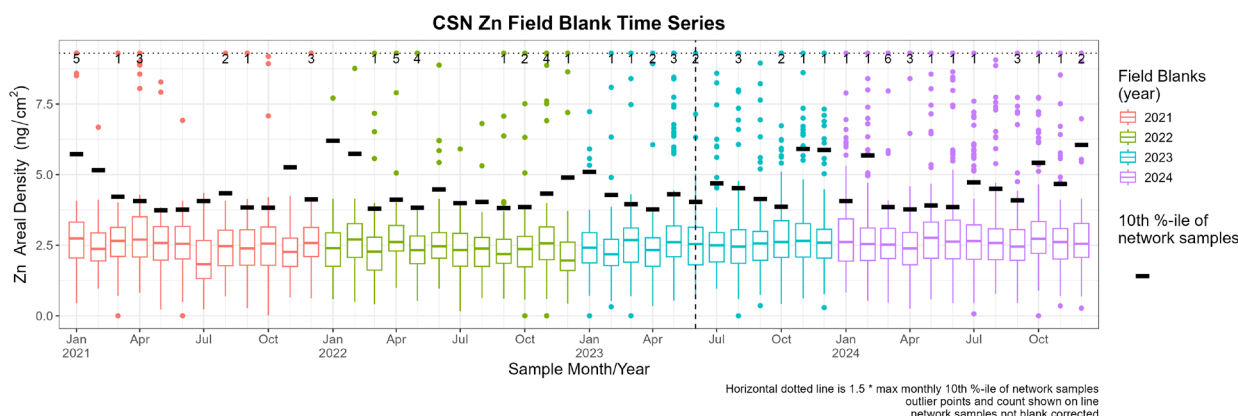


Figure 4-25: Time series of zinc (Zn) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.



4.1.3.5 Optical Absorption Field Blanks

Field blank mass loadings for tau_633 (Figure 4-26) 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*.

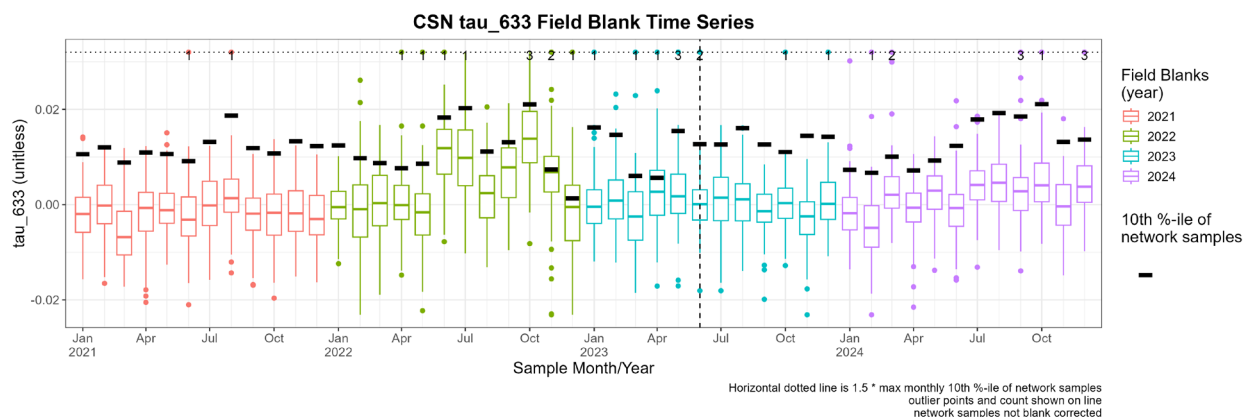
$$\tau_{abs} = \ln\left(\frac{1-r}{t}\right)$$

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

CSN fAbs data was collected for several years but delivery to AQS started May 2022. An effort to validate and deliver past data was completed for data back to August 2020.

In Figure 4-26, 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 $1.5 \times \text{IQR}$ (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond $1.5 \times \text{IQR}$. Outlier points that are off scale are plotted at the $Q3 + 1.5 \times \text{IQR}$ boundary shown by the horizontal dotted line.

Figure 4-26: Time series of tau_633 measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2021 through December 31, 2024.



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 60 PTFE laboratory blanks, 60 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 the 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 months closest to the sampling month, since gravimetry is performed on less than 50 field blanks per month. Field blanks are collected once per month, for each filter type, per site, 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, 2024 through December 31, 2024) are compared to those calculated using the same method from the previous reporting period (samples collected January 1, 2023 through December 31, 2023) (Table 4-5).

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 in MDL $\geq 50\%$ between those reported for the previous reporting period (2023) and the current reporting period (2024). 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	2023 (previous reporting period)		2024 (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	6.2	12	6.9
Al	25	30	45	39	38
As	2.7	1.2	0.0	1.2	0.1
Ba	59	33	11	37	6.6
Br	2.3	1.2	16	1.2	13
Ca	7.6	13	86	20	73
Cd	23	14	4.9	14	4.5
Ce	88	42	4.8	41	4.5
Cl	11	5.5	41	10	32
Co	2.0	1.5	4.6	2.5	0.7
Cr	2.6	2.5	26	4.1	19
Cs	46	27	5.4	27	5.1
Cu	2.5	4.9	15	3.8	19
Fe	3.3	19	90	28	82
In	33	15	5.8	16	5.1
K	11	6.6	97	10	97
Mg	19	48	15	50	15
Mn	2.9	2.9	30	3.1	27
Na	55	91	24	96	23
Ni	1.9	1.4	24	1.7	20
P	16	3.7	5.3	2.5	10
Pb	6.4	7.4	16	10	7.4
Rb	2.6	3.3	6.7	3.5	4.8

Species	EPA Attachment D	2023 (previous reporting period)		2024 (current reporting period)	
	Typical MDL, ng/m ³	Average MDL, ng/m ³	% Above MDL	Average MDL, ng/m ³	% Above MDL
S	9.9	3.7	100	4.0	100
Sb	52	18	5.3	16	7.0
Se	2.6	2.6	7.0	2.6	7.1
Si	19	14	86	26	74
Sn	36	17	6.2	17	6.1
Sr	3.5	2.9	11	3.7	6.4
Ti	5.3	4.0	40	4.9	35
V	3.9	1.2	3.0	1.2	2.6
Zn	3.5	7.3	59	4.5	78
Zr	23	14	7.4	14	7.5
Ammonium	25	13	91	13	87
Chloride	27	35	65	35	66
Nitrate	22	82	97	46	99
Potassium Ion	24	26	62	19	65
Sodium Ion	30	22	53	19	65
Sulfate	35	48	100	48	99
Elemental Carbon (EC1)	95	20	100	10	100
Elemental Carbon (EC2)	63	10	100	8.5	100
Elemental Carbon (EC3)	63	6.0	64	6.6	40
Elemental Carbon (ECR)	63	4.1	100	0.3	100
Elemental Carbon (ECT)	63	3.5	100	0.03	100
Organic Carbon (OC1)	63	22	54	23	52
Organic Carbon (OC2)	63	22	100	24	100
Organic Carbon (OC3)	95	70	98	48	99
Organic Carbon (OC4)	95	36	99	21	100
Organic Carbon (OCR)	63	142	100	100	100
Organic Carbon (OCT)	63	142	100	100	100
Organic Pyrolyzed (OPR)	95	29	93	22	96
Organic Pyrolyzed (OPT)	63	29	97	22	98
Soil	NA	104	93	185	84
Reconstructed Mass	NA	466	100	445	100
fAbs	NA	1.8	87	1.4	92
PM2.5 (88502)	7500	3710	87	4570	80

The differences in MDL from 2023 to 2024 are not unexpected from previous year's changes. The parameters with $\geq 50\%$ change in MDL are: Ca, Cl, Co, Cr, K, Si, EC1, ECTR, ECTT and Soil. There are often changes due to filter lots, handling changes, improved methods, or atmospheric changes. We continue to monitor MDLs for changes, explanations of changes, and potential improvements.

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 2024.

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

4.2.1 Sample Shipping and Handling

4.2.1.1 RTI Shipping and Handling

Issues identified over the course of the contract year for shipping and handling included:

1. Occasional contact from sites via email and on the Field Sampling Chain of Custody (FSCOC) form indicated sites received modules at times with screws that were not fully tightened according to the site operator. In each instance the screws were tightened by the site prior to sampling. Sites also continue to reach out when they receive a module that does not have the top and bottom components sitting flush together. In some cases, the gap between the two is minimal and is a perceived flaw in the manufacturing of an individual module. In other cases, it is clear the screws were not tightened evenly causing the gap. In each case the operator at the site has loosened and re-tightened the screws. This issue is observed approximately twice per calendar year.
2. 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 most prominent during times of 1-in-6 sampling field blanks, where the cartridge for sampling was not loaded with a blank filter in position 4 of the URG cartridge.
 - Staff were reminded of this requirement, as needed, and the frequency of this issue decreased over the course of the year.
 - In cases where the site informs us in a timely manner of missing filters, a replacement set is sent to the site to allow it to collect a valid sample.
3. In a few instances, filters were reloaded after collecting an 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 once every three to four months. Staff who make the error are made aware of the mistake 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.
4. There were three instances brought to the attention of the SHAL where the ID printed on the Null form did not match the ID on the FSCOC. In each case, the site was instructed to correct the Null form ID or it was changed when samples were received back in the

SHAL lab. Additionally, there was one shipment where some sites received the paperwork for a different site – all these issues were resolved after samples were received back after collection and this event did not lead to any invalidated samples.

- These events were most likely the result of a simple paperwork mix-up. No additional actions are expected to be taken at this time.
5. There were a dozen or so sets shipped to sites which were missing the FSCOC paperwork. All the components were loaded correctly, but there was a new technician who had neglected to include the paperwork. In each instance where sites requested the missing FSCOC, it was provided. In many cases, sites were emailed the paperwork before sampling occurred. This incident did not result in any sampling events being invalidated due to missing paperwork as all the information was appropriately captured prior to data entry.
 - The technician who made the error was retrained on the processes of the lab and it has not been an issue since it first occurred.
 6. UC Davis and RTI continue to work together when there is a suspected filter swap occurring between two filters of the same type. A filter swap is defined as a filter physically being placed in a Petri slide with an ID which does not match the information assigned in the database system; the most common filter swap is between sequential events which are processed at the same time (i.e. a June 3rd filter being placed in an assigned June 6th Petri slide). In cases where the unique PTFE filter ID does not match the aliquot label of the Petri slide, the issue is resolved by comparing the sampling event information with the filter ID in the SHAL database. In instances where a nylon or quartz filter have a suspected swap, all available information is reviewed to determine if the events are swapped. In each case of a swap, it has been the same site with a swap occurring between two consecutive sampling dates on a 1-in-3 schedule.
 - When there is an uptick in the amount of swaps, or suspected swaps, UC Davis supplies a list of the suspected swaps and RTI is able to determine if an individual staff member was responsible. During the times of increased filter swaps, staff who are primarily responsible are informed and re-trained on the processes to prevent further swaps.
 7. 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 omitting the comment. It is infrequent and can be quickly resolved through communication between UC Davis and RTI. RTI has implemented 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.
 8. There were occasional instances where two or more filters were mistakenly loaded into a single cassette for sampling.
 - This is still periodically seen, though infrequently. It is estimated this is observed approximately once every three months. Should frequency of the issues increase, additional steps will be taken to ensure resolution.

9. There were two packages lost by UPS in 2024. The Karnack (48-203-0002) site's 2a cooler was lost by UPS on or around 1/19/24. EPA submitted a claim and new components for sampling were assigned to the site for this set. A Bakersfield California Ave (collocated) (06-029-0014) 2a set was lost by UPS on or around 3/6/24. New components for sampling were assigned to the site for this set. There were also two packages that were deemed undeliverable by UPS and returned to RTI; one of these led to an invalidated sampling event, and the other was resolved by sending a replacement set for sample collection.
10. Two instances occurred in 2024 where a leaking icepack caused a contamination of the samples prior to collection. In both instances, a replacement set was sent and a valid collection event occurred.
11. With a change in the shipping scheduling for 2025, the URG sampler was observed to have programmed schedule issues starting with the first sampling event of the calendar year. Additional information and resolution will be provided in the 2025 report.

4.2.1.2 UC Davis Filter Handling

On April 1, 2024, a single CSN PTFE filter from batch 24-01 was left on the counter overnight prior to optical analysis instead of being returned to the refrigerator. A filter level flag and comments were added to the database for this filter. The analyst who made the mistake was informed and reminded of proper procedure. See NR-0028 for further details.

Two refrigerators storing CSN samples from batches 24-02 to 24-04 did not have their daily temperatures recorded on Monday August 5, 2024. The temperature from the previous Friday and the following Tuesday were both within specifications. Staff were reminded of the need to record daily temperatures for all refrigerators. See NR-0031 for further information.

The daily temperature reading for the refrigerator storing PTFE filters preparing for optical analysis was not recorded on Monday September 16, 2024. Samples from batch 24-06 were stored in the refrigerator at the time. The temperatures from the Friday before and following day were both within specifications. Staff were reminded of the proper procedure for recording refrigerator temperatures daily. See NR-0032 for further details.

On Friday January 17, 2025, the quartz refrigerator did not have the temperature recorded for the day as specified in UCD CSN SOP 903. CSN quartz samples from batches 24-08, 24-09, and 24-10 were stored in the refrigerator at the time. The temperatures recorded the day before and the following Tuesday (Monday was a holiday) were within specifications. Staff were reminded of the requirement to record the temperature daily. See NR-0034 for further details.

4.2.2 Gravimetric Analysis

The gravimetry lab did not experience any quality issues affecting CSN data during the 2024 reporting period. There was a timepoint near the end of the month in June where the automatic weighing system stopped functioning and post-sampled filters which were tare weighed on the autohandler had to be post-weighed manually. This information was provided to UC Davis, and any appropriate flags were applied to the data.

As previously mentioned, there were six instances where filters were mistakenly post-weighed outside their permissible window due to the temperature and timeliness of return of the filters to the lab. In all instances the data was flagged with a TS code.

4.2.3 Elemental Analysis

4.2.3.1 X-ray Intensity Drop on XRF-3

On April 12, 2024 XRF-3 showed an unexplained drop in X-ray intensities for light elements. All sample analyses were stopped. The instrument was analyzing IMPROVE samples at the time. Prior to any intensity drops, XRF-3 had analyzed CSN samples from batch 24-01. Troubleshooting by the lab and the manufacturer did not find a definitive cause. In November 2024 the X-ray tube was replaced and the instrument was recalibrated. Some CSN samples from batch 24-09 were analyzed while the X-rays were stable until December 2024 when the intensity drops reoccurred, this time with heavier elements, so all sample analysis was again stopped. Troubleshooting with the manufacturer continued until ultimately the X-ray detector was replaced in December 2025. Testing continues to determine if the detector was the root cause. UC Davis is tracking this issue on IR-0024.

4.2.3.2 XRF Lab Deviations

Deviation DV-0012, which introduces criteria for QC of elemental replicate measures, was still in effect during this reporting period. Also, deviation DV-0015, which removes the element zinc from the monthly NIST SRM QC check, is still in effect for this reporting period. Both deviations predate the 2024 sampling year, however, due to resource constraints the edits to the SOP have not been finalized. This is expected to be completed in 2026.

4.2.4 Ion Analysis

During this reporting period there were no corrective action incidents reported by the ions laboratory.

4.2.5 Carbon Analysis

The quartz filter punch size was incorrectly entered into one of the TOA analyzers. This occurred March 19 – 22, 2024 after the autoloader was removed from the system (which has a different punch size). The issue was noticed and all sample results were reprocessed with the correct punch size before the data were delivered. See NR-0027 for more details.

In October 2024 during a document review, it was discovered that the Spectroscopist did not have the Sucrose Standard Generation Form (UCD CSN TI 402H Appendix A) independently QC checked by another qualified person to catch issues in preparation of the sucrose dilutions. Each sucrose dilution is tested on the TOA analyzers using current calibrations after creation which would catch any issues in the preparation, so there was no impact on the data. Staff in the Carbon Analysis Lab were retrained to ensure the form was properly reviewed in the future. See NR-0033 for further details.

On January 15, 2025, during a routine carbon sample reanalysis, it was discovered that the quartz filter punch size entered into the instrument was incorrect. This affected multiple instruments and multiple samples analyzed that day. Similar instances occurred on February 13, 2025 and March 5, 2025. This affected quartz samples from batches 24-10, 24-11, and 24-12. In all cases the

results were reprocessed with the correct punch size before final data delivery. The instrument software requires manual entry of the punch size, so an automated database check was added to the carbon lab daily QC web application to help catch these errors sooner. See NR-0035 for further details.

In June 2025, after replacing the HeOx compressed gas for the TOA instruments, a dip in the FID response at the start of the HeOx phase of analysis was observed on all instruments. All QC checks continued to pass; however, the dip was visible in the thermograms and was not normal. A similar event happened in October 2023 and was traced to a specific lot of HeOx gas supplied by Linde. No other causes could be confirmed this time, so it was decided that the HeOx gas cylinder should be exchanged again. The HeOx cylinder causing the issue was from a different lot this time but also filled by Linde. A replacement HeOx cylinder from a different lot was installed and the issue was resolved. Since then, we have switched to a new gas supplier, Matheson. UC Davis tracks this issue on IR-0025.

4.2.6 Optical Absorption

During this reporting period there were no corrective action incidents reported by the optical analysis laboratory.

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 evolve 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 and ending September 2023, the bromine (Br) and chlorine (Cl) are marked invalid with the ‘AL – Voided by Operator’ null code for any filters reanalyzed at XRF.

Beginning with filters from October 2023, the bromine (Br) and chlorine (Cl) are marked invalid with the ‘AR – Lab Error’ null code for any filters reanalyzed at XRF. This reanalysis is not an actual lab error, but it is the code selected by EPA for this instance. The AR code is currently applied as part of deviation DV-0018 to UCD CSN SOP 302. This report will be updated if another change is made in the future.

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 requirement to invalidate. Section 5.5.3.1 of UC Davis CSN QAPP has another justification due to the volatility of Br and Cl.

4.2.7.3 January 2024 DART Delivery Incorrect Dataset

The CSN January 2024 dataset delivered to DART was incorrect initially because the unvalidated dataset was delivered. This means that state and local air agency validators reviewed the uncorrected data. Some concentrations and reporting statistics differ between DART and AQS.

This was discovered once data returned from DART to UC Davis. The wrong object, or dataset, in R was used in the last steps of validation and data preparation before posting data to delivery.DartExport, and then delivered to DART. The delivered dataset was the original processed data, prior to any Level 1 validation. Some of the affected parameters are: Analytical MDLs, dummy filter records, some gravimetric mass corrections, a nylon field blank, some reanalysis results, and C1 qualifier codes.

After a review of the changes applied during Level 1 validation, AQRC put together a list of the impacts. It was determined that most of them were minor, but were corrected for AQS delivery. Affected sites and validators were contacted with the correct information and given a chance to review the changes. The problem was attributed to human error and the fact that the Validation script generates multiple datasets that are not necessary, leading to the possibility of selecting the wrong one. The script was updated to ensure only the necessary working dataset is present. The supervisor retrained the employee on the process and there have been no further issues with delivery since then. UC Davis tracked this issue on NR-0030.

4.2.8 Technical System Audit

The EPA worked with Battelle (Columbus, OH) to conduct an audit of RTI's CSN and IMPROVE operations on March 11-12, 2025. The UC Davis Quality Manager was also on-site for the audit. The audit covered sample handling, shipping, gravimetric analysis, ion analysis, data validation, quality control at each step, as well as other topics.

At the time, RTI was performing ions analysis on the November and December 2024 batches. UC Davis operations were outside the scope of the audit.

The final audit report was delivered to RTI and UC Davis on August 21, 2025. The report had two findings and one concern. After some discussions, RTI responded to the audit report with corrective action forms for the two findings and a response to the concern. The EPA requested additional information in a meeting on October 9, 2025, which was provided by RTI. The process is still ongoing as of the publication of this report.

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 2026.

At RTI, no CSN internal audit took place in 2024. The next internal audit will likely take place in 2026.

4.3 Filter Acceptance Testing

Quartz filter acceptance testing is performed by both RTI and UC Davis. A minimum of 2% of filters received are used for testing for any given lot of filters received from the manufacturer. RTI receives the initial filters and performs acceptance testing. The filters are then pre-fired by RTI and sent to UC Davis for Carbon analysis. The results are transmitted back to RTI so the filters can be deployed once they pass the testing.

Nylon filter acceptance testing is performed by RTI for Ion analysis. A minimum of 2% of filters received are used for testing for any given lot of filters received from the manufacturer.

PTFE filter acceptance testing is performed by RTI for Gravimetric analysis and sample handling. A minimum of 2% of filters received are used for testing for any given lot of filters received from the manufacturer, additionally all PTFE filters are visually inspected prior to their use in sample collection for pinholes or other imperfections.

4.3.1 Quartz Filter Testing

All filter lot samples provided to the test laboratory passed the average $\leq 1.5 \mu\text{g}/\text{cm}^2$ TC testing criteria. Results are provided in Table 4-6.

Average results for a lot are what determines the acceptability of use, and all instances of the above criteria were met. For the individual instances where filters were above the permitted average levels, no actions were taken. If a lot was above the permissible level, quartz filters would be re-treated in a muffle furnace and retested.

Table 4-6: Quartz Filter Acceptance Testing Results [$\mu\text{g}/\text{cm}^2$].

Filter ID	TC [$\mu\text{g}/\text{cm}^2$]	Filter ID	TC [$\mu\text{g}/\text{cm}^2$]
CSNQ0017 Filter 1	0.097	CSNQ0030 Filter 1	0.194
CSNQ0017 Filter 2	0.044	CSNQ0030 Filter 2	0.347
CSNQ0017 Filter 3	0.141	CSNQ0030 Filter 3	0.071
CSNQ0017 Filter 4	-0.013	CSNQ0030 Filter 4	0.199
CSNQ0017 Filter 5	0.025	CSNQ0030 Filter 5	0.363
CSNQ0017 Filter 6	-0.061	CSNQ0030 Filter 6	0.157
CSNQ0017 Filter 7	0.058	CSNQ0030 Filter 7	-0.032
CSNQ0017 Filter 8	0.024	CSNQ0030 Filter 8	0.434
CSNQ0017 Filter 9	-0.002	CSNQ0030 Filter 9	0.122
CSNQ0017 Filter 10	-0.078	CSNQ0030 Filter 10	0.096
CSNQ0017 Filter 11	0.006	CSNQ0030 Filter 11	0.338

Filter ID	TC [ug/cm2]
CSNQ0017 Filter 12	0.079
Average	0.027
CSNQ0018 Filter 1	0.056
CSNQ0018 Filter 2	0.195
CSNQ0018 Filter 3	-0.081
CSNQ0018 Filter 4	-0.060
CSNQ0018 Filter 5	-0.086
CSNQ0018 Filter 6	0.006
CSNQ0018 Filter 7	-0.064
CSNQ0018 Filter 8	-0.052
CSNQ0018 Filter 9	-0.067
CSNQ0018 Filter 10	-0.047
CSNQ0018 Filter 11	-0.095
CSNQ0018 Filter 12	-0.062
Average	-0.030
CSNQ0019 Filter 1	-0.064
CSNQ0019 Filter 2	0.003
CSNQ0019 Filter 3	0.052
CSNQ0019 Filter 4	0.326
CSNQ0019 Filter 5	0.165
CSNQ0019 Filter 6	-0.013
CSNQ0019 Filter 7	-0.122
CSNQ0019 Filter 8	-0.084
CSNQ0019 Filter 9	-0.071
CSNQ0019 Filter 10	-0.137
CSNQ0019 Filter 11	-0.090
CSNQ0019 Filter 12	-0.071
Average	-0.009
CSNQ0020 Filter 1	0.017
CSNQ0020 Filter 2	0.001
CSNQ0020 Filter 3	-0.025
CSNQ0020 Filter 4	0.056
CSNQ0020 Filter 5	0.133
CSNQ0020 Filter 6	0.010
CSNQ0020 Filter 7	-0.117
CSNQ0020 Filter 8	-0.178
CSNQ0020 Filter 9	-0.013
CSNQ0020 Filter 10	-0.164
CSNQ0020 Filter 11	0.014
CSNQ0020 Filter 12	-0.015

Filter ID	TC [ug/cm2]
CSNQ0030 Filter 12	0.164
Average	0.204
CSNQ0031 Filter 1	0.011
CSNQ0031 Filter 2	0.137
CSNQ0031 Filter 3	0.109
CSNQ0031 Filter 4	0.005
CSNQ0031 Filter 5	0.334
CSNQ0031 Filter 6	0.119
CSNQ0031 Filter 7	0.015
CSNQ0031 Filter 8	0.083
CSNQ0031 Filter 9	-0.019
CSNQ0031 Filter 10	0.115
CSNQ0032 Filter 11	0.440
CSNQ0032 Filter 12	0.043
Average	0.111
CSNQ0033 Filter 1	0.089
CSNQ0033 Filter 2	0.219
CSNQ0033 Filter 3	0.044
CSNQ0033 Filter 4	0.168
CSNQ0033 Filter 5	0.115
CSNQ0033 Filter 6	0.119
CSNQ0033 Filter 7	0.004
CSNQ0033 Filter 8	0.086
CSNQ0033 Filter 9	0.200
CSNQ0033 Filter 10	0.060
CSNQ0033 Filter 11	0.471
CSNQ0033 Filter 12	0.225
Average	0.150
CSNQ0034 Filter 1	0.053
CSNQ0034 Filter 2	0.239
CSNQ0034 Filter 3	0.162
CSNQ0034 Filter 4	0.089
CSNQ0034 Filter 5	-0.001
CSNQ0034 Filter 6	0.162
CSNQ0034 Filter 7	-0.175
CSNQ0034 Filter 8	0.176
CSNQ0034 Filter 9	0.182
CSNQ0034 Filter 10	0.064
CSNQ0034 Filter 11	0.836
CSNQ0034 Filter 12	0.356

Filter ID	TC [ug/cm2]
Average	-0.023
CSNQ0021 Filter 1	-0.061
CSNQ0021 Filter 2	-0.066
CSNQ0021 Filter 3	-0.081
CSNQ0021 Filter 4	0.152
CSNQ0021 Filter 5	0.128
CSNQ0021 Filter 6	-0.043
CSNQ0021 Filter 7	-0.164
CSNQ0021 Filter 8	-0.019
CSNQ0021 Filter 9	-0.073
CSNQ0021 Filter 10	-0.262
CSNQ0021 Filter 11	0.062
CSNQ0021 Filter 12	-0.148
Average	-0.048
CSNQ0022 Filter 1	-0.061
CSNQ0022 Filter 2	-0.106
CSNQ0022 Filter 3	0.078
CSNQ0022 Filter 4	0.074
CSNQ0022 Filter 5	0.407
CSNQ0022 Filter 6	-0.105
CSNQ0022 Filter 7	-0.102
CSNQ0022 Filter 8	-0.095
CSNQ0022 Filter 9	-0.063
CSNQ0022 Filter 10	-0.170
CSNQ0022 Filter 11	-0.112
CSNQ0022 Filter 12	-0.182
Average	-0.036
CSNQ0023 Filter 1	0.252
CSNQ0023 Filter 2	0.701
CSNQ0023 Filter 3	-0.014
CSNQ0023 Filter 4	0.008
CSNQ0023 Filter 5	0.178
CSNQ0023 Filter 6	-0.032
CSNQ0023 Filter 7	0.423
CSNQ0023 Filter 8	0.275
CSNQ0023 Filter 9	-0.069
CSNQ0023 Filter 10	0.001
CSNQ0023 Filter 11	-0.006
CSNQ0023 Filter 12	-0.105
Average	0.134

Filter ID	TC [ug/cm2]
Average	0.178
CSNQ0035 Filter 1	0.435
CSNQ0035 Filter 2	0.504
CSNQ0035 Filter 3	0.401
CSNQ0035 Filter 4	0.142
CSNQ0035 Filter 5	0.017
CSNQ0035 Filter 6	0.073
CSNQ0035 Filter 7	1.366
CSNQ0035 Filter 8	0.126
CSNQ0035 Filter 9	0.242
CSNQ0035 Filter 10	0.124
CSNQ0035 Filter 11	0.071
CSNQ0035 Filter 12	-0.117
Average	0.282
CSNQ0036 Filter 1	0.110
CSNQ0036 Filter 2	0.026
CSNQ0036 Filter 3	-0.001
CSNQ0036 Filter 4	0.666
CSNQ0036 Filter 5	0.612
CSNQ0036 Filter 6	0.440
CSNQ0036 Filter 7	0.172
CSNQ0036 Filter 8	0.064
CSNQ0036 Filter 9	0.466
CSNQ0036 Filter 10	0.064
CSNQ0036 Filter 11	0.270
CSNQ0036 Filter 12	-0.087
Average	0.234
CSNQ0037 Filter 1	0.192
CSNQ0037 Filter 2	0.198
CSNQ0037 Filter 3	0.348
CSNQ0037 Filter 4	0.391
CSNQ0037 Filter 5	-0.126
CSNQ0037 Filter 6	0.013
CSNQ0037 Filter 7	0.556
CSNQ0037 Filter 8	0.248
CSNQ0037 Filter 9	0.341
CSNQ0037 Filter 10	-0.173
CSNQ0037 Filter 11	-0.018
CSNQ0037 Filter 12	0.236
Average	0.184

Filter ID	TC [ug/cm2]
CSNQ0024 Filter 1	-0.039
CSNQ0024 Filter 2	0.003
CSNQ0024 Filter 3	-0.102
CSNQ0024 Filter 4	0.123
CSNQ0024 Filter 5	0.239
CSNQ0024 Filter 6	0.042
CSNQ0024 Filter 7	0.103
CSNQ0024 Filter 8	-0.075
CSNQ0024 Filter 9	-0.061
CSNQ0024 Filter 10	0.217
CSNQ0024 Filter 11	0.165
CSNQ0024 Filter 12	-0.027
Average	0.049
CSNQ0025 Filter 1	0.106
CSNQ0025 Filter 2	0.010
CSNQ0025 Filter 3	0.083
CSNQ0025 Filter 4	0.137
CSNQ0025 Filter 5	0.098
CSNQ0025 Filter 6	0.231
CSNQ0025 Filter 7	0.166
CSNQ0025 Filter 8	0.105
CSNQ0025 Filter 9	-0.157
CSNQ0025 Filter 10	0.020
CSNQ0025 Filter 11	0.128
CSNQ0025 Filter 12	0.208
Average	0.094
CSNQ0026 Filter 1	-0.085
CSNQ0026 Filter 2	-0.125
CSNQ0026 Filter 3	0.038
CSNQ0026 Filter 4	-0.189
CSNQ0026 Filter 5	-0.070
CSNQ0026 Filter 6	-0.106
CSNQ0026 Filter 7	0.260
CSNQ0026 Filter 8	-0.016
CSNQ0026 Filter 9	-0.078
CSNQ0026 Filter 10	0.079
CSNQ0026 Filter 11	-0.040
CSNQ0026 Filter 12	-0.128
Average	-0.038
CSNQ0027 Filter 1	0.108

Filter ID	TC [ug/cm2]
CSNQ0038 Filter 1	0.053
CSNQ0038 Filter 2	0.854
CSNQ0038 Filter 3	0.553
CSNQ0038 Filter 4	0.185
CSNQ0038 Filter 5	0.327
CSNQ0038 Filter 6	0.650
CSNQ0038 Filter 7	0.320
CSNQ0038 Filter 8	0.503
CSNQ0038 Filter 9	1.336
CSNQ0038 Filter 10	1.422
CSNQ0038 Filter 11	0.027
CSNQ0038 Filter 12	0.478
Average	0.559
CSNQ0039 Filter 1	-0.076
CSNQ0039 Filter 2	-0.006
CSNQ0039 Filter 3	-0.033
CSNQ0039 Filter 4	0.228
CSNQ0039 Filter 5	0.733
CSNQ0039 Filter 6	-0.018
CSNQ0039 Filter 7	3.296
CSNQ0039 Filter 8	0.623
CSNQ0039 Filter 9	0.131
CSNQ0039 Filter 10	0.533
CSNQ0039 Filter 11	0.576
CSNQ0039 Filter 12	-0.084
Average	0.492
CSNQ0040 Filter 1	-0.051
CSNQ0040 Filter 2	0.108
CSNQ0040 Filter 3	0.241
CSNQ0040 Filter 4	0.034
CSNQ0040 Filter 5	-0.046
CSNQ0040 Filter 6	0.109
CSNQ0040 Filter 7	0.060
CSNQ0040 Filter 8	0.576
CSNQ0040 Filter 9	0.854
CSNQ0040 Filter 10	0.123
CSNQ0040 Filter 11	-0.006
CSNQ0040 Filter 12	0.265
Average	0.189
CSNQ0041 Filter 1	0.136

Filter ID	TC [ug/cm2]
CSNQ0027 Filter 2	0.150
CSNQ0027 Filter 3	-0.076
CSNQ0027 Filter 4	-0.158
CSNQ0027 Filter 5	-0.037
CSNQ0027 Filter 6	-0.017
CSNQ0027 Filter 7	0.088
CSNQ0027 Filter 8	0.100
CSNQ0027 Filter 9	-0.005
CSNQ0027 Filter 10	0.069
CSNQ0027 Filter 11	0.200
CSNQ0027 Filter 12	-0.074
Average	0.029
CSNQ0028 Filter 1	0.507
CSNQ0028 Filter 2	0.216
CSNQ0028 Filter 3	0.148
CSNQ0028 Filter 4	0.118
CSNQ0028 Filter 5	0.458
CSNQ0028 Filter 6	0.551
CSNQ0028 Filter 7	0.017
CSNQ0028 Filter 8	0.065
CSNQ0028 Filter 9	0.085
CSNQ0028 Filter 10	0.066
CSNQ0028 Filter 11	0.135
CSNQ0028 Filter 12	0.712
Average	0.256
CSNQ0029 Filter 1	0.384
CSNQ0029 Filter 2	0.146
CSNQ0029 Filter 3	0.036
CSNQ0029 Filter 4	0.178
CSNQ0029 Filter 5	0.207
CSNQ0029 Filter 6	1.063
CSNQ0029 Filter 7	0.033
CSNQ0029 Filter 8	0.191
CSNQ0029 Filter 9	0.073
CSNQ0029 Filter 10	0.188
CSNQ0029 Filter 11	0.265
CSNQ0029 Filter 12	0.249
Average	0.251

Filter ID	TC [ug/cm2]
CSNQ0041 Filter 2	-0.010
CSNQ0041 Filter 3	0.730
CSNQ0041 Filter 4	0.714
CSNQ0041 Filter 5	-0.023
CSNQ0041 Filter 6	1.791
CSNQ0041 Filter 7	1.368
CSNQ0041 Filter 8	0.068
CSNQ0041 Filter 9	0.085
CSNQ0041 Filter 10	0.118
CSNQ0041 Filter 11	0.320
CSNQ0041 Filter 12	0.067
Average	0.447
CSNQ0042 Filter 1	1.369
CSNQ0042 Filter 2	0.149
CSNQ0042 Filter 3	0.059
CSNQ0042 Filter 4	-0.028
CSNQ0042 Filter 5	-0.006
CSNQ0042 Filter 6	0.356
CSNQ0042 Filter 7	0.092
CSNQ0042 Filter 8	-0.048
CSNQ0042 Filter 9	-0.140
CSNQ0042 Filter 10	-0.067
CSNQ0042 Filter 11	-0.012
CSNQ0042 Filter 12	0.147
Average	0.156
Max Result	3.296

4.3.2 Nylon Acceptance Testing

All filter lot samples provided to the test laboratory passed the average $\leq 1\mu\text{g}/\text{filter}$ testing criteria for each anion and cation. Results are provided in Table 4-7. Acceptance testing for filters CSNN0002 Filter 156 through CSNN0002 Filter 318 was performed in 2024.

Average results for a lot are what determines the acceptability of use, and all instances of the above criteria were met. For the individual instances where filters were above the permitted average levels, no actions were taken. If a lot was above the permissible level, nylon filters would be further examined and the manufacturer would be contacted or discussions would commence about additional filter cleaning processes to be conducted at RTI.

Table 4-7: Nylon Filter Acceptance Testing Results.

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	$\mu\text{g}/\text{filter}$	$\mu\text{g}/\text{filter}$	$\mu\text{g}/\text{filter}$	$\mu\text{g}/\text{filter}$	$\mu\text{g}/\text{filter}$	$\mu\text{g}/\text{filter}$
CSNN0002Filter156	0.13	0.20	0.00	0.07	0.04	0.00
CSNN0002Filter157	0.15	0.25	0.00	0.10	0.04	0.00
CSNN0002Filter158	0.07	0.17	0.00	0.07	0.04	0.00
CSNN0002Filter159	0.18	0.26	0.00	0.11	0.04	0.00
CSNN0002Filter160	0.10	0.17	0.00	0.07	0.04	0.06
CSNN0002Filter161	0.11	0.19	0.00	0.07	0.04	0.00
CSNN0002Filter162	0.16	0.28	0.00	0.11	0.04	0.00
CSNN0002Filter163	0.09	0.18	0.00	0.07	0.04	0.00
CSNN0002Filter164	0.11	0.18	0.00	0.06	0.04	0.00
CSNN0002Filter165	0.11	0.18	0.00	0.07	0.04	0.06
CSNN0002Filter166	0.11	0.18	0.26	0.15	0.04	0.00
CSNN0002Filter167	0.13	0.24	0.00	0.07	0.04	0.00
CSNN0002Filter168	0.11	0.27	0.00	0.10	0.04	0.00
CSNN0002Filter169	0.06	0.16	0.00	0.07	0.03	0.00
CSNN0002Filter170	0.09	0.22	0.00	0.09	0.04	0.00
CSNN0002Filter171	0.13	0.18	0.13	0.11	0.04	0.00
CSNN0002Filter172	0.11	0.18	0.19	0.10	0.04	0.06
CSNN0002Filter173	0.09	0.17	0.00	0.08	0.04	0.00
CSNN0002Filter174	0.09	0.33	0.00	0.13	0.04	0.06
CSNN0002Filter175	0.08	0.20	0.00	0.09	0.04	0.00
CSNN0002Filter176	0.08	0.29	0.00	0.09	0.04	0.00
CSNN0002Filter177	0.07	0.28	0.00	0.09	0.04	0.00
CSNN0002Filter178	0.12	0.16	0.00	0.09	0.04	0.00
CSNN0002Filter179	0.03	0.22	0.09	0.09	0.04	0.00
CSNN0002Filter180	0.05	0.16	0.00	0.07	0.04	0.06
CSNN0002Filter181	0.10	0.17	0.00	0.07	0.04	0.00
CSNN0002Filter182	0.10	0.27	0.00	0.08	0.04	0.00
CSNN0002Filter183	0.12	0.22	0.00	0.09	0.04	0.00

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter184	0.15	0.20	0.09	0.09	0.04	0.00
CSNN0002Filter185	0.08	0.29	0.00	0.09	0.03	0.00
CSNN0002Filter186	0.05	0.50	0.10	0.18	0.04	0.00
CSNN0002Filter187	0.10	0.33	0.00	0.10	0.04	0.00
CSNN0002Filter188	0.03	0.17	0.00	0.07	0.04	0.00
CSNN0002Filter189	0.11	0.20	0.00	0.08	0.04	0.00
CSNN0002Filter190	0.08	0.26	0.00	0.11	0.04	0.00
CSNN0002Filter191	0.10	0.19	0.00	0.07	0.04	0.00
CSNN0002Filter192	0.14	0.24	0.00	0.09	0.04	0.00
CSNN0002Filter193	0.10	0.37	0.00	0.14	0.04	0.00
CSNN0002Filter194	0.08	0.21	0.00	0.09	0.04	0.00
CSNN0002Filter195	0.11	0.21	0.00	0.08	0.04	0.00
CSNN0002Filter196	0.11	0.24	0.00	0.08	0.04	0.00
CSNN0002Filter197	0.05	0.26	0.00	0.08	0.04	0.00
CSNN0002Filter198	0.12	0.32	0.00	0.13	0.04	0.00
CSNN0002Filter199	0.08	0.18	0.00	0.06	0.04	0.00
CSNN0002Filter200	0.12	0.18	0.19	0.11	0.04	0.00
CSNN0002Filter201	0.11	0.17	0.24	0.15	0.04	0.00
CSNN0002Filter202	0.10	0.18	0.00	0.08	0.04	0.00
CSNN0002Filter203	0.09	0.30	0.00	0.11	0.04	0.06
CSNN0002Filter204	0.06	0.69	0.00	0.20	0.04	0.00
CSNN0002Filter205	0.10	0.29	0.00	0.07	0.04	0.06
CSNN0002Filter206	0.33	0.41	0.00	0.08	0.05	0.17
CSNN0002Filter207	0.21	0.00	0.00	0.11	0.05	0.00
CSNN0002Filter208	0.24	0.30	0.00	0.09	0.05	0.16
CSNN0002Filter209	0.25	0.34	0.00	0.12	0.06	0.20
CSNN0002Filter210	0.16	0.29	0.00	0.11	0.05	0.16
CSNN0002Filter211	0.19	0.00	0.00	0.10	0.05	0.00
CSNN0002Filter212	0.20	0.00	0.00	0.12	0.05	0.00
CSNN0002Filter213	0.17	0.00	0.00	0.11	0.05	0.16
CSNN0002Filter214	0.35	0.42	0.00	0.14	0.06	0.20
CSNN0002Filter215	0.22	0.31	0.00	0.13	0.06	0.18
CSNN0002Filter216	0.29	0.00	0.00	0.20	0.05	0.17
CSNN0002Filter217	0.19	0.00	0.00	0.14	0.06	0.00
CSNN0002Filter218	0.22	0.35	0.00	0.11	0.06	0.18
CSNN0002Filter219	0.25	0.30	0.00	0.13	0.05	0.00
CSNN0002Filter220	0.28	0.00	0.00	0.10	0.06	0.00
CSNN0002Filter221	0.18	0.25	0.00	0.11	0.05	0.18
CSNN0002Filter222	0.17	0.00	0.00	0.08	0.06	0.00

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter223	0.13	0.00	0.00	0.09	0.05	0.15
CSNN0002Filter224	0.14	0.00	0.00	0.10	0.06	0.00
CSNN0002Filter225	0.18	0.00	0.00	0.09	0.06	0.15
CSNN0002Filter226	0.24	0.00	0.00	0.11	0.06	0.00
CSNN0002Filter227	0.22	0.27	0.00	0.10	0.06	0.00
CSNN0002Filter228	0.25	0.00	0.00	0.10	0.05	0.00
CSNN0002Filter229	0.24	0.00	0.00	0.13	0.05	0.00
CSNN0002Filter230	0.43	0.33	0.00	0.15	0.05	0.00
CSNN0002Filter231	0.36	0.00	0.00	0.09	0.05	0.00
CSNN0002Filter232	0.22	0.28	0.00	0.10	0.05	0.00
CSNN0002Filter233	0.36	0.31	0.00	0.11	0.06	0.18
CSNN0002Filter234	0.32	0.33	0.00	0.11	0.07	0.21
CSNN0002Filter235	0.25	0.00	0.00	0.16	0.08	0.18
CSNN0002Filter236	0.27	0.00	0.00	0.12	0.11	0.18
CSNN0002Filter237	0.19	0.00	0.72	0.12	0.26	0.18
CSNN0002Filter238	0.32	0.57	0.00	0.20	0.17	0.27
CSNN0002Filter239	0.28	0.00	0.00	0.10	0.16	0.18
CSNN0002Filter240	0.27	0.00	0.31	0.11	0.16	0.17
CSNN0002Filter241	0.18	0.00	0.20	0.11	0.16	0.20
CSNN0002Filter242	0.19	0.00	0.00	0.12	0.17	0.19
CSNN0002Filter243	0.25	0.00	0.00	0.09	0.07	0.16
CSNN0002Filter244	0.22	0.00	0.00	0.10	0.11	0.16
CSNN0002Filter245	0.15	0.24	0.00	0.09	0.06	0.16
CSNN0002Filter246	0.20	0.38	0.00	0.08	0.06	0.16
CSNN0002Filter247	0.28	0.37	0.00	0.09	0.06	0.20
CSNN0002Filter248	0.18	0.00	0.00	0.16	0.10	0.34
CSNN0002Filter249	0.27	0.43	0.00	0.15	0.06	0.19
CSNN0002Filter250	0.41	0.53	0.00	0.32	0.08	0.89
CSNN0002Filter251	0.29	0.50	0.00	0.12	0.06	0.00
CSNN0002Filter252	0.29	0.00	0.00	0.09	0.06	0.17
CSNN0002Filter253	0.18	0.00	0.00	0.08	0.06	0.18
CSNN0002Filter254	0.30	0.37	0.00	0.15	0.06	0.19
CSNN0002Filter255	0.24	0.33	0.00	0.11	0.06	0.18
CSNN0002Filter256	0.28	0.20	0.00	0.10	0.04	0.00
CSNN0002Filter257	0.21	0.00	0.00	0.09	0.04	0.00
CSNN0002Filter258	0.19	0.00	0.00	0.08	0.04	0.06
CSNN0002Filter259	0.25	0.00	0.00	0.12	0.03	0.08
CSNN0002Filter260	0.27	0.00	0.00	0.10	0.03	0.00
CSNN0002Filter261	0.25	0.24	0.03	0.12	0.03	0.10

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter262	0.18	0.12	0.05	0.11	0.04	0.05
CSNN0002Filter263	0.15	0.15	0.00	0.11	0.11	0.07
CSNN0002Filter264	0.29	0.22	0.00	0.12	0.24	0.10
CSNN0002Filter265	0.26	0.00	0.00	0.10	0.48	0.08
CSNN0002Filter266	0.17	0.00	0.00	0.11	0.65	0.07
CSNN0002Filter267	0.25	0.00	0.00	0.12	2.10	0.10
CSNN0002Filter268	0.22	0.00	0.00	0.12	3.66	0.13
CSNN0002Filter269	0.20	0.12	0.00	0.09	3.65	0.11
CSNN0002Filter270	0.26	0.00	0.00	0.16	0.06	0.09
CSNN0002Filter271	0.29	0.00	0.79	0.16	0.19	0.11
CSNN0002Filter272	0.19	0.00	0.87	0.13	0.18	0.09
CSNN0002Filter273	0.21	0.00	0.00	0.11	0.04	0.07
CSNN0002Filter274	0.22	0.00	0.00	0.10	0.04	0.11
CSNN0002Filter275	0.16	0.00	0.00	0.10	0.06	0.06
CSNN0002Filter276	0.30	0.00	0.00	0.12	0.06	0.07
CSNN0002Filter277	0.27	0.00	0.00	0.11	0.03	0.06
CSNN0002Filter278	0.25	0.16	0.02	0.11	0.03	0.09
CSNN0002Filter279	0.26	0.18	0.03	0.08	0.03	0.00
CSNN0002Filter280	0.34	0.21	0.00	0.10	0.03	0.07
CSNN0002Filter281	0.41	0.00	0.00	0.24	0.04	0.13
CSNN0002Filter282	0.16	0.00	0.00	0.11	0.03	0.05
CSNN0002Filter283	0.20	0.00	0.00	0.14	0.03	0.08
CSNN0002Filter284	0.21	0.25	0.00	0.10	0.03	0.07
CSNN0002Filter285	0.16	0.00	0.00	0.10	0.03	0.05
CSNN0002Filter286	0.18	0.22	0.00	0.09	0.03	0.07
CSNN0002Filter287	0.19	0.20	0.00	0.12	0.03	0.09
CSNN0002Filter288	0.15	0.24	0.00	0.11	0.03	0.11
CSNN0002Filter289	0.24	0.00	0.00	0.09	0.05	0.15
CSNN0002Filter290	0.19	0.00	0.00	0.10	0.04	0.05
CSNN0002Filter291	0.24	0.32	0.00	0.09	0.05	0.10
CSNN0002Filter292	0.18	0.00	0.00	0.08	0.03	0.07
CSNN0002Filter293	0.32	0.12	0.00	0.15	0.04	0.07
CSNN0002Filter294	0.22	0.00	0.00	0.11	0.04	0.06
CSNN0002Filter295	0.31	0.19	0.00	0.11	0.05	0.06
CSNN0002Filter296	0.20	0.00	0.00	0.15	0.08	0.05
CSNN0002Filter297	0.17	0.15	0.00	0.07	0.03	0.00
CSNN0002Filter298	0.18	0.00	0.00	0.08	0.12	0.00
CSNN0002Filter299	0.17	0.00	0.00	0.08	0.23	0.06
CSNN0002Filter300	0.00	0.00	0.00	0.00	0.03	0.08

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter301	0.06	0.00	0.00	0.00	0.00	0.00
CSNN0002Filter302	0.07	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter303	0.05	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter304	0.09	0.09	0.00	0.00	0.00	0.00
CSNN0002Filter305	0.07	0.00	0.00	0.00	0.00	0.00
CSNN0002Filter306	0.06	0.09	0.00	0.00	0.04	0.08
CSNN0002Filter307	0.08	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter308	0.03	0.06	0.00	0.00	0.04	0.08
CSNN0002Filter309	0.06	0.18	0.00	0.00	0.04	0.00
CSNN0002Filter310	0.05	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter311	0.00	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter312	0.05	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter313	0.06	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter314	0.04	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter315	0.05	0.00	0.00	0.00	0.04	0.08
CSNN0002Filter316	0.04	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter317	0.06	0.11	0.00	0.00	0.04	0.00
CSNN0002Filter318	0.05	0.22	0.00	0.04	0.04	0.09
CSNN0002Filter319	0.04	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter320	0.12	0.00	0.00	0.09	0.04	0.08
CSNN0002Filter321	0.05	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter322	0.04	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter323	0.06	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter324	0.06	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter325	0.00	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter326	0.05	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter327	0.76	0.72	0.00	0.36	0.04	0.62
CSNN0002Filter328	0.04	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter329	0.03	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter330	2.80	0.76	10.84	7.40	0.00	0.63
CSNN0002Filter331	0.07	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter332	0.04	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter333	0.05	0.12	0.00	0.00	0.03	0.00
CSNN0002Filter334	0.04	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter335	0.06	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter336	0.00	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter337	0.06	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter338	0.03	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter339	0.07	0.00	0.00	0.00	0.03	0.00

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter340	0.07	0.00	0.00	0.00	0.00	0.00
CSNN0002Filter341	0.00	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter342	0.07	0.00	0.00	0.00	0.04	0.00
CSNN0002Filter343	0.03	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter344	0.05	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter345	0.10	0.11	0.00	0.03	0.03	0.08
CSNN0002Filter346	0.08	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter347	0.04	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter348	0.26	0.51	2.40	0.20	0.66	0.14
CSNN0002Filter349	0.06	0.00	0.00	0.02	0.03	0.00
CSNN0002Filter350	0.09	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter351	0.11	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter352	0.10	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter353	0.09	0.33	0.00	0.00	0.03	0.08
CSNN0002Filter354	0.11	0.33	0.00	0.01	0.03	0.08
CSNN0002Filter355	0.11	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter356	0.10	0.24	0.00	0.00	0.03	0.09
CSNN0002Filter357	0.12	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter358	0.05	0.15	0.00	0.00	0.03	0.08
CSNN0002Filter359	0.11	0.14	0.00	0.00	0.03	0.09
CSNN0002Filter360	0.09	0.16	0.00	0.00	0.03	0.08
CSNN0002Filter361	0.10	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter362	0.07	0.35	0.11	0.04	0.03	0.09
CSNN0002Filter363	0.05	0.04	0.00	0.00	0.03	0.08
CSNN0002Filter364	0.07	0.40	0.00	0.00	0.03	0.09
CSNN0002Filter365	0.06	0.12	0.04	0.00	0.03	0.00
CSNN0002Filter366	0.07	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter367	0.13	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter368	0.16	0.15	0.33	0.14	0.03	0.08
CSNN0002Filter369	0.12	0.00	0.00	0.01	0.03	0.08
CSNN0002Filter370	0.08	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter371	0.06	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter372	0.13	0.11	0.00	0.07	0.03	0.09
CSNN0002Filter373	0.08	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter374	0.19	0.07	0.00	0.06	0.03	0.08
CSNN0002Filter375	0.08	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter376	0.18	0.00	0.00	0.03	0.03	0.08
CSNN0002Filter377	0.12	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter378	0.12	0.17	0.00	0.00	0.03	0.08

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter379	0.06	0.15	0.00	0.00	0.03	0.08
CSNN0002Filter380	0.06	0.07	0.00	0.00	0.03	0.08
CSNN0002Filter381	0.08	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter382	0.09	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter383	0.06	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter384	0.04	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter385	0.12	0.12	0.00	0.02	0.03	0.00
CSNN0002Filter386	0.07	0.00	0.00	0.01	0.03	0.08
CSNN0002Filter387	0.08	0.00	0.00	0.00	0.00	0.08
CSNN0002Filter388	0.10	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter389	0.13	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter390	0.07	0.00	0.00	0.00	0.03	0.08
CSNN0002Filter391	0.07	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter392	0.14	0.00	0.00	0.04	0.03	0.08
CSNN0002Filter393	0.07	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter394	0.12	0.13	0.00	0.01	0.00	0.08
CSNN0002Filter395	0.03	0.00	0.00	0.00	0.00	0.00
CSNN0002Filter396	0.09	0.00	0.00	0.00	0.00	0.08
CSNN0002Filter397	0.07	0.10	0.00	0.00	0.00	0.00
CSNN0002Filter398	0.13	0.08	0.00	0.00	0.00	0.00
CSNN0002Filter399	0.05	0.00	0.00	0.00	0.03	0.00
CSNN0002Filter400	0.04	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter401	0.06	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter402	0.05	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter403	0.02	0.00	0.00	0.12	0.11	0.13
CSNN0002Filter404	0.03	0.00	0.00	0.12	0.11	0.13
CSNN0002Filter405	0.03	0.00	0.00	0.12	0.12	0.13
CSNN0002Filter406	0.02	0.00	0.00	0.12	0.12	0.13
CSNN0002Filter407	0.00	0.00	0.00	0.12	0.12	0.13
CSNN0002Filter408	0.03	0.00	0.00	0.12	0.11	0.13
CSNN0002Filter409	0.01	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter410	0.02	0.00	0.00	0.15	0.12	0.12
CSNN0002Filter411	0.01	0.00	0.00	0.11	0.12	0.12
CSNN0002Filter412	0.02	0.00	0.00	0.12	0.11	0.13
CSNN0002Filter413	0.03	0.00	0.00	0.11	0.11	0.12
CSNN0002Filter414	0.02	0.00	0.00	0.11	0.11	0.12
CSNN0002Filter415	0.05	0.00	0.00	0.11	0.13	0.13
CSNN0002Filter416	0.00	0.00	0.00	0.11	0.13	0.13
CSNN0002Filter417	0.00	0.00	0.00	0.12	0.11	0.13

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
CSNN0002Filter418	0.01	0.32	0.00	0.13	0.12	0.15
CSNN0002Filter419	0.00	0.00	0.00	0.11	0.13	0.12
CSNN0002Filter420	0.09	0.00	0.00	0.22	0.08	0.13
CSNN0002Filter421	0.08	0.00	0.00	0.11	0.13	0.12
CSNN0002Filter422	0.05	0.00	0.00	0.11	0.13	0.12
CSNN0002Filter423	0.00	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter424	0.06	0.00	0.00	0.11	0.13	0.13
CSNN0002Filter425	0.01	0.00	0.00	0.11	0.14	0.12
CSNN0002Filter426	0.01	0.00	0.00	0.11	0.14	0.13
CSNN0002Filter427	0.76	0.79	0.00	0.42	0.13	0.87
CSNN0002Filter428	0.02	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter429	0.04	0.00	0.00	0.11	0.14	0.12
CSNN0002Filter430	2.88	0.00	10.94	7.54	0.00	0.75
CSNN0002Filter431	0.03	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter432	0.00	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter433	0.04	0.00	0.00	0.12	0.11	0.13
CSNN0002Filter434	0.03	0.00	0.00	0.13	0.12	0.13
CSNN0002Filter435	0.03	0.00	0.00	0.11	0.12	0.13
CSNN0002Filter436	0.04	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter437	0.03	0.00	0.00	0.11	0.11	0.12
CSNN0002Filter438	0.02	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter439	0.08	0.00	0.00	0.13	0.11	0.14
CSNN0002Filter440	0.02	0.00	0.00	0.11	0.11	0.12
CSNN0002Filter441	0.00	0.00	0.00	0.11	0.11	0.12
CSNN0002Filter442	0.04	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter443	0.08	0.00	0.00	0.12	0.11	0.00
CSNN0002Filter444	0.01	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter445	0.00	0.00	0.00	0.12	0.11	0.13
CSNN0002Filter446	0.09	0.00	0.00	0.12	0.11	0.14
CSNN0002Filter447	0.02	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter448	0.17	0.57	2.40	0.25	0.80	0.30
CSNN0002Filter449	0.03	0.00	0.00	0.11	0.12	0.12
CSNN0002Filter450	0.01	0.00	0.00	0.11	0.11	0.13
CSNN0002Filter451	0.03	0.00	0.00	0.11	0.11	0.14
CSNN0002Filter452	0.04	0.00	0.00	0.11	0.11	0.12
CSNN0002Filter453	0.27	0.35	0.00	0.18	0.11	0.25
CSNN0002Filter454	0.05	0.34	0.00	0.13	0.11	0.19
CSNN0002Filter455	0.05	0.00	0.00	0.11	0.11	0.13

	chloride	nitrate	sulfate	sodium	ammonium	potassium
	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter	µg/filter
Average	0.15	0.11	0.10	0.13	0.10	0.08
Max Result	2.88	0.79	10.94	7.54	3.66	0.89

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, none of the 480 filters targeted for visual inspection were found to have quality issues. Throughout the sample loading process approximately 50 filters were observed to have minor disqualifying defects or were mistakenly contaminated prior to sample collection and were discarded prior to being used in the network.

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.

For completeness, the AR null code is used when an invalid event is 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, or filters were improperly loaded - including when the modules were not completely tightened as detailed in section 4.2.1.

In 2024, Table 4-3 notes the AR code was used 3 times for PTFE samples, 13 times for nylon samples, and 21 times for Quartz samples. There were 72 additional AR codes applied to nylon field blanks due to the denuder contamination investigation noted in section 3.1.5.

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

Note that 2024 was the final year of CSN cold shipping to and from the sites. As of 2025, there is no longer a 4 °C requirement and ice packs are no longer provided for site shipments. The TT flag would only be applied in two situations: (1) shipment between laboratories, which still uses ice packs and has a 4 °C requirement, and (2) storage temperatures above 4 °C.

Table 5-1: TT flags applied to filters sampled in 2024 (field blanks excluded).

Batch	PTFE	Nylon	Quartz	Total
2024-01	31	31	31	93
2024-02	27	27	27	81
2024-03	66	66	66	198

Batch	PTFE	Nylon	Quartz	Total
2024-04	77	77	77	231
2024-05	1,039	82	1,040	2,161
2024-06	129	128	1,035	1,292
2024-07	155	155	155	465
2024-08	116	116	116	348
2024-09	230	230	229	689
2024-10	173	173	173	519
2024-11	114	114	114	342
2024-12	180	180	180	540

5.2 Leak Testing

During the 2024 calendar year, all SASS modules for collection on PTFE and nylon filters, and all cassettes used for collection on quartz filters were tested using an in-house leak test device. Guidance from the manufacturer detailing permissible vacuum pressure loss was used to determine pass/fail criteria. Over the course of the year, it was measured that six URG cassettes and three SASS modules experienced a leak test failure. All failing cassettes and modules were refurbished by replacement of O-rings and all passed leak tests after their initial failures.

5.3 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 SOPs.

5.3.1 Summary of QC Requirements

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	$< \pm 15 \mu\text{g}$ 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	$< \pm 15 \mu\text{g}$ difference	2.12 Sec. 10.5	Laboratory contamination
Calibration / Verification				
Balance Calibration	1/year	Manufacturers spec. $< \pm 2^\circ \text{C}$	2.12 Sec. 9.3 2.12, Sec. 4.3.8	Verification of equipment operation Verification of equipment operation
Temp. Calibration	1/year	$< \pm 2\%$	2.12, Sec. 4.3.8	Verification of equipment operation
RH Calibration	1/year			
Accuracy				
Balance Audit	1/year	$< \pm 0.003 \text{ mg}$ or manufacturers specs, whichever is tighter	2.12 Sec. 11.2.7 2.12 Sec. 10.6	Laboratory technician operation Balance accuracy/stability
Balance Check (50, 100, 300, and 500 mg) working standards	beginning, every 10 th sample, end	$< \pm 3 \mu\text{g}$ from certified value		
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 10 th 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 from sample end date if receipt temperature ≤4 °C; ≤30 days if receipt temperature >4 °C and ambient collection temperature ≤ receipt temperature (TT flag applied); or ≤10 days from sample end date 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 2024
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	< 2.1°C Standard Deviation (SD) over 24 hr.	Requirement met for all filters.
Humidity Range	All Filters	24-hr mean 30% - 40% Relative Humidity (RH) or within ±5% sampling RH but ≥ 20%RH	Requirement met for all filters.
Humidity Control	All Filters	< 5.1% SD over 24 hr.	Requirement met for all filters.
Pre/post Sampling RH	All Filters	difference in 24-hr means < ± 5.1% RH	Requirement met for all filters.
Balance	All Filters	located in filter conditioning environment	Requirement met for all filters.

5.3.2 Summary of QC Checks

Following the quality requirements listed in Table 5-3, a working standard (bracketing the mass of the filter) is weighed with each weighing session at the start, end, and after every ten masses are recorded. Four sets of standard masses were utilized during the 2024 CSN project year, one set of 300 mg and 500 mg weighing sets (#1) were used between January 1, 2024 through September 1, 2024, a second 300 mg and 500 mg weighing set (#2) was used from September 2, 2024 through December 6, 2024, an additional 300 mg and 500 mg set (#3) were used from December 7, 2024 through December 31, 2024; one additional 300 mg and 500 mg set (#4) was used for the period requiring manual weighing. Trend charts over time for each can be found in Figures 5-1 through 5-8. Dotted lines represent the QC bounds.

Figure 5-1: 300 mg standard mass #1 (with certified mass being 300.000 mg).

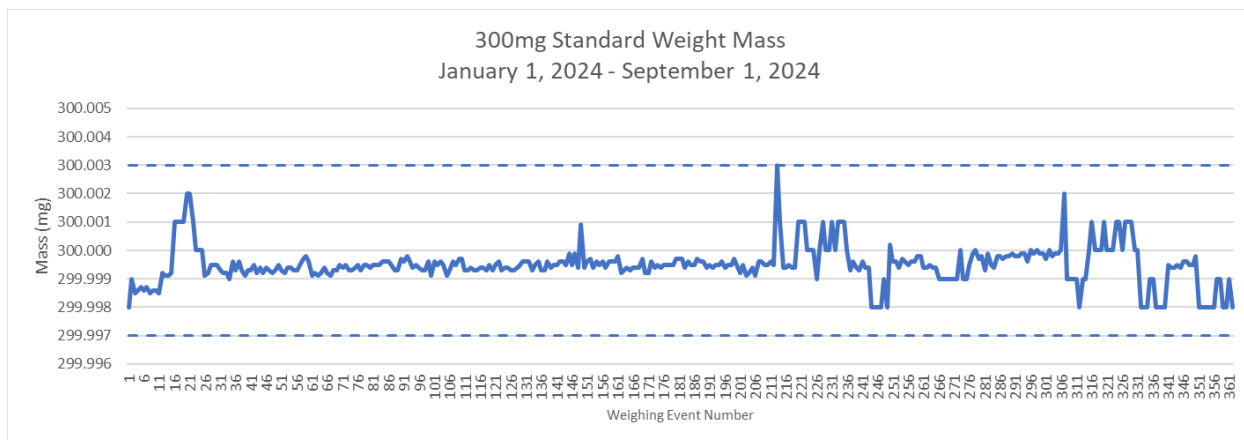


Figure 5-2: 500 mg standard mass #1 (with certified mass being 499.995 mg).

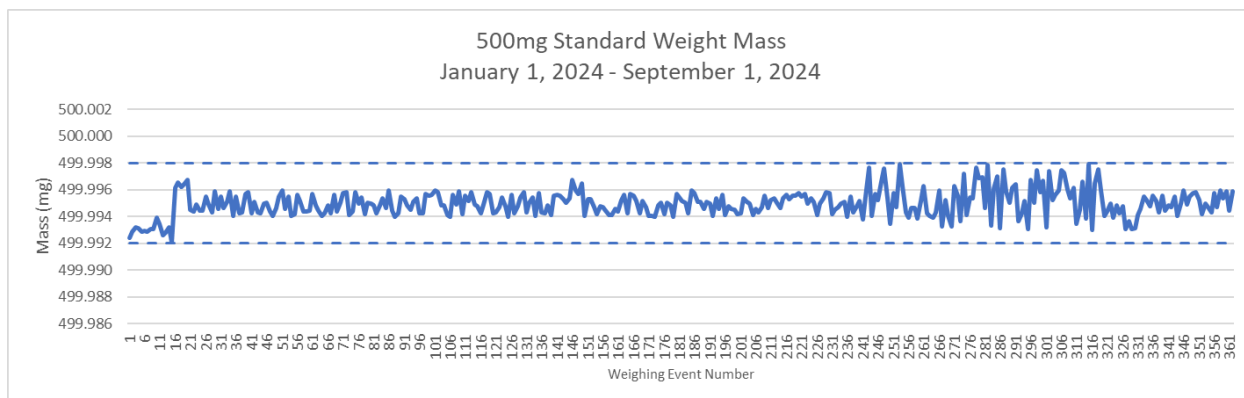


Figure 5-3: 300 mg standard mass #2 (with certified mass being 299.993 mg).

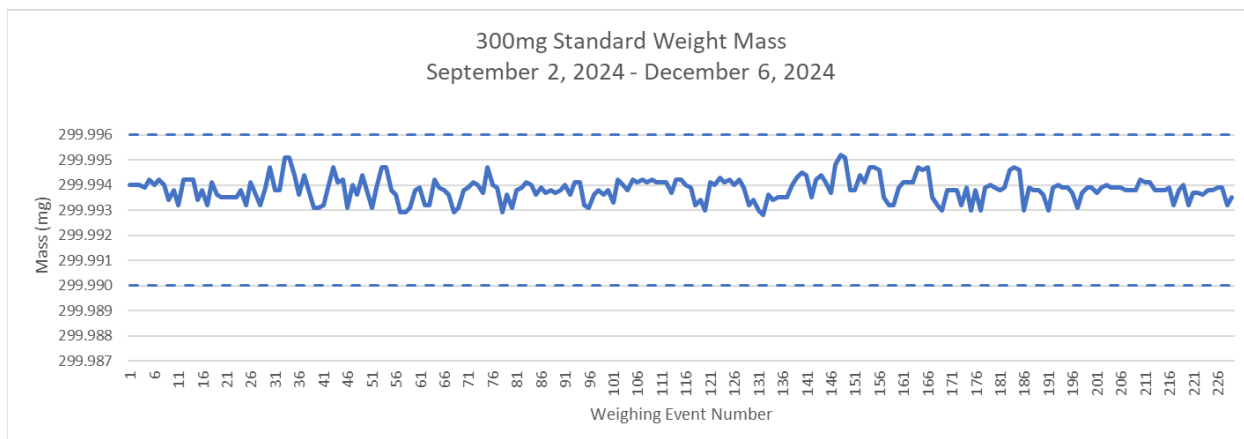


Figure 5-4: 500 mg standard mass #2 (with certified mass being 499.998 mg).

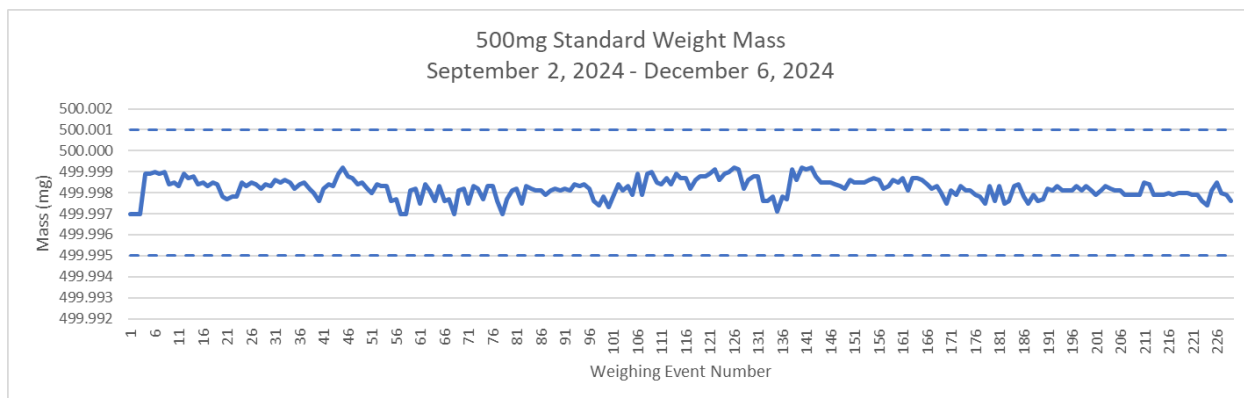


Figure 5-5: 300 mg standard mass #3 (with certified mass being 300.008 mg).

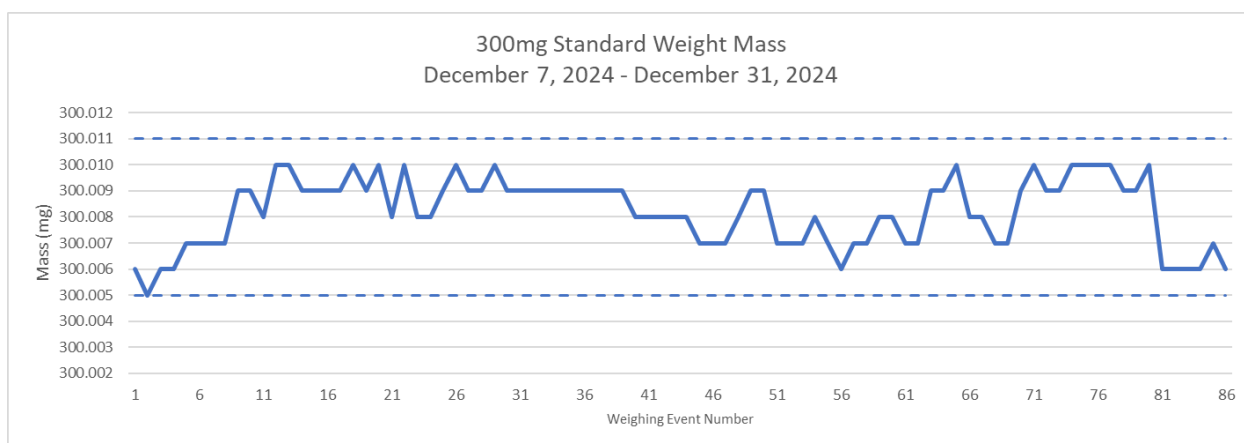


Figure 5-6: 500 mg standard mass #3 (with certified mass being 500.005 mg).

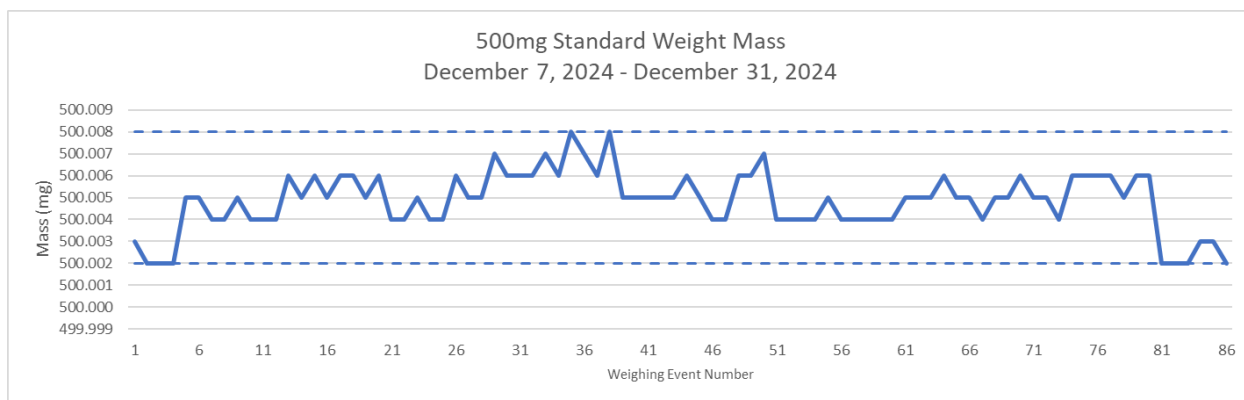


Figure 5-7: 300 mg standard manual weighing mass #4 (with certified mass being 300.000 mg).

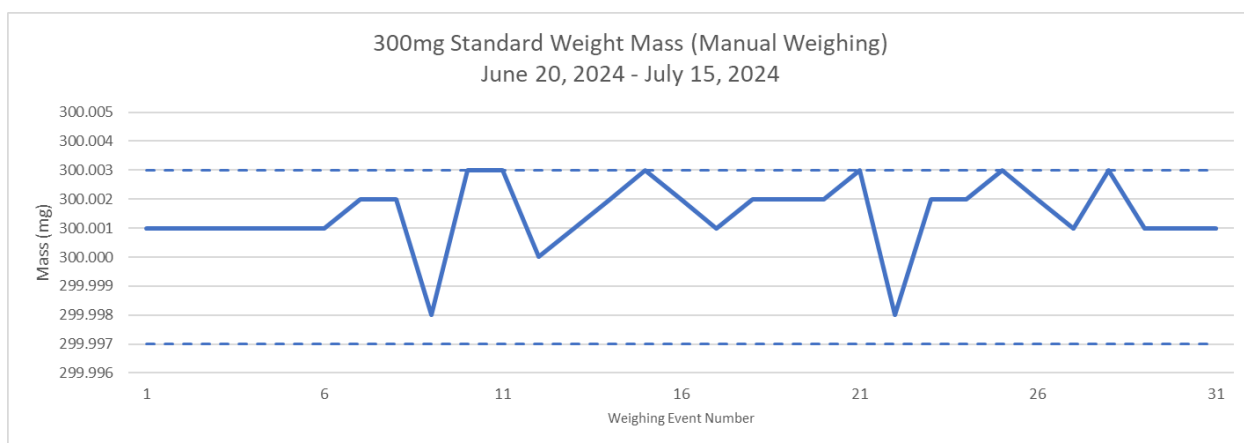
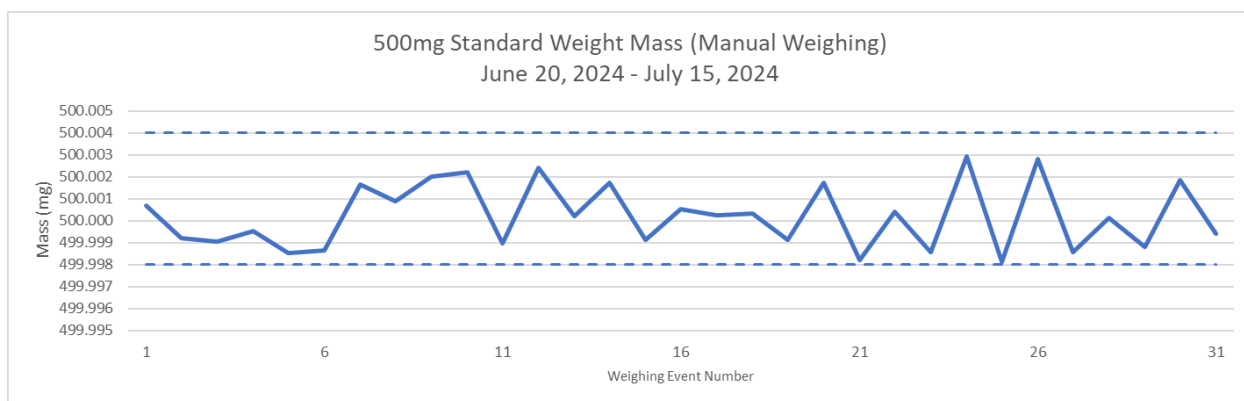


Figure 5-8: 500 mg standard manual weighing mass #4 (with certified mass being 500.001 mg).

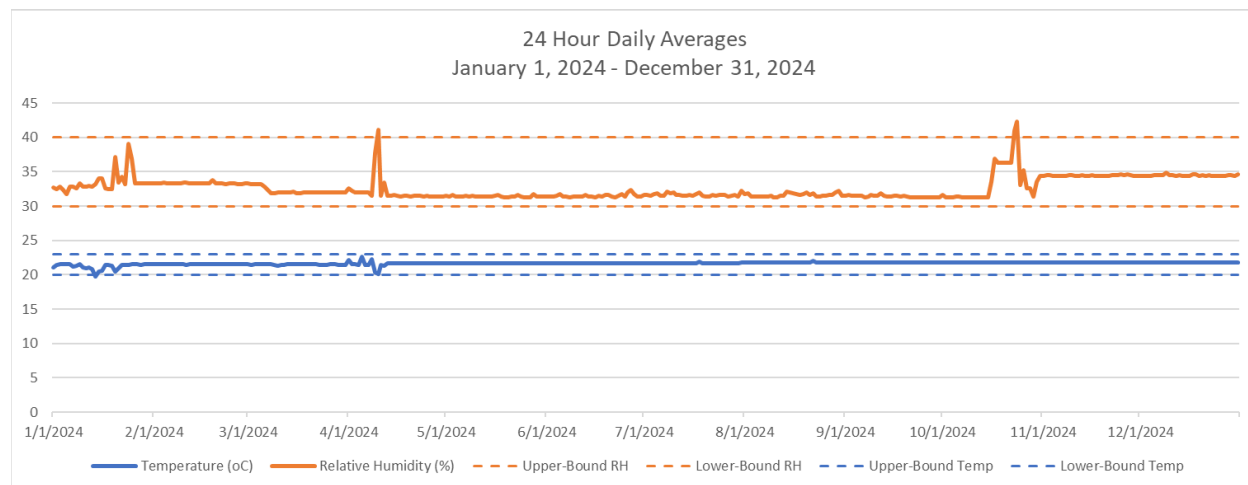


5.3.3 Summary of Environmental Chamber Parameters

Following the quality requirements listed in Table 5-3 — 24-hr averages for relative humidity and temperature, collected at 5-minute intervals — are provided in Figure 5-9. 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 5-9: 24-hr daily average of environmental chamber conditions.



5.3.4 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 4.1.2.3 and Section 7.5, respectively.

5.3.5 Audits, Performance Evaluations, Training, and Accreditations

5.3.5.1 System Audits

The prime contractor (UC Davis) did not conduct any audit of the RTI Gravimetric Laboratory during this reporting period. As discussed in 4.2.8, EPA worked with Battelle to perform an audit of RTI for CSN on March 11th and 12th of 2025.

5.3.5.2 Performance Evaluations

UC Davis and RTI participated in the 2024 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/2025-01/2024_megape_report_final_508.pdf.

5.3.5.3 Training

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

5.3.5.4 Accreditations

The RTI gravimetry lab is accredited by the State of Louisiana Department of Environmental Quality, LELAP/NELAP; LAB ID # 04017.

5.3.6 Summary of Filter Blanks

Over the sampling period (January 1, 2024 through December 31, 2024) there were 210 valid PTFE gravimetric filter field blanks that were weighed. Field Blank gravimetric values are reviewed as part of regular validation by UC Davis. Field Blank values are used to calculate MDL for gravimetric concentrations.

In the table below, note that sample handling transferred from WSP to RTI during the June 2023 sample collection.

Table 5-4: PTFE PM_{2.5} gravimetric filter field blank statistics in µg/filter (samples collected 1/1/2024 through 12/31/2024).

PM _{2.5} Parameter	2020	2021	2022	2023	2024
Count	202	306	297	261	210
Median (µg/filter)	5	7	6	10	14.5
Average (µg/filter)	8.0	7.7	10.2	12.3	18.9
Min (µg/filter)	0	-12	-3	-2	-2
Max (µg/filter)	154	116	197	94	176
StdDev (µg/filter)	13.8	8.5	18.9	11.3	17.8

5.4 RTI Ion Chromatography Laboratory

The RTI Ion Chromatography Laboratory, as a subcontractor to UC Davis, received and analyzed extracts from nylon filters for batches January 2024 through December 2024, covering the sampling period January 1, 2024 through December 31, 2024. Routine analysis of these samples was performed March 07, 2024 through March 06, 2025. Both routine analysis and reanalysis were performed March 07, 2024 through April 19, 2025. Using ion chromatography, RTI analyzed for both anions (chloride [Cl⁻], nitrate [NO₃⁻], and sulfate [SO₄²⁻]) and cations (sodium [Na⁺], ammonium [NH₄⁺], and potassium [K⁺]) using five Thermo Dionex ICS systems and four Thermo Dionex Aquion systems (six anion systems: A11, A12, A13, A17, A10, and A8; three cation systems: C11, C9, and C10) and reported the results of those analyses to UC Davis. Table 5-5 details the analysis dates for each batch of data, including both routine analysis and reanalysis.

Table 5-5: 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 (2024)	Analysis Batch #	IC Analysis Dates
January	January	3-7-2024 – 5-10-2024
February	February	4-10-2024 – 6-13-2024
March	March	5-9-2024 – 7-15-2024

Sampling Month (2024)	Analysis Batch #	IC Analysis Dates
April	April	6-12-2024 – 8-05-2024
May	May	7-9-2024 – 9-16-2024
June	June	8-5-2024 – 10-14-2024
July	July	9-06-2024 – 11-15-2024
August	August	10-04-2024- 12-18-2024
September	September	11-06-2024 – 1-21-2025
October	October	12-10-2024 – 2-13-2025
November	November	01-15-2025 – 3-24-2025
December	December	02-12-2025 – 4-19-2025

5.4.1 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, ICS-6000 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 5-6. 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 5-6: 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 Percent Difference (RPD) < 10% at 10x MDL or higher RPD < 200% at MDL and up to 10x MDL	Investigate; reanalyze
Spiked sample extract	2 per set of 50 samples	Recoveries within 90 to 110% of target values	Investigate; reanalyze
Reagent blanks	One reagent blank per reagent used (DI H ₂ O and/or eluent); at least one per day	No limit set; the data is compiled for comparability studies; < 10 times MDL	Investigate; reanalyze
Round Robin (External QA by USGS)	4 per month	Not applicable; data reported and compared annually	Investigate

Activity	Frequency	Acceptance Criteria	Corrective Action
Reanalysis	5% of all samples, reanalyzed on a different day and as requested	MDL to 10 times MDL: RPD up to 200%, 10 to 100 times MDL: RPD < 20%, >100 times MDL: RPD < 10%	Investigate and reanalyze samples if needed

5.4.2 Summary of QC Results

RTI followed the acceptance criteria stated in Table 5-6. 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.

5.4.2.1 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.

5.4.2.2 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 5-7 and 5-8 lists the concentrations.

Table 5-7: Target concentrations of anion CCV check standards for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024).

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

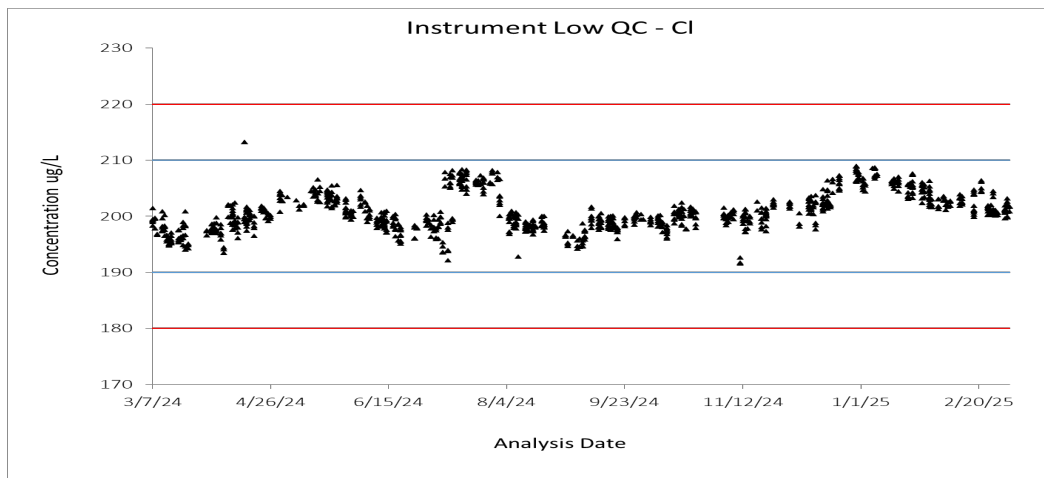
Table 5-8: Target concentrations of cation CCV check standards for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024).

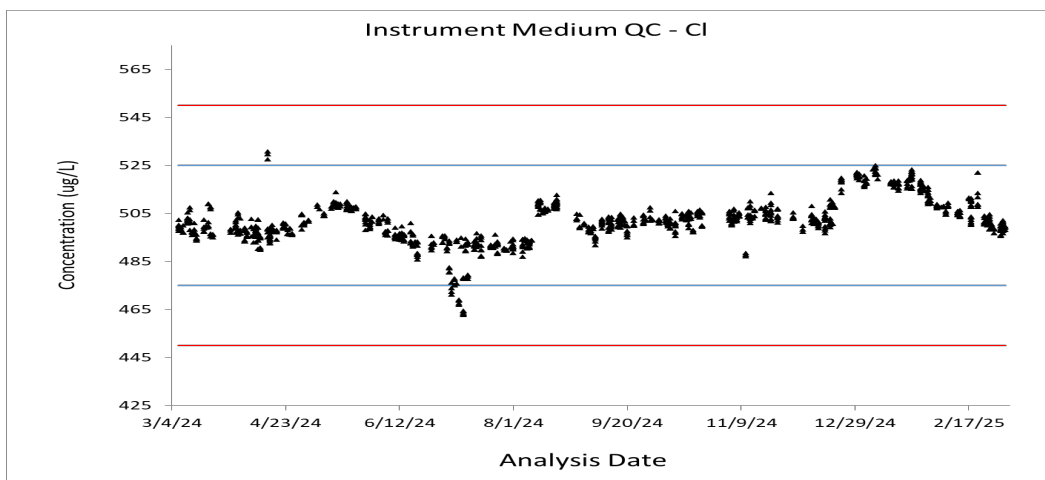
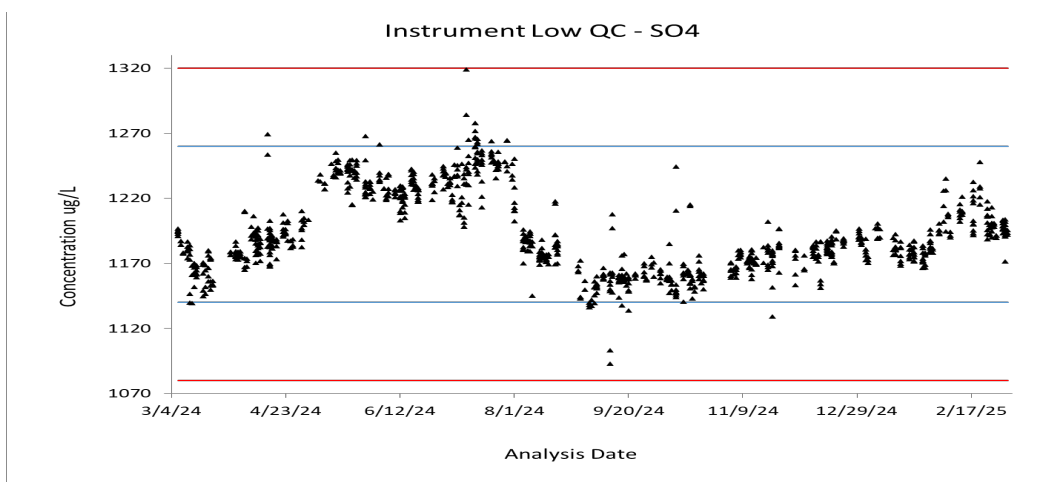
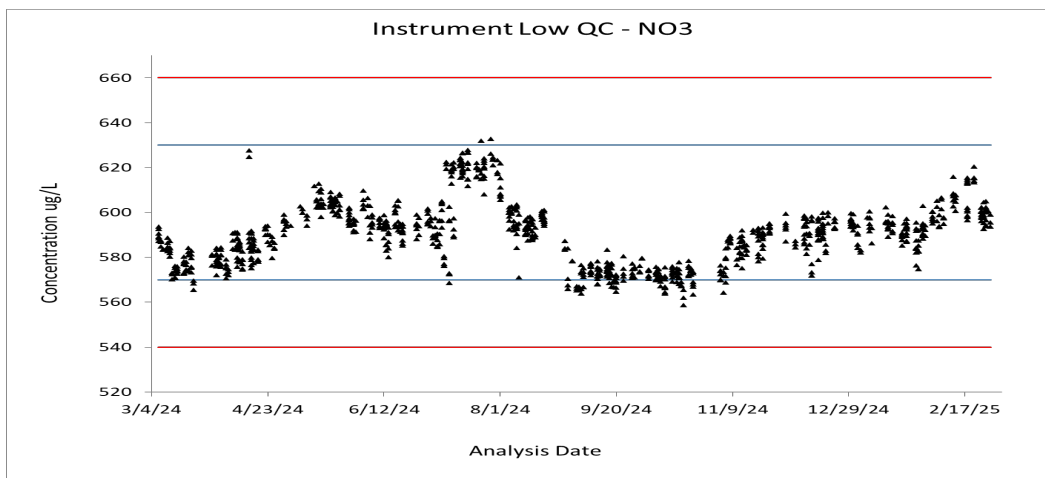
QC Sample	Na ⁺ (ppb)	NH ₄ ⁺ (ppb)	K ⁺ (ppb)
Instrument Low QC	20	20	20
Instrument Medium QC	250	250	250
Instrument Medium-High QC	750	750	750
Instrument High QC	2000	2000	2000

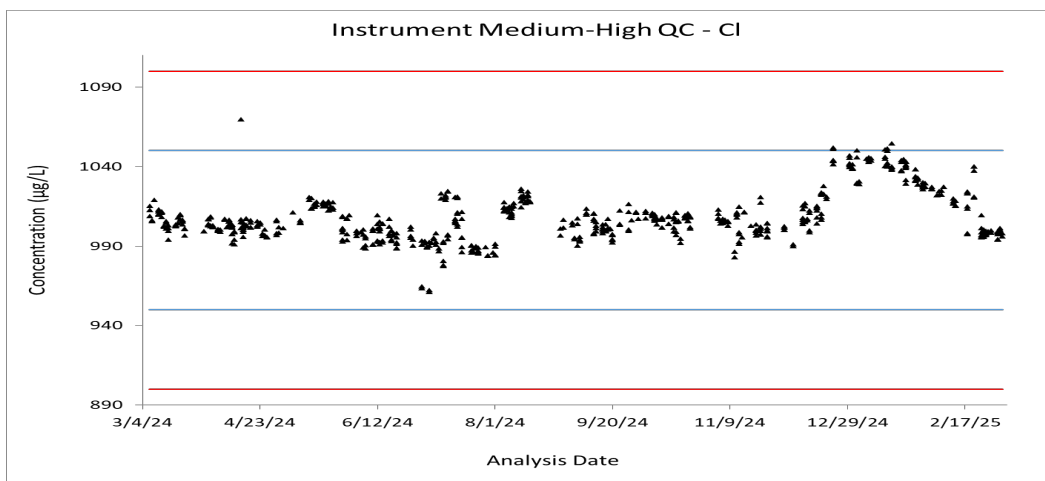
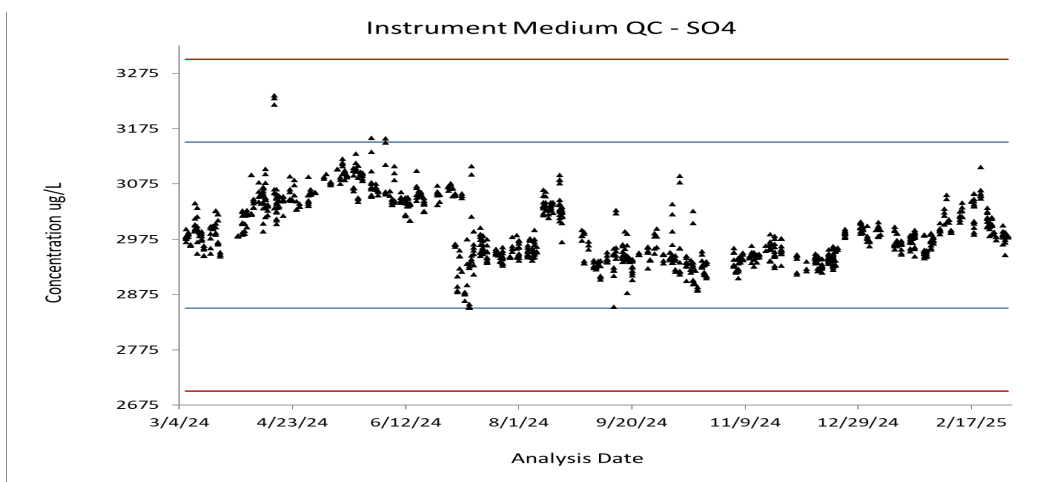
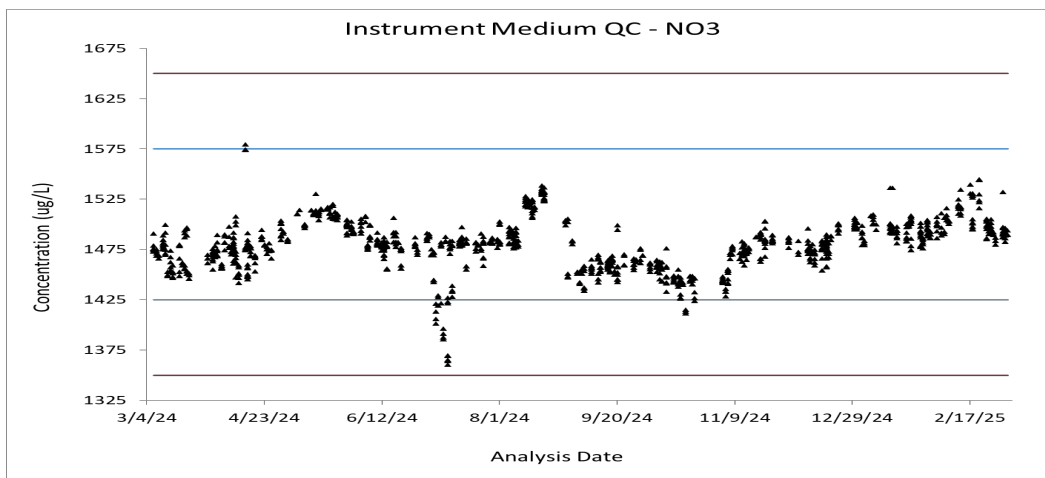
At least two CCV check standards are analyzed immediately after the calibration standards and a single CCV check standard is analyzed after every ten samples. When an instrument CCV check standard fails the acceptance criteria by falling outside of the control limits, impacted samples are reanalyzed. 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 5-10) and cation (Figure 5-11) 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.

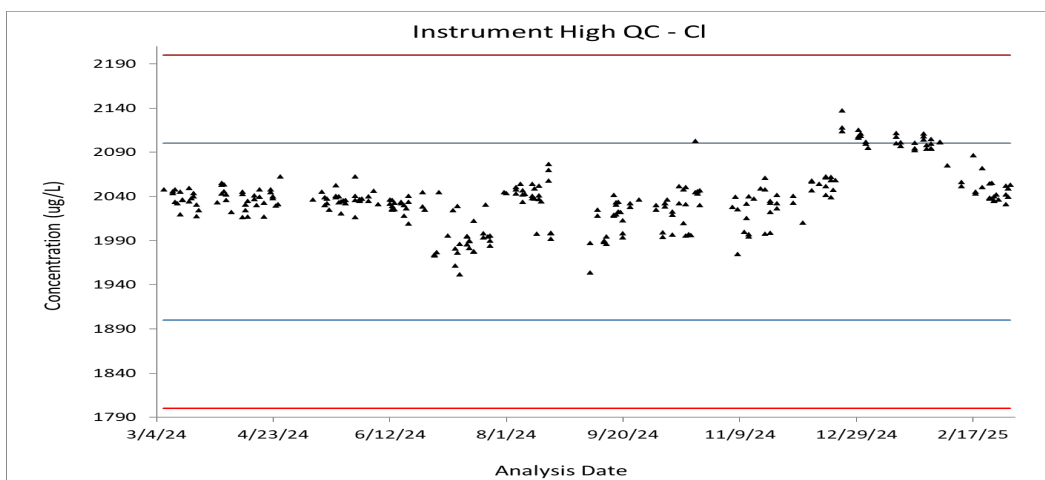
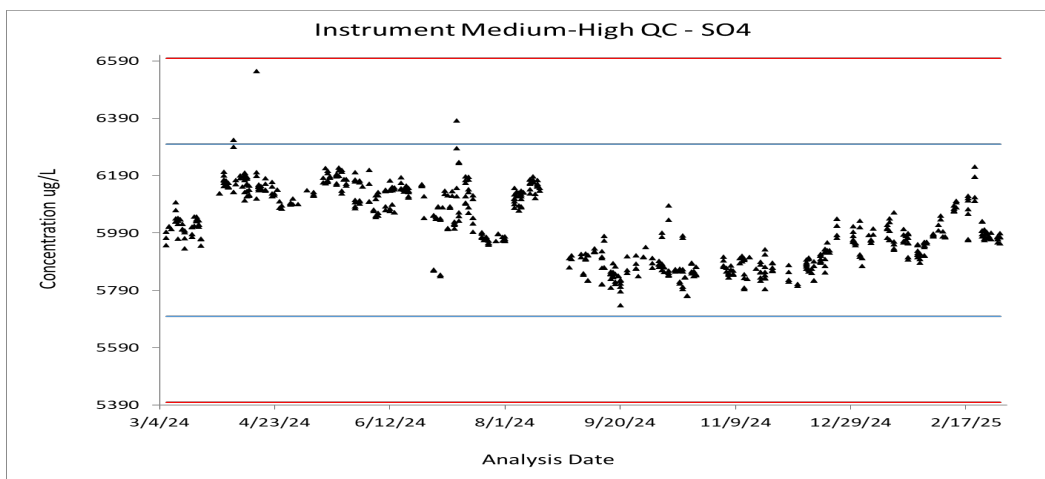
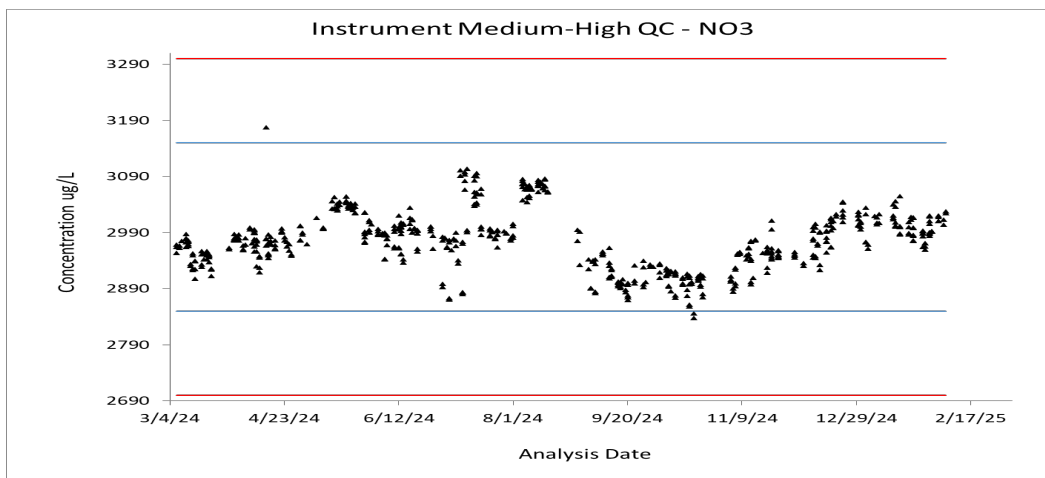
In the control chart below, red lines show upper and lower control limits set at $\pm 10\%$ of the nominal concentrations for the low, medium, medium-high, and high standards. Blue lines show upper and lower warning limits.

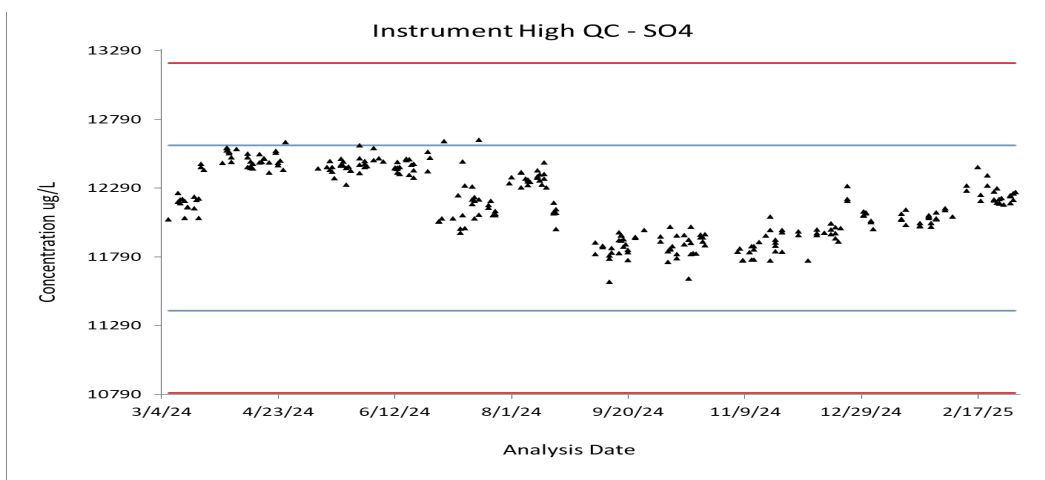
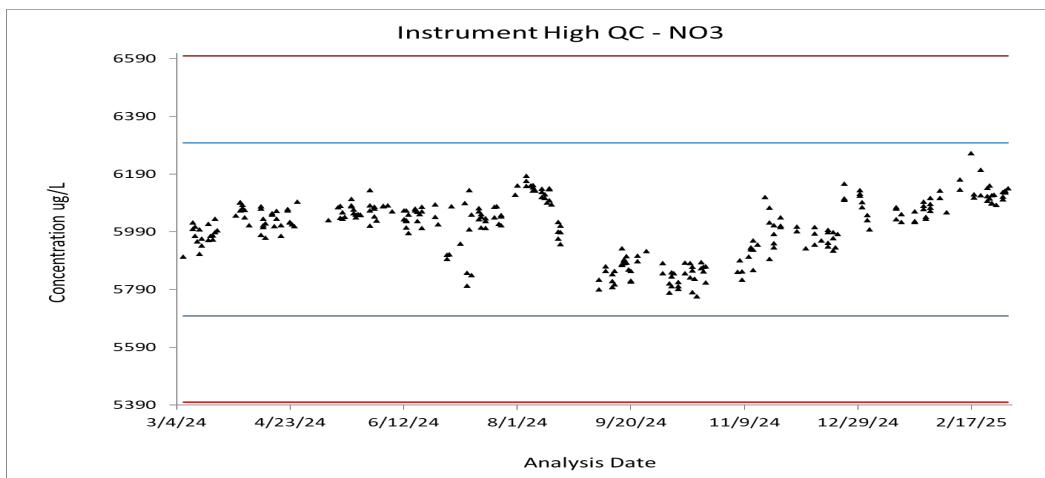
Figure 5-10: Control charts for anion CCV check standards at low, medium, medium-high, and high concentrations measured in units of $\mu\text{g/L}$ (see Table 5-6) for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024).





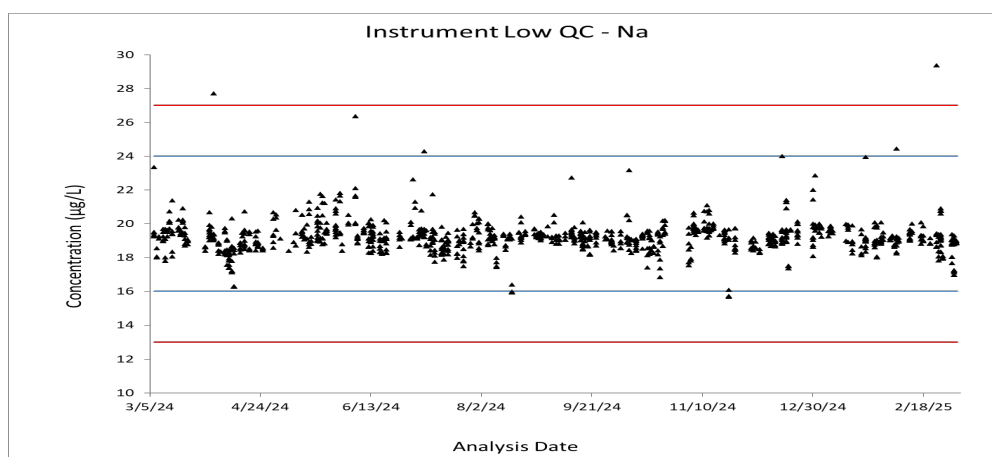


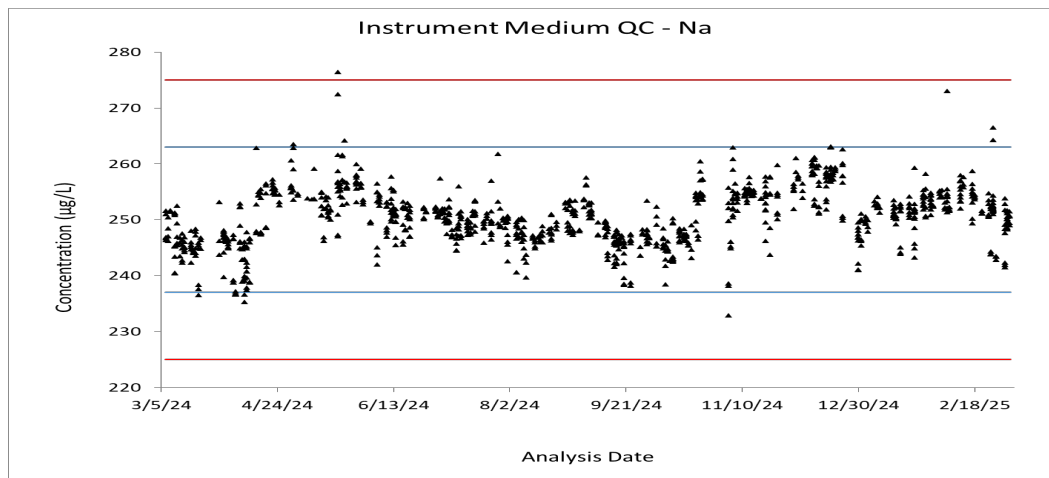
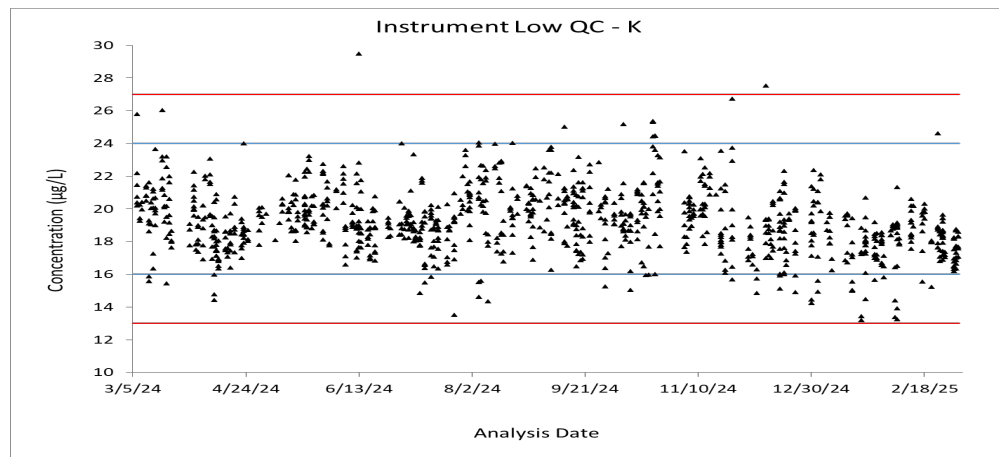
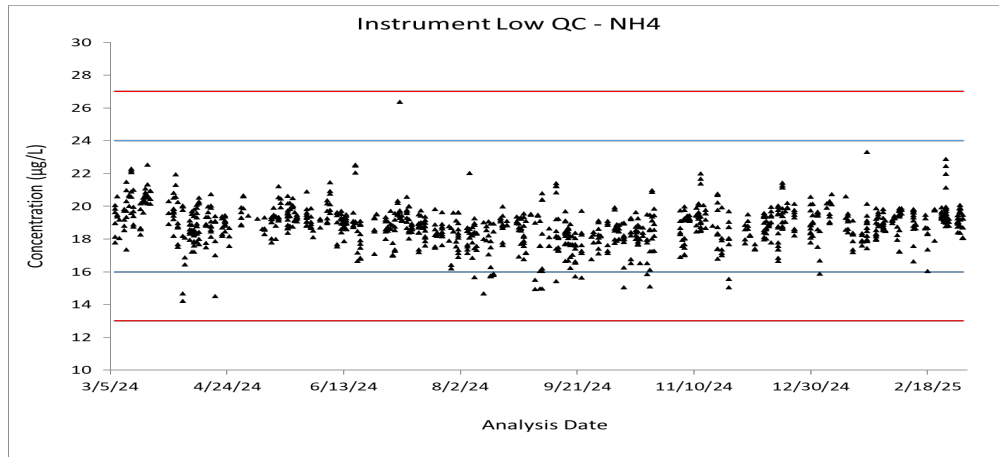


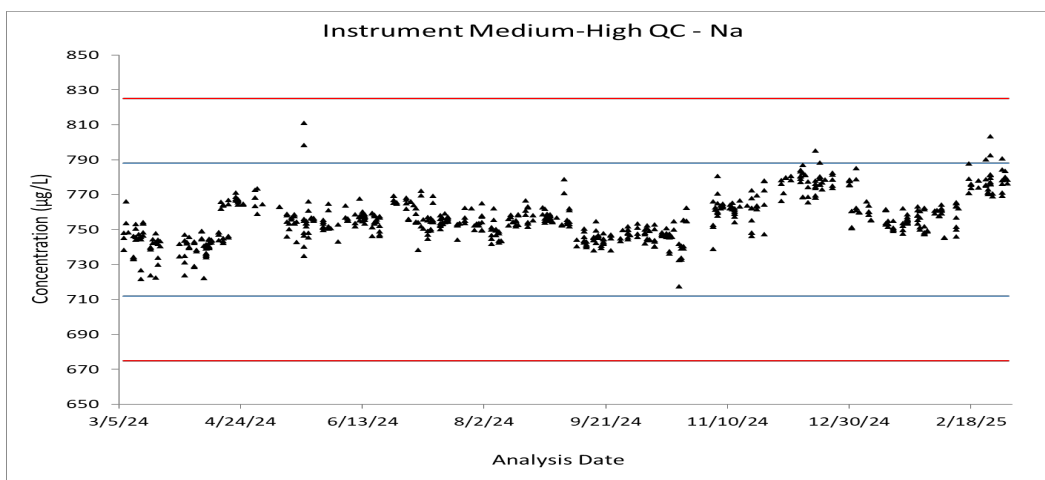
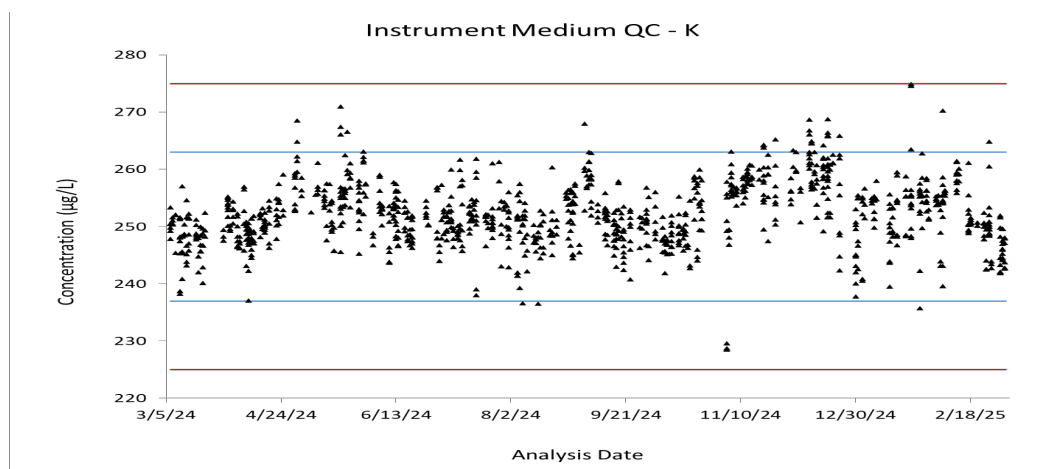
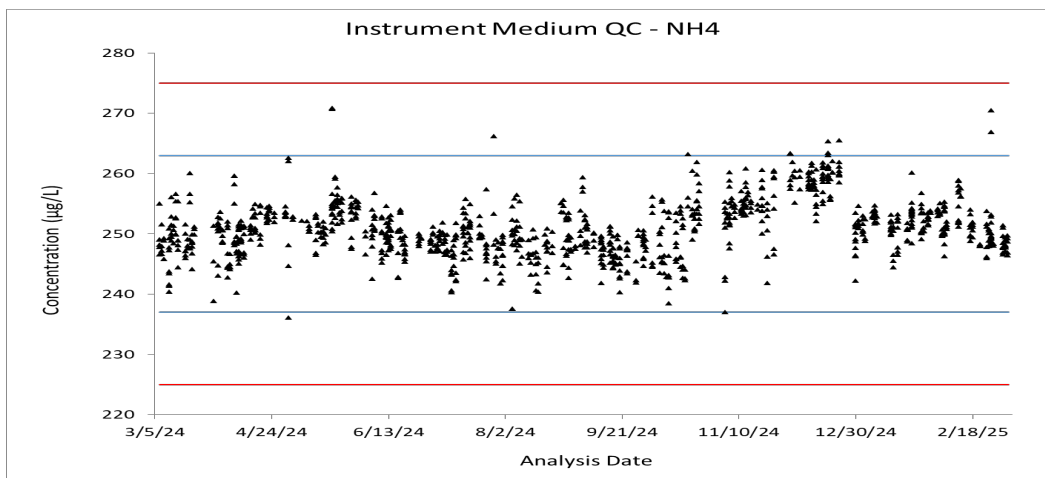


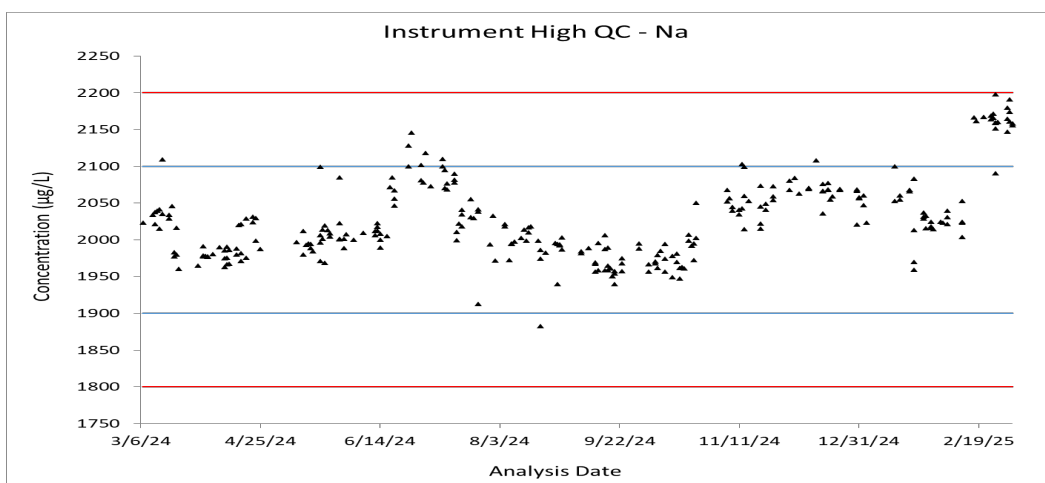
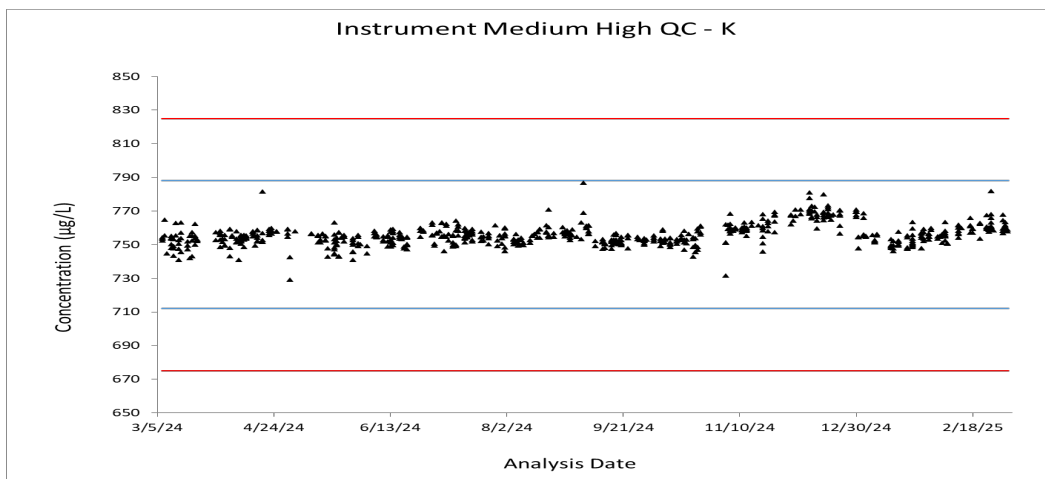
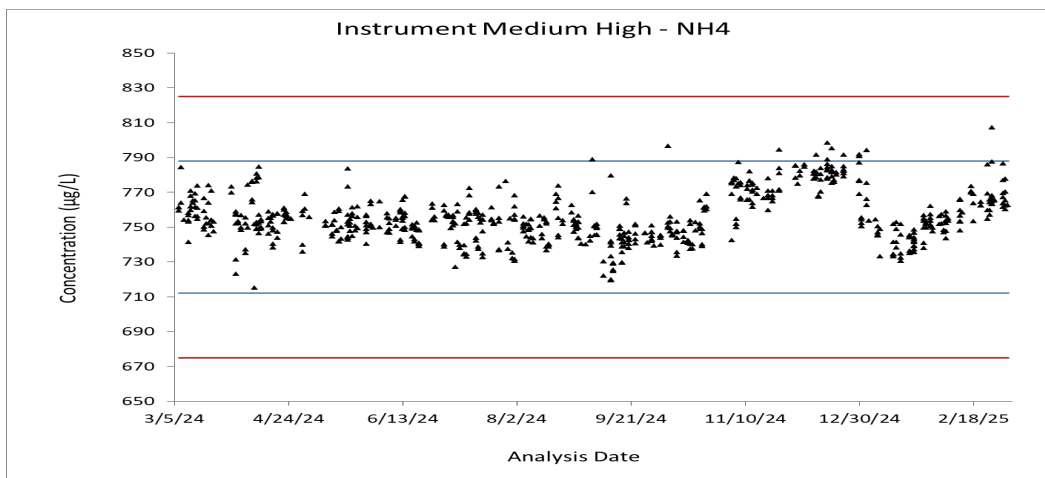
In the control charts below, red lines show upper and lower control limits set at $\pm 35\%$ of the nominal concentrations for the low standards and $\pm 10\%$ of the nominal concentrations for the medium, medium-high, and high standards. Blue lines show upper and lower warning limits.

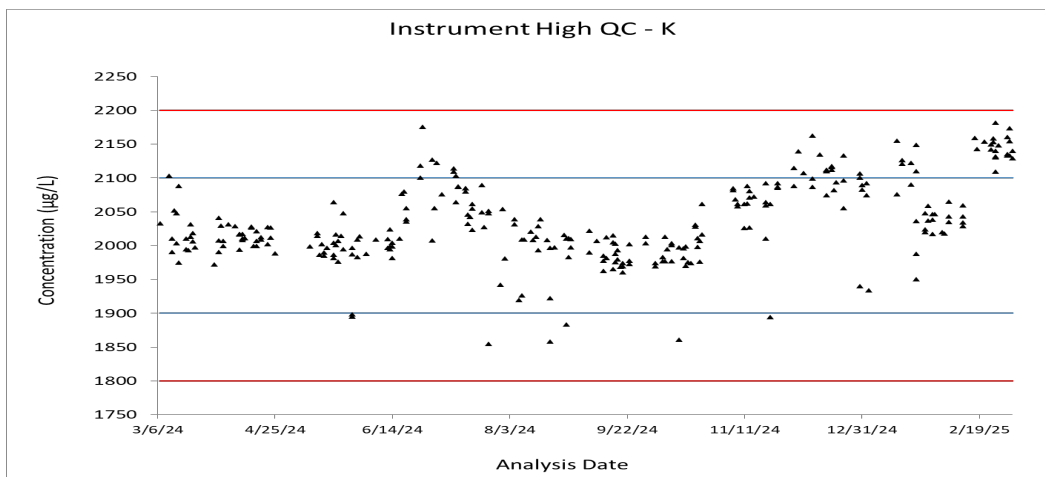
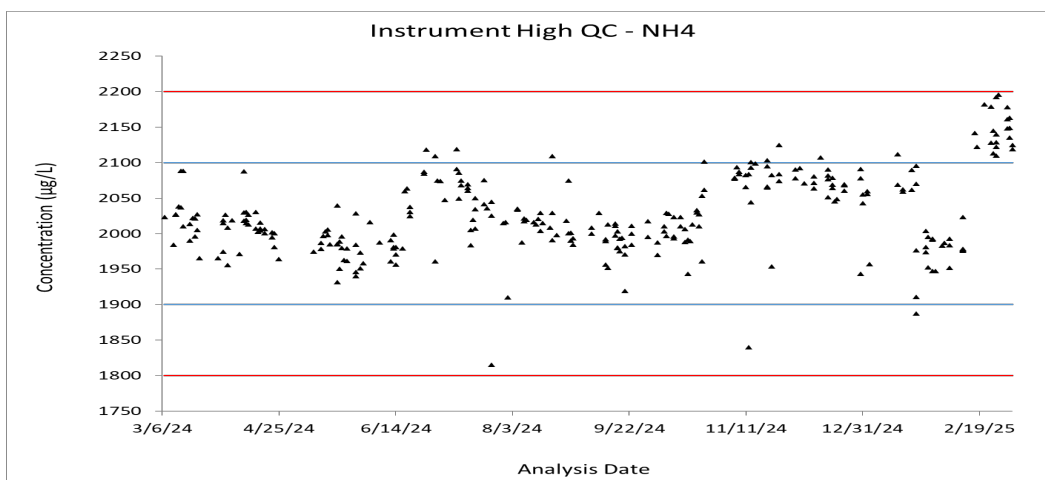
Figure 5-11: Control charts for cation CCV check standards at low, medium, medium-high, and high concentrations measured in units of $\mu\text{g/L}$ (see Table 5-7) for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024).







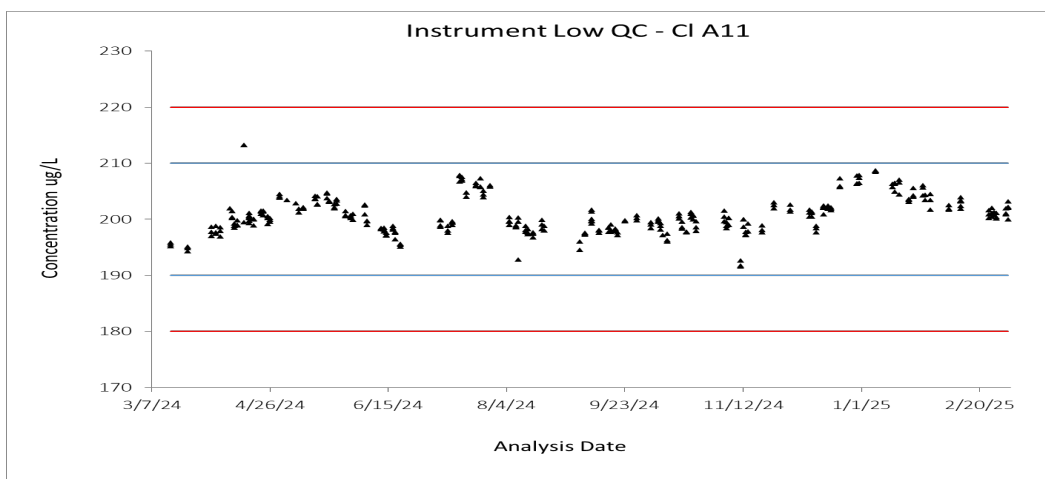
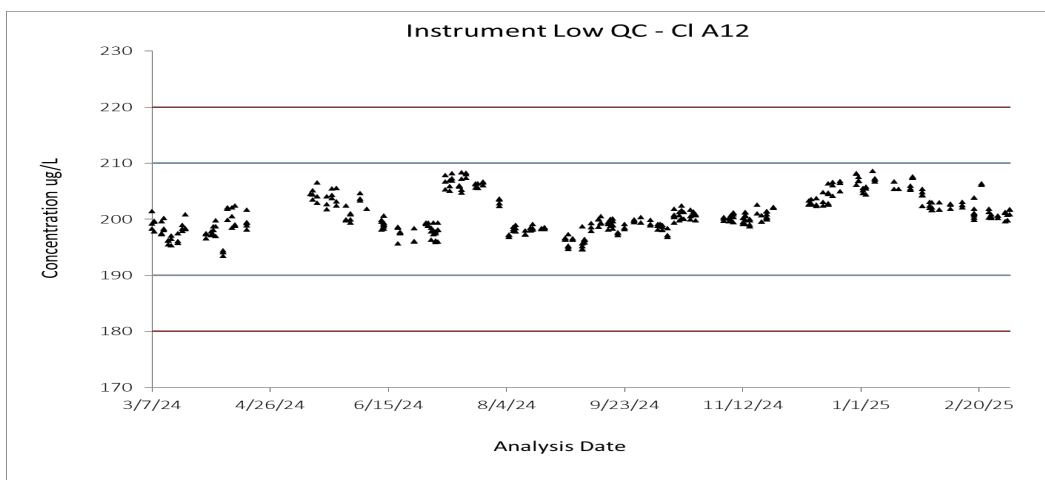
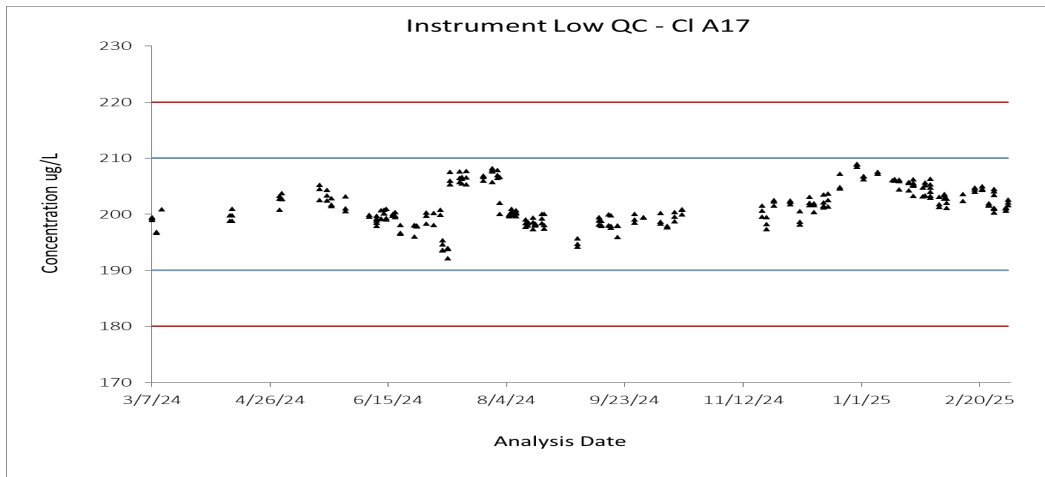


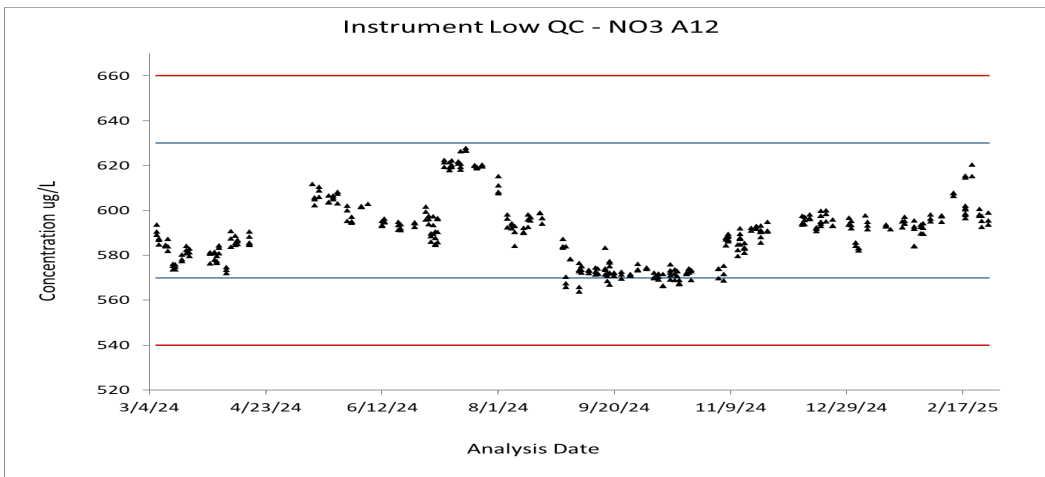
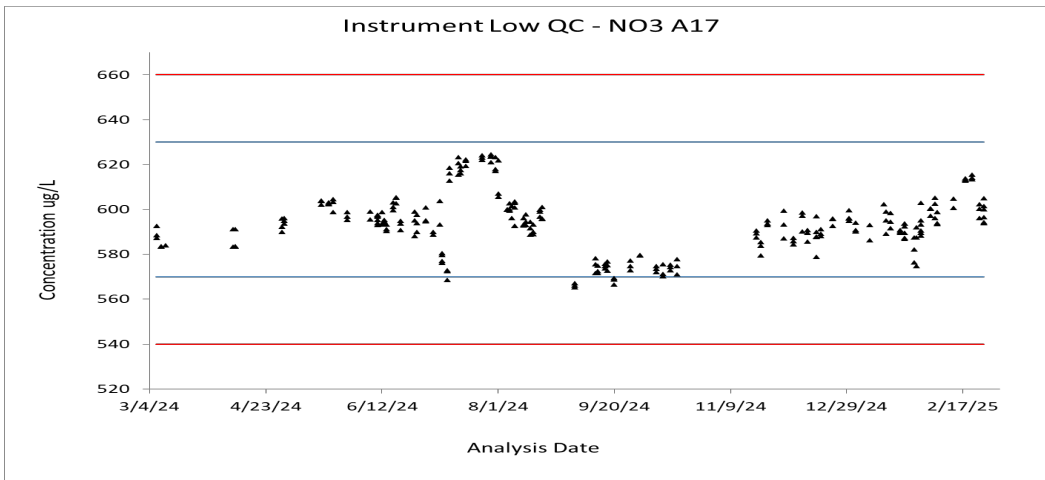
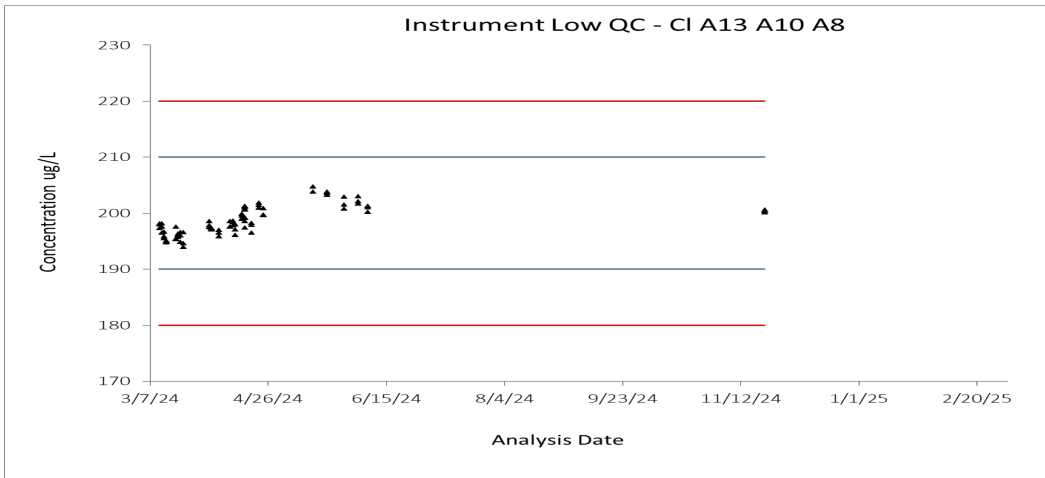


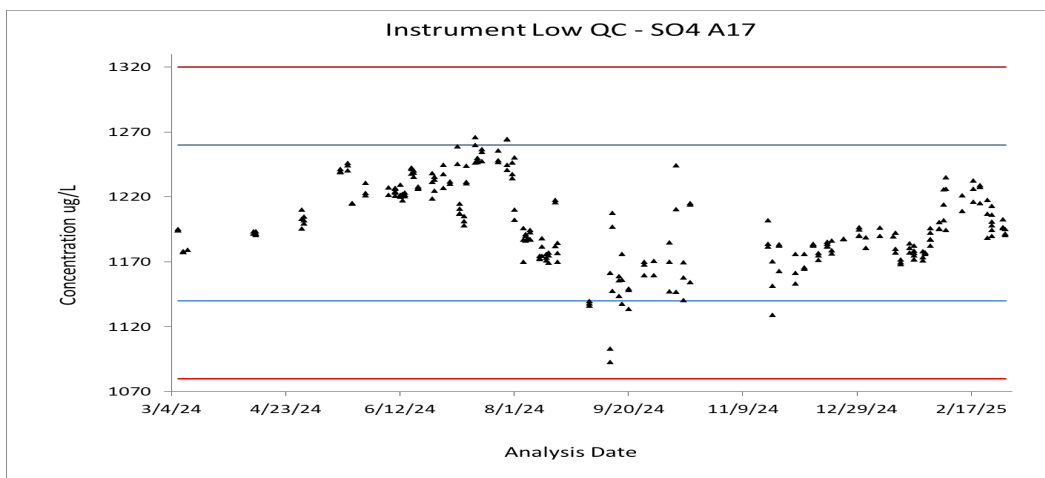
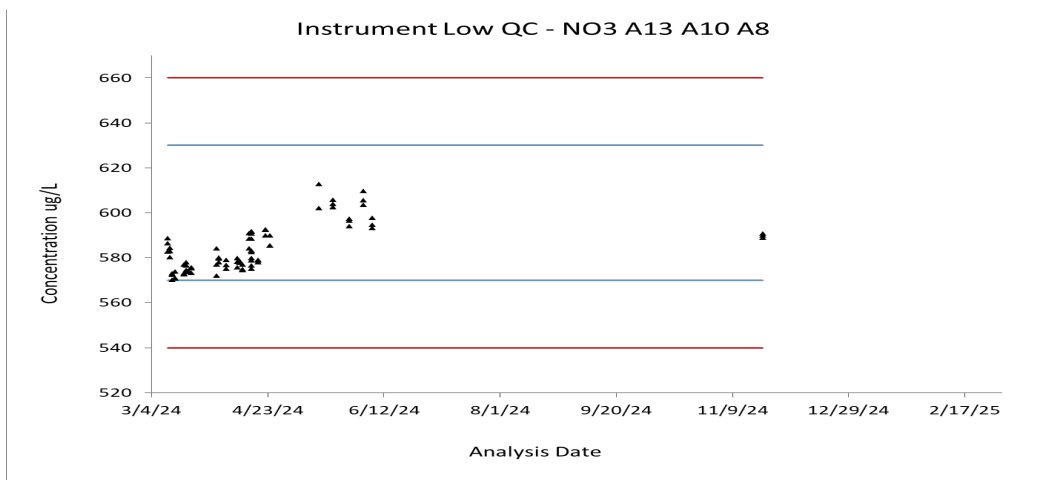
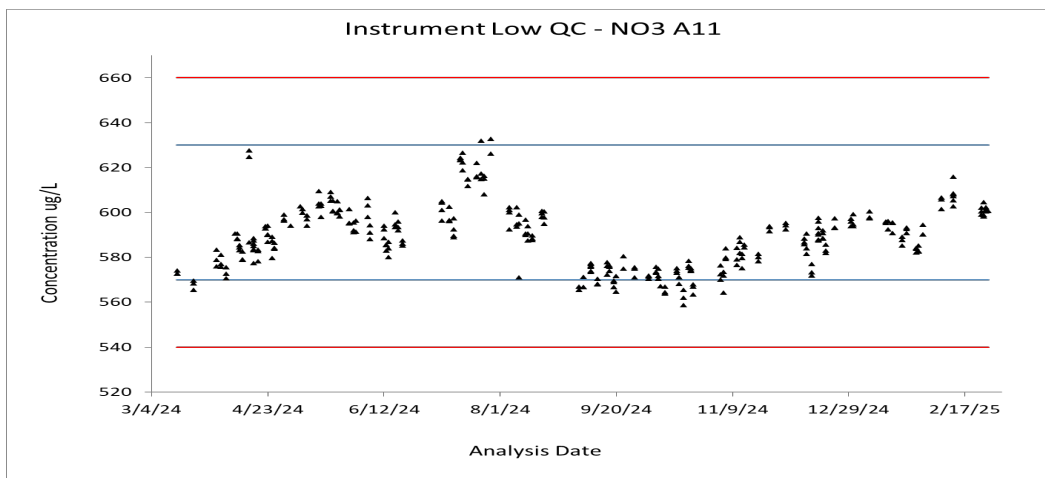
To demonstrate instrument-to-instrument performance, control charts for the lowest CCV check standards were generated where Aquion instruments A11, A12, & A17; ICS 3000 systems A8 & A10; and ICS 6000 system A13 are compared for anions (Figure 5-12). Aquions instruments C9, C10, and C11 are compared for cations (Figure 5-13). The control charts illustrate consistent performance between instruments. Results for A8, A10 and A13 are combined as these systems primarily support anion-only analyses for other projects and used as needed to support this project.

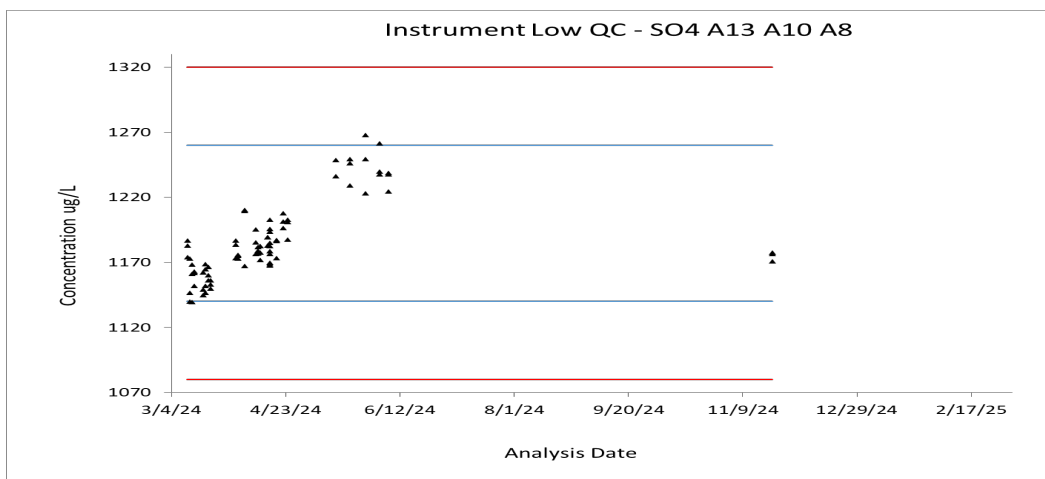
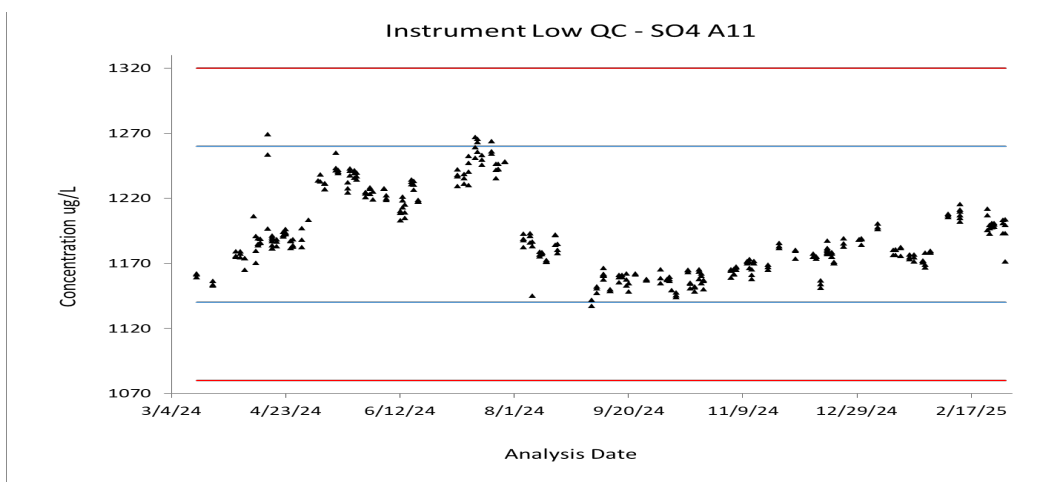
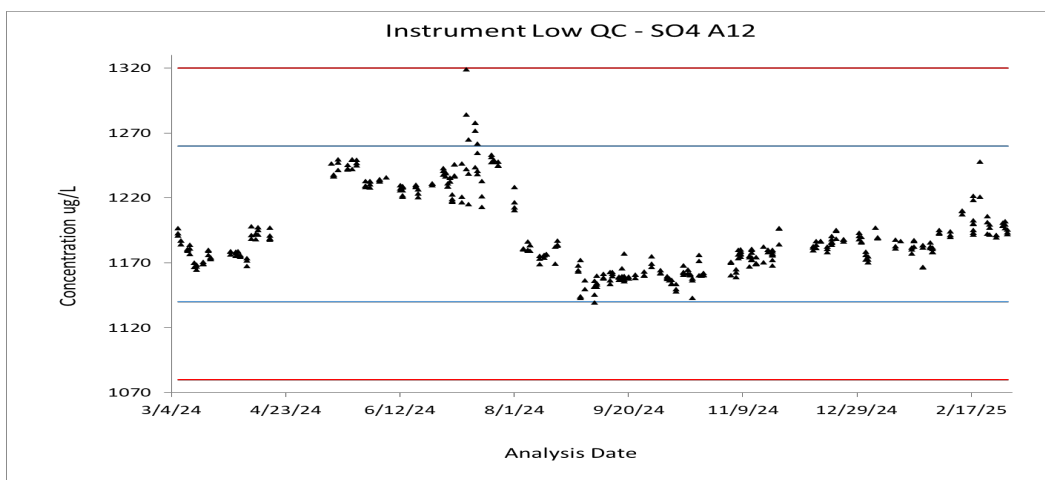
In the control charts below, red lines show upper and lower control limits set at $\pm 10\%$ of the nominal concentrations. Blue lines show upper and lower warning limits.

Figure 5-12: Control charts for anion CCV check standards showing comparability between instruments at low concentrations for this analysis period (see Table 5-7).



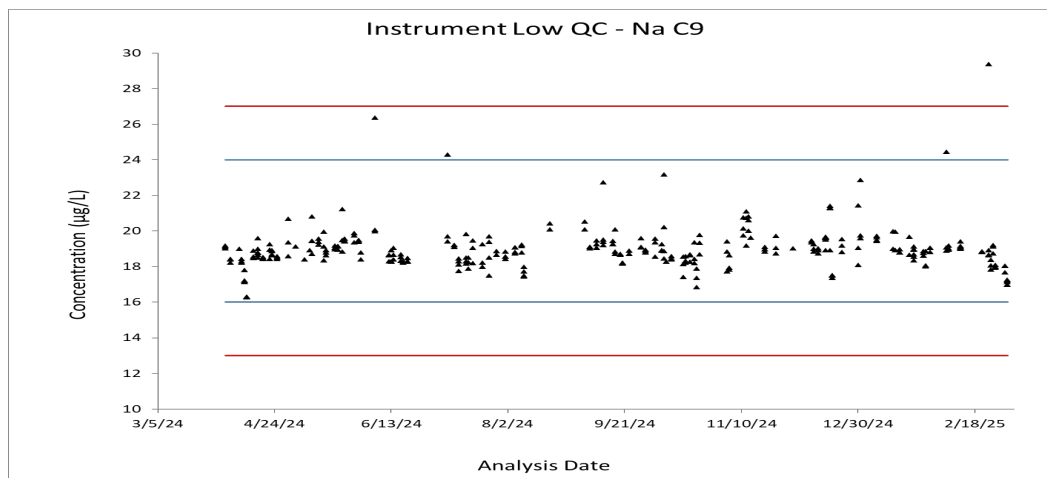
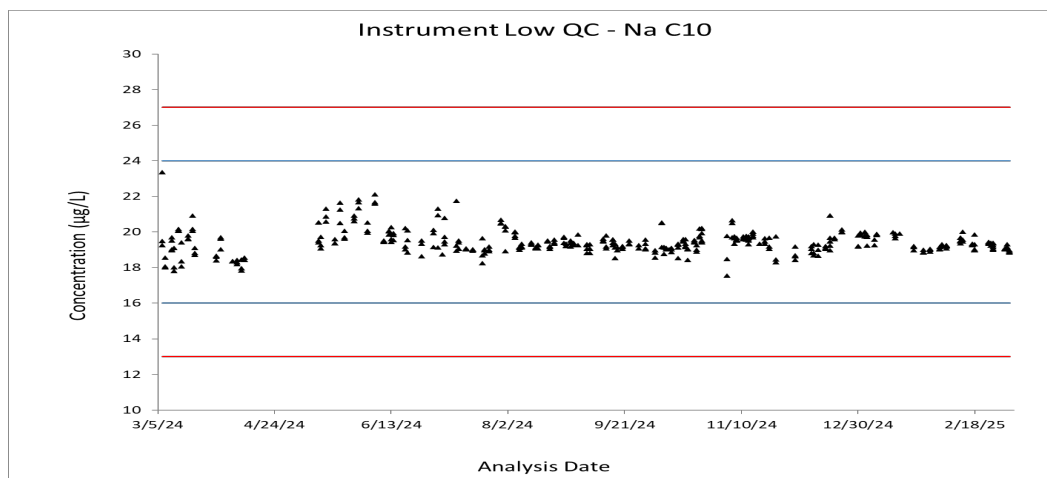
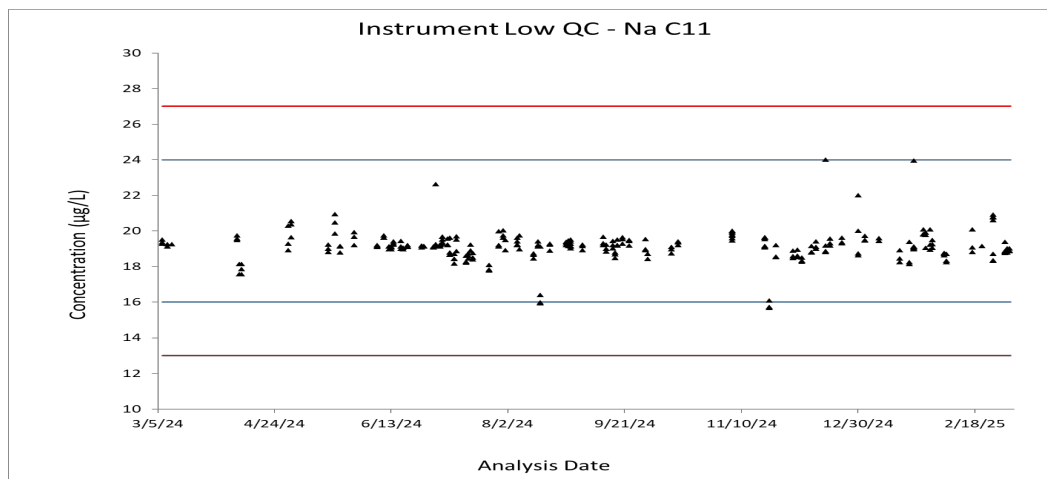


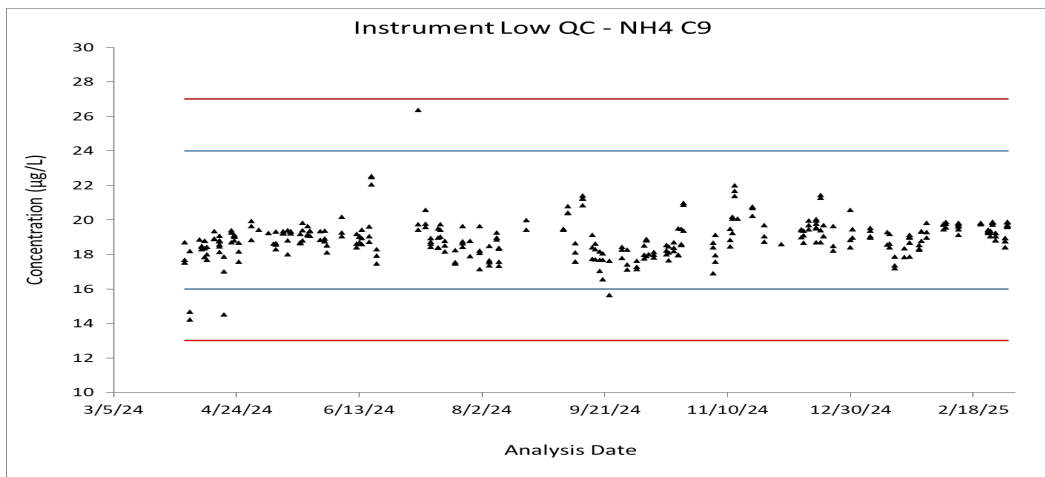
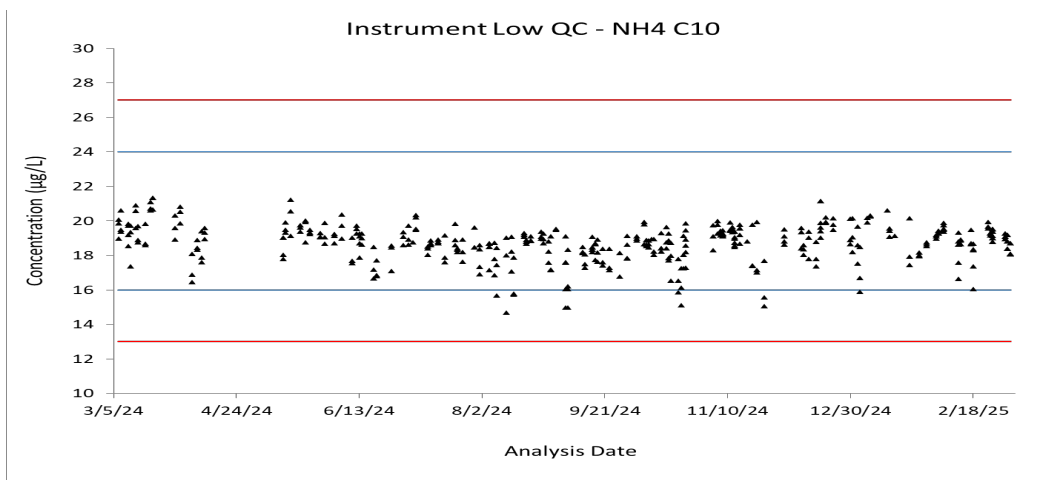
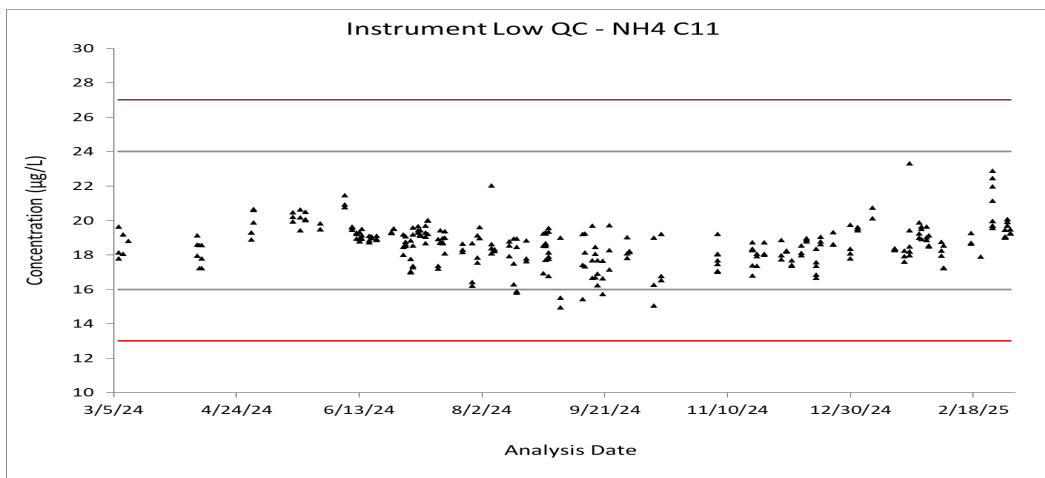


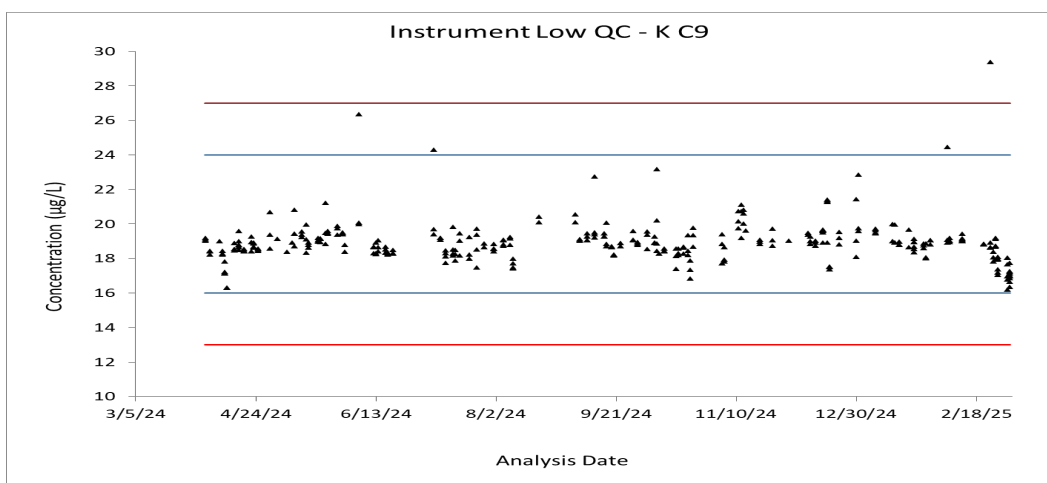
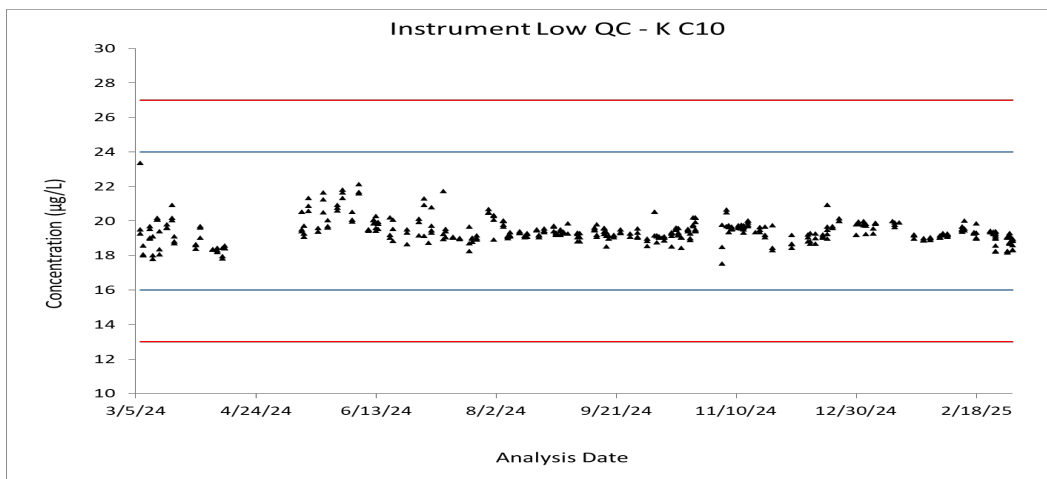
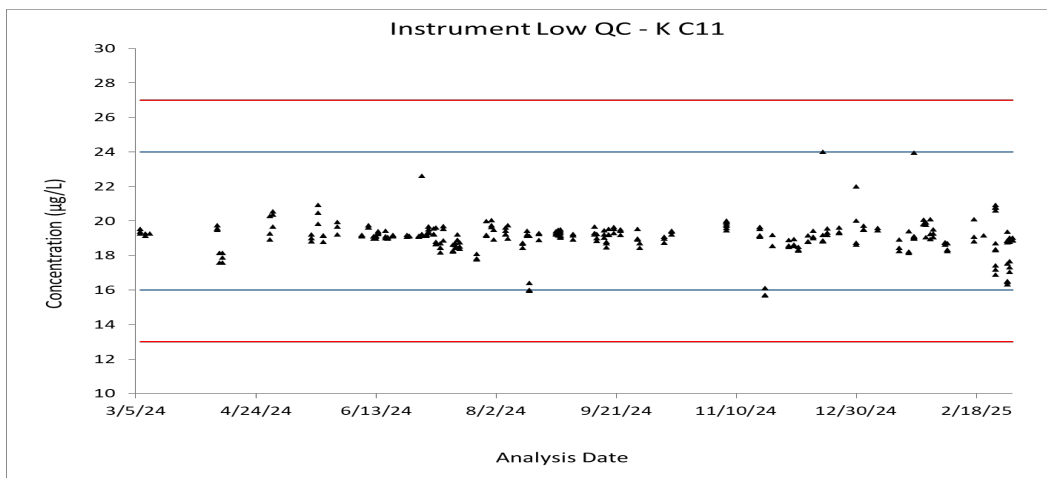


In the following control charts, red lines show upper and lower control limits set at $\pm 35\%$ of the nominal concentrations. Blue lines show upper and lower warning limits.

Figure 5-13: Control charts for cation CCV check standards showing comparability between instruments at low concentrations for this analysis period.



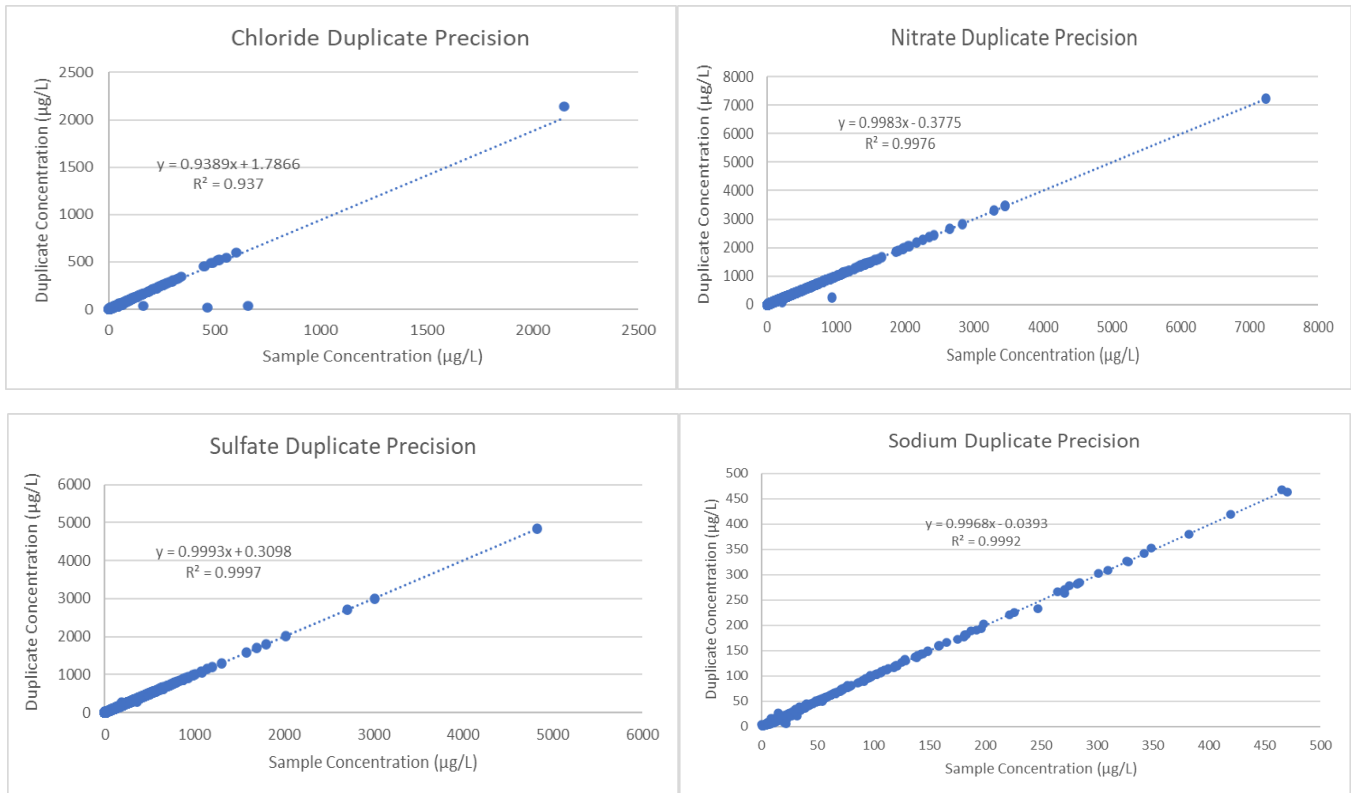


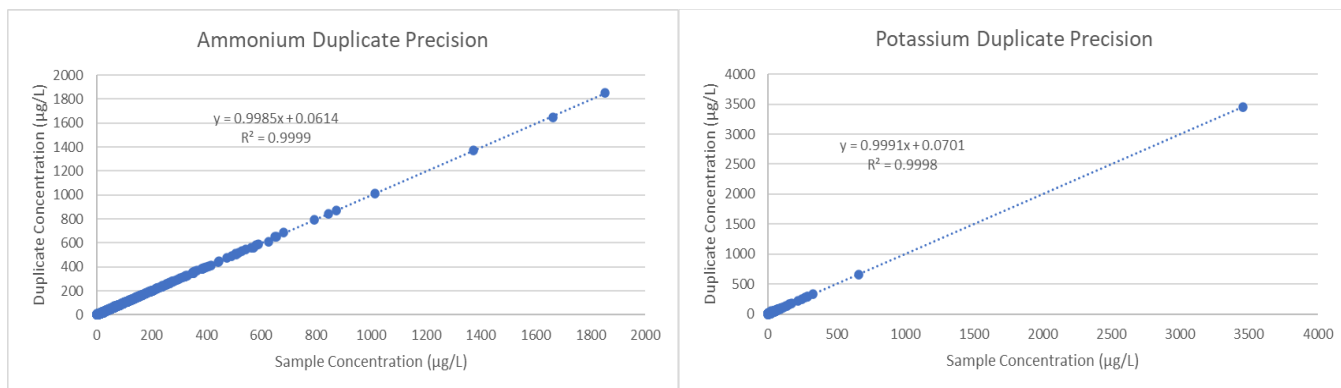


5.4.2.3 Duplicate Samples

Duplicate analysis results are obtained from two different aliquots of the same filter sample extract run on the same instrument sequentially; there are three sets of duplicate samples for every 50 samples analyzed. The relative percent difference (RPD) for duplicate samples must be within $\pm 10\%$ when sample concentrations are greater than ten times the analytical MDL and within $\pm 200\%$ when sample concentrations are at or up to ten times the analytical MDL. During the analysis period when samples collected during 2024 were analyzed (March 7, 2024 through March 6, 2025), there were a total of 879 duplicate samples analyzed for anions (Figure 5-14), there were ten cases where the RPD did not meet the acceptance criteria. Also during this analysis period, there were a total of 871 duplicate samples analyzed for cations (Figure 5-14), with fourteen cases where the RPD did not meet the acceptance criteria. When duplicate precision or recovery results fail to meet the acceptance criteria, the associated quality control data are reviewed to identify the cause of failure. If the root cause cannot be determined, or if contamination or another analytical issue is suspected to have impacted additional samples within the batch, a subset of samples (typically 5) is reanalyzed. This reanalysis is performed to verify whether the issue is isolated or affects the analytical batch. If we find evidence that the issue affected the broader analytical batch, the entire batch of samples is reanalyzed. We found one case in a single batch where we reanalyzed the entire batch of samples.

Figure 5-14: Ion duplicate analysis results for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024). Cases that did not meet the acceptance criteria, as described in section 5.3.2.3, are included in these figures.

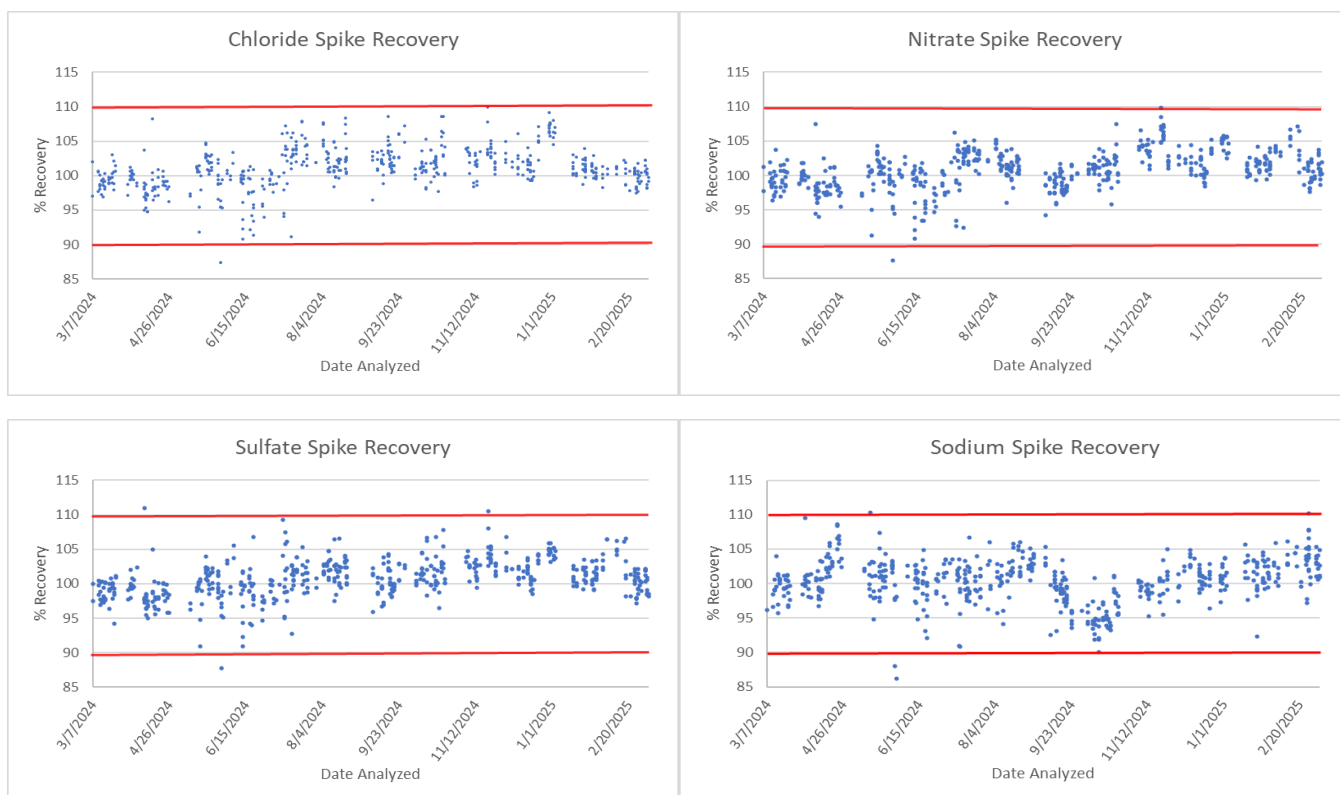


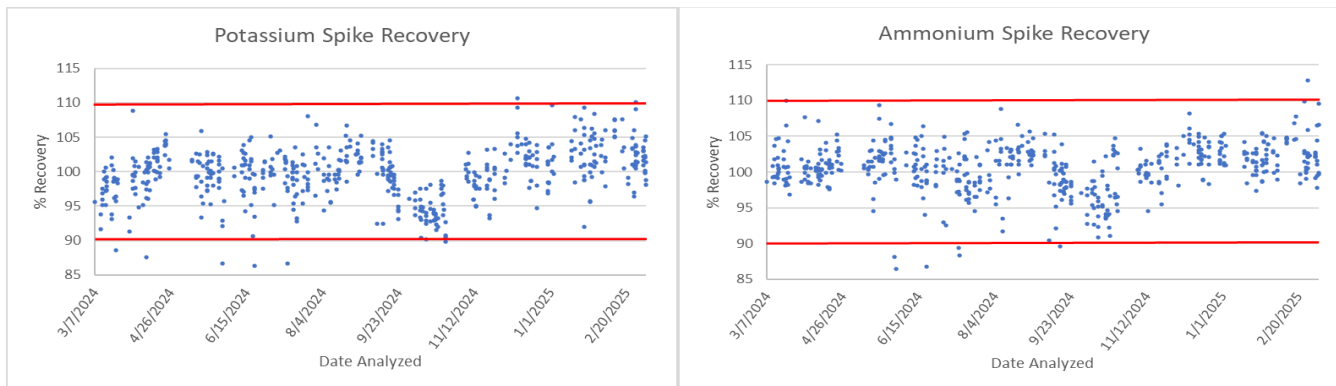


5.4.2.4 Spiked Sample Extracts

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 576 matrix spikes were analyzed for anions. There were eighteen cases where either chloride, nitrate, or sulfate failed spike recovery criteria (Figure 5-15); samples were reanalyzed for all cases. A total of 575 matrix spikes were analyzed for cations. There were 22 cases where spiked samples failed to meet recovery criteria of 90-110% for either sodium, ammonium, or potassium spiked samples (Figure 5-15); samples were reanalyzed for all cases. In the figures below, the red lines are drawn to indicate the acceptable recovery limits of 90% to 110%.

Figure 5-15: Time series of recovery (%) for anion and cation of matrix spikes for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024).

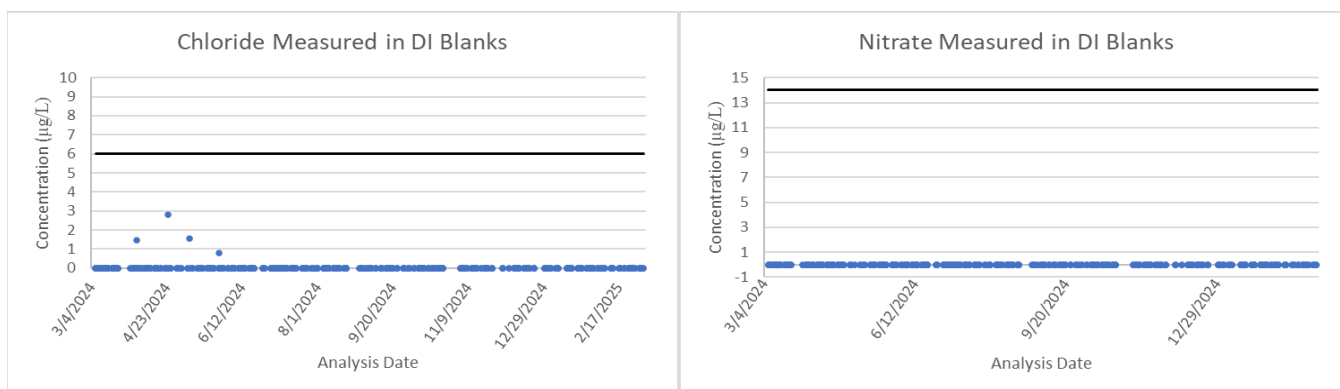




5.4.2.5 Reagent Blanks and Spikes

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 20 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 5-16: Concentrations of anions and cations in DI water blanks for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024). Black line indicates the analytical method detection limit.



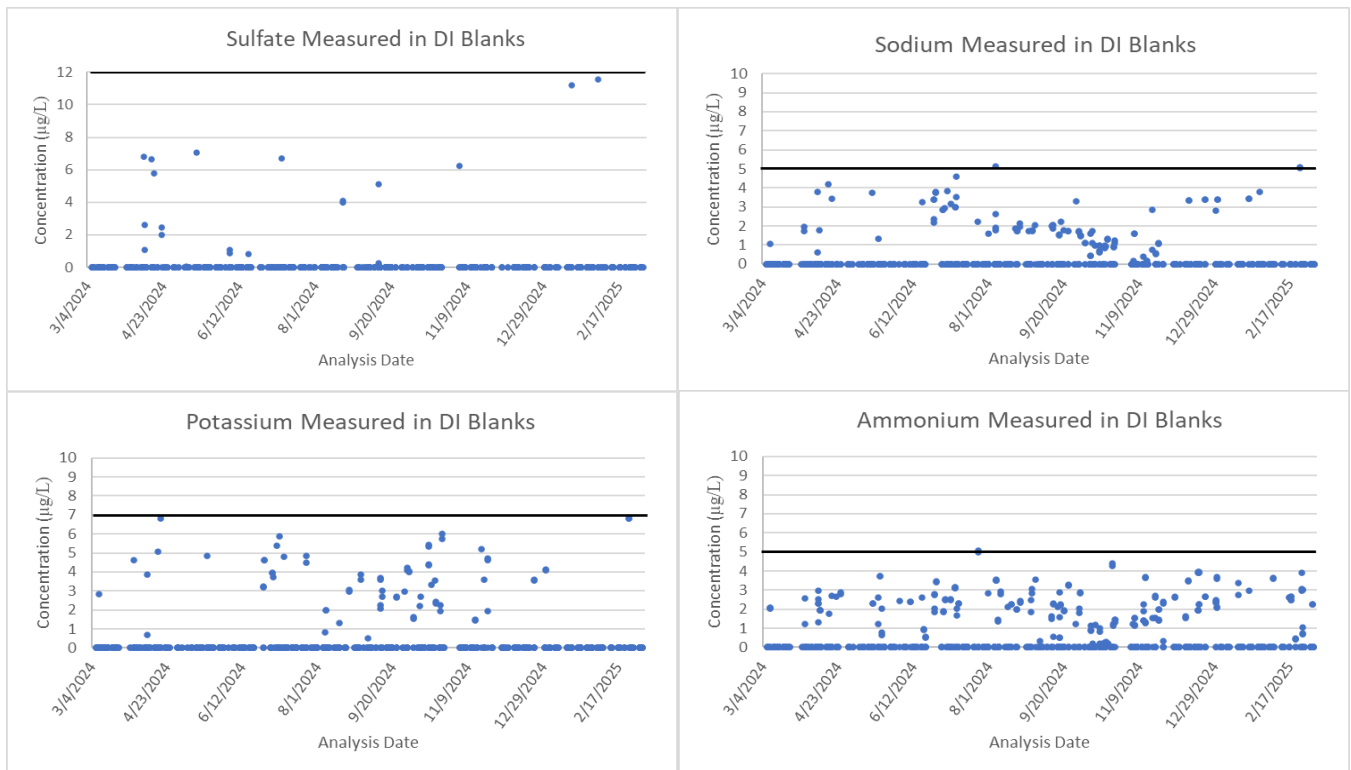
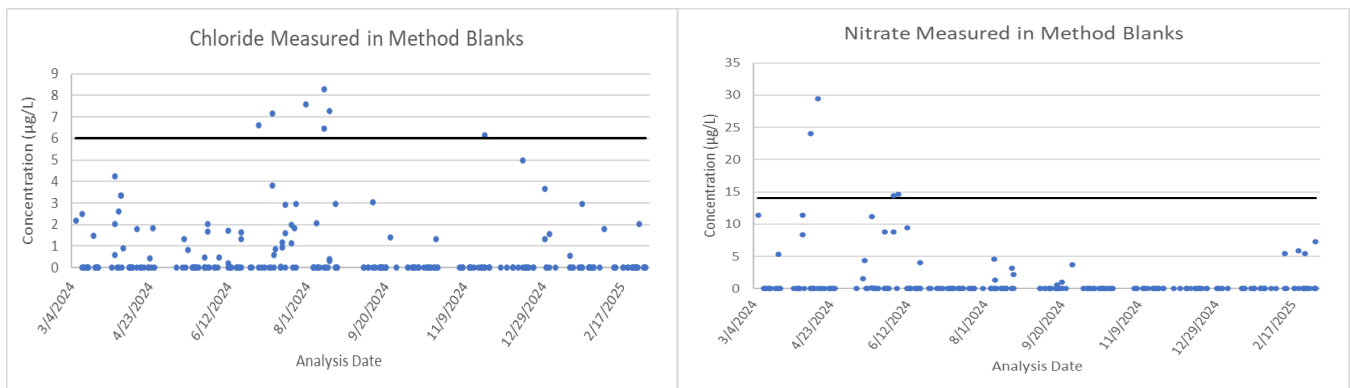
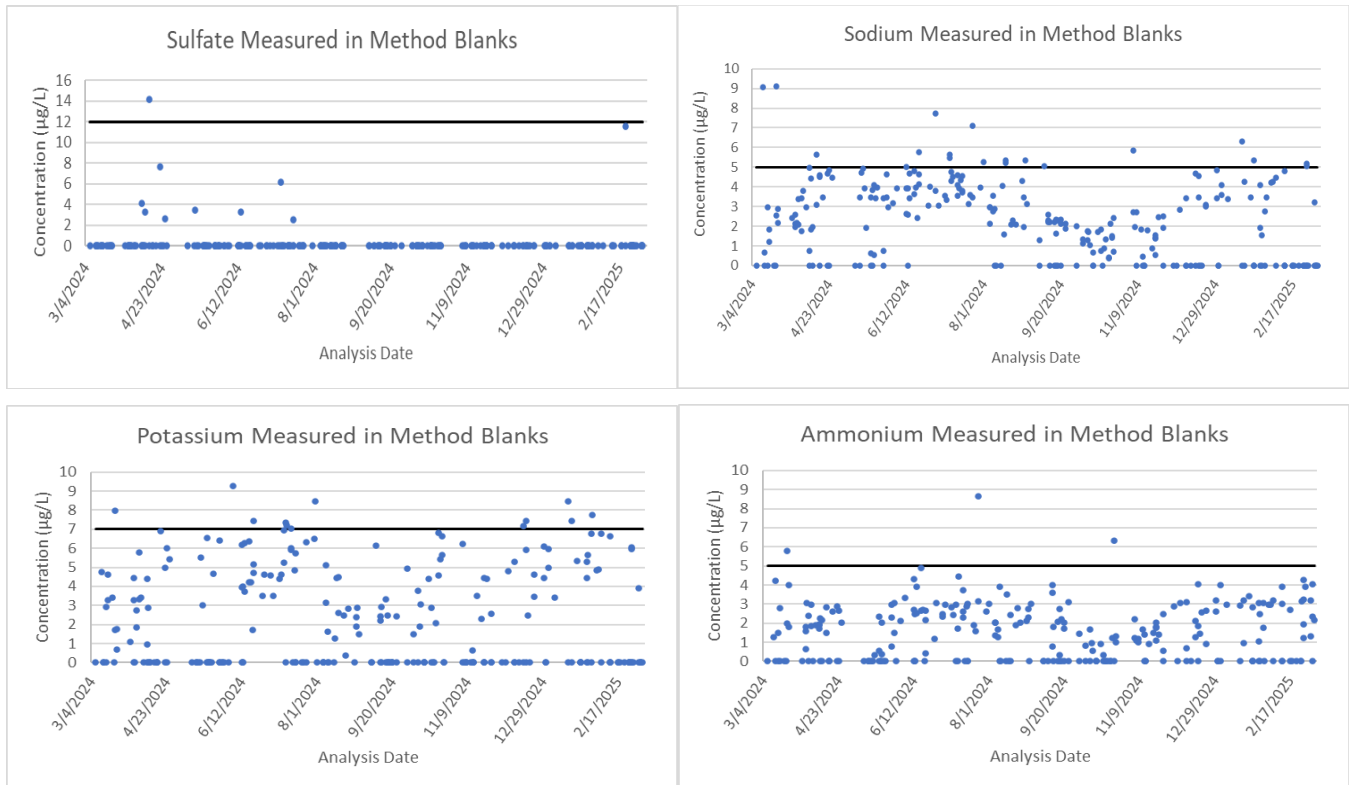


Figure 5-17: Concentrations of anions and cations in method blanks for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024). Black line indicates the analytical method detection limit.





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 5-9 and Table 5-10) 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 5-18 and Figure 5-19) have more frequent outliers relative to the CCV check standards (Figure 5-10 and Figure 5-11), 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 April of 2024, following preparation of a new LCS spiking solution. The LCS Low checks were within reasonable limits after the solution was discarded and re-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 5-9: Target concentrations for anion LCS for the analysis period 03/07/2024 through 03/06/2025 (samples collected 1/1/2024 through 12/31/2024).

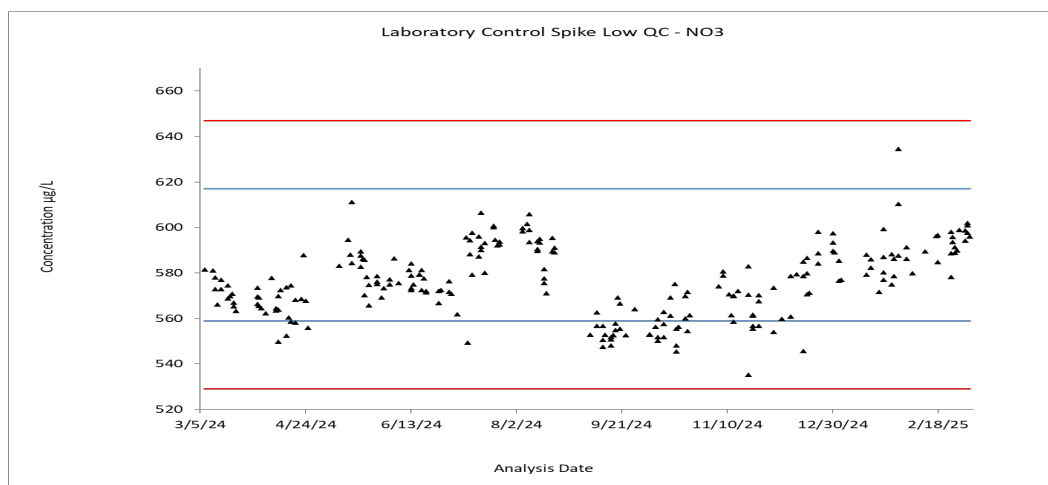
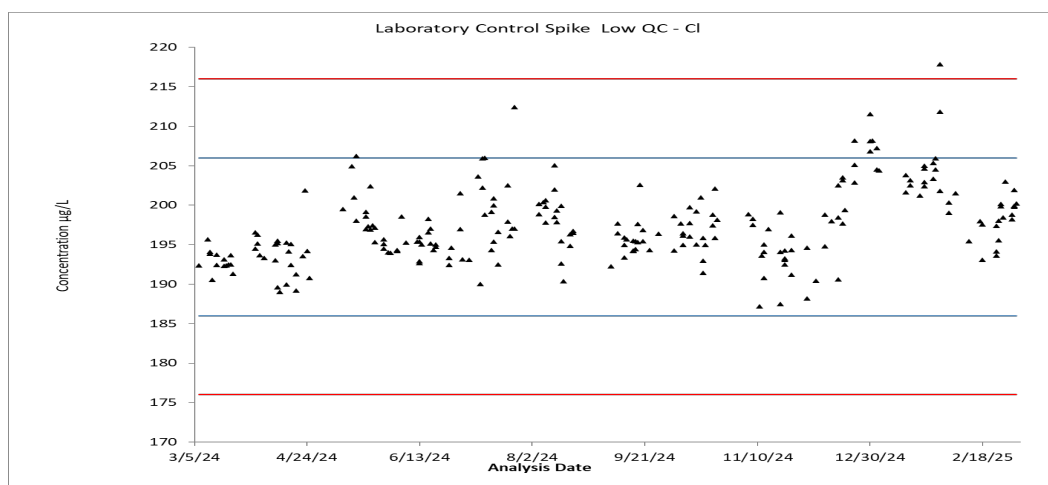
QC Sample	Cl ⁻ (ppb)	NO ₃ ⁻ (ppb)	SO ₄ ²⁻ (ppb)
LCS Low	196	588	1180
LCS Medium	476	1430	2860
LCS High	2000	6000	12000

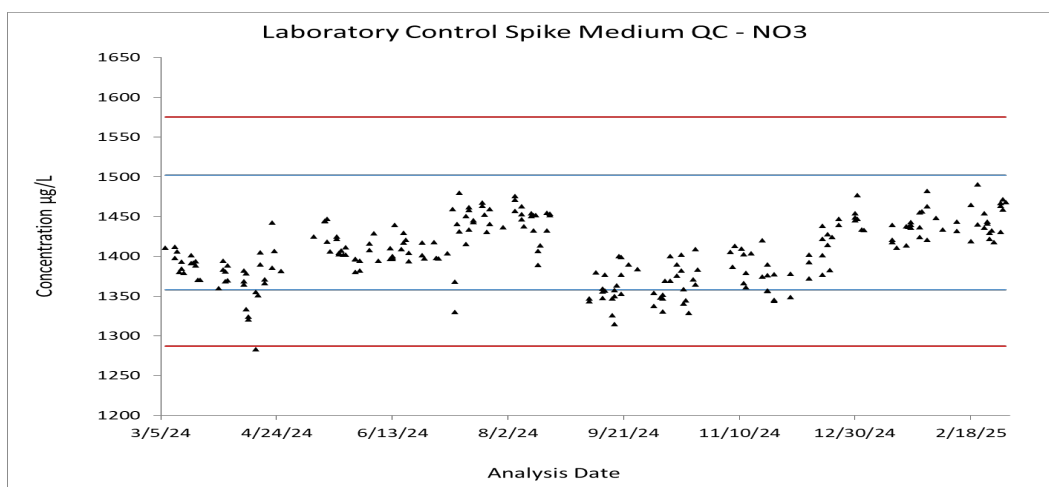
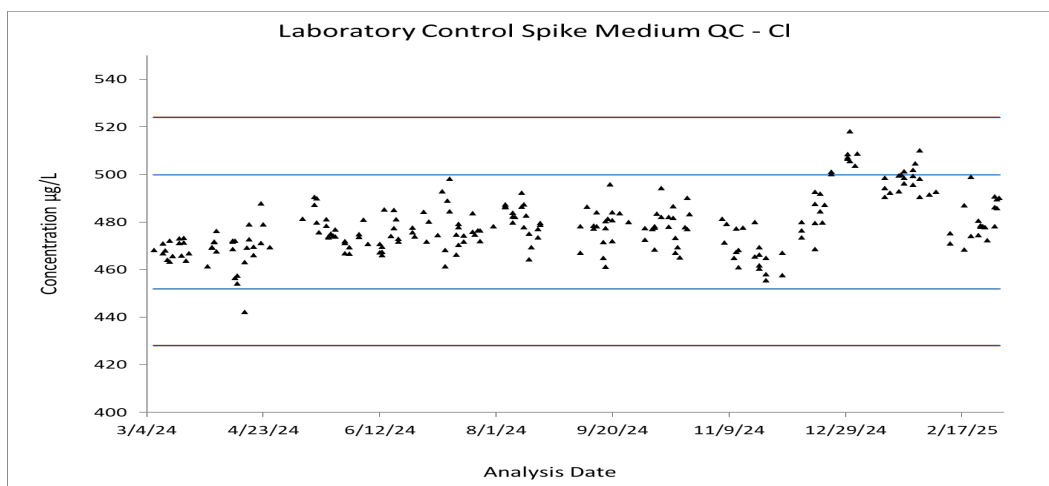
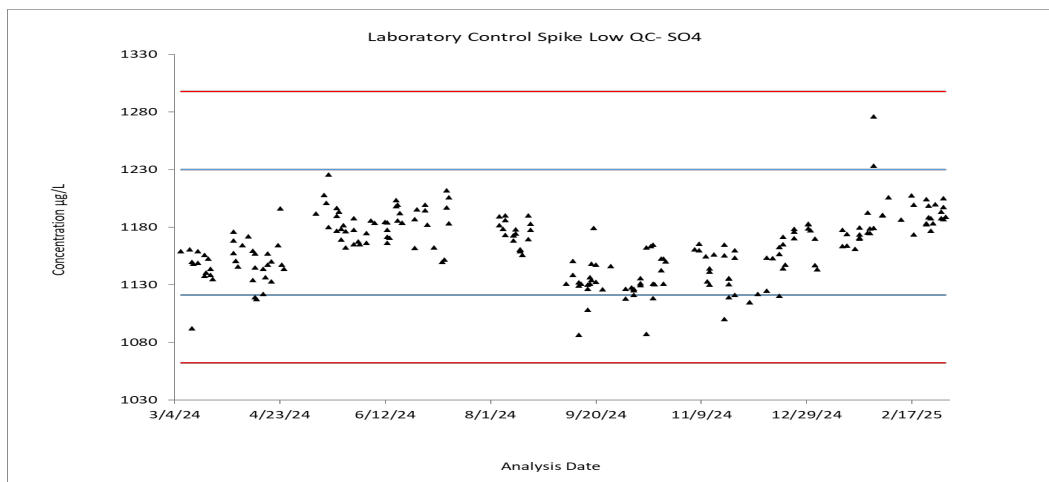
Table 5-10: Target concentrations for cation LCS for the analysis period 3/17/2023 through 03/05/2024 (samples collected 1/1/2023 through 12/31/2023).

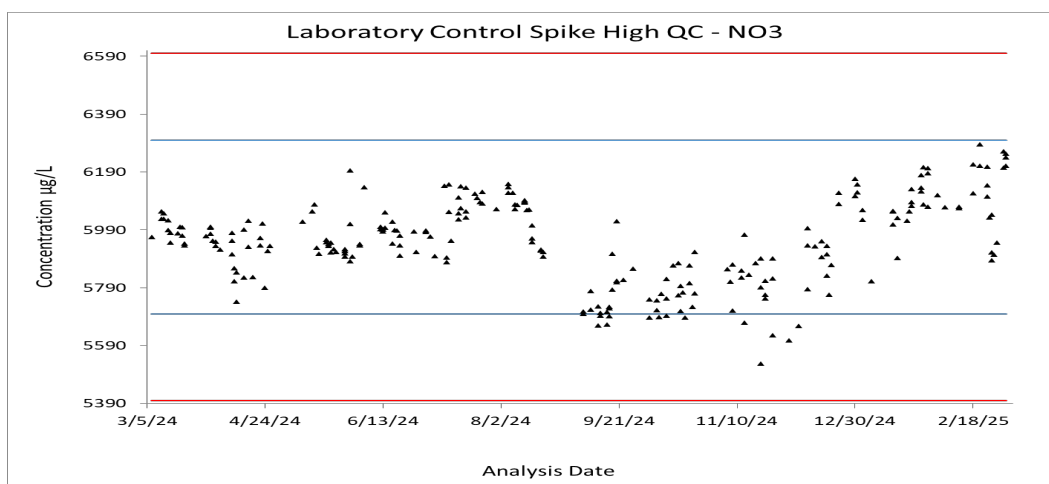
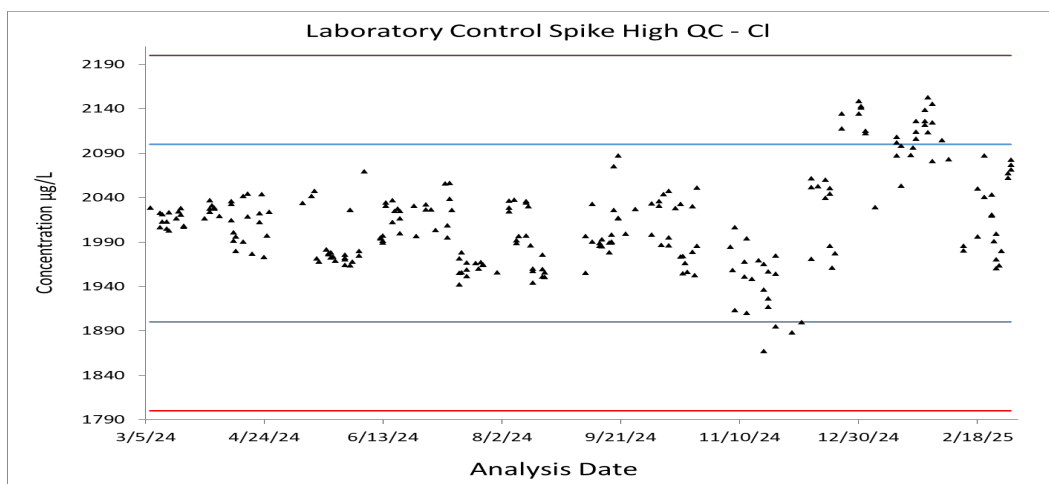
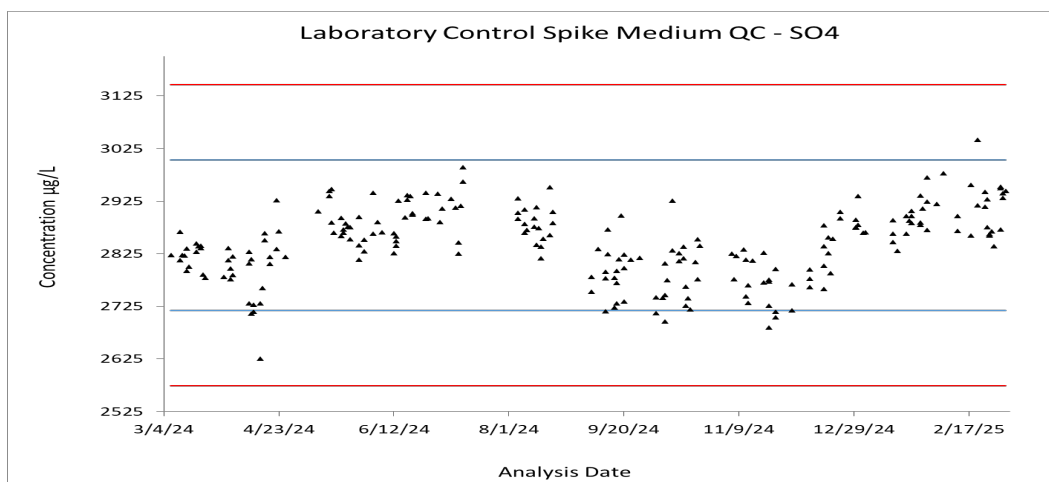
QC Sample	Na ⁺ (ppb)	NH ₄ ⁺ (ppb)	K ⁺ (ppb)
LCS Low	20	20	20
LCS Medium	276	276	276
LCS High	769	769	769

In Figures 5-18 and 5-19 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 5-18: Control charts for anion LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024).







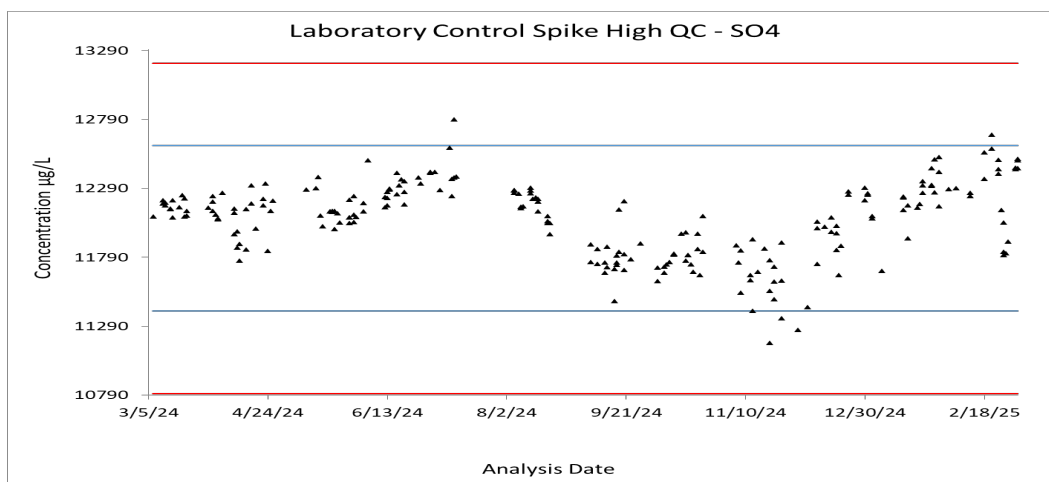
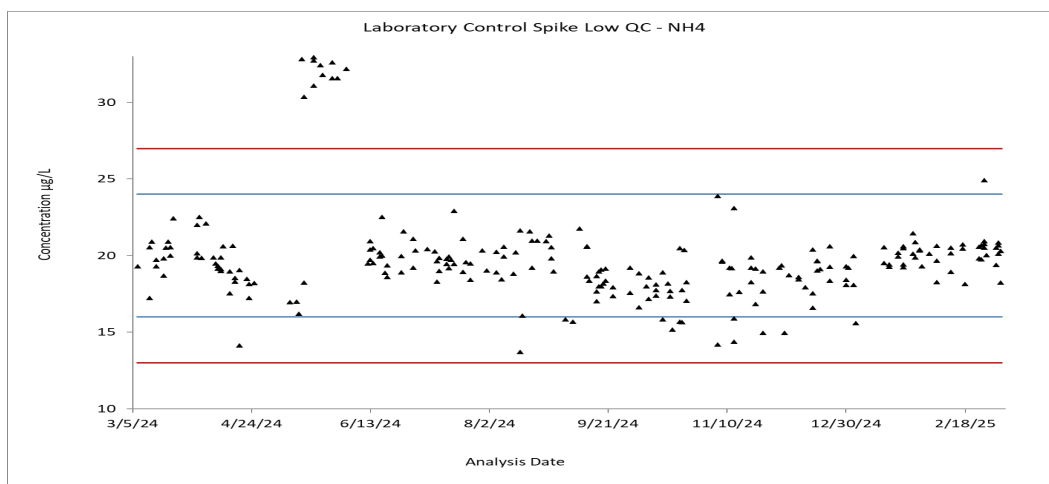
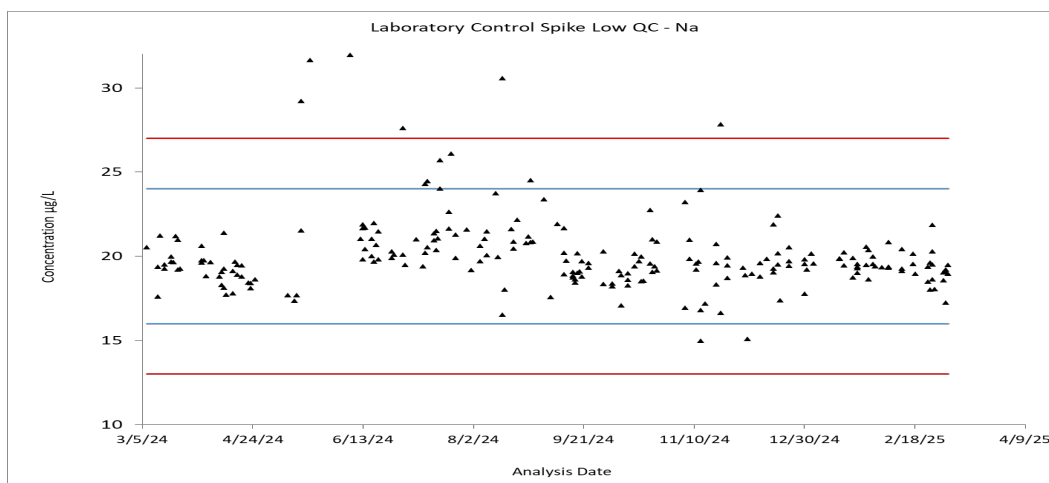
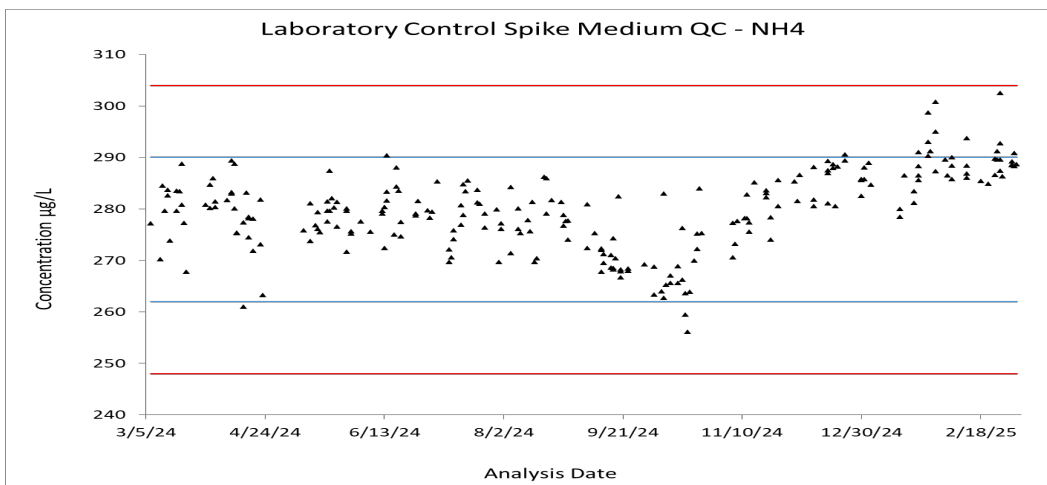
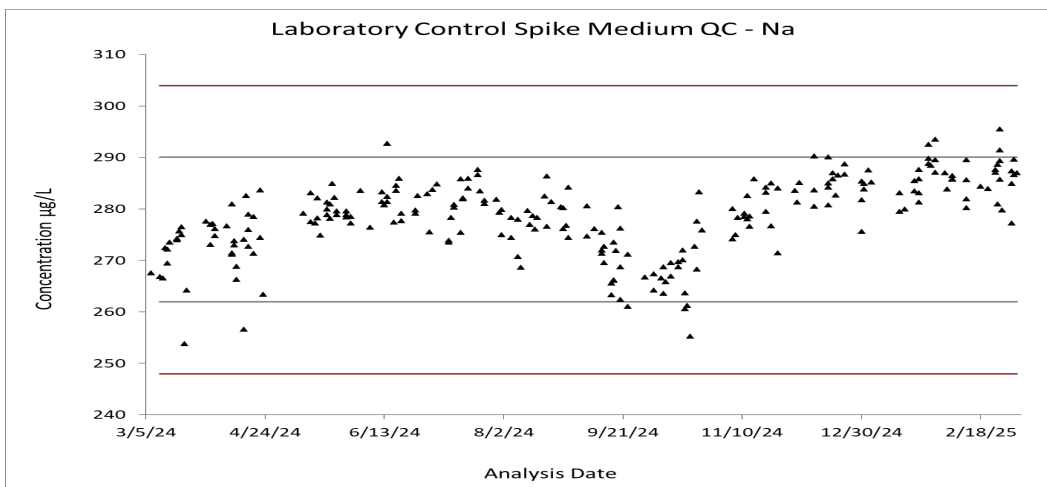
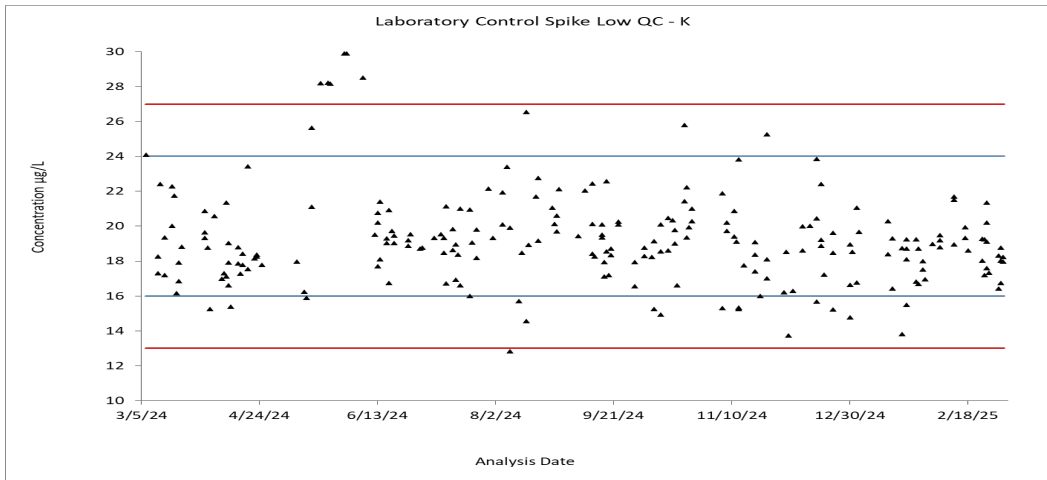
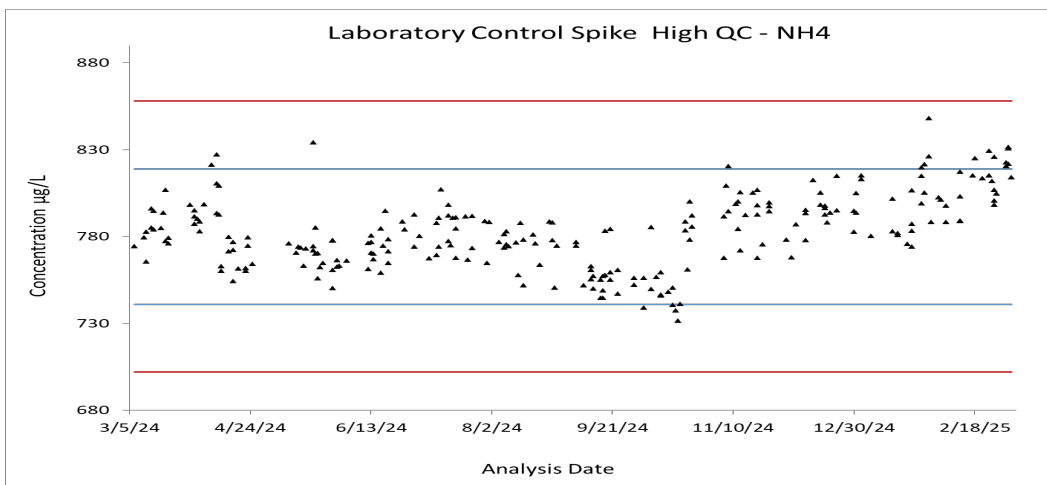
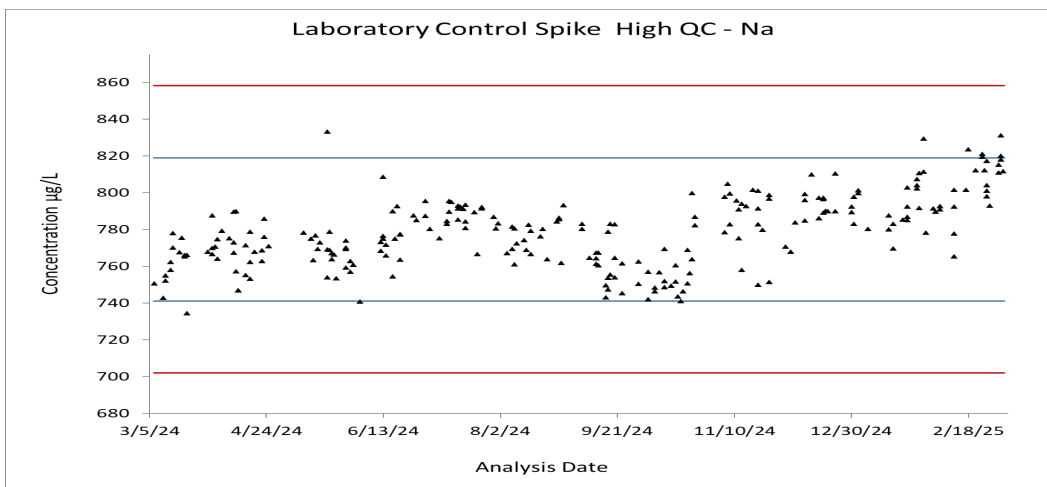
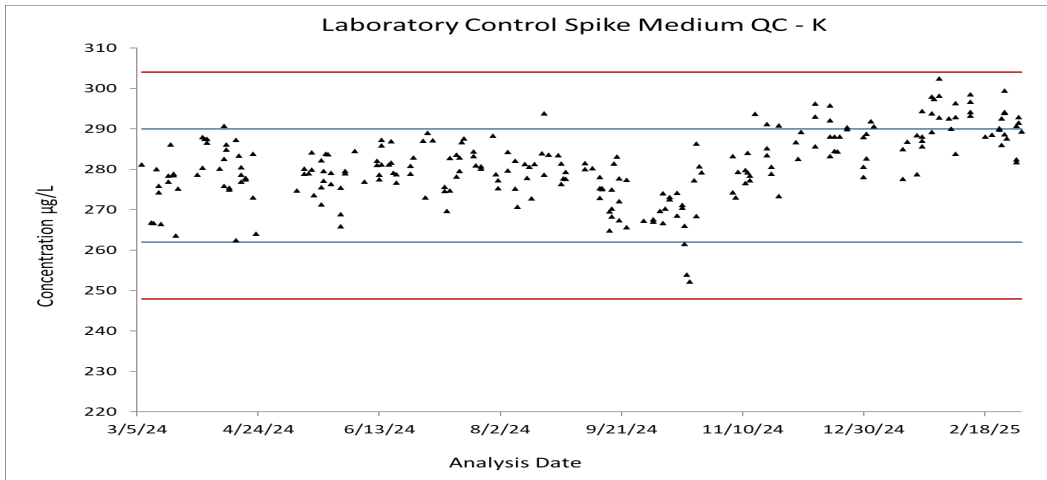
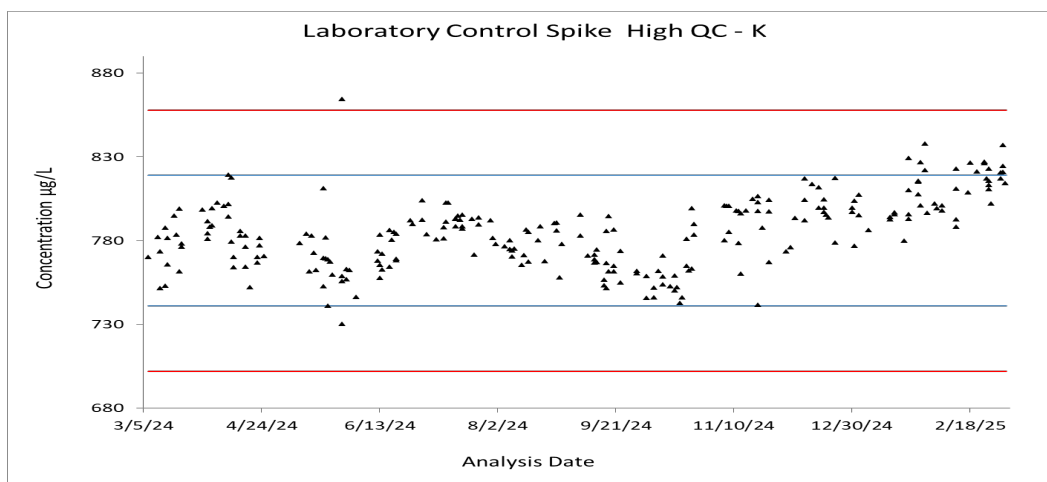


Figure 5-19: Control charts for cation LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024).









5.4.2.6 *Environment and Climate Change Canada Proficiency Testing Program*

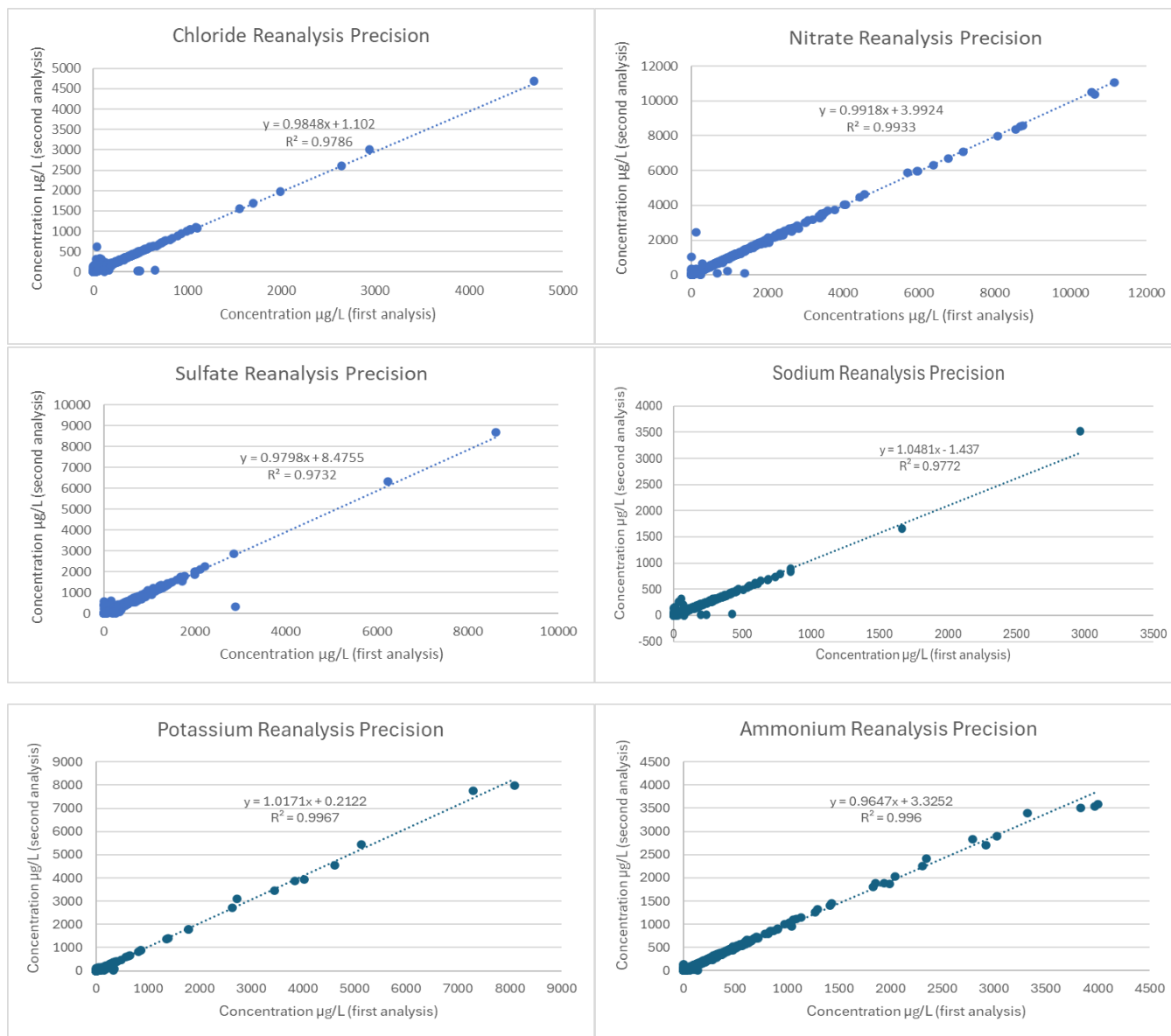
The RTI Ions Chromatography Laboratory participated in the Proficiency Testing Program administered by Environment and Climate Change Canada. For this study, RTI analyzed ten rainwater samples and results were compared against other participating laboratories. RTI received an overall “Good” quality rating score for its participation in the Winter 2024 study. A copy of the report is available upon request.

5.4.2.7 *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 5-6, 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 flagged during analyst review will also be reanalyzed for issues such as poor peak integration 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 3,166 samples reanalyzed for anions and 3,135 samples reanalyzed for cations (Figure 5-20). Less than 1.10% 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 5-20: Ion reanalysis results for the analysis period 3/07/2024 through 3/06/2025 (samples collected 1/1/2024 through 12/31/2024).



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 4.1.2.2 and Section 7.5, respectively.

5.4.4 Audits, Performance Evaluations, Training, and Accreditations

5.4.4.1 System Audits

The prime contractor (UC Davis) did not conduct any audit of the RTI Ion Chromatography Laboratory during this reporting period. As discussed in Section 4.2.8, EPA worked with Battelle to perform an audit of RTI for CSN on March 11th and 12th of 2025.

5.4.4.2 Performance Evaluations

RTI participated in the 2024 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/2025-01/2024_megape_report_final_508.pdf.

5.4.4.3 Training

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

5.4.4.4 Accreditations

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

5.4.5 Summary of Filter Blanks

5.4.5.1 Field Blanks

Over the sampling period (January 1, 2024 through December 31, 2024) there were 1,528 valid nylon filter field blanks. Table 5-11 and Table 5-12 summarize the field blank statistics.

Table 5-11: Nylon filter field blank statistics in µg/mL for the analysis period 3/7/2024 through 3/6/2025 (samples collected 1/1/2024 through 12/31/2024).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl ⁻	1528	0.008	0.011	0.001	0.366	0.016
NO ₃ ⁻	1528	0.007	0.010	0.000	0.662	0.031
SO ₄ ²⁻	1528	0.000	0.007	0.000	0.973	0.038
Na ⁺	1528	0.005	0.007	0.000	0.691	0.021
NH ₄ ⁺	1528	0.005	0.005	0.000	0.149	0.006
K ⁺	1528	0.005	0.006	0.000	0.331	0.010

Table 5-12: Nylon filter field blank statistics in µg/filter (extraction volume 25 mL) for the analysis period 3/24/2023 through 3/5/2024 (samples collected 1/1/2024 through 12/31/2024).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl ⁻	1528	0.209	0.265	0.035	9.150	0.402
NO ₃ ⁻	1528	0.165	0.259	0.000	16.538	0.769
SO ₄ ²⁻	1528	0.000	0.184	0.000	24.324	0.955
Na ⁺	1528	0.133	0.174	0.000	17.263	0.514
NH ₄ ⁺	1528	0.122	0.130	0.000	3.722	0.147
K ⁺	1528	0.136	0.143	0.000	8.275	0.237

5.4.5.2 Laboratory Blanks

As described in Section 4.1.3.6 – beginning with the July 1, 2020 sampling period – five nylon laboratory blanks are shipped with each batch of routine filters to the analysis laboratory and are analyzed. A total of 60 nylon laboratory blanks were analyzed during the current reporting period, where each set of laboratory blanks were analyzed either before or straight after the routine analysis of the associated batch. Table 5-13 and Table 5-14 summarize the laboratory blank statistics.

Table 5-13: Nylon filter laboratory blank statistics in µg/mL for the analysis period 3/7/2024 through 3/6/2025 (samples collected 1/1/2024 through 12/31/2024).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl ⁻	60	0.004	0.004	0.000	0.009	0.002
NO ₃ ⁻	60	0.005	0.005	0.000	0.042	0.006
SO ₄ ²⁻	60	0.000	0.001	0.000	0.007	0.001
Na ⁺	60	0.004	0.004	0.002	0.006	0.001
NH ₄ ⁺	60	0.003	0.003	0.001	0.005	0.001
K ⁺	60	0.004	0.004	0.000	0.008	0.002

Table 5-14: Nylon filter laboratory blank statistics in µg/filter (extraction volume 25 mL) for the analysis period 3/7/2024 through 3/6/2025 (samples collected 1/1/2024 through 12/31/2024).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl ⁻	60	0.090	0.092	0.007	0.212	0.050
NO ₃ ⁻	60	0.135	0.135	0.000	1.057	0.158
SO ₄ ²⁻	60	0.000	0.015	0.000	0.165	0.033
Na ⁺	60	0.090	0.093	0.045	0.148	0.024
NH ₄ ⁺	60	0.080	0.077	0.026	0.125	0.028
K ⁺	60	0.109	0.102	0.000	0.201	0.040

5.5 UC Davis X-ray Fluorescence Laboratory

The UC Davis X-ray Fluorescence Laboratory received and analyzed PTFE filters from samples collected January 1, 2024 through December 31, 2024. 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 22, 2024 through April, 23, 2025 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 5-15 for details.

Table 5-15: Sampling months during 2024 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	24-01	2024-03-22 - 2024-04-06	2024-03-22 - 2024-04-05	2024-03-22 - 2024-04-04	2024-03-22 - 2024-05-15	2024-03-22 - 2024-04-06
February	24-02	2024-04-19 - 2024-05-03	2024-04-19 - 2024-05-04	NA	2024-04-20 - 2024-06-18	2024-04-20 - 2024-05-04
March	24-03	2024-05-19 - 2024-06-05	2024-05-19 - 2024-06-05	NA	2024-05-19 - 2024-07-18	2024-05-19 - 2024-06-05
April	24-04	2024-06-25 - 2024-07-07	2024-06-19 - 2024-07-07	NA	2024-06-25 - 2024-08-07	2024-06-19 - 2024-07-07
May	24-05	2024-07-24 - 2024-08-23	2024-07-24 - 2024-08-09	NA	2024-07-24 - 2024-09-18	2024-07-24 - 2024-08-09
June	24-06	2024-08-04 - 2024-09-10	2024-08-23 - 2024-09-11	NA	2024-09-03 - 2024-09-11	2024-08-23 - 2024-10-16
July	24-07	NA	2024-09-12 - 2024-10-03	NA	2024-09-11 - 2024-11-18	2024-09-11 - 2024-10-03
August	24-08	2024-10-25 - 2024-12-13	2024-10-24 - 2024-11-10	NA	2024-10-25 - 2024-11-12	2024-10-25 - 2024-11-11
September	24-09	2024-11-25 - 2024-12-06	2024-11-23 - 2024-12-06	2024-11-23 - 2024-12-06	2024-11-23 - 2025-01-22	2024-11-23 - 2024-12-06
October	24-10	2024-12-19 - 2025-02-12	2024-12-19 - 2025-01-05	NA	2024-12-20 - 2025-02-21	2024-12-19 - 2025-01-05
November	24-11	2025-01-22 - 2025-02-25	2025-01-23 - 2025-02-07	NA	2025-01-23 - 2025-04-02	2025-01-23 - 2025-02-26
December	24-12	2025-02-07 - 2025-03-18	2025-02-25 - 2025-03-27	NA	2025-02-25 - 2025-04-01	2025-02-26 - 2025-04-23
All Months	24-01 to 24-12	2024-03-22 - 2025-03-18	2024-03-22 - 2025-03-27	2024-03-22 - 2024-12-06	2024-03-22 - 2025-04-02	2024-03-22 - 2025-04-23

5.5.1 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 5-16.

Table 5-16: 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	$\leq$ 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 $\pm 10\%$ 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 $\pm 10\%$ 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 UC Davis-made 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. Reference loadings of UC Davis-made ME-RM samples are determined using the mean of five measurements on each of at least three EDXRF instruments (15 or more total measurements) for each element. The standard deviation used for acceptance limits (see Table 5-16) is calculated from these same measurements.

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.

5.5.2 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.

5.5.2.1 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 5-21 and Figure 5-22 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 ten samples from 2024 were reanalyzed for suspected zinc contamination. Of those, two were found to have zinc contamination and the reanalysis result was reported. For the rest the original valid result was reported.

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 5-21: Analysis results from daily PTFE blanks for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-15 for corresponding sampling dates). Elements Na through Zn shown.

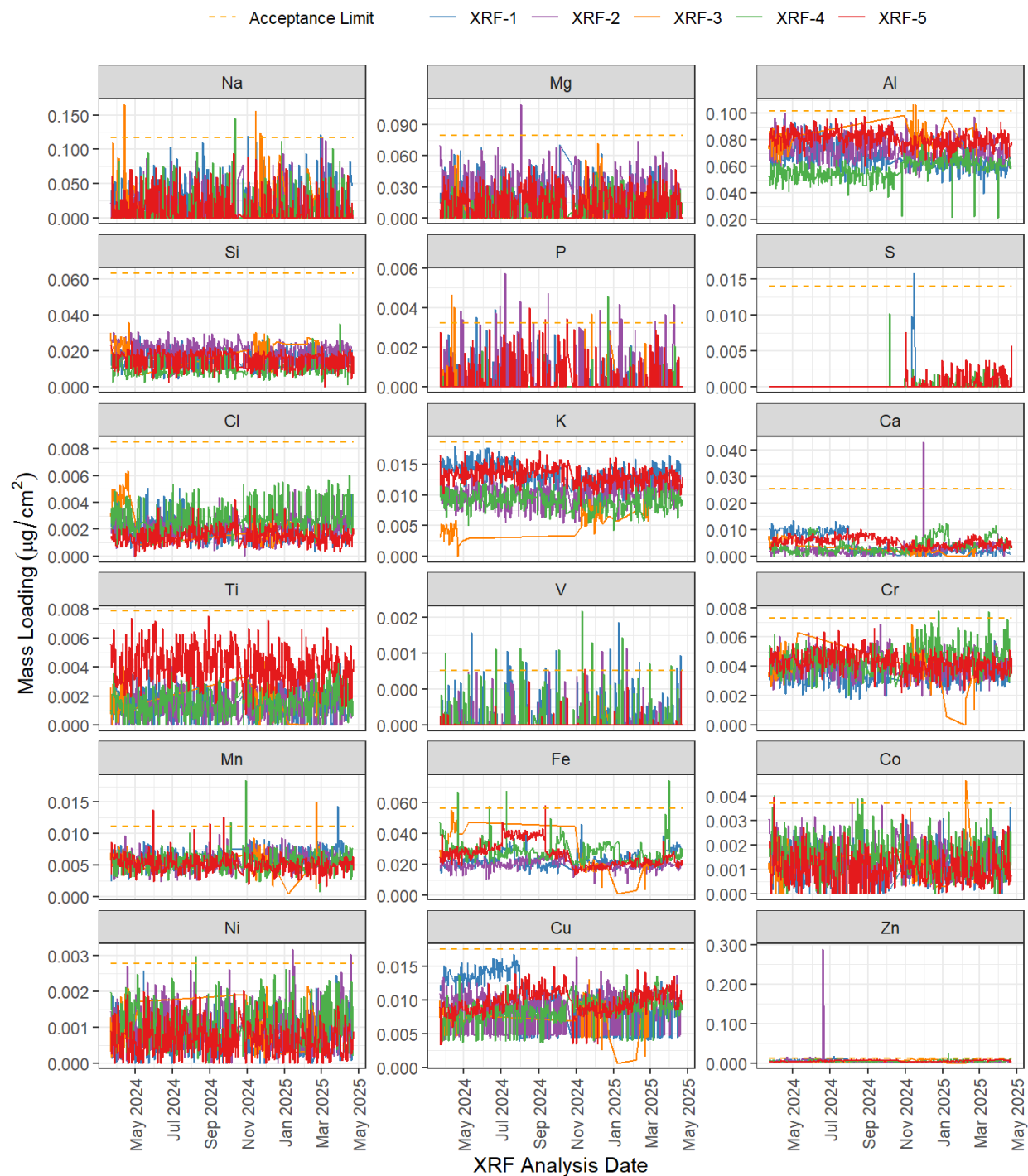
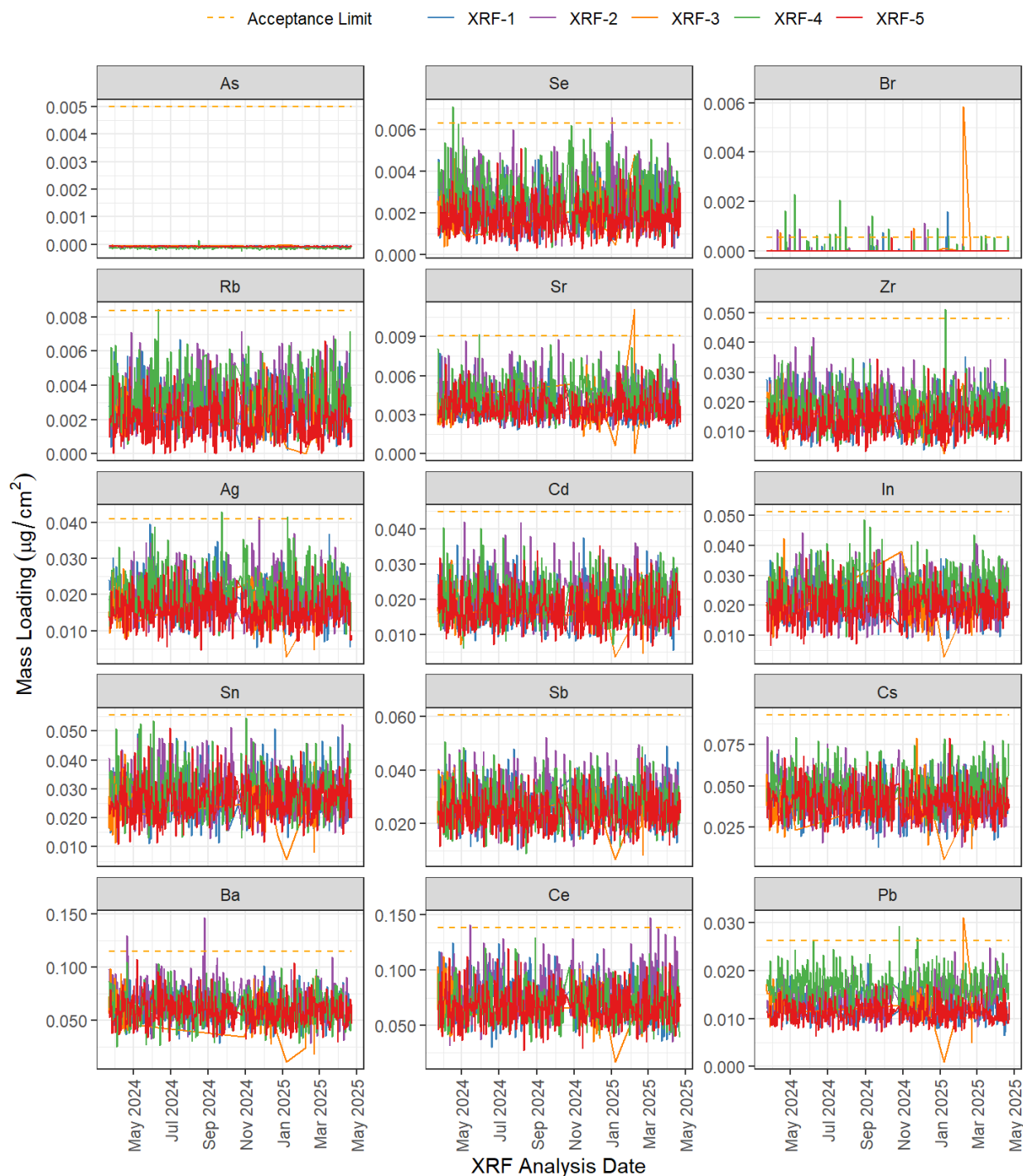


Figure 5-22: Analysis results from daily PTFE blanks for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-15 for corresponding sampling dates). Elements As through Pb shown.



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 5-16. 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 5-17 through 5-21 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 in the tables 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 5-16. The daily QC-ME results for all instruments passed QC criteria for the entire analysis period of this report.

Note that RSD stands for Relative Standard Deviation.

Table 5-17: Descriptive statistics of XRF-1 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 252.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.537	1.295	1.782	0	0	5.3
Si	0.595	0.518	0.739	0	0	2.9
S	12.229	11.219	13.712	0	0	2.0
K	1.747	1.600	1.955	0	0	1.1
Ca	1.683	1.517	1.854	0	0	0.7
Cr	0.739	0.665	0.813	0	0	0.8
Fe	2.075	1.829	2.235	0	0	2.0
Zn	0.289	0.250	0.306	0	0	2.6
As	0.504	0.454	0.555	0	0	1.4
Se	0.373	0.336	0.410	0	0	1.2
Rb	0.173	0.157	0.191	0	0	1.9
Sr	0.168	0.149	0.183	0	0	2.0
Cd	0.226	0.195	0.256	1.6	0	4.8
Sn	0.264	0.225	0.300	0	0	4.9
Pb	0.067	0.048	0.088	0	0	8.7

Table 5-18: Descriptive statistics of XRF-2 results (µg/cm²) of the daily UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 233.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.474	1.253	1.686	0	0	2.1
Si	0.607	0.478	0.724	0	0	3.5
S	11.791	10.714	13.095	0	0	1.2
K	1.691	1.532	1.872	0	0	0.7
Ca	1.626	1.457	1.781	0	0	1.0
Cr	0.702	0.635	0.776	0	0	0.9
Fe	1.987	1.740	2.127	0	0	0.9
Zn	0.281	0.241	0.294	0.4	0	1.4
As	0.484	0.434	0.530	0	0	1.4
Se	0.358	0.322	0.394	0	0	1.5
Rb	0.167	0.150	0.184	0	0	2.3
Sr	0.162	0.145	0.177	0	0	2.0
Cd	0.220	0.182	0.245	0.4	0	4.9
Sn	0.257	0.214	0.288	0	0	4.7
Pb	0.063	0.043	0.083	0.9	0	10.9

Table 5-19: Descriptive statistics of XRF-3 results (µg/cm²) of the daily UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 28.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.351	1.060	1.558	0	0	4.7
Si	0.625	0.470	0.732	0	0	2.9
S	11.051	10.007	12.230	0	0	1.4
K	1.583	1.447	1.768	0	0	0.7
Ca	1.577	1.427	1.744	3.6	0	3.2
Cr	0.673	0.611	0.747	3.6	0	3.3
Fe	1.929	1.700	2.077	0	0	2.5
Zn	0.259	0.234	0.286	0	0	2.5
As	0.465	0.425	0.519	3.6	0	2.7
Se	0.322	0.297	0.363	3.6	0	3.4
Rb	0.162	0.148	0.180	3.6	0	3.2
Sr	0.156	0.142	0.173	0	0	2.4
Cd	0.213	0.181	0.246	0	0	5.4
Sn	0.246	0.214	0.284	0	0	4.0
Pb	0.066	0.043	0.080	0	0	7.7

Table 5-20: Descriptive statistics of XRF-4 results (µg/cm²) of the daily UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 362.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.462	1.381	1.811	3.0	0	2.3
Si	1.584	1.344	1.768	0	0	2.3
S	11.476	10.591	12.944	0	0	1.1
K	1.752	1.598	1.953	0	0	1.0
Ca	1.692	1.514	1.850	0	0	0.9
Cr	0.518	0.463	0.565	0	0	1.3
Fe	1.981	1.731	2.116	0	0	1.5
Zn	0.218	0.186	0.227	1.9	0	2.0
As	0.614	0.540	0.661	0	0	1.5
Se	0.278	0.255	0.312	0	0	2.4
Rb	0.188	0.169	0.207	0	0	2.0
Sr	0.191	0.170	0.208	0	0	1.9
Cd	0.288	0.252	0.320	0	0	3.2
Sn	0.179	0.146	0.203	0.6	0	18.9
Pb	0.157	0.132	0.176	0	0	6.0

Table 5-21: Descriptive statistics of XRF-5 results (µg/cm²) of the daily UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 291.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.442	1.116	1.655	0	0	2.3
Si	2.303	2.066	2.626	0	0	1.8
S	8.384	7.449	9.104	0	0	0.9
K	1.434	1.273	1.556	0	0	0.6
Ca	1.247	1.119	1.368	0	0	1.3
Cr	0.100	0.088	0.108	0	0	2.0
Fe	1.359	1.188	1.453	0.3	0	1.2
Zn	0.104	0.089	0.108	3.8	0	2.3
As	0.583	0.522	0.638	0	0	0.9
Se	0.104	0.092	0.112	0	0	2.3
Rb	0.163	0.147	0.180	0	0	1.8
Sr	0.177	0.159	0.194	0	0	1.8
Cd	0.311	0.279	0.341	0	0	3.4
Sn	0.024	-0.001	0.049	0.3	0	28.7
Pb	0.237	0.214	0.262	0	0	2.8

5.5.2.2 Results of Weekly QC Checks

Weekly QC checks include analysis of a UC Davis produced ME-RM (different than the daily ME-RM). Weekly results are compared to acceptance criteria of +/- 10% of the reference values

for the relevant elements, as listed in Table 5-16. 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 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 5-16.

Tables 5-22 through 5-26 show the EDXRF statistics of the weekly UC Davis ME-RM through 4/23/2025.

Table 5-22: Descriptive statistics of XRF-1 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 57.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.533	1.171	1.745	0	0	3.8
Si	2.453	2.160	2.659	0	0	1.5
S	8.799	7.877	9.627	0	0	1.1
K	1.508	1.344	1.642	0	0	0.5
Ca	1.362	1.188	1.452	0	0	1.2
Cr	0.106	0.094	0.115	0	0	2.1
Fe	1.427	1.256	1.535	0	0	1.6
Zn	0.108	0.093	0.114	1.8	0	2.5
As	0.621	0.557	0.681	0	0	1.1
Se	0.111	0.097	0.119	0	0	2.2
Rb	0.173	0.156	0.190	0	0	1.8
Sr	0.188	0.169	0.207	0	0	1.6
Cd	0.327	0.293	0.365	0	0	3.4
Pb	0.253	0.228	0.280	0	0	3.4

Table 5-23: Descriptive statistics of XRF-2 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 58.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.531	1.171	1.745	0	0	2.3
Si	2.482	2.160	2.659	0	0	2.6
S	8.906	7.877	9.627	0	0	1.1
K	1.514	1.344	1.642	0	0	0.8
Ca	1.371	1.188	1.452	0	0	1.1
Cr	0.105	0.094	0.115	0	0	2.1
Fe	1.437	1.256	1.535	0	0	0.8
Zn	0.108	0.093	0.114	0	0	1.9
As	0.630	0.557	0.681	0	0	1.4
Se	0.112	0.097	0.119	0	0	2.6
Rb	0.176	0.156	0.190	0	0	2.2
Sr	0.189	0.169	0.207	0	0	1.8
Cd	0.330	0.293	0.365	0	0	3.9
Pb	0.254	0.228	0.280	0	0	3.0

Table 5-24: Descriptive statistics of XRF-3 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 15.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.551	1.171	1.745	0	0	3.0
Si	2.529	2.160	2.659	0	0	1.3
S	8.824	7.877	9.627	0	0	1.3
K	1.503	1.344	1.642	0	0	0.5
Ca	1.374	1.188	1.452	0	0	2.0
Cr	0.104	0.094	0.115	0	0	1.8
Fe	1.399	1.256	1.535	0	0	2.0
Zn	0.107	0.093	0.114	0	0	2.5
As	0.619	0.557	0.681	0	0	3.2
Se	0.110	0.097	0.119	0	0	2.1
Rb	0.173	0.156	0.190	0	0	3.4
Sr	0.184	0.169	0.207	6.7	0	3.5
Cd	0.327	0.293	0.365	0	0	3.4
Pb	0.255	0.228	0.280	0	0	3.6

Table 5-25: Descriptive statistics of XRF-4 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 59.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.378	1.171	1.745	0	0	4.3
Si	2.351	2.160	2.659	0	0	2.2
S	8.778	7.877	9.627	0	0	1.6
K	1.511	1.344	1.642	0	0	1.5
Ca	1.374	1.188	1.452	0	0	1.9
Cr	0.107	0.094	0.115	0	0	2.3
Fe	1.427	1.256	1.535	0	0	1.7
Zn	0.108	0.093	0.114	0	0	2.4
As	0.641	0.557	0.681	0	0	1.6
Se	0.112	0.097	0.119	0	0	2.6
Rb	0.175	0.156	0.190	0	0	1.9
Sr	0.190	0.169	0.207	0	0	1.8
Cd	0.331	0.293	0.365	0	0	4.1
Pb	0.256	0.228	0.280	0	0	2.8

Table 5-26: Descriptive statistics of XRF-5 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-14 for corresponding sampling dates), N = 60.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.518	1.171	1.745	0	0	2.9
Si	2.372	2.160	2.659	0	0	1.8
S	8.827	7.877	9.627	0	0	1.3
K	1.516	1.344	1.642	0	0	0.9
Ca	1.351	1.188	1.452	0	0	1.6
Cr	0.106	0.094	0.115	0	0	1.6
Fe	1.424	1.256	1.535	0	0	1.3
Zn	0.107	0.093	0.114	0	0	1.7
As	0.625	0.557	0.681	0	0	1.1
Se	0.111	0.097	0.119	0	0	1.9
Rb	0.174	0.156	0.190	0	0	1.6
Sr	0.189	0.169	0.207	0	0	1.6
Cd	0.332	0.293	0.365	0	0	3.0
Pb	0.251	0.228	0.280	0	0	2.5

5.5.2.3 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. The reference value for the weekly UC Davis-made ME-RM is calculated

as detailed in section 5.4.1, the mean of five measurements each from at least three EDXRF instruments:

$$Ref_i = \frac{1}{N} (\sum_5^1 XRF1_i + \sum_5^1 XRF2_i + \sum_5^1 XRF3_i + \dots),$$

where $XRF1_i$, $XRF2_i$, $XRF3_i$ are the mass loadings of the i^{th} element measured by at least three instruments, “...” indicates up to all five instruments can be used (all operational instruments, at the time of determination, are used), and N is the total number of results of all instruments used.

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

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

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

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

The precision is estimated by,

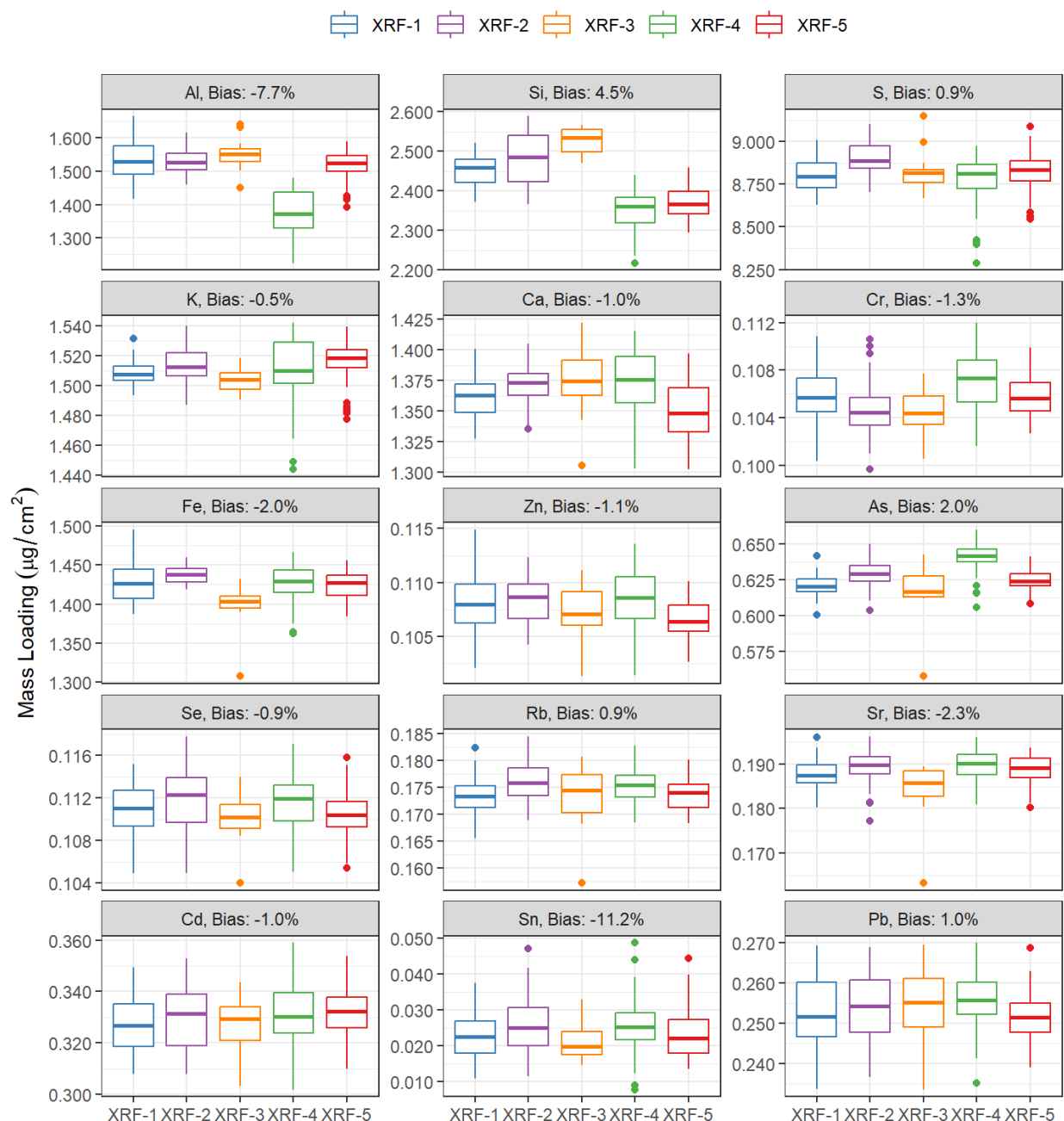
$$Precision_i = \sqrt{\frac{n \sum_{j=1}^n d_{i,j}^2 - (\sum_{j=1}^n d_{i,j})^2}{n(n-1)}}$$

The results from this analysis, for the elements listed for the weekly ME-RM in Table 5-16, averaged over the UC Davis ME-RM samples used during the analysis period, are presented in Table 5-27. 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 5-23 for the weekly ME-RM sample. In that figure, bias shown in plot labels is the maximum instrument bias as defined above. 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 $1.5 \times IQR$ (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond $1.5 \times IQR$.

Table 5-27: Precision and bias of all EDXRF instruments from the weekly UC Davis ME-RM calculated for the analysis period 3/22/2024 through 4/23/2025 (see Table 5-15 for corresponding sampling dates). Only elements listed in Table 5-16 for the weekly UC ME-RM are evaluated.

Element	XRF-1 Bias %	XRF-2 Bias %	XRF-3 Bias %	XRF-4 Bias %	XRF-5 Bias %	XRF-1 Prec. %	XRF-2 Prec. %	XRF-3 Prec. %	XRF-4 Prec. %	XRF-5 Prec. %
Al	2.7	2.5	3.9	-7.7	1.7	3.9	2.4	3.2	4.0	3.0
Si	1.4	2.5	4.5	-2.9	-2.0	1.5	2.7	1.3	2.2	1.7
S	-0.3	0.9	0.0	-0.6	0.0	1.1	1.1	1.3	1.6	1.3
K	-0.2	0.1	-0.5	-0.1	0.3	0.5	0.8	0.5	1.5	0.9
Ca	-0.2	0.4	0.7	0.7	-1.0	1.2	1.1	2.0	1.9	1.5
Cr	0.0	-1.0	-1.3	1.2	0.0	2.1	2.0	1.8	2.3	1.6
Fe	0.0	0.7	-2.0	0.0	-0.2	1.6	0.8	2.0	1.7	1.3
Zn	0.3	0.5	-0.5	0.5	-1.1	2.5	1.9	2.5	2.4	1.6
As	-1.2	0.2	-1.6	2.0	-0.6	1.1	1.4	3.1	1.6	1.1
Se	-0.3	0.7	-0.9	0.4	-0.6	2.2	2.6	2.1	2.7	1.9
Rb	-0.7	0.9	-0.7	0.5	-0.5	1.8	2.2	3.4	1.9	1.6
Sr	-0.5	0.3	-2.3	0.5	0.2	1.6	1.9	3.5	1.8	1.6
Cd	-0.8	0.0	-1.0	0.5	0.5	3.4	3.9	3.4	4.1	3.0
Sn	-5.4	7.8	-11.2	5.6	-5.1	26.0	32.0	23.2	32.6	27.1
Pb	-0.3	0.1	0.5	1.0	-0.9	3.4	3.0	3.6	2.8	2.5

Figure 5-23: Instrumental comparison using the weekly UC Davis ME-RM, QC|ME-47-W|MTL5089.



5.5.2.4 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 reference values and uncertainty for the samples of the reanalysis set are determined as the mean and standard deviation respectively of five initial measurements each from all five instruments taken at the time the ME-RMs were produced. 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 5-24 shows the mean z-score plots during the analysis period. No issues were observed in the z-scores for this analysis period.

Figure 5-24: Inter-instrument comparison by z-score of monthly reanalysis sample set. The orange dashed lines indicate the mean z-score acceptance criteria of ± 1 .



5.5.2.5 Calibration Verification with NIST SRM 2783

The EDXRF measurement of NIST SRM 2783 certified/reference mass loadings is monitored monthly for selected elements with loadings at least three times higher than the EDXRF analytical method detection limits. It should be noted that the NIST certification of elemental concentrations expired 9/1/2021. NIST SRM 2783 is out of stock and NIST has not indicated they will recertify the SRM. No other air particulate on filter media SRM exists, therefore, UC Davis continues to analyze SRM 2783. The error, calculated as the difference between the measured and certified/reference mass loading relative to the certified/reference mass loading, is plotted for each instrument and provides a measure of instrument stability and accuracy. The error is compared to element specific acceptance criteria calculated as $\pm$ the root-mean-squared-

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

The NIST SRM 2783 results from this analysis period (3/22/2024 through 4/23/2025) are shown in Figure 5-25, while Table 5-28 summarizes the calibrations performed during this analysis period. All EDXRF instruments underwent routine annual calibrations in October 2023. XRF-1 had a recalibration due to a shift in X-ray intensities in December 2023. XRF-1 then underwent another recalibration after the X-ray intensities shifted again and the cause was found to be debris on the detector window which was removed, see investigation report, IR-0020. All EDXRF instruments underwent another annual calibration in October 2024, except XRF-3, which was calibrated in November 2024 after an X-ray tube replacement.

In the past Zn exceedances have been a recurring issue due to sporadic Zn contamination from the instrument as discussed previously. 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 5-25: Error of each EDXRF instrument from the NIST SRM 2783 standard run monthly for the analysis period 3/22/2024 through 4/23/2025.

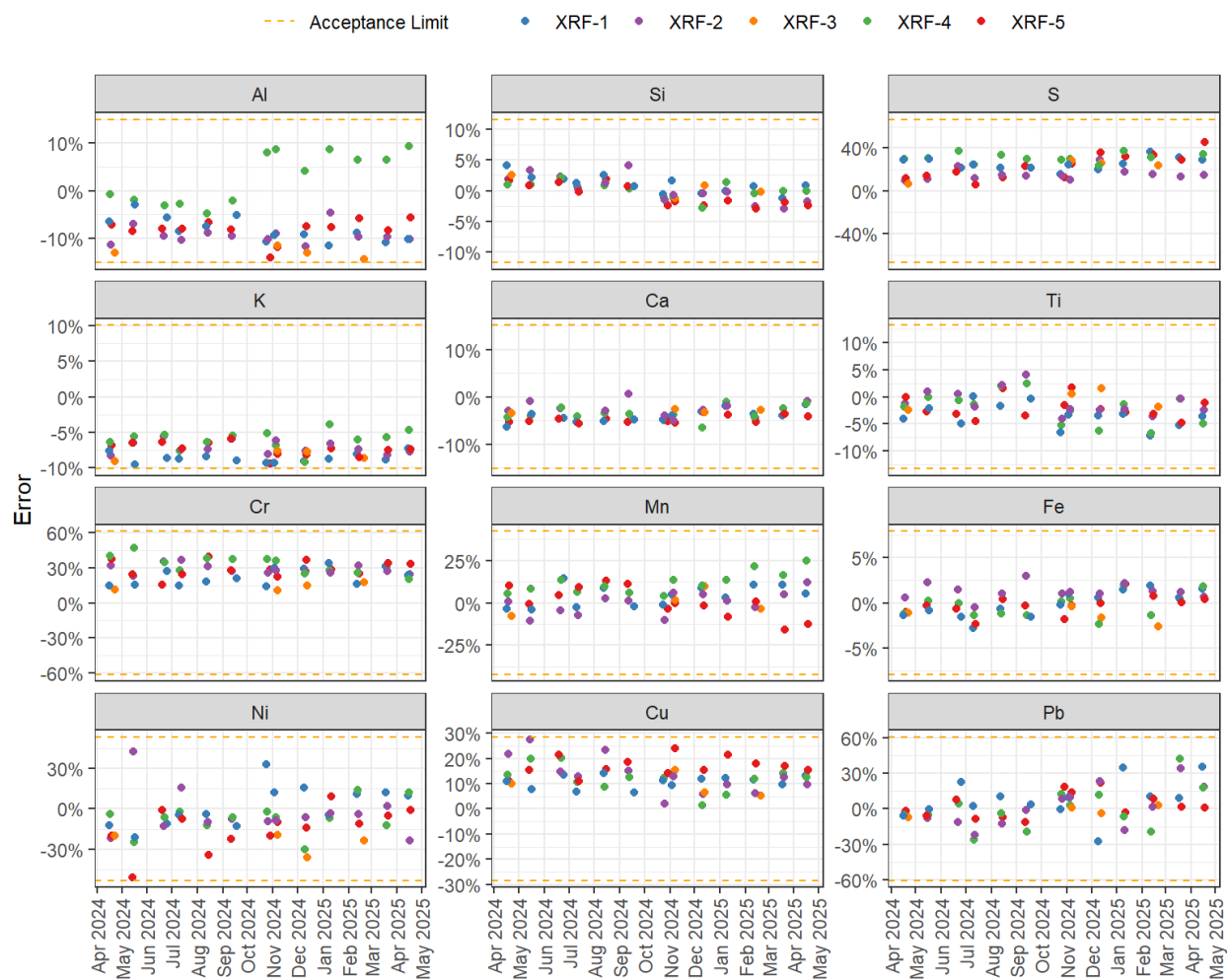


Table 5-28: Dates for calibrations performed on each EDXRF instrument during this analysis period (3/22/2024 through 4/23/2025).

EDXRF Instrument	Calibration Date	Reason for Calibration	Range of Sample Dates Analyzed
XRF-2	2023-10-24	Annual Calibration	2024-01-01 - 2024-07-29
XRF-4	2023-10-24	Annual Calibration	2024-01-01 - 2024-07-29
XRF-3	2023-10-25	Annual Calibration	2024-01-01 - 2024-01-31
XRF-5	2023-10-25	Annual Calibration	2024-01-01 - 2024-07-29
XRF-1	2023-10-26	Annual Calibration	None
XRF-1	2023-12-07	Recalibration due to intensity shift	None
XRF-1	2023-12-21	Recalibration after cleaning detector window	2024-01-01 - 2024-06-29
XRF-1	2024-10-23	Annual Calibration	2024-08-01 - 2024-12-29
XRF-4	2024-10-23	Annual Calibration	2024-07-29 - 2024-12-29
XRF-2	2024-10-24	Annual Calibration	2024-08-01 - 2024-12-29
XRF-5	2024-10-25	Annual Calibration	2024-08-01 - 2024-12-29
XRF-3	2024-11-07	Annual Calibration	2024-09-03 - 2024-09-30

5.5.3 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 4.1.2.3 and Section 7.5, respectively.

5.5.4 Audits, Performance Evaluations, Training, and Accreditations

5.5.4.1 System Audits

No system audits were performed during this analysis period.

5.5.4.2 Performance Evaluations

UC Davis participated in the 2024 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/2025-01/2024_megape_report_final_508.pdf.

5.5.4.3 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.

5.5.4.4 Accreditations

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

5.5.5 Summary of Filter Blanks

5.5.5.1 Field Blanks

Over the sampling period (January 1, 2024 through December 31, 2024) there were 1,601 valid PTFE filter field blanks. Table 5-29 summarizes the field blank statistics.

Table 5-29: PTFE filter field blank statistics for the 2024 sampling analysis period 3/22/2024 through 3/14/2025 (samples collected 1/1/2024 through 12/31/2024).

Species	Count	Median (µg/cm ²)	Average (µg/cm ²)	Min (µg/cm ²)	Max (µg/cm ²)	St. Dev. (µg/cm ²)
Ag	1601	0.019	0.019	0.006	0.042	0.006
Al	1601	0.081	0.082	0.043	0.275	0.021
As	1601	0.000	0.000	0.000	0.000	0.000
Ba	1601	0.063	0.064	0.024	0.115	0.015
Br	1601	0.000	0.000	0.000	0.006	0.000
Ca	1601	0.003	0.006	0.000	0.246	0.013
Cd	1601	0.019	0.020	0.006	0.043	0.006
Ce	1601	0.073	0.075	0.028	0.163	0.018
Cl	1601	0.002	0.003	0.000	0.124	0.005
Co	1601	0.001	0.001	0.000	0.005	0.001
Cr	1601	0.005	0.007	0.002	0.209	0.012
Cs	1601	0.043	0.044	0.014	0.089	0.012
Cu	1601	0.009	0.009	0.003	0.044	0.003
Fe	1601	0.021	0.031	0.010	0.661	0.043
In	1601	0.022	0.022	0.008	0.049	0.007
K	1601	0.013	0.013	0.001	0.289	0.010
Mg	1601	0.011	0.015	0.000	0.131	0.018
Mn	1601	0.006	0.006	0.002	0.019	0.002
Na	1601	0.000	0.018	-0.006	0.470	0.030
Ni	1601	0.001	0.002	0.000	0.067	0.004
P	1601	0.000	0.000	0.000	0.017	0.001
Pb	1601	0.013	0.014	0.006	0.027	0.003
Rb	1601	0.003	0.003	0.000	0.008	0.001
S	1601	0.000	0.002	0.000	0.389	0.021
Sb	1601	0.027	0.027	0.007	0.059	0.007
Se	1601	0.002	0.002	0.000	0.007	0.001
Si	1601	0.019	0.020	0.001	0.506	0.019
Sn	1601	0.028	0.028	0.011	0.056	0.008
Sr	1601	0.004	0.004	0.002	0.010	0.001
Ti	1601	0.002	0.002	0.000	0.023	0.002
V	1601	0.000	0.000	0.000	0.002	0.000
Zn	1601	0.003	0.003	0.000	0.031	0.002
Zr	1601	0.017	0.017	0.003	0.042	0.006

5.5.5.2 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 5-30 summarizes the laboratory blank statistics.

Table 5-30: PTFE filter laboratory blank statistics for the 2024 sampling analysis period 4/5/2024 through 3/13/2025 (samples collected 1/1/2024 through 12/31/2024).

Species	Count	Median ($\mu\text{g}/\text{cm}^2$)	Average ($\mu\text{g}/\text{cm}^2$)	Min ($\mu\text{g}/\text{cm}^2$)	Max ($\mu\text{g}/\text{cm}^2$)	St. Dev. ($\mu\text{g}/\text{cm}^2$)
Ag	60	0.020	0.019	0.007	0.030	0.005
Al	60	0.075	0.073	0.021	0.105	0.014
As	60	0.000	0.000	0.000	0.000	0.000
Ba	60	0.064	0.065	0.032	0.101	0.015
Br	60	0.000	0.000	0.000	0.000	0.000
Ca	60	0.003	0.003	0.000	0.008	0.002
Cd	60	0.020	0.020	0.010	0.039	0.006
Ce	60	0.073	0.075	0.044	0.130	0.019
Cl	60	0.002	0.002	0.000	0.005	0.001
Co	60	0.001	0.001	0.000	0.004	0.001
Cr	60	0.004	0.004	0.003	0.007	0.001
Cs	60	0.047	0.047	0.020	0.089	0.013
Cu	60	0.009	0.009	0.003	0.013	0.002
Fe	60	0.019	0.019	0.010	0.028	0.003
In	60	0.022	0.024	0.009	0.043	0.007
K	60	0.013	0.013	0.006	0.020	0.003
Mg	60	0.006	0.012	0.000	0.044	0.014
Mn	60	0.006	0.006	0.003	0.008	0.001
Na	60	0.000	0.015	0.000	0.119	0.026
Ni	60	0.001	0.001	0.000	0.002	0.001
P	60	0.000	0.000	0.000	0.003	0.001
Pb	60	0.013	0.014	0.008	0.021	0.004
Rb	60	0.003	0.003	0.000	0.006	0.002
S	60	0.000	0.000	0.000	0.001	0.000
Sb	60	0.026	0.027	0.012	0.048	0.007
Se	60	0.002	0.002	0.001	0.005	0.001
Si	60	0.017	0.015	0.004	0.031	0.006
Sn	60	0.030	0.029	0.009	0.046	0.009
Sr	60	0.004	0.004	0.002	0.006	0.001
Ti	60	0.002	0.003	0.000	0.007	0.002
V	60	0.000	0.000	0.000	0.001	0.000
Zn	60	0.003	0.003	0.001	0.007	0.001
Zr	60	0.017	0.017	0.004	0.030	0.006

5.6 UC Davis Thermal Optical Analysis Laboratory

The UC Davis Thermal Optical Analysis (TOA) Laboratory received and analyzed quartz filters from batches 24-01 through 24-12, covering the field sampling period beginning from January 1, 2024 through December 31, 2024. Analyses of these samples were performed March 7, 2024

through April 17, 2025. 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 5-31: Sampling months in 2024 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 (2024)	Analysis Batch #	TOA Analysis Dates
January	24-01	03/07/2024 – 04/02/2024
February	24-02	04/03/2024 – 04/24/2024
March	24-03	05/08/2024 – 05/31/2024
April	24-04	06/12/2024 – 07/09/2024
May	24-05	07/10/2024 – 08/05/2024
June	24-06	08/14/2024 – 09/12/2024
July	24-07	09/13/2024 – 11/14/2024
August	24-08	10/14/2024 – 12/17/2024
September	24-09	11/12/2024 – 12/11/2024
October	24-10	12/11/2024 – 01/16/2025
November	24-11	01/16/2025 – 03/25/2025
December	24-12	02/11/2025 – 04/17/2025
All months	24-01 to 24-12	03/07/2024 – 04/17/2025

5.6.1 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 CH₄/He mixture gas cylinder is replaced or a consistent one-side bias is observed with the daily single-point sucrose standard check, whichever comes first). Maintenance is performed as needed by trained laboratory staff. Quality control procedures are described in *UCD CSN SOP #402* and are summarized in Table 5-32.

Table 5-32: 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	$TC \leq 1.0 \mu\text{g C/cm}^2$	Repeat analysis. If same result, check filter lot for possible contamination and perform pre-firing
Instrument Blank Check	Beginning of analysis day	TC between -0.3 and $0.3 \mu\text{g C/cm}^2$	Repeat analysis. If same result, check instrument and gas lines for possible contamination
Single-point Sucrose Standard Check	Beginning of analysis day	TC within $\pm 7\%$ of the calculated value	Repeat analysis. If same result, run a different sucrose solution to determine if the problem is with the solution or instrument. If former, make new sucrose solution. If latter, perform multi-point calibration to determine new calibration constant
Calibration Peak Area Check	Every analysis	Within $\pm 10\%$ of the daily average value for a specific instrument	Void analysis result; Repeat analysis with second filter punch
Laser Performance Check	Beginning of analysis day	Laser Transmittance signal for Instrument blank > 5000	First check laser-sample-detector alignment and/or examine top oven window for frosting or debris; replace laser source when necessary
Network Sample Replicates	Every 20 th network sample analysis	Within $\pm 10\%$ RPD when $TC > 10 \mu\text{g C/cm}^2$ within $\pm 20\%$ RPD when $ECR > 2.5 \mu\text{g C/cm}^2$ or Within $\pm 1 \mu\text{g/cm}^2$ when $TC \leq 10 \mu\text{g C/cm}^2$ Within $\pm 0.5 \mu\text{g/cm}^2$ when $ECR \leq 2.5 \mu\text{g C/cm}^2$.	Investigate instrument and sample anomalies. Analyze the third punch on a different analyzer
Inter-instrument Comparison Check	Weekly	Within $\pm 10\%$ RPD* when $TC > 10 \mu\text{g C/cm}^2$ Within $\pm 20\%$ RPD when $ECR > 2.5 \mu\text{g C/cm}^2$ or Within $\pm 1 \mu\text{g/cm}^2$ when $TC \leq 10 \mu\text{g C/cm}^2$ Within $\pm 0.5 \mu\text{g/cm}^2$ when $ECR \leq 2.5 \mu\text{g C/cm}^2$ *RPD for each analyzer is calculated against the average measurement from all analyzers	Analyze a second punch from the same sample on the failed analyzer. If same result, analyzer taken offline and investigated for the root cause of the failure
Multi-point Sucrose Standard Check	Every six months or after major instrument repair or change of calibration gas cylinder	NA ^a	Calculate new calibration constant based on calibration slope and update in the IMPROVE_A protocol parameter file
Temperature Calibrations	Every six months or after major instrument repair	NA	Change the temperature offset values in the IMPROVE_A protocol parameter file accordingly

^a NA: Not Applicable.

5.6.2 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. Thermogram review had not been performed on every sample analysis, as per the SOP, in the 2023 report. Beginning with batch 23-11, DV-0017 was initiated to capture the actual procedure which instead performed thermogram checks on sample analyses that failed other QC or validation checks. During the 2024 sampling year software automations were put into place to monitor sample thermograms and report any anomalies. Anomalous thermograms are reviewed by trained senior lab staff or the Laboratory Manager weekly and corrective action is taken as needed. More details about this change in thermogram review are discussed in Section 4.2.5 (Corrective Actions). Samples impacted by failure to meet QC acceptance criteria outlined in Table 5-32 are reanalyzed.

5.6.2.1 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 5-33 lists the number of blanks analyzed during the report period and their areal density statistics.

Table 5-33: Statistics of daily quartz filter laboratory blank and instrument blank total carbon (TC) analyses on all carbon analyzers for the analysis period 03/07/2024 through 04/17/2025 (samples collected 1/1/2024 through 12/31/2024).

Blank Type	Count	Median ($\mu\text{g}/\text{cm}^2$)	Average ($\mu\text{g}/\text{cm}^2$)	Min ($\mu\text{g}/\text{cm}^2$)	Max ($\mu\text{g}/\text{cm}^2$)	St.Dev. ($\mu\text{g}/\text{cm}^2$)	# Exceedance
Laboratory Blank	1394	0.23	0.28	-1.39	4.81	0.34	38
Laboratory Blank - R*	51	0.07	0.14	-0.44	1.11	0.31	1
Instrument Blank	1387	-0.06	-0.06	-0.59	0.35	0.11	17
Instrument Blank - R*	28	-0.15	-0.15	-0.52	0.10	0.14	3

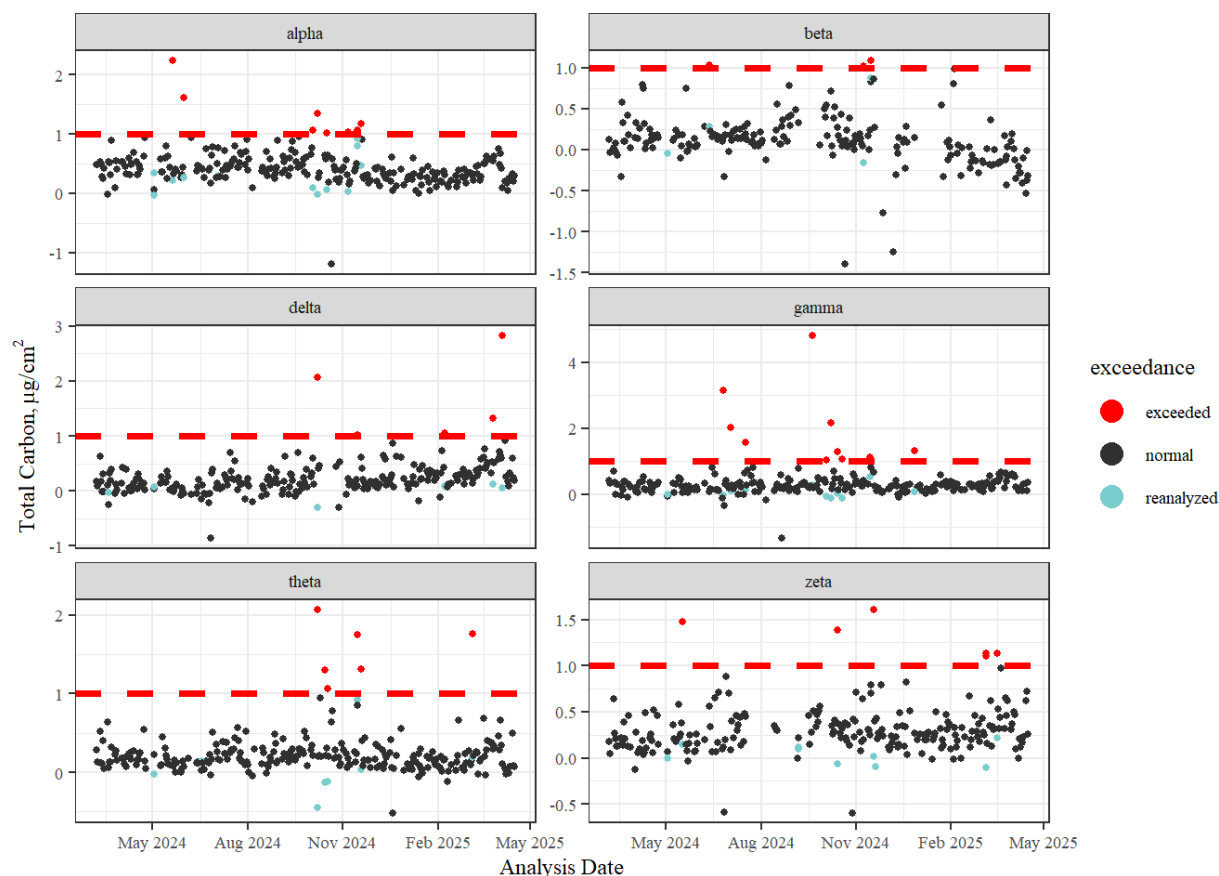
*Laboratory/Instrument Blank - R: Repeated laboratory/instrument blank when original analysis fails the acceptance criteria.

For laboratory blanks (QB), if the TC areal density exceeds $1.0 \mu\text{g C}/\text{cm}^2$, a second punch is taken from the same blank filter lot and 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, the issue will be investigated and no samples will be analyzed until the issue is resolved. 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 H₂ gas cylinder

change. Figure 5-26 and Figure 5-27 show the results of daily laboratory and instrument blanks, respectively, analyzed by each instrument during this reporting period.

Figure 5-26 shows the results of daily analyses of laboratory blanks by each instrument. In most cases, the repeated QB analysis is satisfactory. In the figure, the red dashed horizontal line indicates the acceptance criteria of $1.0 \mu\text{g C/cm}^2$ for total carbon areal density. For cases when the acceptance criteria were exceeded (red points), a repeat analysis (blue points) was performed.

Figure 5-26: Total carbon results of daily quartz filter laboratory blanks from each analyzer for the analysis period 03/07/2024 through 04/17/2025 (samples collected 1/1/2024 through 12/31/2024).

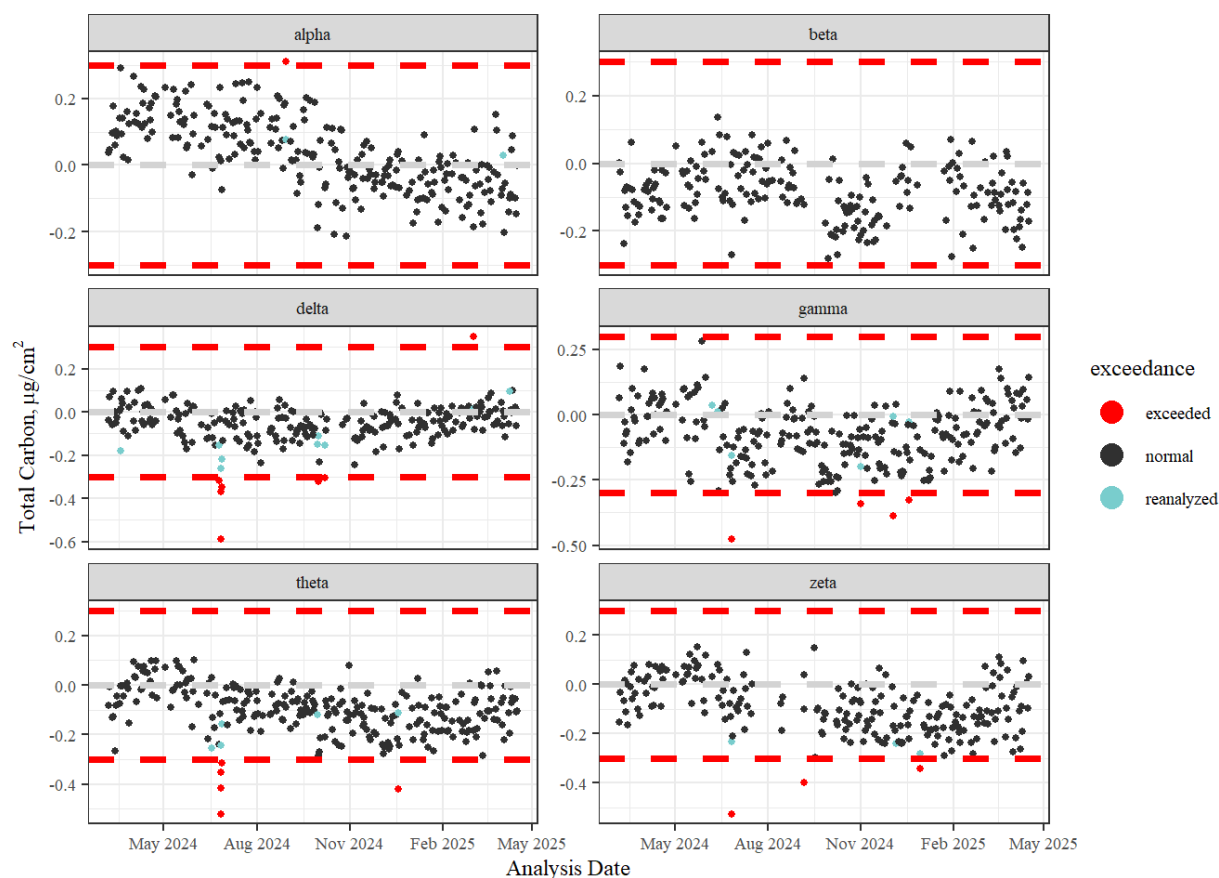


Instrument blank (IB) analysis is performed following the laboratory blank analysis by reusing the sample punch. The instrument blank acceptance criteria is TC within $\pm 0.3 \mu\text{g C/cm}^2$. When the instrument blank fails to meet the QC criteria (red points in Figure 5-27), analysis is repeated (blue points in Figure 5-27). If the Instrument Blank-R analysis still exceeds the acceptance limit (three cases during the report period; Table 5-33), the operator checks the instrument and gas line for possible contamination and examines the stability of the FID baseline from thermograms. The analysis results from instrument (and laboratory) blanks must be acceptable before continuing with analysis of the sucrose standard.

Figure 5-27 shows the results of daily analyses of instrument blanks by each instrument. Horizontal dash lines in red color indicate the acceptance criteria of $\pm 0.3 \mu\text{g C/cm}^2$ for total carbon areal density. For cases when the acceptance criteria were exceeded (red points), a repeated analysis was performed (blue points). Multiple instances of reanalysis of the IB are

indicated in the Figure between June 25 to 27, 2024 on four of the instruments due to a new HeOx gas cylinder change. The new gas cylinder was changed to one from a different manufacturer lot which resolved this issue. More details can be found in section 4.2.5 and investigation report, IR-0018.

Figure 5-27: Results of daily instrument blanks from each analyzer for the analysis period 03/07/2024 through 04/17/2025 (samples collected 1/1/2024 through 12/31/2024).



5.6.2.2 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 5-34 summarizes the concentrations of all sucrose standard solutions generated for calibrating the carbon analyzers on a semi-annual basis (or as needed). Sucrose calibration standards cover a wide range of the TC levels from 2.11 $\mu\text{g C}/\text{cm}^2$ through 210.5 $\mu\text{g C}/\text{cm}^2$, 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 5-34: Sucrose solution standard concentrations in µgC/cm² at 10 µL.

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*	varies (10 – 50)

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

Upon completion of the Sucrose|15 analysis, the measured TC is compared against the reference value (i.e. calculated TC) provided in Table 5-34. 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, an investigation is opened to determine if there is an issue with the instrument. Table 5-35 summarizes the statistics of the daily sucrose check. There were 68 exceedances out of the 1484 sucrose analyses during the report period. All repeat-analyses of the sucrose solution showed acceptable results (Figure 5-28).

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

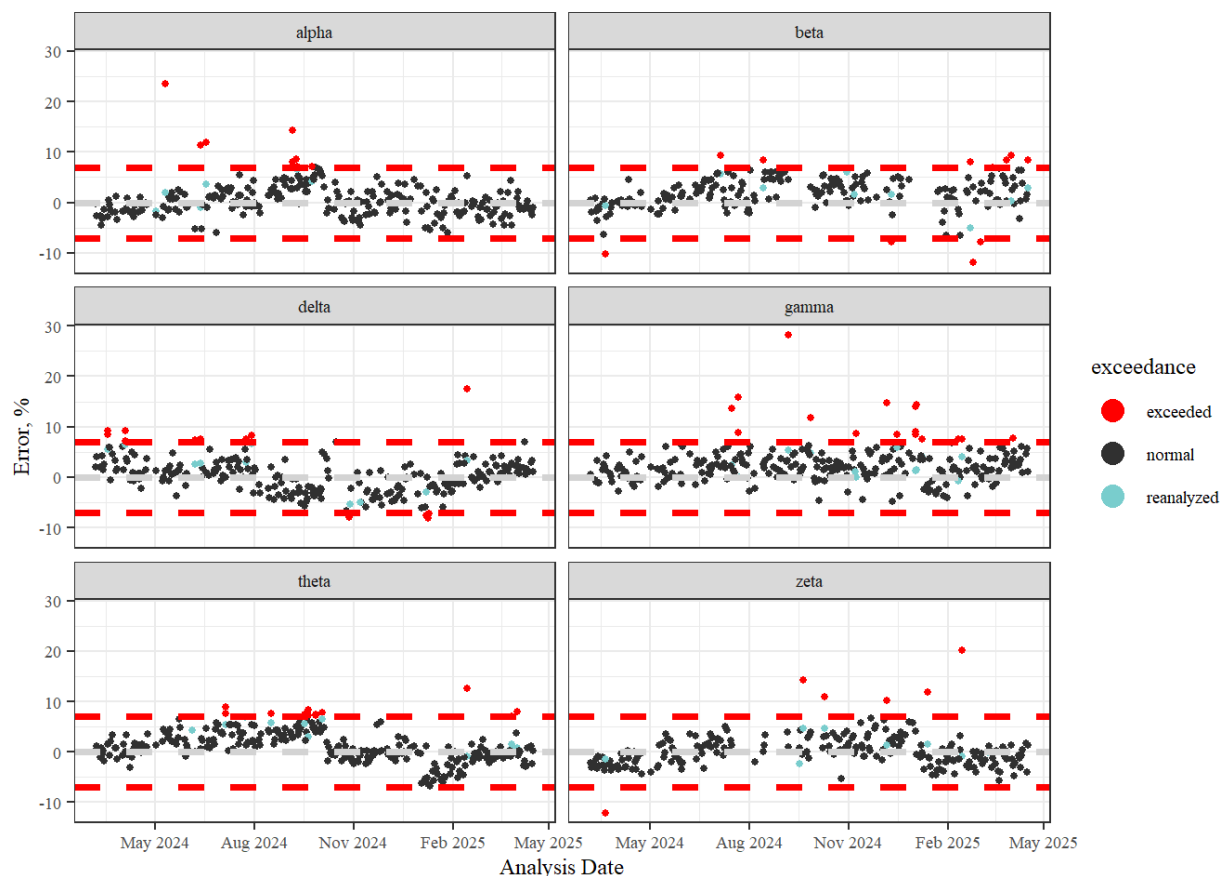
(Eq. 5-1)

Table 5-35: Statistics of daily single-point sucrose standard total carbon analyses on all carbon analyzers for the analysis period 03/07/2024 through 04/17/2025 (samples collected 1/1/2024 through 12/31/2024).

Analyzer	Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
Alpha	262	0.10	0.51	-5.95	23.59	3.44	9
Beta	212	1.79	1.73	-11.83	9.42	3.26	11
Delta	251	0.51	0.30	-8.10	17.56	3.58	14
Gamma	268	1.98	2.37	-4.85	28.25	3.55	16
Theta	269	0.89	1.20	-6.86	12.65	3.13	12
Zeta	222	-0.00	0.23	-12.04	20.17	3.40	6

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

Figure 5-28: Results of daily single-point sucrose calibration standard check for the analysis period 03/07/2024 through 04/17/2025 (samples collected 1/1/2024 through 12/31/2024) for all instruments.



5.6.2.3 Calibration Peak Area Check

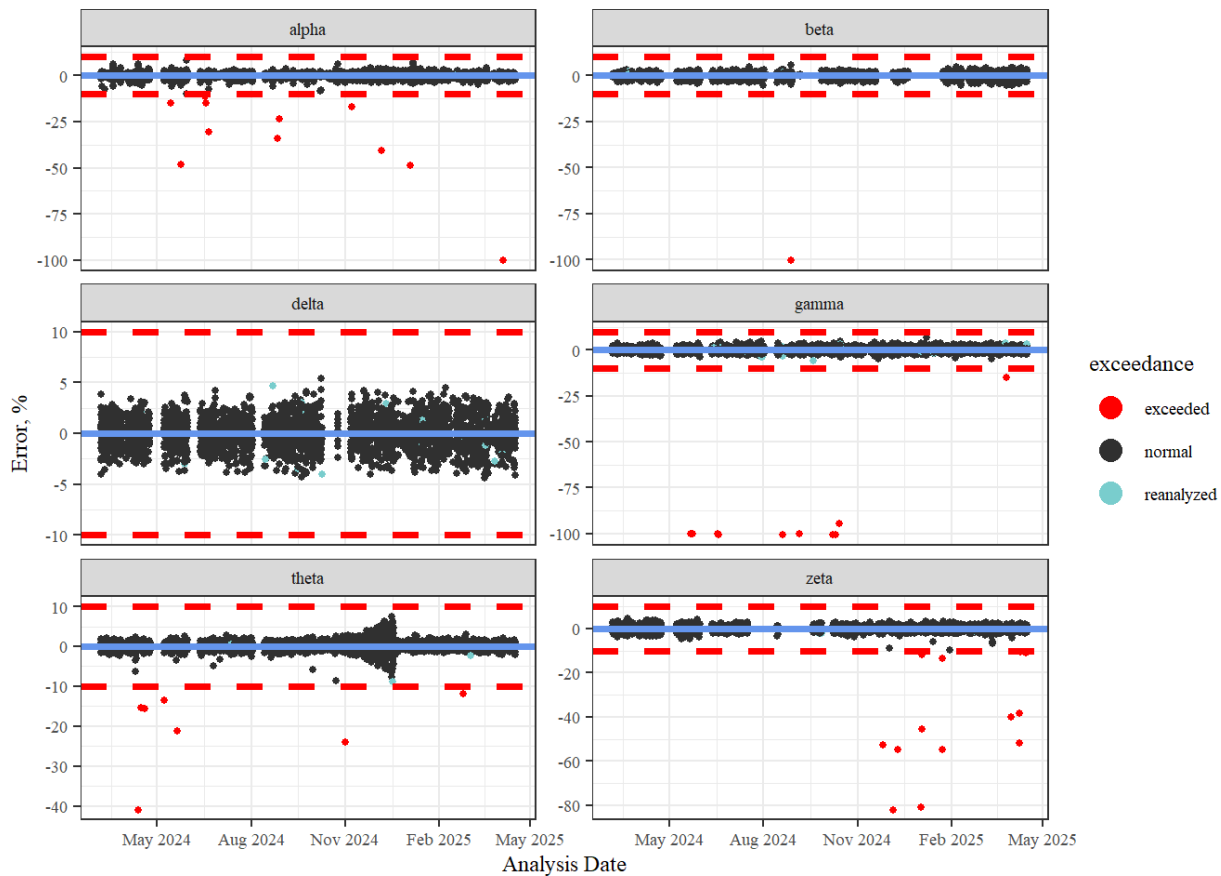
At the end of each analysis, a fixed amount of methane (CH_4) from a cylinder containing 5% CH_4 in helium is injected into the system as an internal gaseous standard. The CH_4 peak area is quantified and compared to the average peak area of all analyses performed on that instrument on that day. If the error (calculated using Equation 5-2) exceeds $\pm 10\%$ acceptance criteria, the analysis result is voided; the flowrate of the calibration gas and sample oven pressure are verified; corrective actions (if applicable) are taken immediately after the problem is identified; and the analysis is repeated using a second filter punch analyzed on the original analyzer (or on a different analyzer if the original analyzer is not available). A pattern of increasing variability in the CH_4 peak area error typically indicates an aging methanator oven which is then replaced. Table 5-36 summarizes the statistics of the calibration peak area checks. There were 42 exceedances during this reporting period. All affected samples were reanalyzed with acceptable results. Most exceedances are due to the FID flame going out at the start or during an analysis.

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

Table 5-36: Statistics of internal calibration peak area check on all carbon analyzers for the analysis period 03/07/2024 through 04/17/2025 (samples collected 01/01/2024 through 12/29/2024).

Analyzer	Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
Alpha	2959	0.11	-0.13	-99.99	8.17	2.96	11
Beta	2317	0.24	-0.04	-100.20	5.90	2.63	1
Delta	2753	0.02	0.00	-4.43	5.37	1.56	0
Gamma	2971	-0.06	-0.31	-100.74	7.07	5.64	10
Theta	2917	-0.02	-0.06	-40.87	7.36	1.64	7
Zeta	2453	0.07	-0.23	-81.98	4.37	3.74	13

Figure 5-29: Results of internal calibration area check for the analysis period 03/07/2024 through 04/17/2025 (samples collected 01/01/2024 through 12/29/2024). Red dashed lines indicate the acceptance criteria of $\pm 10\%$ error from the mean value. For cases when calibration area exceeded the acceptance criteria (red points), a repeated analysis (blue points) was performed and the original analysis was voided. The pattern in theta's plot around December 2024 shows an aging methanator oven which was replaced on 12/19/2024.



5.6.2.4 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 5-30 shows the filter reflectance and transmittance initial readings for all instrument blank analyses during the report period. There were no low laser signals during this reporting period. Jumps and discontinuities in the laser signals for individual instruments are the result of instrument maintenance requiring laser realignment.

In the following figure, the red dashed line indicates the acceptance criteria of 5000 a.u. of the laser signal. Different analyzers are indicated by data point color.

Figure 5-30: Laser initial readings (top: Transmittance; bottom: Reflectance) of the instrumental blank analysis for the analysis period 03/07/2024 through 04/17/2025 (samples collected 01/01/2024 through 12/29/2024).



5.6.2.5 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 5-37 lists the acceptance criteria for replicate analysis and the summary statistics from this reporting period. A total of 758 replicate analyses were performed out of the 15,866 samples and field blanks. For cases that exceeded the acceptance criteria, a third punch (if available) was analyzed on a different analyzer, and all three sets of results (routine, replicate, and reanalysis) from the same filter are compared to determine analysis validity. Instrument anomaly and/or deposit inhomogeneity are also examined. During this reporting period, there was a total of 22 TC exceedances and 20 ECR exceedances. A third punch from samples with exceedances were analyzed on a third analyzer. As noted in Table 5-37, all reanalysis of exceedances passed the QC criteria. Figure 5-31 shows the results of the replicate analyses. The original failed analyses are invalidated in the database and not plotted in this figure.

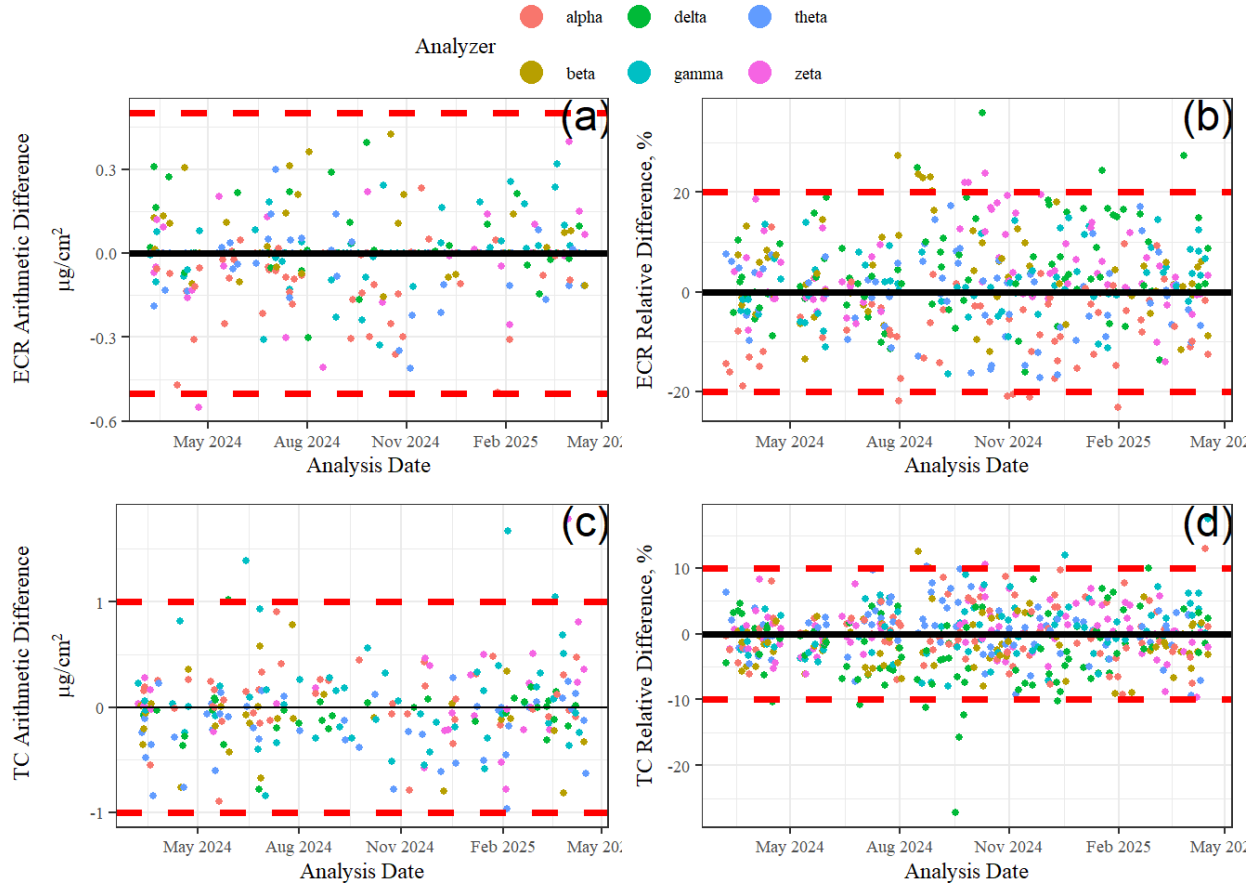
Table 5-37: Acceptance criteria and the summary statistics of the replicate analyses for the analysis period 03/07/2024 through 04/17/2025 (samples collected 01/01/2024 through 12/29/2024).

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	758	22	22
ECR	*RPD < ±20% when ECR > 2.5 µg /cm ² or Absolute difference <±0.5 µg/cm ² when ECR ≤2.5 µg/cm ²	758	20	20

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

In the following figure, 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). The invalidated original results are not plotted.

Figure 5-31: Results of CSN replicate analysis for ECR (Panel a and b) and TC (Panel c and d) for the analysis period 03/07/2024 through 04/17/2025 (samples collected 01/01/2024 through 12/29/2024).



5.6.2.6 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 cm² punches. A total of 60 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 ($Measured_i$) 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/cm² and ECR > 2.5 µg C/cm²) are based on the relative difference (%) by dividing the difference between the measurement of a given analyzer (i) and the average value for the same PC sample obtained from all analyzers used in comparison by the average value using the equation as follows:

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

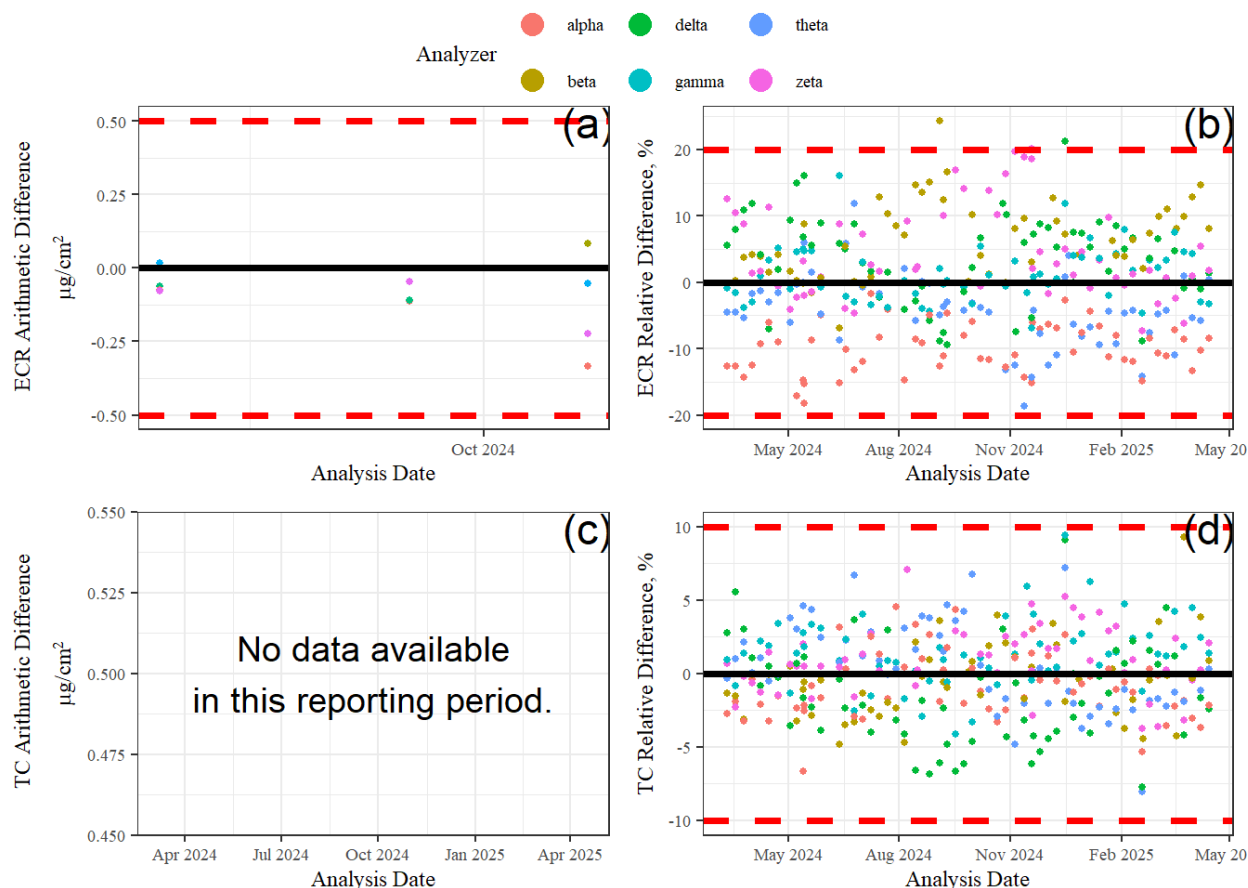
The acceptance criteria for inter-instrument comparison at low filter loadings ($TC \leq 10 \mu\text{g C/cm}^2$ and $ECR \leq 2.5 \mu\text{g C/cm}^2$) are based on the arithmetic difference between the measurement from a given analyzer and the average value for the same PC sample obtained from all analyzers used in each comparison. The acceptance criteria for inter-instrumental check are the same as that for the network sample replicates (See Table 5-32 for details). Exceeding the acceptance criteria results in further investigation of the instrument, and reanalysis of the performance check sample. Table 5-38 summarizes the statistics of instrument bias for ECR and TC. There were three exceedances during this reporting period.

Table 5-38: 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. Note, no PC samples had $10 \mu\text{g/cm}^2$ or less TC during this analysis period. The analysis period covers the dates starting from 03/07/2024 through 04/17/2025 (samples collected 01/01/2024 through 12/29/2024).

Relative difference (%) for high filter loadings (Acceptance limit: $\pm 10\%$ for TC and $\pm 20\%$ for ECR)								
ECR > $2.5 \mu\text{g/cm}^2$					TC > $10 \mu\text{g/cm}^2$			
Analyzer	Count	Median	Mean	St. Dev.	Count	Median	Mean	St. Dev.
Alpha	57	-10.29	-9.99	3.73	60	-1.23	-0.81	2.29
Beta	53	6.29	6.33	5.80	54	-0.46	-0.47	2.62
Delta	58	5.04	3.67	6.53	60	-1.73	-1.47	3.41
Gamma	57	0.80	1.23	4.25	60	1.32	1.39	2.36
Theta	58	-4.37	-4.27	5.41	61	0.29	0.46	2.92
Zeta	55	2.12	4.48	7.02	55	0.68	0.93	2.24
Arithmetic difference for low filter loadings (Acceptance limit: $\pm 1 \mu\text{g/cm}^2$ for TC and $\pm 0.5 \mu\text{g/cm}^2$ for ECR)								
ECR: 0 - $2.5 \mu\text{g/cm}^2$					TC: 0 - $10 \mu\text{g/cm}^2$			
Analyzer	Count	Median	Mean	St. Dev.	Count	Median	Mean	St. Dev.
Alpha	3	-0.11	-0.17	0.14	0	NA	NA	NA
Beta	1	0.08	0.08	NA	0	NA	NA	NA
Delta	2	-0.09	-0.09	0.03	0	NA	NA	NA
Gamma	3	-0.05	-0.05	0.06	0	NA	NA	NA
Theta	3	-0.08	-0.12	0.09	0	NA	NA	NA
Zeta	3	-0.11	-0.17	0.14	0	NA	NA	NA

Figure 5-32 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 5-32: Results of the weekly performance check samples by each analyzer for ECR (Panel a and b) and TC (Panel c and d). Note, no PC samples had 10 $\mu\text{g}/\text{cm}^2$ or less TC during this analysis period. The analysis period covers the dates starting from 03/07/2024 through 04/17/2025 (samples collected 01/01/2024 through 12/29/2024).



5.6.2.7 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 5-34 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 5-39 summarizes the multi-point sucrose calibrations performed during this reporting period.

Table 5-39: Summary of multi-point sucrose calibration performed for the analysis period 03/07/2024 through 04/17/2025 (samples collected 01/01/2024 through 12/29/2024).

Analyzer	Calibration Date	Slope	r ²	Calibration Constant
Alpha ¹	3/6/2024	1.0028	0.9999	19.7984
Delta ¹	3/6/2024	0.9851	0.9996	19.6626
Gamma ¹	3/6/2024	0.9951	0.9999	20.2746
Theta ¹	3/6/2024	0.9707	0.9999	21.4338
Zeta ¹	3/6/2024	1.0404	1	20.9278
Beta ¹	3/7/2024	1.0390	1	19.8292
Delta ²	4/4/2024	1.0265	1	19.0939
Delta ¹	8/6/2024	1.0034	0.9998	19.0292
Gamma ¹	8/6/2024	0.9856	1	20.5708
Theta ¹	8/6/2024	0.9607	0.9997	22.3106
Alpha ¹	8/6/2024	0.9510	0.9994	20.8185
Beta ¹	8/7/2024	0.9500	1	20.8900
Zeta ¹	8/7/2024	0.9914	1	21.1093
Beta ²	9/5/2024	1.0214	0.9997	20.4523
Delta ²	10/2/2024	0.9600	1	19.7400
Alpha ²	10/4/2024	1.0424	0.9995	19.9717
Theta ²	10/4/2024	1.0595	0.9999	21.0577
Delta ²	10/15/2024	1.0500	1	18.7400
Delta ²	10/28/2024	0.9500	1	19.6600
Delta ⁴	11/5/2024	1.0046	0.9995	19.5700
Delta ³	1/9/2025	0.9553	1	20.4857
Alpha ¹	2/13/2025	0.9960	1	20.0519
Beta ¹	2/13/2025	0.9779	1	20.9145
Zeta ¹	2/13/2025	1.0284	0.9992	20.5264
Gamma ¹	2/13/2025	1.0132	0.9994	20.8572
Theta ¹	2/13/2025	1.0131	0.9996	21.4307
Delta ¹	2/13/2025	0.9693	0.9993	20.5020

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 Sucrose calibration performed after replacing main oven.

5.6.2.8 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 5-40 summarizes the temperature calibrations performed on each analyzer during this reporting period.

Table 5-40: Summary of the temperature calibrations performed on each analyzer for the analysis period 03/07/2024 through 04/17/2025 (samples collected 01/01/2024 through 12/29/2024).

Analyzer	Calibration Date	Reason
Alpha	4/3/2024	Semi-annual temperature calibration
Beta	4/3/2024	Semi-annual temperature calibration
Zeta	4/3/2024	Semi-annual temperature calibration
Delta	4/25/2024	Following oven replacement
Gamma	6/6/2024	Semi-annual temperature calibration
Theta	6/6/2024	Semi-annual temperature calibration
Zeta	7/24/2024	Following oven replacement
Beta	8/30/2024	Part of high EC troubleshooting
Alpha	9/13/2024	Semi-annual temperature calibration
Beta	9/24/2024	Following front oven thermocouple replacement
Zeta	9/30/2024	Following front oven thermocouple replacement
Zeta	10/2/2024	Following oven heating coil replacement
Zeta	10/3/2024	Following re-wrapping of front oven heating coil
Alpha	10/10/2024	Following front oven thermocouple replacement
Delta	10/16/2024	Following repositioning of front oven thermocouple
Delta	10/23/2024	Following front oven thermocouple replacement
Delta	11/1/2024	Following oven replacement
Gamma	12/12/2024	Semi-annual temperature calibration
Theta	12/12/2024	Semi-annual temperature calibration

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 Carbon Laboratory during this reporting period.

5.6.4.2 Performance Evaluations

The UC Davis Thermal Optical Analysis Laboratory participated in the ERLAP 2025 OCEC Interlaboratory Comparison. Eight quartz filter samples were analyzed on Theta with the EUSAAR protocol at AQRC. Our results showed low bias in TC and OC, and a high bias for EC when compared to the assigned values. A review of the results and QC procedures determined that the instrument was functioning well, but the carbon measurement is difficult to reproduce consistently. See the references section of this report for more details (JRC142729).

5.6.4.3 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.

5.6.4.4 Accreditations

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

5.6.5 Summary of Filter Blanks

5.6.5.1 Field Blanks

Over the sampling period (January 1, 2024 through December 31, 2024) there were 1,536 valid quartz filter field blanks. Table 5-41 summarizes the field blank statistics.

Table 5-41: Quartz filter field blank statistics for the analysis period 03/07/2024 through 04/017/2025 (samples collected 01/1/2024 through 12/31/2024). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).

Species	Count	Median ($\mu\text{g}/\text{cm}^2$)	Average ($\mu\text{g}/\text{cm}^2$)	Min ($\mu\text{g}/\text{cm}^2$)	Max ($\mu\text{g}/\text{cm}^2$)	St. Dev. ($\mu\text{g}/\text{cm}^2$)
EC1	1536	0.019	0.031	-0.165	1.337	0.062
EC2	1536	0.048	0.055	-0.162	1.312	0.057
EC3	1536	0.007	0.010	-0.185	0.490	0.024
ECR	1536	0.000	0.001	-0.005	1.103	0.032
ECT	1536	0.000	0.001	-0.005	0.696	0.022
OC1	1536	0.131	0.148	-0.074	0.725	0.084
OC2	1536	0.311	0.329	0.029	2.012	0.143
OC3	1536	0.452	0.503	0.088	2.417	0.237
OC4	1536	0.107	0.126	-0.579	1.870	0.117
OCR	1536	1.126	1.199	-0.716	7.058	0.532
OCT	1536	1.126	1.199	-0.716	7.465	0.535
OPR	1536	0.078	0.094	-0.514	2.030	0.105
OPT	1536	0.078	0.094	-0.514	2.030	0.108
TCTC	1536	1.126	1.200	-0.714	8.161	0.543

5.6.5.2 Laboratory Blanks Supplied by RTI

Five quartz laboratory blanks are shipped from the Sample Handling Laboratory (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 5.5.2.1, as the laboratory blanks are from the same filter lots as the CSN sample filters. The RTI laboratory blanks are pre-fired by RTI and 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 5-42, 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 5-42: Quartz filter laboratory blank statistics for the analysis period 04/02/2024 through 03/13/2025 (samples collected 01/1/2024 through 12/31/2024). 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 ($\mu\text{g}/\text{cm}^2$)	Average ($\mu\text{g}/\text{cm}^2$)	Min ($\mu\text{g}/\text{cm}^2$)	Max ($\mu\text{g}/\text{cm}^2$)	St.Dev. ($\mu\text{g}/\text{cm}^2$)
EC1	60	-0.006	0.004	-0.045	0.529	0.047
EC2	60	0.009	0.013	-0.032	0.406	0.038
EC3	60	0.006	0.009	-0.029	0.178	0.022
ECR	60	0.000	0.000	-0.003	0.009	0.001
ECT	60	0.000	0.000	-0.003	0.001	0.000
OC1	60	0.038	0.039	-0.002	0.087	0.020
OC2	60	0.050	0.055	0.010	0.369	0.030
OC3	60	0.102	0.175	0.013	6.778	0.452
OC4	60	-0.027	-0.009	-0.162	1.004	0.103
OCR	60	0.186	0.286	-0.160	8.602	0.617
OCT	60	0.186	0.286	-0.160	8.602	0.617
OPR	60	0.015	0.026	-0.096	0.770	0.088
OPT	60	0.015	0.027	-0.096	0.770	0.088
TCTC	60	0.186	0.286	-0.159	8.601	0.617

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

5.7 UC Davis Optical Absorption Laboratory

The UC Davis Optical Absorption Laboratory received and analyzed PTFE filters from batches 2024-01 through 2024-12, covering the field sampling period beginning from January 1, 2024 through December 31, 2024. Analyses of these samples were performed April 10, 2024 through April 23, 2025. The Hybrid Integrating Plate and Sphere (HIPS) instrument was used for all analysis. This instrument uses a 633 nm 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 5-43: Sampling months in 2024 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 (2024)	Analysis Batch #	HIPS Analysis Dates
January	2024-01	2024-04-10 - 2024-05-15
February	2024-02	2024-05-09 - 2024-06-20
March	2024-03	2024-06-12 - 2024-07-18
April	2024-04	2024-07-11 - 2024-08-08
May	2024-05	2024-08-14 - 2024-09-19
June	2024-06	2024-09-17 - 2024-10-22
July	2024-07	2024-10-22 - 2024-11-19
August	2024-08	2024-11-20 - 2024-12-19
September	2024-09	2024-12-19 - 2025-01-23
October	2024-10	2025-02-18 - 2025-02-25
November	2024-11	2025-02-20 - 2025-04-03
December	2024-12	2025-03-13 - 2025-04-23
All Months	2024-01:2024-12	2024-04-10 - 2025-04-23

5.7.1 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 $\pm 3\%$ 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 5-44.

Table 5-44: UC Davis quality control measures for carbon analysis by HIPS.

Analysis	Frequency	Criterion	Corrective Action
Verification Set	Daily	Within $\pm 3\%$ 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 $\pm 1\%$ of the accepted values	Reanalysis required
Routine Replicates	Once a sample month	Under development*	Under development*

*In March of 2023, UC Davis began collecting routine replicates of CSN filter HIPS analysis. This started with the January 2023 batch of filters on DV-0010. UC Davis has continued to reanalyze ~80 filters each month on the HIPS instrument. Criterion and Corrective Actions will be developed at a later time when enough data is collected and resources are available.

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 $\pm 2 \times$ 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.

5.7.2 Summary of QC Results

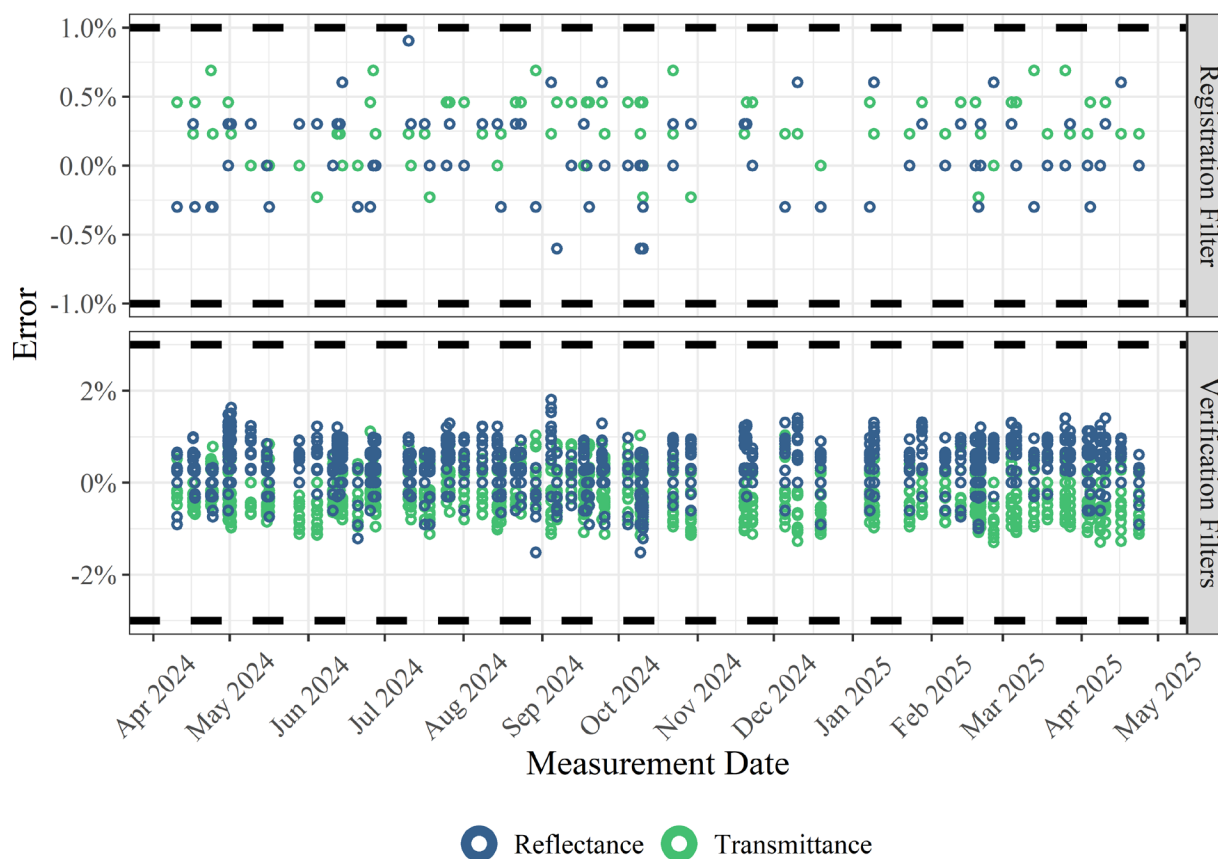
QC tests conducted over the course of the analysis period showed good overall control of the instrument and process. There were occasional acceptance criteria failures, which were investigated promptly and corrected with no impact on sample results. The following summarizes the QC issues which occurred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

5.7.2.1 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 had no failures during the period reported here, see Figure 5-33.

Figure 5-33: HIPS detector response check of the Verification Filter set.

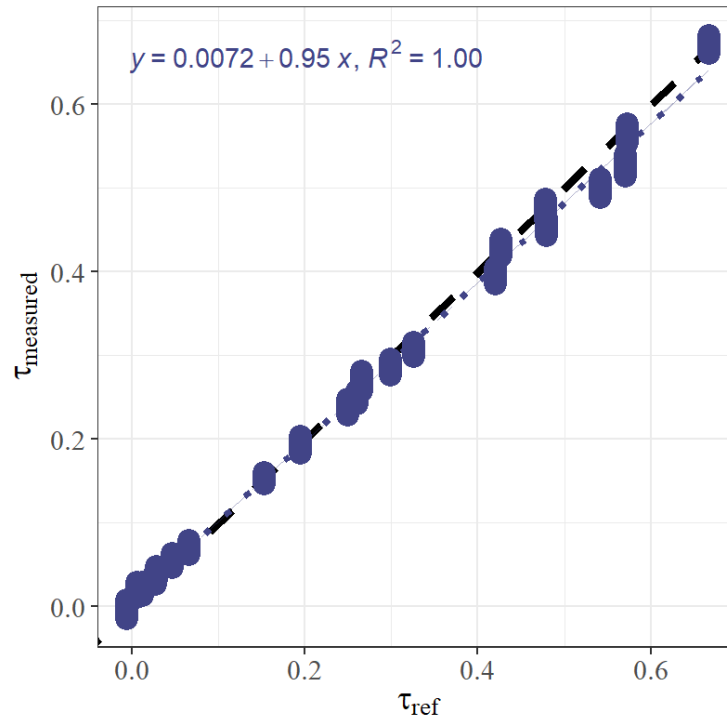


5.7.2.2 Reanalysis Check

The Reanalysis Set verification check is predicated on a field blank calibration using field blanks representative of the sample filters chosen for reanalysis. Calibration of the Reanalysis Set filters is only performed after a major instrument repair or change which would warrant a new calibration. The calibration in use during this reporting period, performed 05/01/2023, did not change. 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 5-34.

Figure 5-34: HIPS linearity check of the Reanalysis Filter set.



Calibration Date  2023-05-01

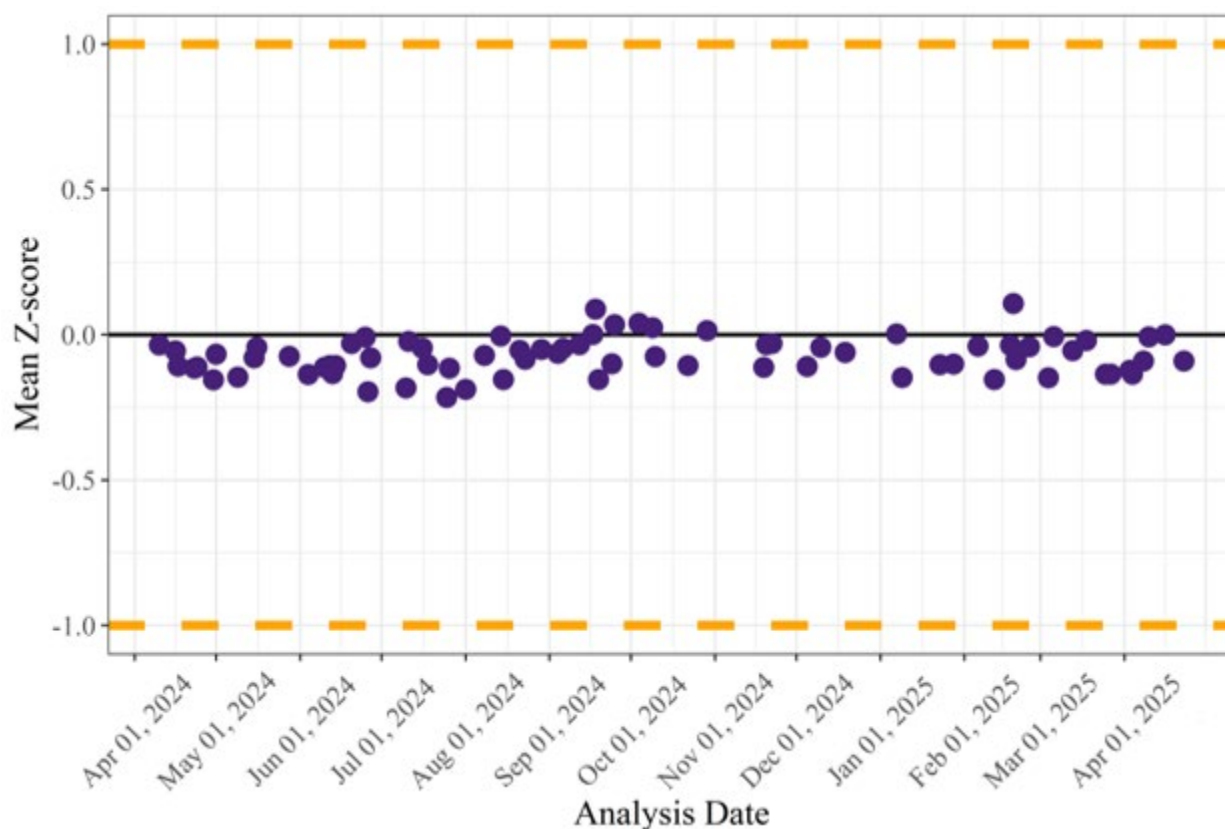
The linearity check passed for the active calibration of the Reanalysis Set. The HIPS instrument had a 100 % passing rate for the reanalysis set measurements within the uncertainty bounds, $\pm 2 \times U_{\tau_{abs}}$.

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 5-35.

Figure 5-35: HIPS reanalysis mean z-score. Horizontal lines demarcate the QC limits of the z-scores.



5.7.3 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

5.7.4 Audits, Performance Evaluations, Training, and Accreditations

5.7.4.1 System Audits

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

5.7.4.2 Performance Evaluations

No performance evaluations were conducted during this reporting period.

5.7.4.3 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.

5.7.4.4 *Accreditations*

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

5.7.5 **Summary of Filter Blanks**

5.7.5.1 *Field Blanks*

Over the sampling period (January 1, 2024 through December 31, 2024) there were 1601 valid PTFE filter field blanks. Table 5-45 summarizes the field blank statistics.

Table 5-45: PTFE filter field blank statistics for the 2024 sampling analysis period 4/10/2024 through 4/04/2025 (samples collected 1/1/2024 through 12/31/2024). Values are expressed as optical depth, which is unitless.

Species	Count	Median	Average	Min	Max	St. Dev.
fAbs	1601	0.001	0.002	-0.023	0.314	0.012

5.7.5.2 *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 5-46 summarizes the laboratory blank statistics.

Table 5-46: PTFE filter laboratory blank statistics for the 2024 sampling analysis period 4/10/2024 through 4/04/2025 (samples collected 1/1/2024 through 12/31/2024). Values are expressed as optical depth, which is unitless.

Species	Count	Median	Average	Min	Max	St. Dev.
fAbs	60	0.005	0.005	-0.011	0.014	0.006

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 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 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**

6.3 Leak Testing

6.4 Number of Events Posted to AQS

Table 6-1 summarizes AQS delivery dates for samples collected January 1, 2024 through December 31, 2024. Data are expected to be delivered to AQS within 160 days after the end of the sampling month. The January and March 2024 deliveries were delayed by an outage of the DART system used by SLT (State, Local, and Tribal) agencies for data validation.

Table 6-1: Summary of data deliveries to AQS for samples collected January 1, 2024 through December 31, 2024.

Sampling Month (2024)	Analysis Batch #	Filter Receipt Date	AQS Delivery Date	Days
January	24-01	March 6, 2024	July 26, 2024	176
February	24-02	April 4, 2024	August 8, 2024	160
March	24-03	May 8, 2024	September 9, 2024	161
April	24-04	June 12, 2024	October 8, 2024	160
May	24-05	July 11, 2024	November 6, 2024	158
June	24-06	August 14, 2024	December 6, 2024	158
July	24-07	September 11, 2024	January 13, 2025	165
August	24-08	October 9, 2024	February 5, 2025	157
September	24-09	November 6, 2024	March 10, 2025	160
October	24-10	December 4, 2024	April 10, 2025	160
November	24-11	January 15, 2025	May 9, 2025	159
December	24-12	February 12, 2025	June 10, 2025	160

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 regularly; 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. UC Davis reviews the QAPP, SOPs, and other project documents annually and revises them on an as-needed basis.

RTI, a subcontractor to AQRC, also released Revision 0 of their QAPP for Filter Handling, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography on November 20th, 2023. There were no revisions to the RTI QAPP for Filter Handling, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography in 2024. RTI reviews the QAPP, SOPs, and other project documents annually and revises them on an as-needed basis.

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 as needed. Revisions are delivered to EPA as they are completed.

7.2.1 UC Davis SOP Revisions

SOPs are updated as procedures are added or modified. They are sent as a package to EPA on a regular basis. SOP revisions since the last QA Report include updates to Data Validation and Sample Receiving and Inventorying. Updates for XRF, Carbon, HIPS, and additional Data Validation are in progress.

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 contract year, six SHAL SOPs and seven SHAL TIs were finalized prior to May 1, 2024. All SOP's for SHAL were utilized in draft format, until they were finalized. The gravimetry lab SOP was finalized and in effect in 2024. The SOP for the Ions laboratory was reviewed and updated on 3/5/2025.

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 uploaded to the UC Davis CSN database by the Sample Handling Laboratory (RTI). 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, RTI gravimetric mass result files are ingested to the UC Davis CSN database by the Sample Handling Lab (RTI).

- 2) *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.
- 3) *UCD CSN TI #801C: Data Validation*
 - a. Level 0: 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.
 - b. Level 1: Several statistical and visual checks are applied and examined. Laboratory reanalyses are requested as needed. Data are flagged with qualifier or null codes.
- 4) *UCD CSN TI #801D: Data for DART* — 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.
- 5) *UCD CSN #TI 801E: CSN Data for AQS* — 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 7.2.
- 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 data files prior to submission to UC Davis.
- Review of acceptance testing results.

7.4 Data Validation and Review

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 are 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 2024 no filters or batches failed the acceptance criteria. Results from OCEC and Ions analysis were reported in Section 4.3 in this report.

7.4.2 Summary of Monthly Data Validation Review Results

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>.

7.4.2.1 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 in 2023 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).

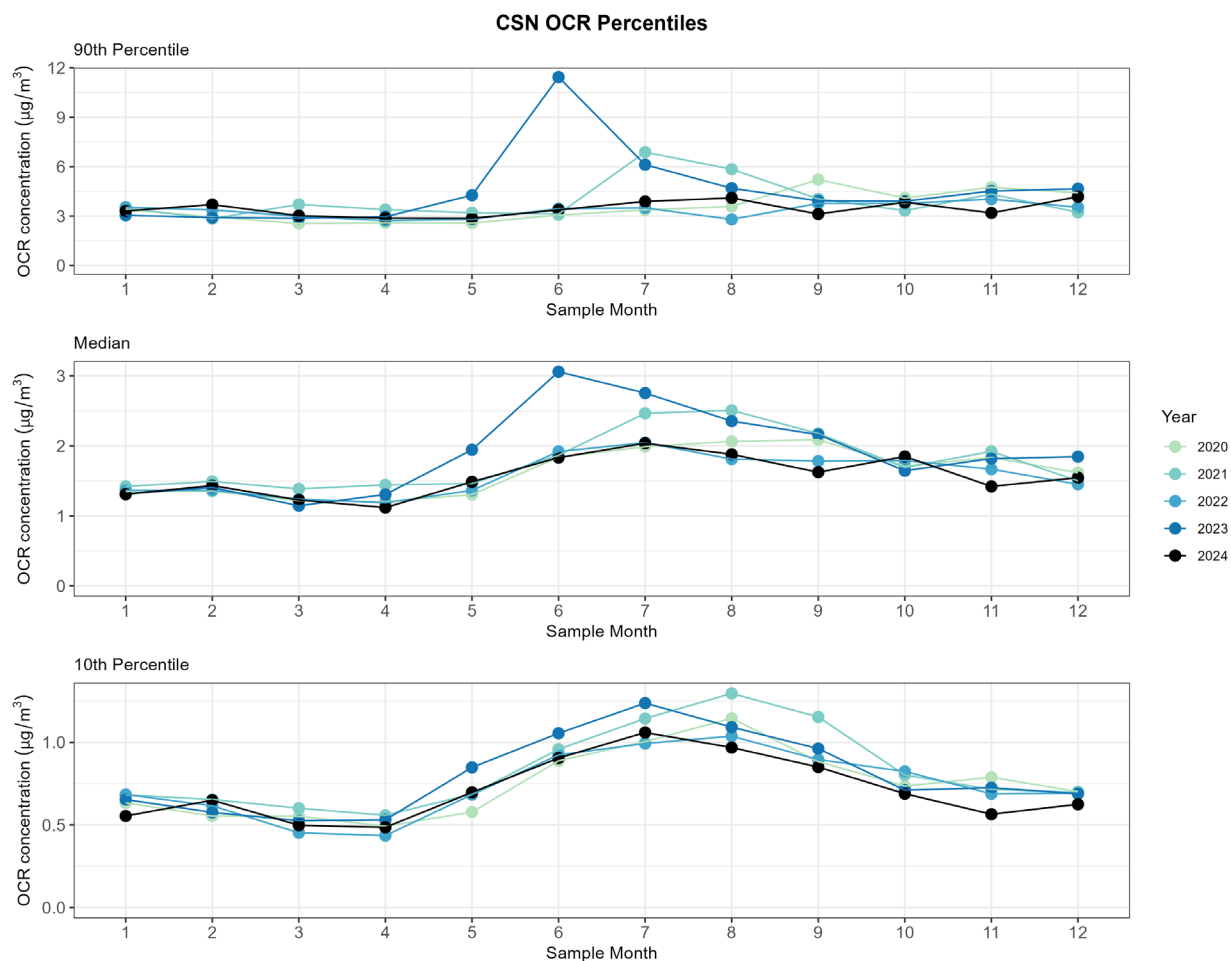
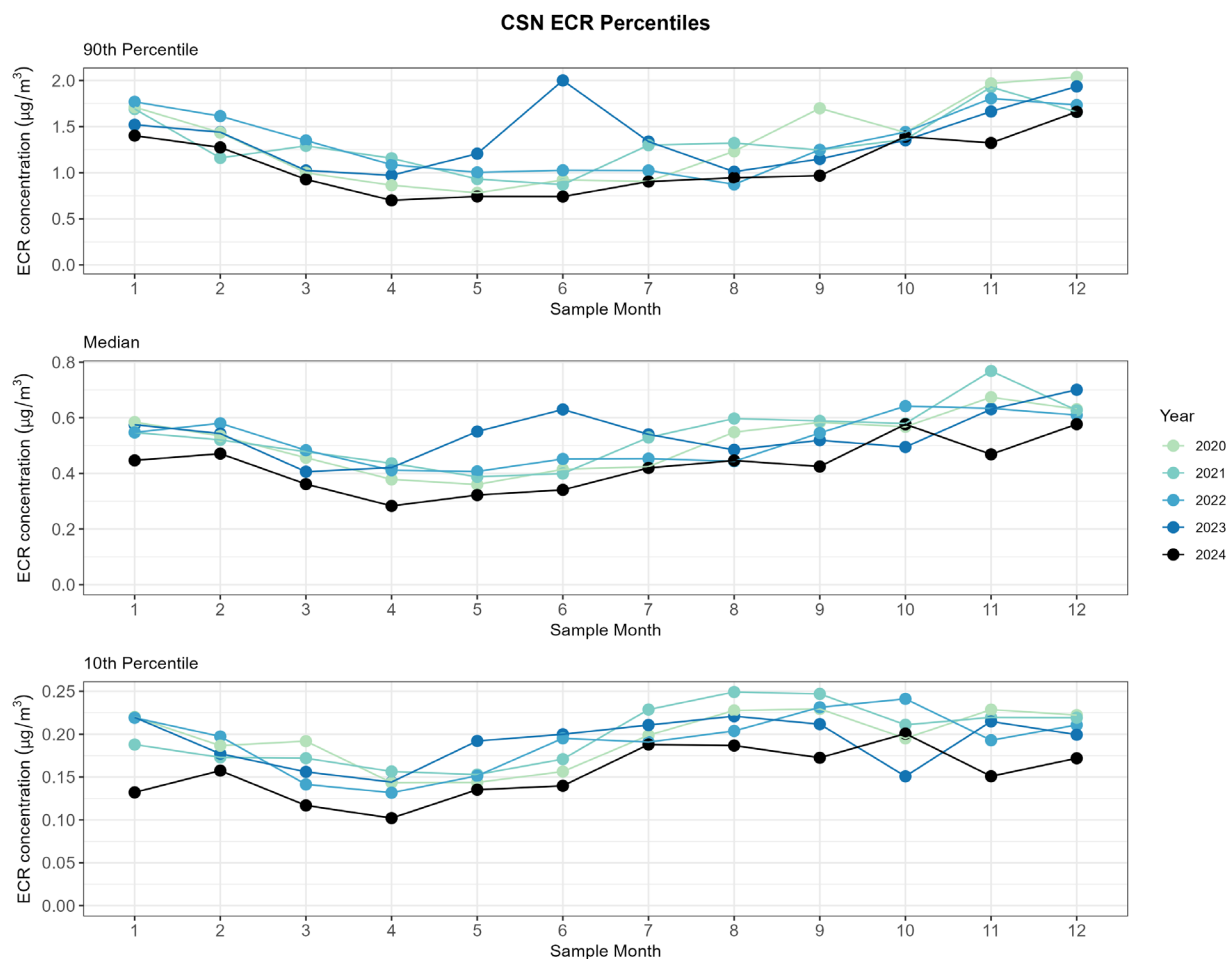
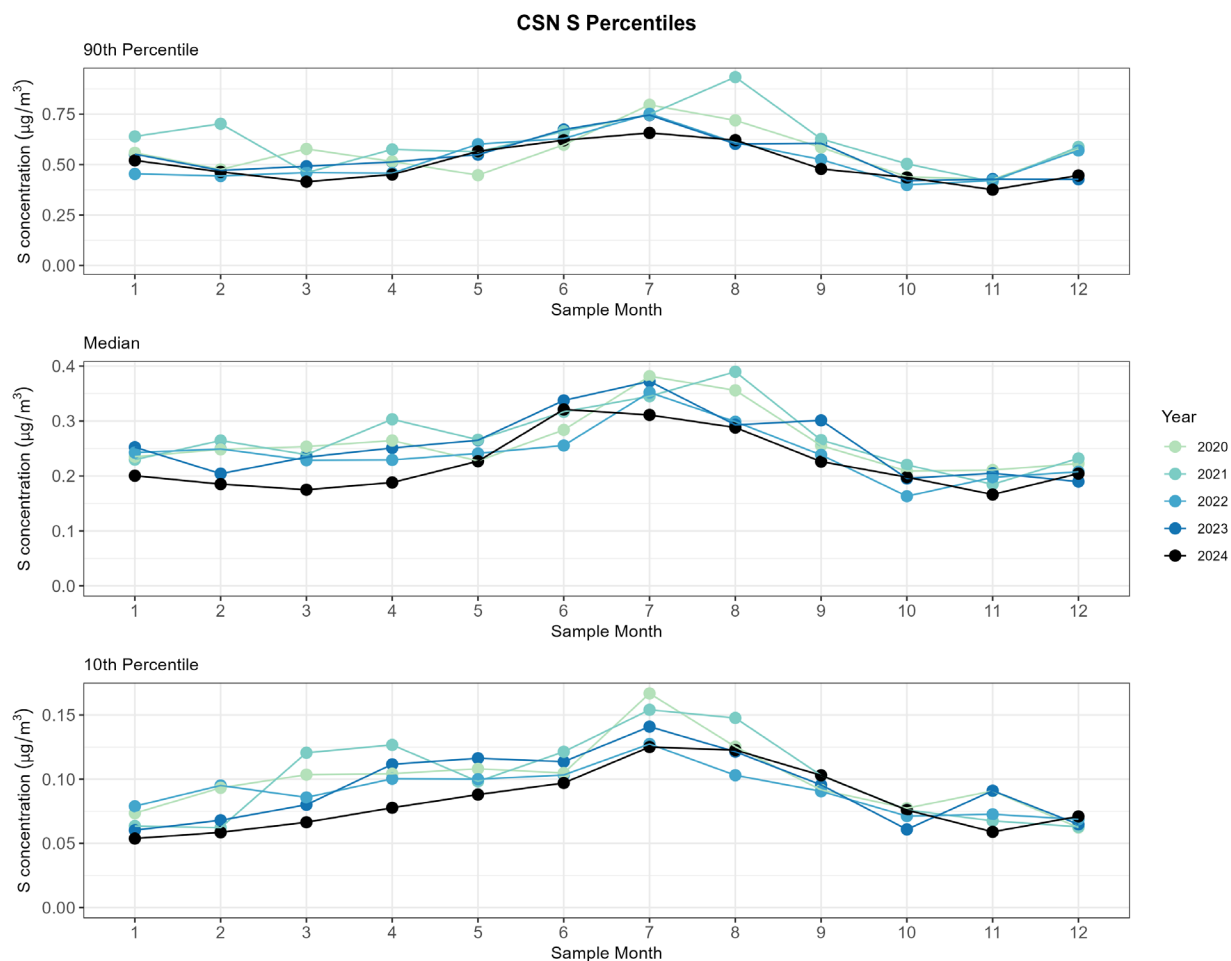


Figure 7-2: Multi-year time series of network-wide elemental carbon by reflectance concentrations (ECR).



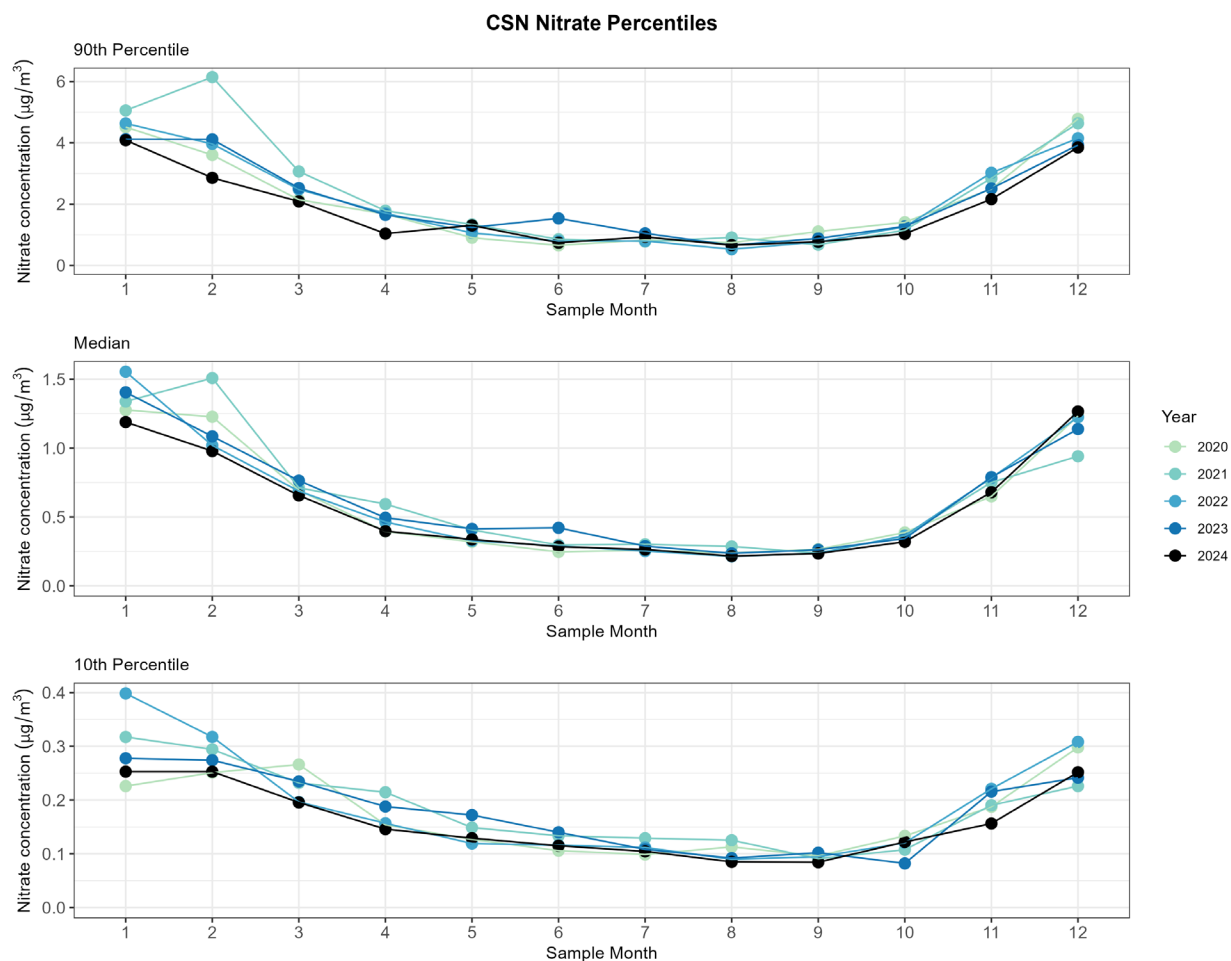
Similar to recent years, the 2024 sulfur concentrations generally continue to be low (Figure 7-3), with reduced seasonal variability.

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



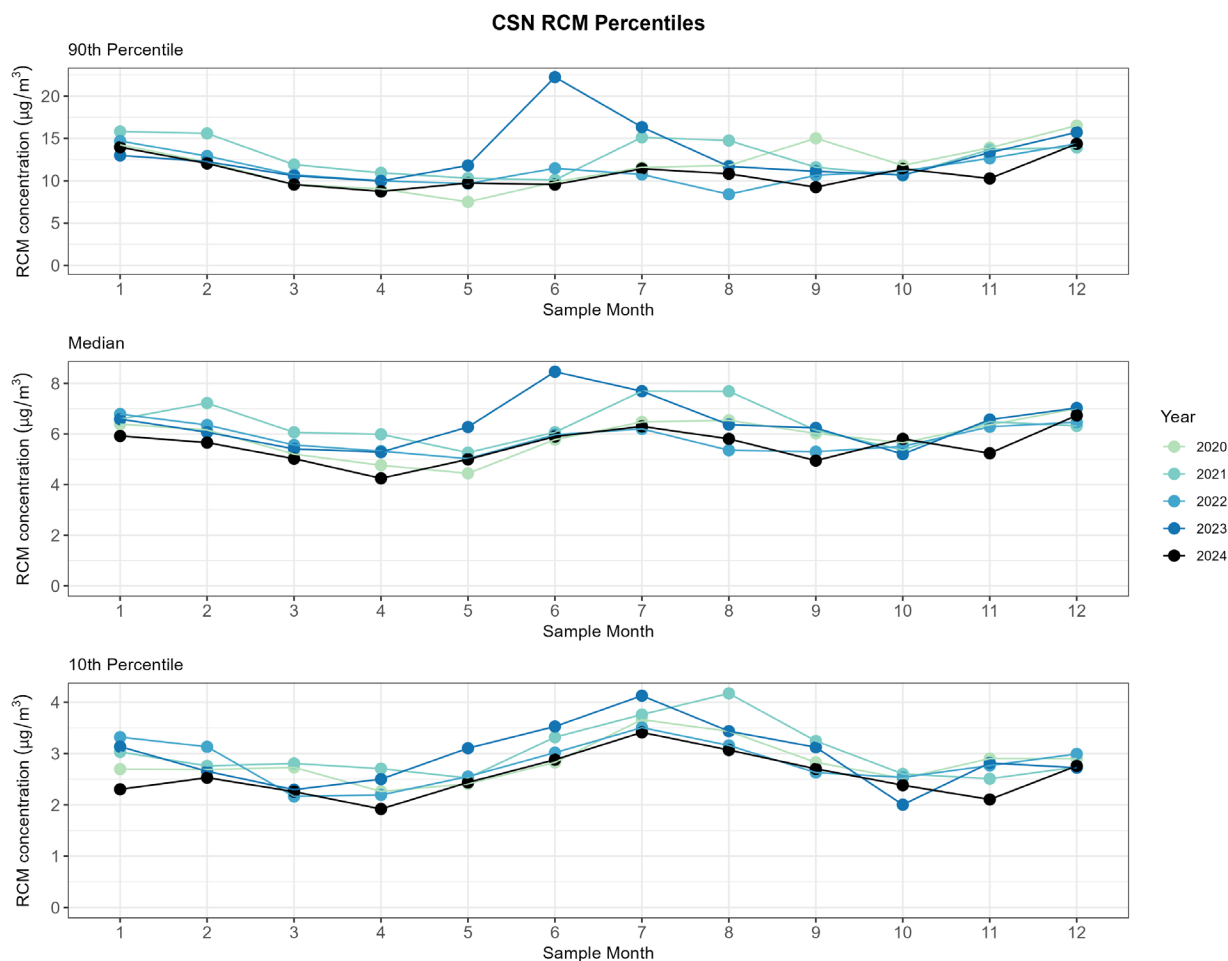
The 2024 nitrate concentrations continue to show strong seasonality with elevated winter concentrations (Figure 7-4).

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



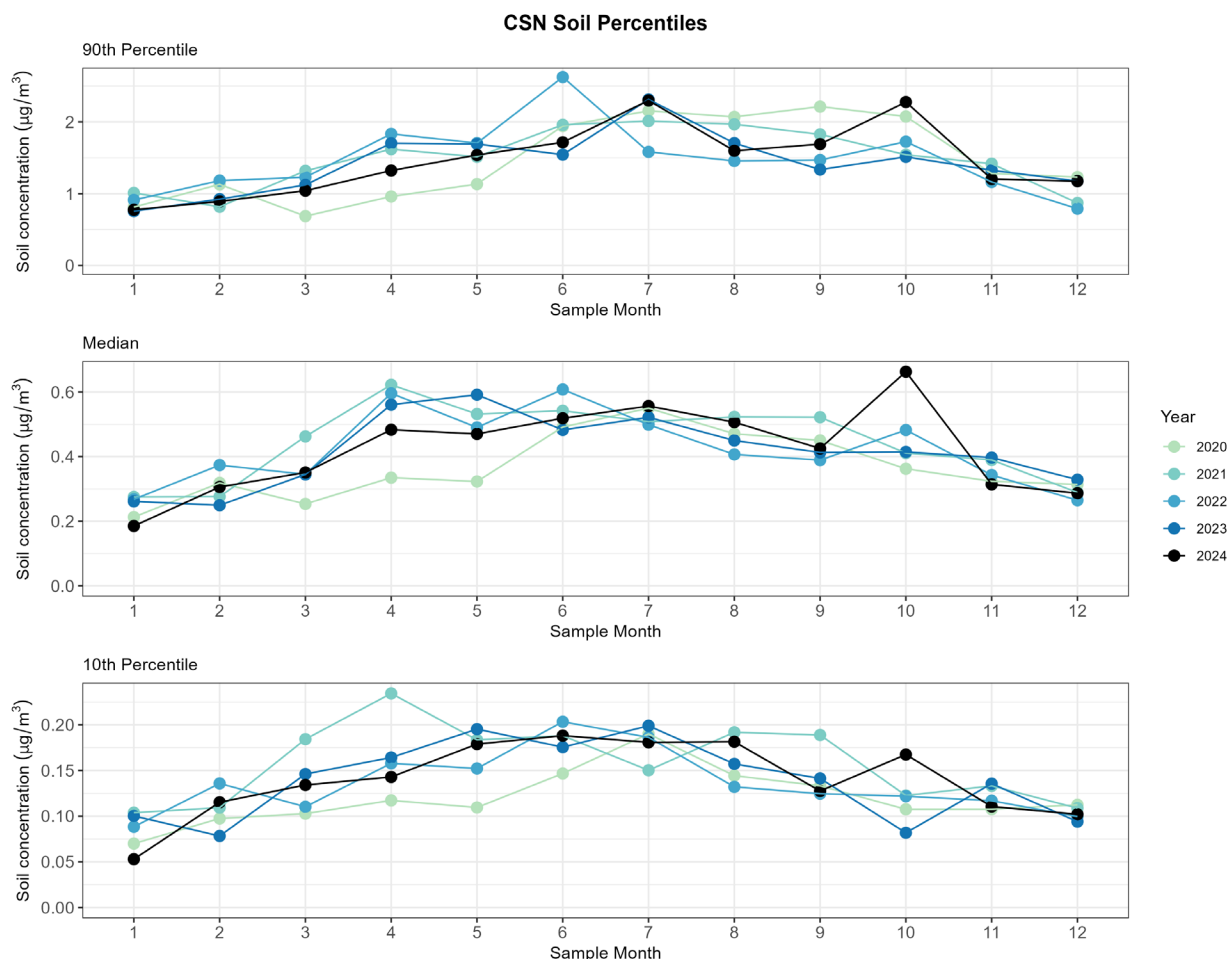
UC Davis calculates and delivers composite variables for reconstructed mass (RCM) and soil. The 2020 through 2024 RCM and soil results are shown in Figure 7-5 and 7-6, respectively. High RCM in spring 2023 was driven by wildfire smoke.

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



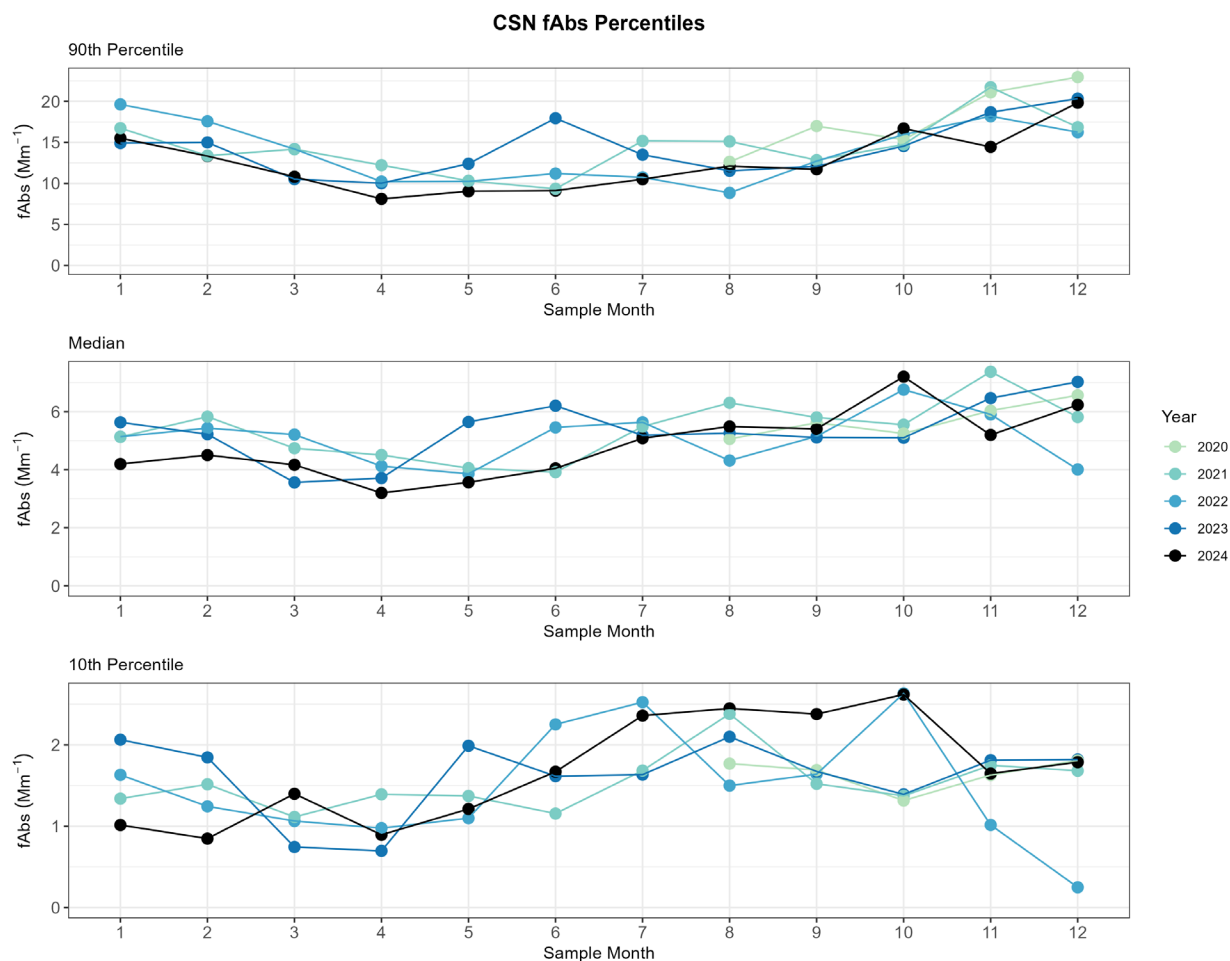
The soil elements in October 2024 peaked to high points for the month in recent years. This includes Al, Si, Ca, Fe, and Ti. Although the Al and Ti peaks are less pronounced. The soil elements peak is as-yet unexplained.

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 depicts data for years 2020-2024. AQRC made an effort to perform some basic validation on measurements taken back to August 2020 and delivered that data for historical context.

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



After the contract transition from WSP to RTI (June 2023 data), 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 time series plots below.

Figure 7-8: Multi-year time series of network-wide chromium (Cr) concentrations.

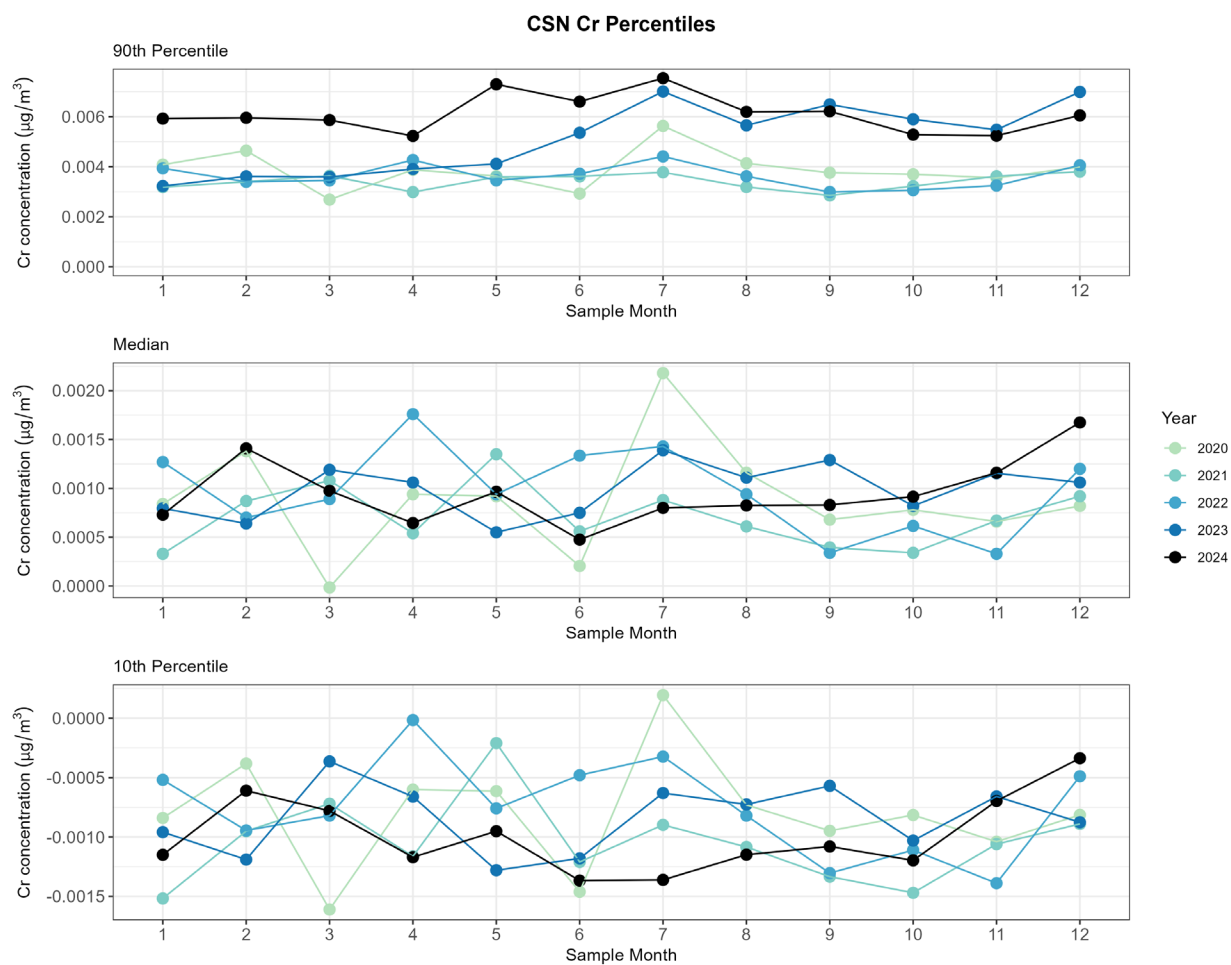


Figure 7-9: Multi-year time series of network-wide nickel (Ni) concentrations.

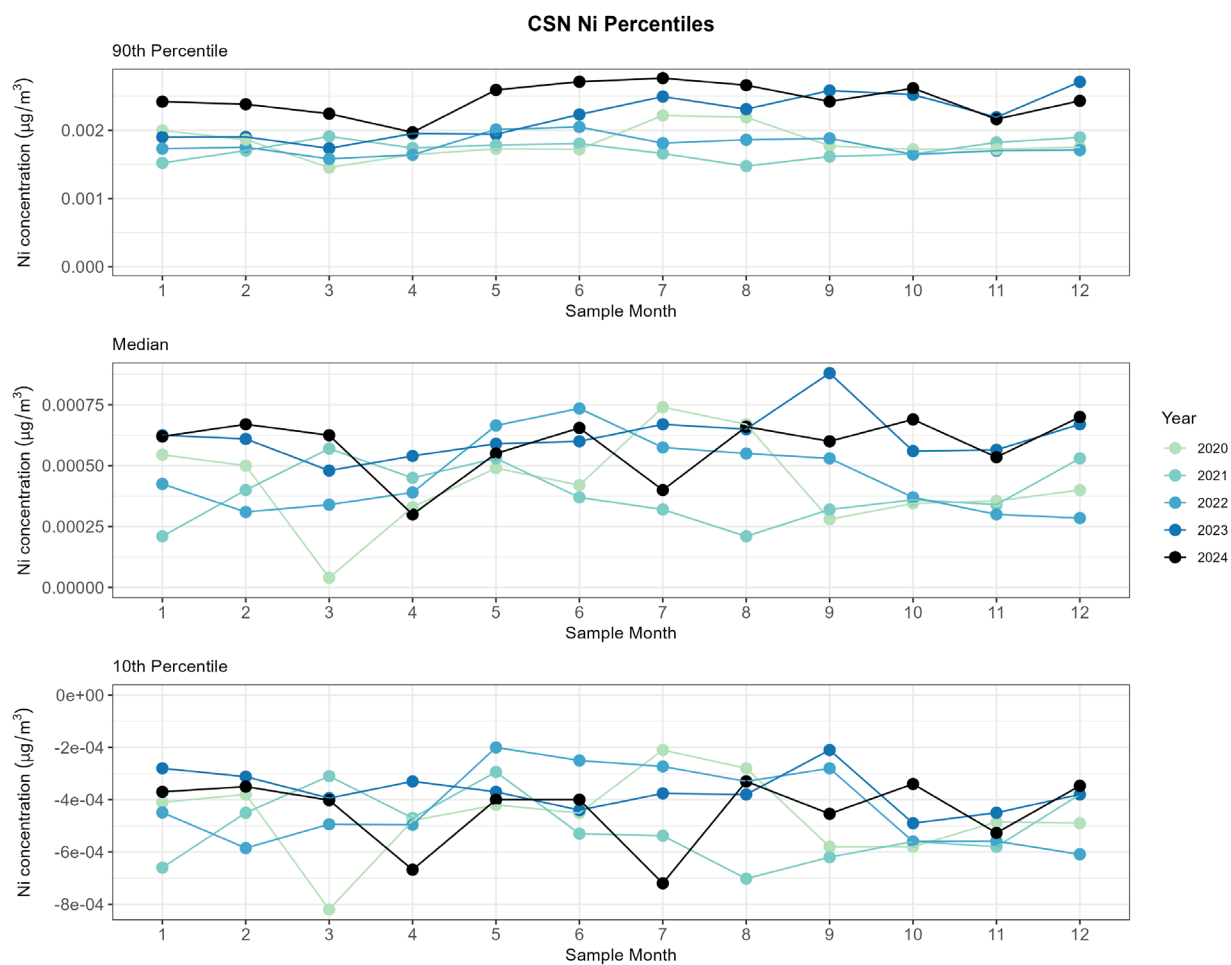
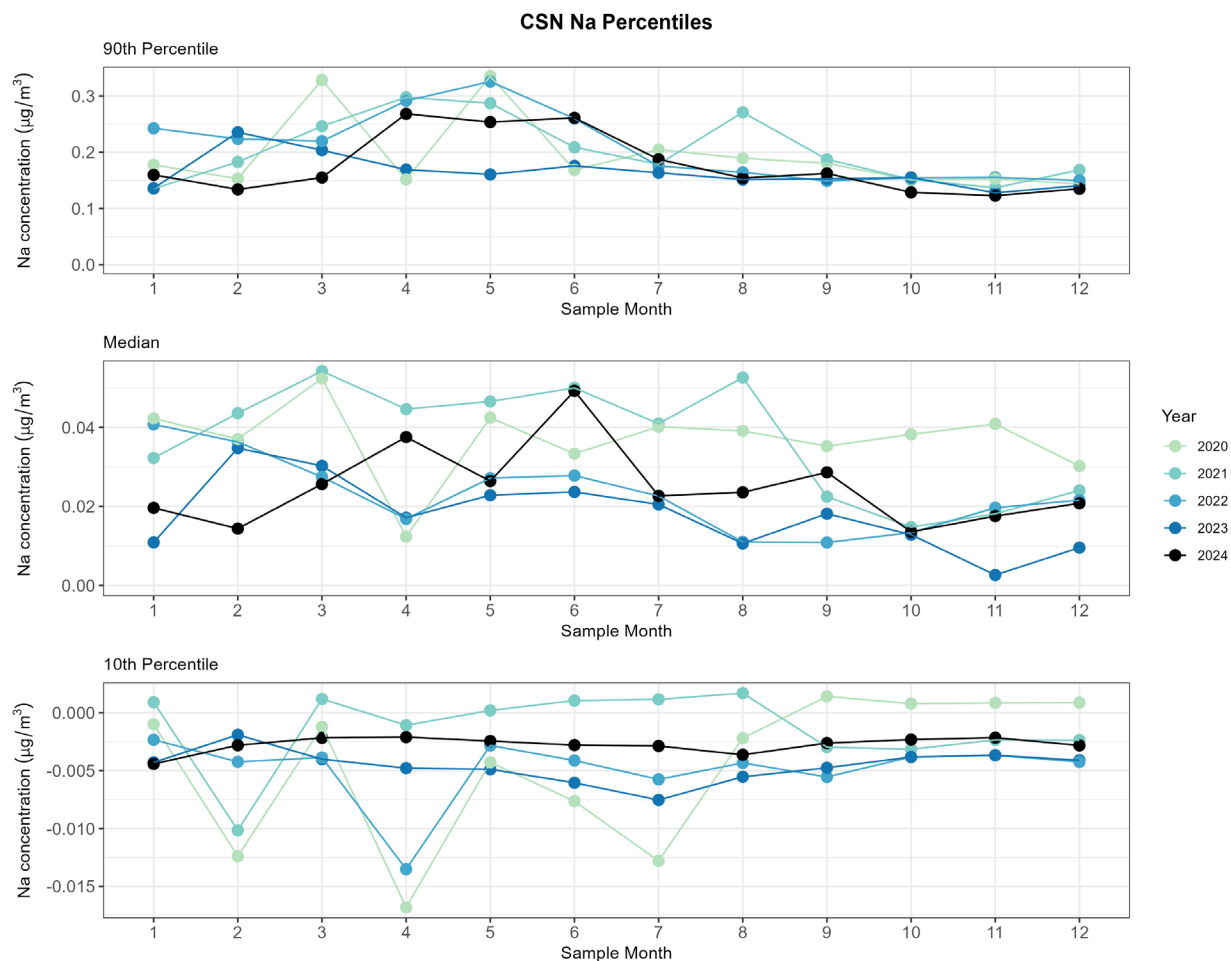
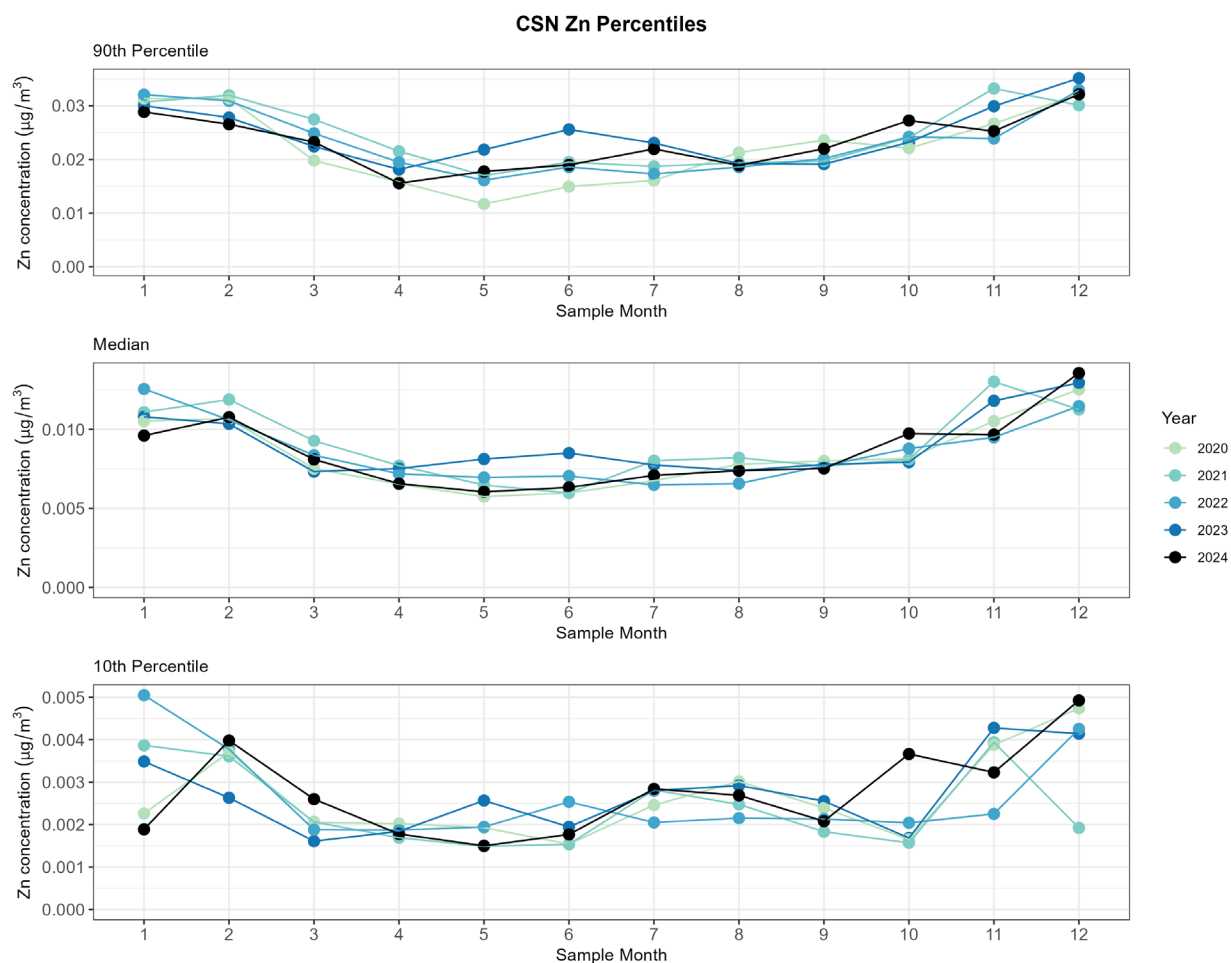


Figure 7-10: Multi-year time series of network-wide sodium (Na) concentrations.



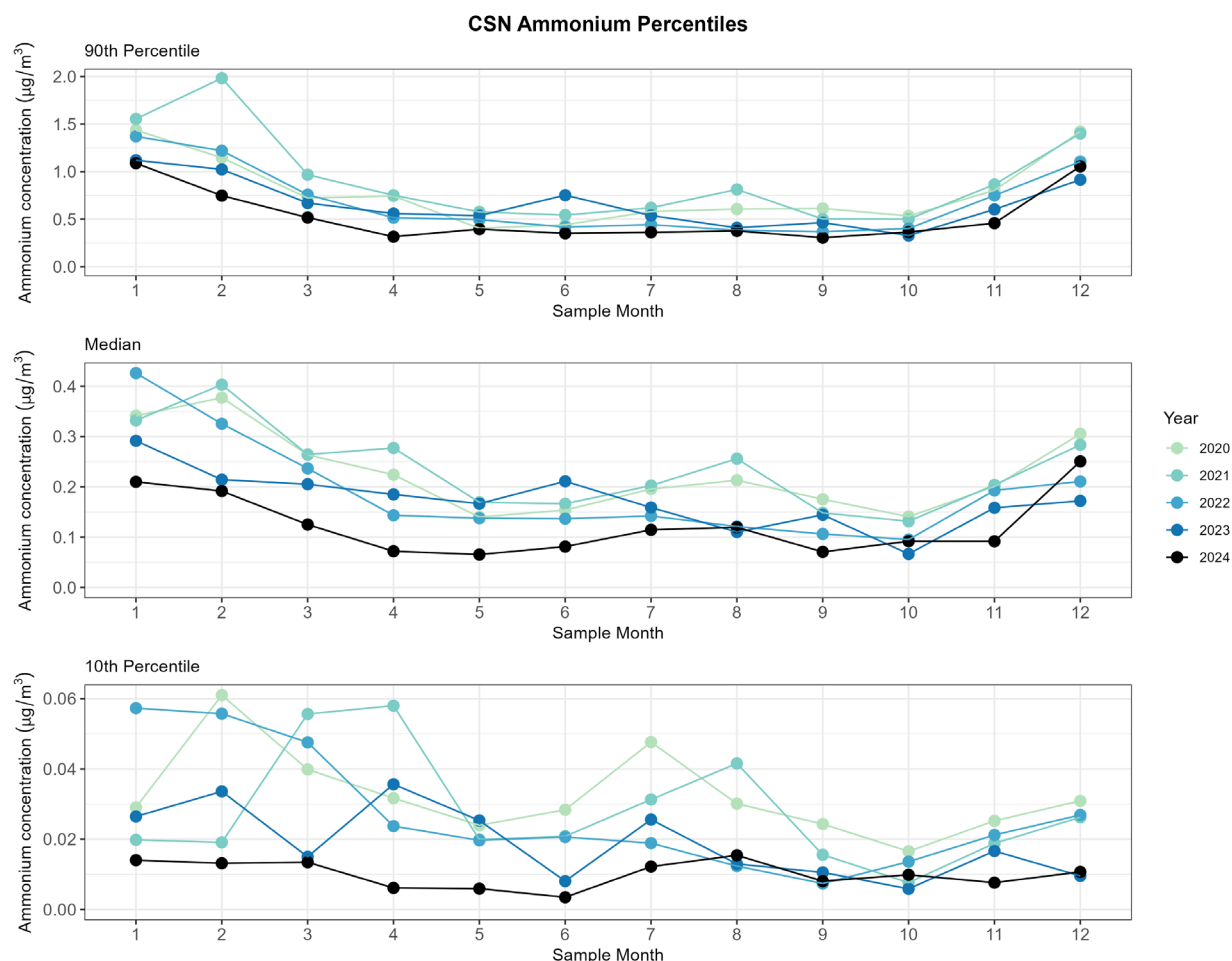
The Zinc time series is below. The 2023 May-July peaks may be tied to fire activity.

Figure 7-11: Multi-year time series of network-wide zinc (Zn) concentrations.



In Figure 7-12 below, the impact of denuder coating contamination can be seen in the lower Ammonium Ion values starting in April 2024 and returning to more-typical levels in July 2024. The ion-balance was disrupted by Sulfur contamination in the Magnesium-Oxide slurry used for recoating denuders.

Figure 7-12: Multi-year time series of network-wide ammonium 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.

7.4.2.2.1 Sulfur versus Sulfate

PTFE filters are analyzed for elemental sulfur using EDXRF, and nylon filters are analyzed for sulfate (SO_4) using IC. The molecular weight of SO_4 (96 g/mol) is three times the atomic weight of S (32 g/mol), so the concentration ratio ($3 \times \text{S}$)/ 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 7-13 shows that S and SO_4 are generally well correlated with a correlation coefficient of 0.92. Figure 7-14 shows the impact of denuder contamination on the $3\text{S}/\text{SO}_4$ ratio experienced in 2024 data.

Figure 7-13: Scatter plot of (3×S) versus SO₄, samples collected January 1, 2024 through December 31, 2024 (2022-2023?data are plotted in gray for comparison). Number of observations in 2024 (complete pairs) is 12,142. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.

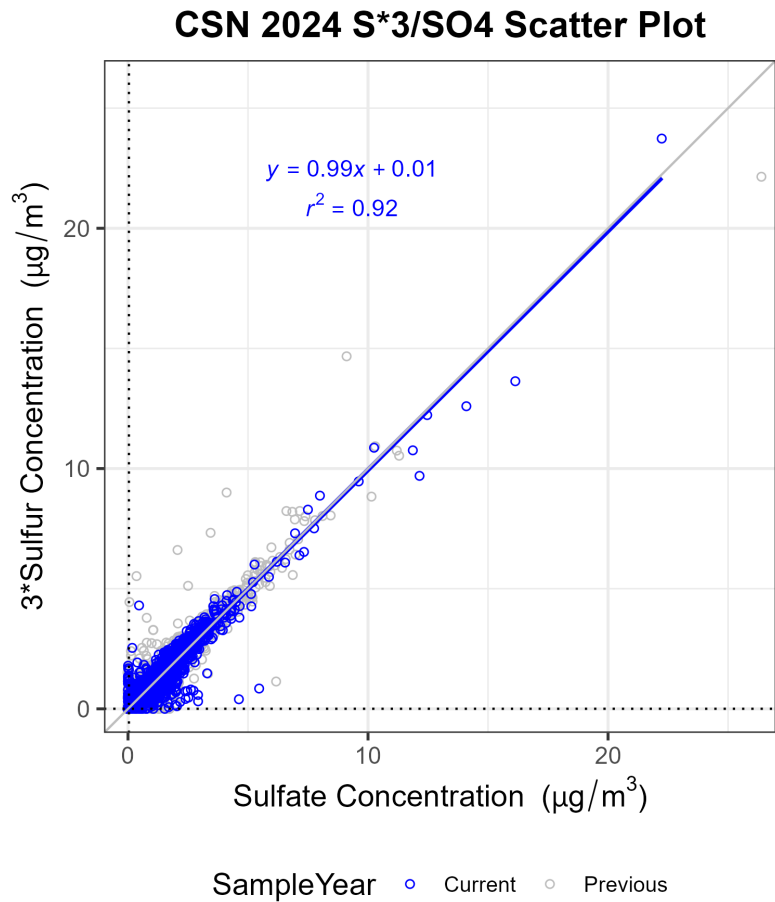
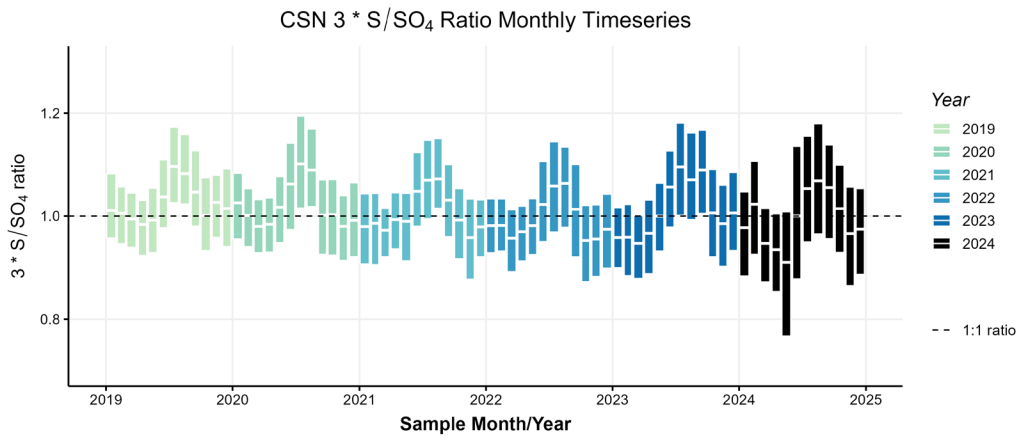


Figure 7-14: Time series of CSN monthly ratio of (3xS) versus SO₄, samples collected from 2019 to 2024.



7.4.2.2.2 Potassium versus Potassium Ion

PTFE filters are analyzed for elemental potassium using EDXRF, and nylon filters are analyzed for potassium ion using IC. Similar to the S/SO₄ ratio relationship, the potassium/potassium ion ratio can be used to identify 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 7-15).

Figure 7-15: Scatter plot of potassium versus potassium ion, samples collected January 1, 2024 through December 31, 2024 (2022-2023 data are plotted in gray for comparison). Number of observations in 2024 (complete pairs) is 12,142. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.

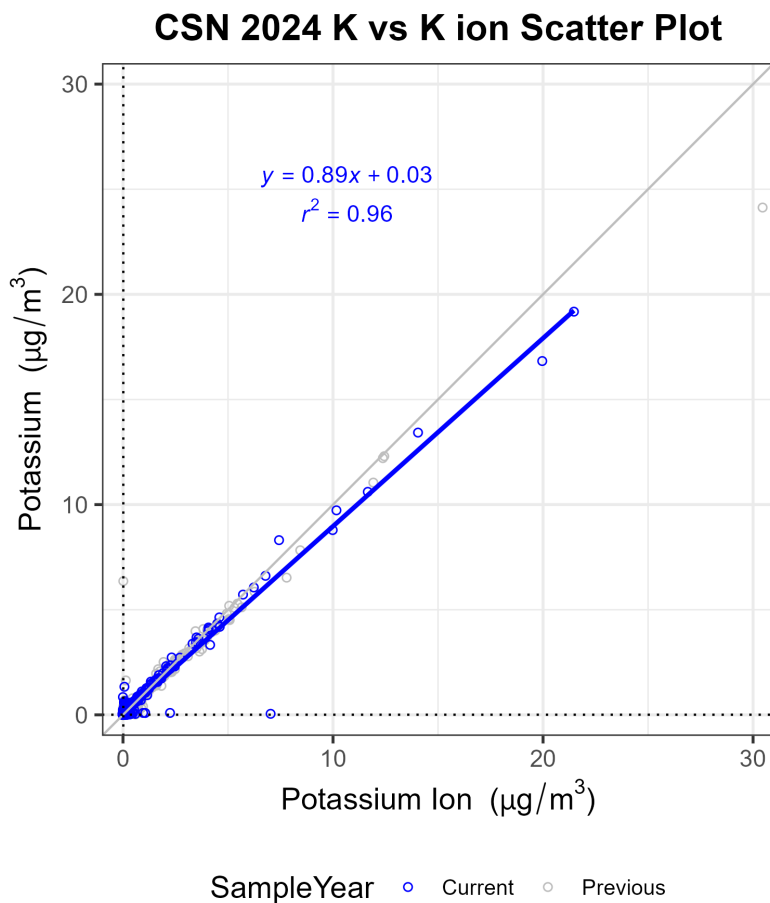
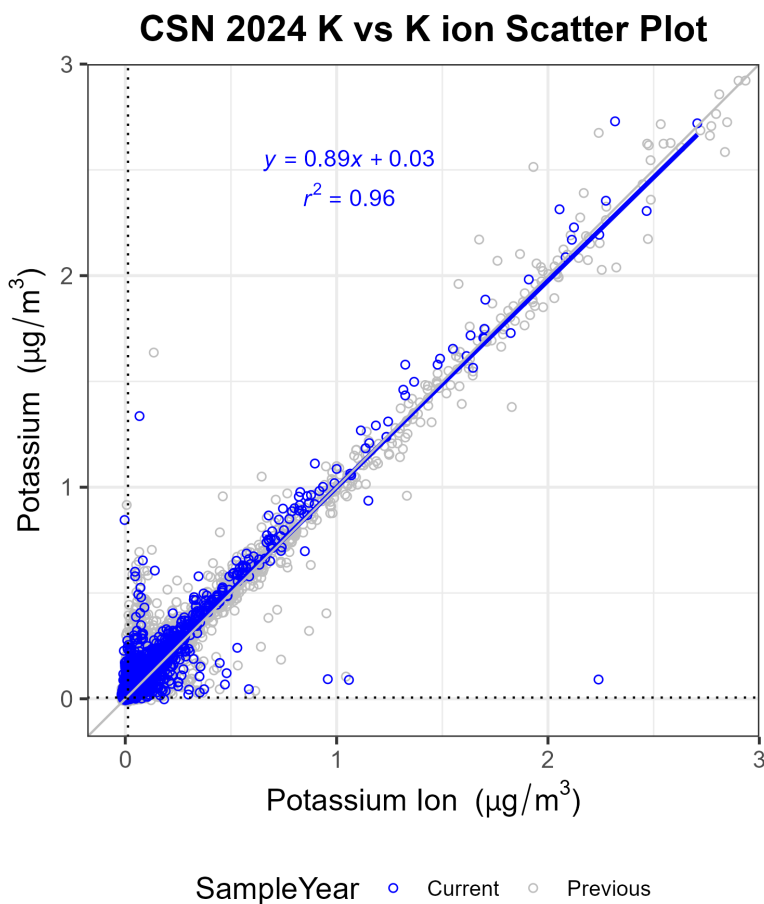


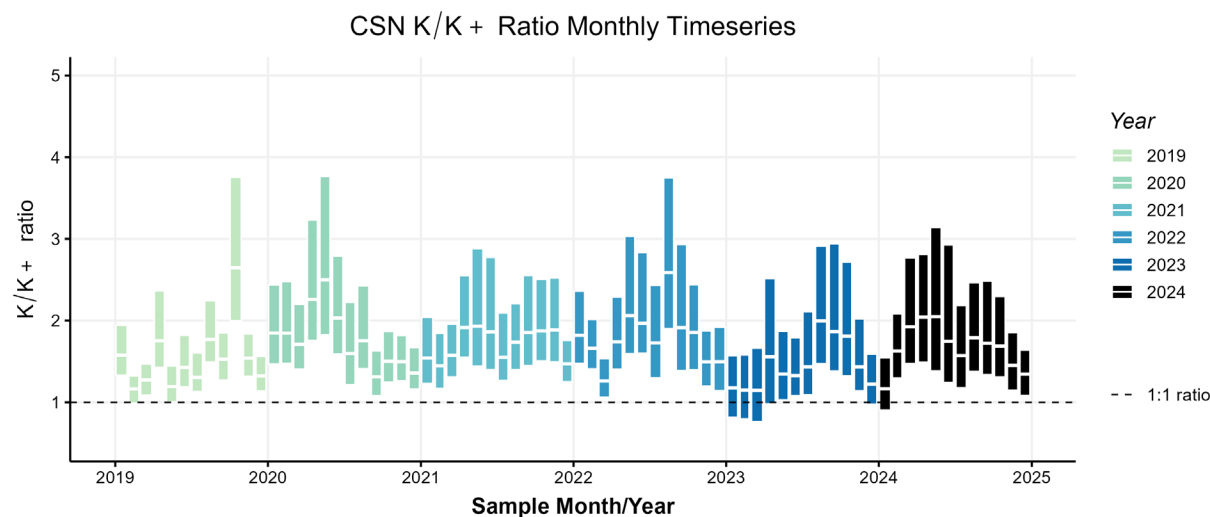
Figure 7-16: Scatter plot of potassium versus potassium ion, samples collected January 1, 2024 through December 31, 2024 (2022-2023 data are plotted in gray for comparison). Zoomed in to typical concentrations. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.



The linear regression is strongly affected by high concentrations of potassium. RTI and UC Davis reviewed their processes to look for a cause. Currently there is no conclusion. Potassium typically comes from smoke or vegetative debris and not soil. The best explanation is that perhaps the elemental measurement by XRF underestimates the higher concentrations because calibration is tuned to typical mass loadings seen in the CSN and no self-absorption correction is applied. At the lower concentrations, the points align more closely with the 1:1 line. One suggested experiment would be to do ions analysis on PTFE filters that have undergone elements measurements, at the typical concentrations, to verify our methods for the bulk of the data.

Figure 7-17 shows the multi-year time series of monthly ratio of K/K^+ over the past years.

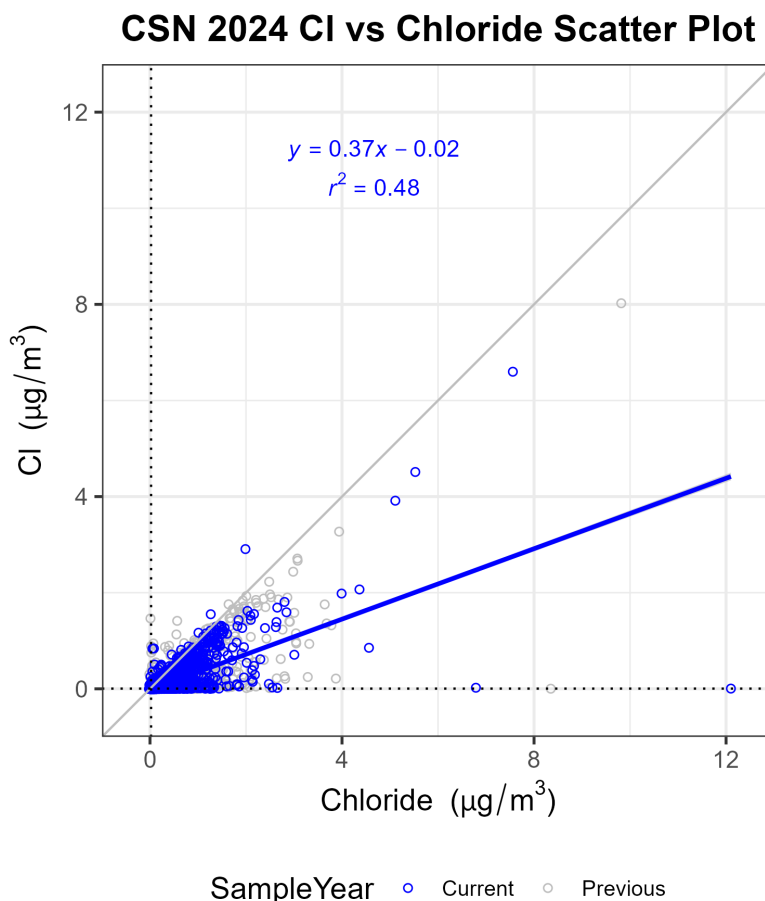
Figure 7-17: Timeseries of CSN monthly ratio of K versus K⁺, samples collected from 2019 to 2024.



7.4.2.2.3 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 7-18). In practice, chloride ion is often measured at higher concentrations than chlorine.

Figure 7-18: Scatter plot of chlorine versus chloride ion, samples collected January 1, 2024 through December 31, 2024 (2022-2023 data are plotted in gray for comparison). Number of observations in 2024 (complete pairs) is 12,040. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.



7.4.2.2.4 PM_{2.5} versus Reconstructed Mass (RCM)

PM_{2.5} mass 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:

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

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

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 PM_{2.5} mass (Figure 7-19). The multi-year monthly ratio plot (Figure 7-20) shows historically low ratios in June 2023, when PM_{2.5} concentrations were highest and driven by Canadian wildfire smoke. When organic mass (OM) is dominated by smoke, the OC-to-OM conversion factor of 1.4 may be too low, resulting in lower RCM/AirNow PM_{2.5} ratios.

Figure 7-19: Scatter plot of reconstructed mass (RCM) versus AirNow PM_{2.5} mass, samples collected January 1, 2024 through December 31, 2024 (2022-2023 data are plotted in gray for comparison). Number of observations in 2024 (complete pairs) is 9,461. Solid gray line indicates 1:1. Solid blue line indicates linear regression fit.

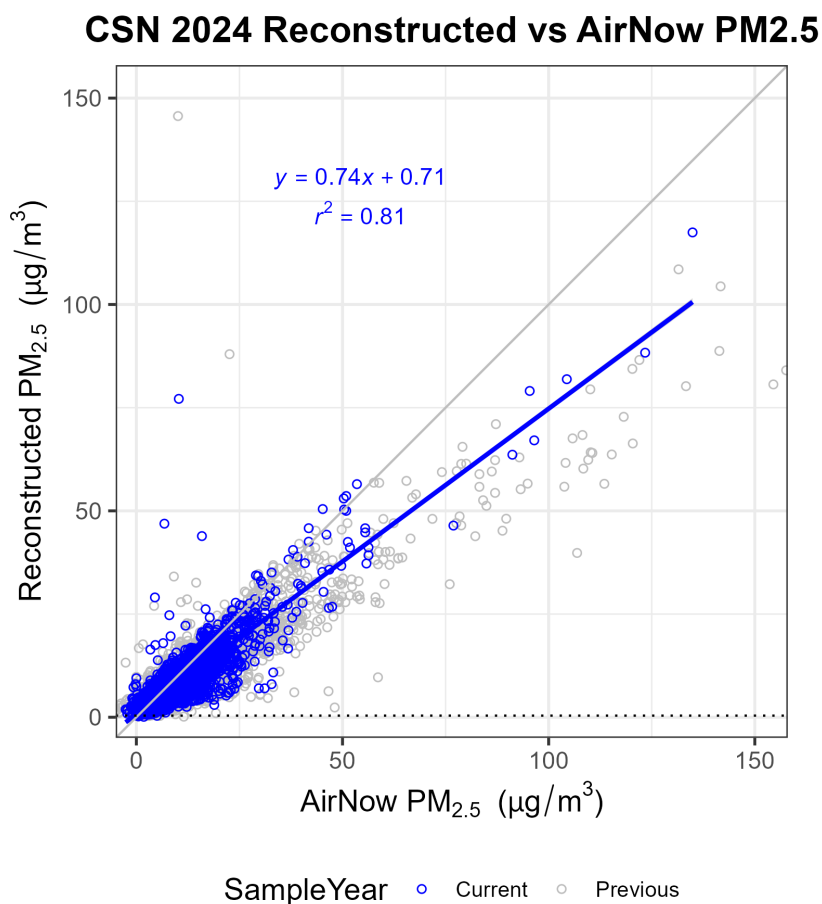
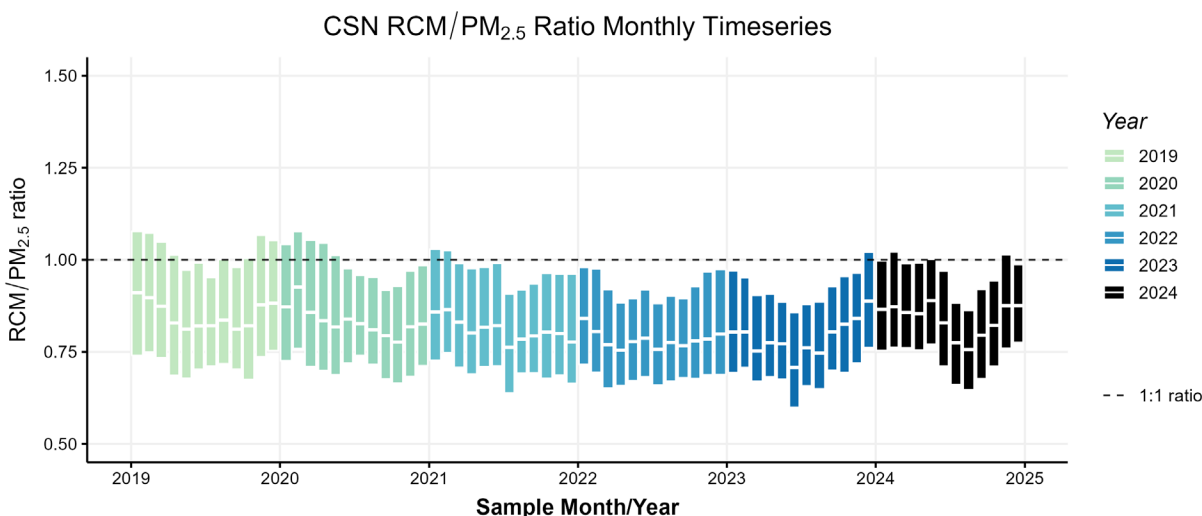


Figure 7-20: Timeseries of monthly ratio of RCM versus PM_{2.5} samples collected from 2019 to 2024.



7.4.2.2.5 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. fAbs data have been validated and delivered to AQS since May 2022.

Figure 7-21: Timeseries of monthly ratio of fAbs versus ECR samples collected from 2022 to 2024.

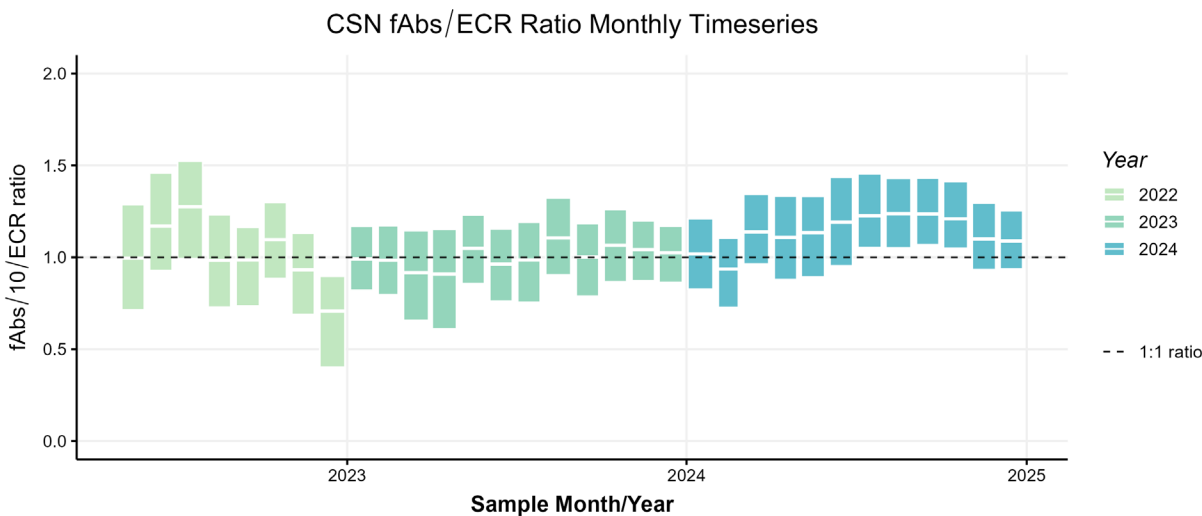
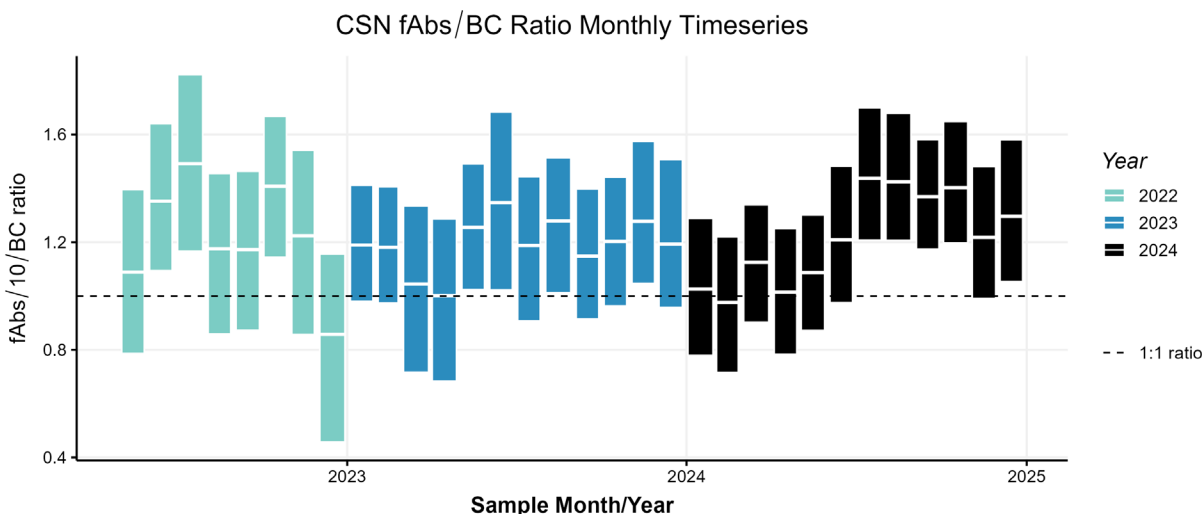


Figure 7-22: Timeseries of monthly ratio of fAbs versus BC samples collected from 2022 to 2024.



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 7-23, elements; Figure 7-24, ions; Figure 7-25, carbon, Figure 7-26, optical).

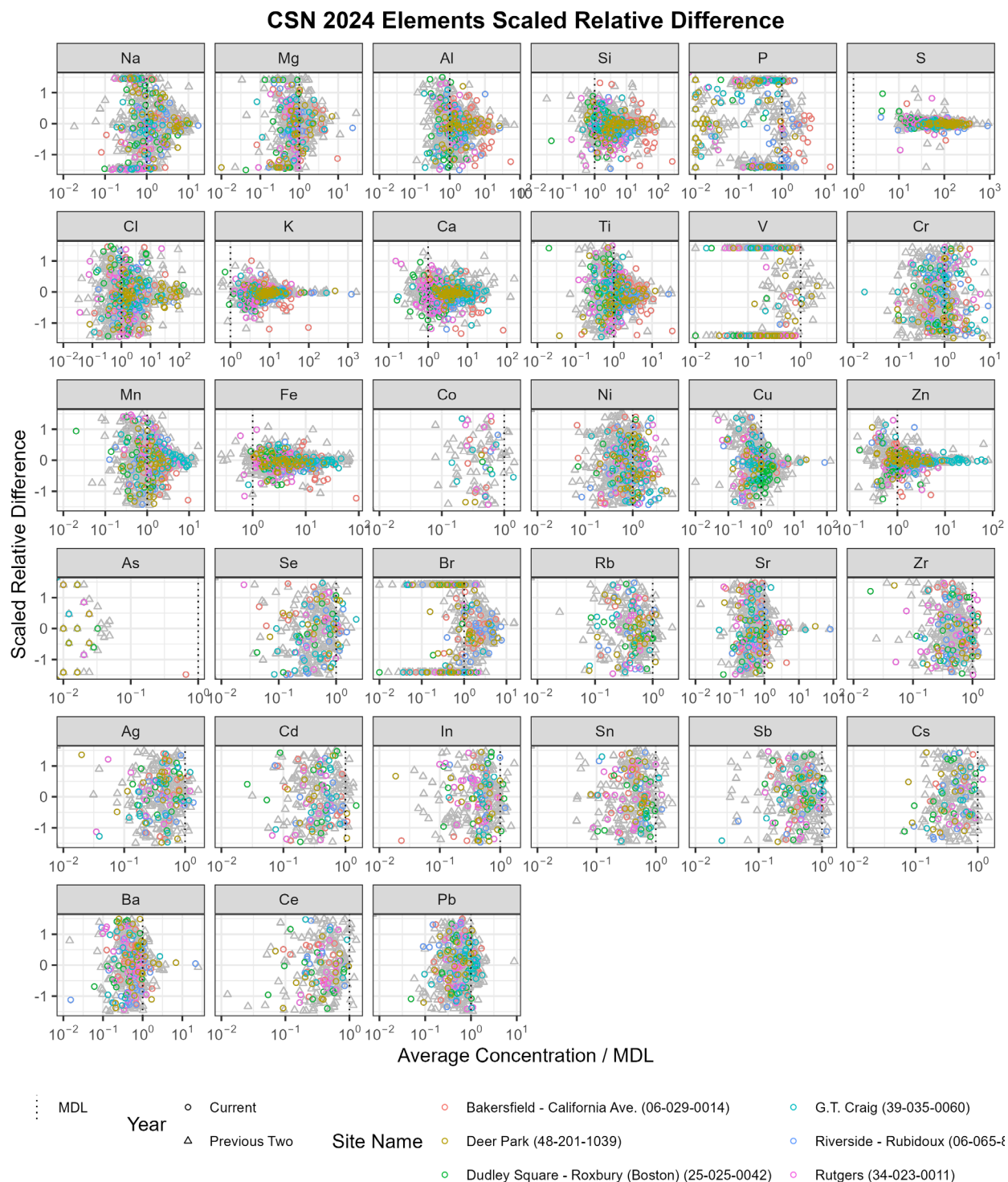
$$\text{Scaled Relative Difference (SRD)} = \frac{(\text{collocated} - \text{routine}) / \sqrt{2}}{(\text{collocated} + \text{routine}) / 2} \quad (\text{Eq. 7-1})$$

The scaled relative differences are $\pm\sqrt{2}$, when one of the two measurements is zero and vary between these limits at concentrations close to the detection limit. The scaled relative differences generally decrease with increasing concentration and are expected to converge to a distribution representative of multiplicative measurement error when the concentration is well above the detection limit. This convergence is not observed for many elements and carbon fractions that are rarely measured above the MDL at the collocated sites.

7.5.1 Collocated Scaled Relative Difference Plots

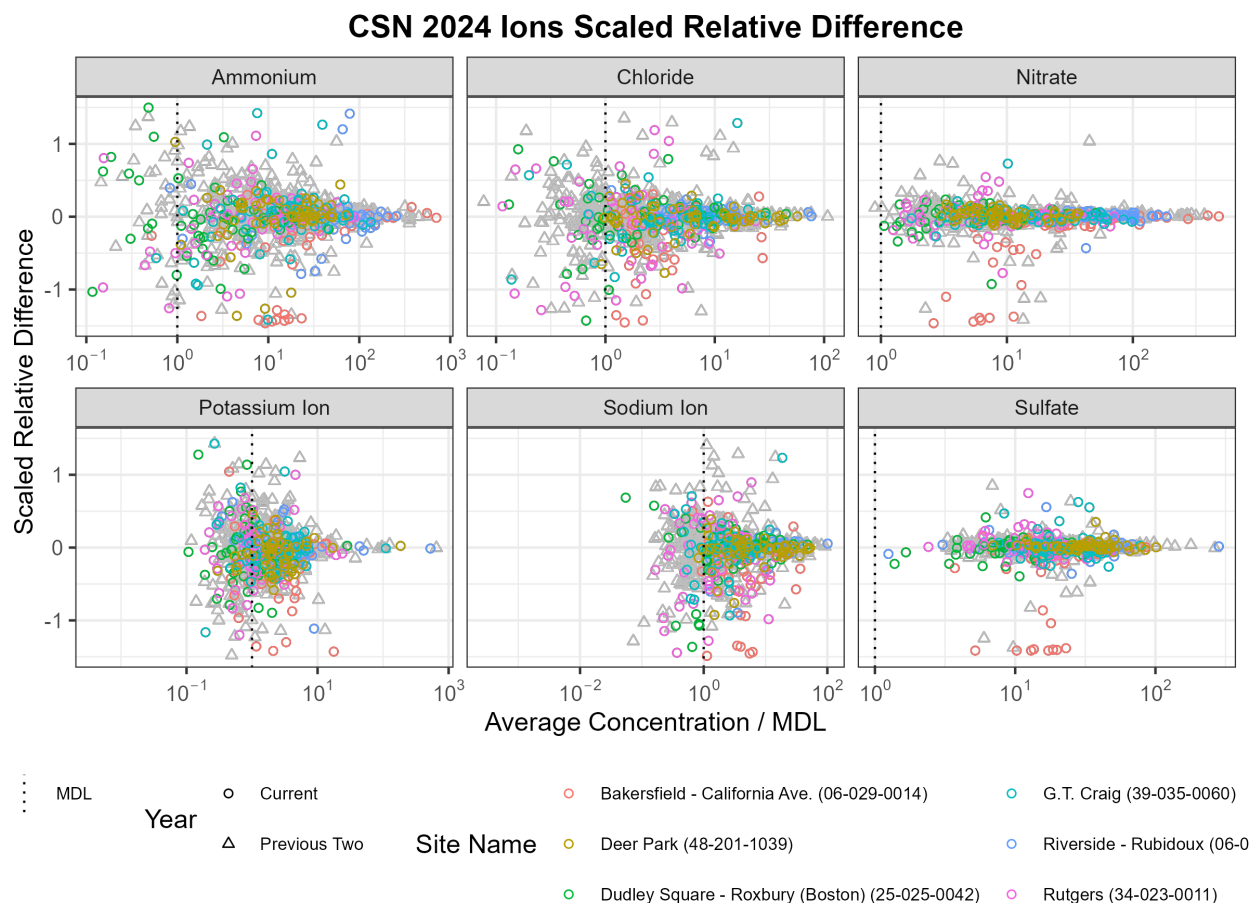
In the following plots, the values used are the delivered concentrations that have been blank corrected. Data from the previous two years (2022-2023, gray triangles) are plotted together with the current year (2024) to allow for direct comparison. Dotted vertical lines indicate MDL.

Figure 7-23: Scaled relative differences for element measurements at sites with collocated samplers across the network (January 1, 2024 through December 31, 2024).



In the Ions SRD plots below, site Bakersfield showed a difference between routine and collocated Ions from May to August 2024 that eventually returned back to normal. The cause was undetermined.

Figure 7-24: Scaled relative differences for ion measurements at sites with collocated samplers across the network (January 1, 2024 through December 31, 2024).



In Figure 7-25 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).

Figure 7-25: Scaled relative differences for carbon measurements at sites with collocated samplers across the network (January 1, 2024 through December 31, 2024).

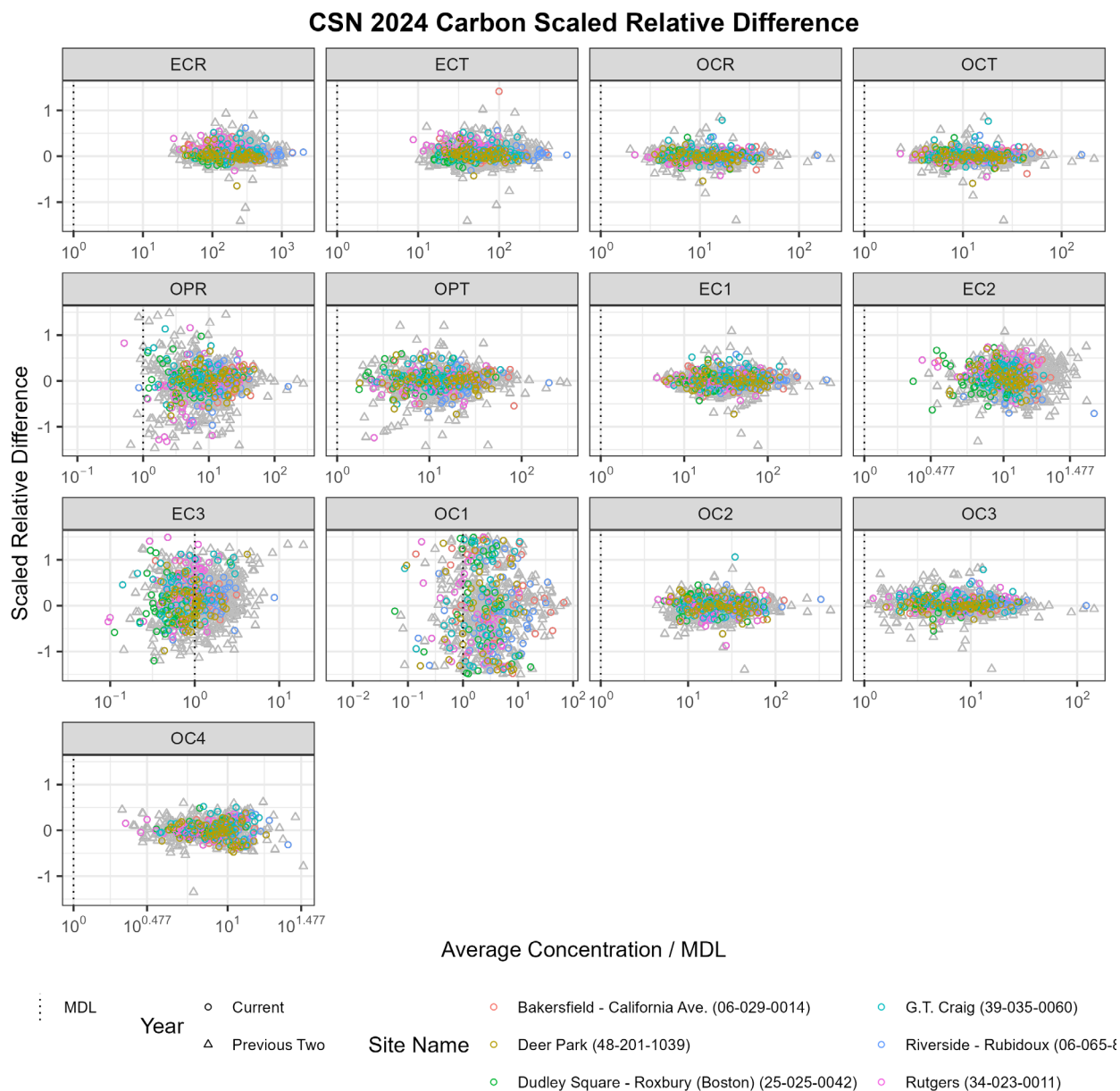
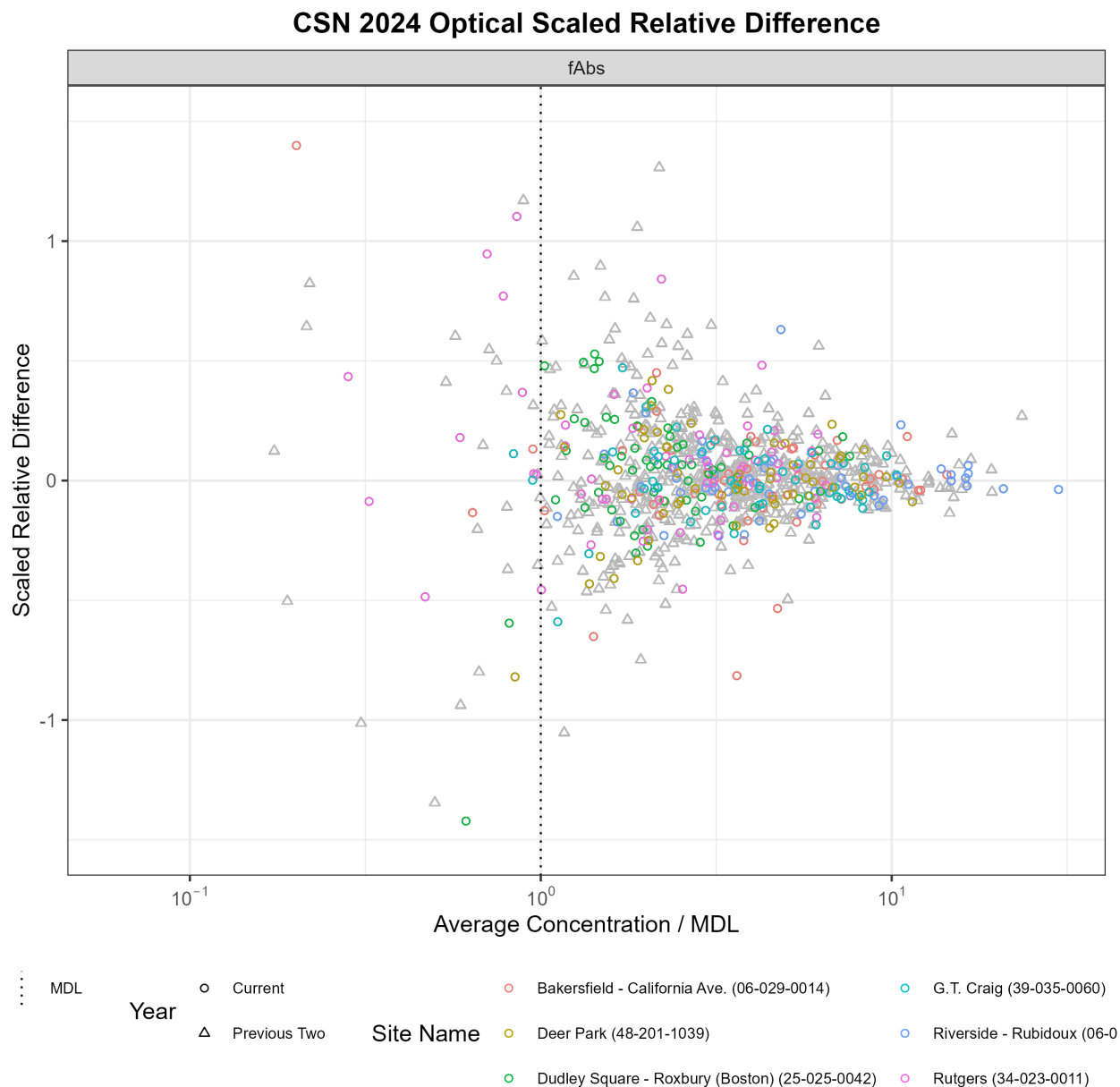


Figure 7-26 Scaled relative differences for optical measurements at sites with collocated samplers across the network (January 1, 2024 through December 31, 2024).



7.5.2 Collocated Precision and Fractional Uncertainty

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, 2024 through December 31, 2024) the fractional uncertainty is calculated from sample pairs collected at CSN collocated sites June 1, 2021 through May 31, 2023, with a minimum of 60 collocated pairs. For species 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.

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

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.

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

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}) value of relative percent difference (RPD) divided by square root of 2, 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.

$$\text{Relative Percent Difference (RPD)}_i = \frac{X_i - Y_i}{(X_i + Y_i)/2} \times 100\% \quad (\text{Eq. 7-4})$$

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

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 40 CFR Part 58, Appendix A § 4.2.1, 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, RPD is calculated using Equation 7-4. The CV upper bound is calculated using Equation 7-6:

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

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 2024 (current reporting period) as well as 2023 (previous reporting period). The CFR CV calculated using Equations 7-4 and 7-6 from collocated samples collected during 2024 (current reporting period) and 2023 (previous reporting period) is also included.

In the Tables 7-1 to 7-4 below, 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, 2020 through May 31, 2022 and used in relevant calculations for samples collected January 1, 2023 through December 31, 2023. CV is calculated from samples collected January 1, 2023 through December 31, 2023.
- For the current reporting period, f is calculated from samples collected June 1, 2021 through May 31, 2023 and used in relevant calculations for samples collected January 1, 2024 through December 31, 2024. CV is calculated from samples collected January 1, 2024 through December 31, 2024.
- 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.

Species	f (%)		f (%) Pairs		CV (%)		CV (%) Pairs		CFR CV (%)		CFR CV (%) Pairs	
	2023	2024	2023	2024	2023	2024	2023	2024	2023	2024	2023	2024
Ag	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Al	15.4	16.6	174	149	10.2	9.8	41	34	29.7	33.1	41	34
As	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Ba	25.0	25.0	0	0	15.5	6.4	2	2	10.9	17.3	2	2
Br	53.8	53.0	171	129	17.5	17.6	14	19	33.7	28.9	14	19
Ca	11.7	11.7	465	449	8.1	8.9	167	115	24.9	25.4	167	115
Cd	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Ce	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Cl	34.0	28.9	181	177	15.1	18.7	51	44	45.1	30.5	51	44
Co	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Cr	25.0	25.0	0	0	2.6	6.7	3	1	110.7	---	3	1
Cs	25.0	25.0	0	0	---	---	0	0	---	---	0	0

	<i>f</i> (%)		<i>f</i> (%) Pairs		CV (%)		CV (%) Pairs		CFR CV (%)		CFR CV (%) Pairs	
Species	2023	2024	2023	2024	2023	2024	2023	2024	2023	2024	2023	2024
Cu	25.0	25.0	41	0	2.9	8.0	7	8	9.3	13.1	7	8
Fe	10.6	10.9	599	566	5.2	8.7	140	144	18.2	23.3	140	144
In	25.0	25.0	0	0	---	---	0	0	---	---	0	0
K	7.4	8.4	644	631	6.7	5.8	278	223	15.7	17.3	278	223
Mg	25.0	25.0	9	0	8.1	18.6	5	8	21.2	28.1	5	8
Mn	25.0	25.0	45	0	7.6	8.7	26	22	17.5	17.6	26	22
Na	19.5	15.9	65	65	16.1	9.7	22	23	24.8	17.0	22	23
Ni	25.0	25.0	1	0	---	4.0	0	1	---	---	0	1
P	25.0	25.0	28	0	---	16.0	0	5	---	32.1	0	5
Pb	25.0	25.0	1	0	12.1	---	1	0	---	---	1	0
Rb	25.0	25.0	0	0	---	---	0	0	---	---	0	0
S	5.3	5.3	679	691	3.9	4.3	318	312	9.5	12.2	318	312
Sb	25.0	25.0	2	0	---	---	0	0	---	---	0	0
Se	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Si	11.7	12.7	457	445	12.7	11.6	187	114	28.2	29.9	187	114
Sn	25.0	25.0	0	0	---	---	0	0	---	---	0	0
Sr	25.0	25.0	1	0	0.8	4.1	3	5	2.8	12.9	3	5
Ti	16.3	15.1	180	134	10.8	13.0	28	23	23.6	41.8	28	23
V	25.0	25.0	8	0	18.5	---	1	0	---	---	1	0
Zn	12.5	12.6	508	437	3.8	6.2	45	109	10.2	10.4	45	109
Zr	25.0	25.0	0	0	---	---	0	0	---	---	0	0

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

	<i>f</i> (%)		<i>f</i> (%) Pairs		CV (%)		CV (%) Pairs		CFR CV (%)		CFR CV (%) Pairs	
Species	2023	2024	2023	2024	2023	2023	2023	2024	2023	2024	2023	2024
fAbs	11.0	11.0	276	138	6.2	6.5	158	186	11.2	12.6	158	186

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

	<i>f</i> (%)		<i>f</i> (%) Pairs		CV (%)		CV (%) Pairs		CFR CV (%)		CFR CV (%) Pairs	
Species	2023	2024	2023	2024	2023	2023	2023	2024	2023	2024	2023	2024
Ammonium	8.5	11.9	600	586	8.3	9.3	260	222	22.8	24.0	260	222
Chloride	6.4	5.5	418	454	3.7	5.4	153	156	16.6	13.8	153	156
Nitrate	4.7	4.5	654	640	3.5	4.3	275	284	11.3	14.2	275	284
Potassium Ion	10.2	9.9	308	233	6.2	6.2	66	70	22.3	13.7	66	70
Sodium Ion	6.3	5.7	362	350	3.5	6.1	130	155	14.3	20.6	130	155
Sulfate	3.6	3.4	677	691	3.0	4.0	314	294	10.6	15.7	314	294

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 (CFR CV) for carbon species.

	f (%)		f (%) Pairs		CV (%)		CV (%) Pairs		CFR CV (%)		CFR CV (%) Pairs	
Species	2023	2024	2023	2024	2023	2024	2023	2024	2023	2024	2023	2024
Elemental Carbon (EC1)	13.8	12.4	667	676	7.9	7.3	319	308	20.3	16.1	319	308
Elemental Carbon (EC2)	28.2	29.7	628	659	21.7	20.5	318	301	32.0	28.0	318	301
Elemental Carbon (EC3)	25.0	29.5	102	143	12.9	20.6	17	2	25.5	32.7	17	2
Elemental Carbon (ECR)	12.4	13.7	666	676	7.8	7.7	319	308	16.8	14.4	319	308
Elemental Carbon (ECT)	15.2	15.9	667	676	9.0	8.9	319	307	18.7	14.9	319	307
Organic Carbon (OC1)	33.8	36.6	269	185	17.7	17.3	59	41	39.1	38.8	59	41
Organic Carbon (OC2)	11.5	12.6	661	670	9.1	9.0	319	310	19.1	16.3	319	310
Organic Carbon (OC3)	10.3	11.5	238	449	5.5	7.0	272	298	16.4	14.1	272	298
Organic Carbon (OC4)	20.5	17.5	456	545	10.3	11.5	297	310	19.1	18.2	297	310
Organic Carbon (OCR)	7.0	8.0	486	611	4.6	4.7	314	309	13.5	10.9	314	309
Organic Carbon (OCT)	6.4	7.1	509	623	4.4	4.7	315	309	13.3	10.9	315	309
Organic Pyrolyzed (OPR)	22.0	22.0	431	458	15.0	14.5	251	269	31.1	27.6	251	269
Organic Pyrolyzed (OPT)	17.9	16.8	583	607	11.7	11.3	297	303	26.8	22.9	297	303

8. References

40 CFR Part 50 Appendix L. Available at
<https://www.govinfo.gov/app/details/CFR-2024-title40-vol2/CFR-2024-title40-vol2-part50-appL>

Code of Federal Regulations. Title 40, Part 58, Appendix A. Available at
<https://www.ecfr.gov/current/title-40/chapter-I/subchapter-C/part-58/appendix-Appendix%20A%20to%20Part%2058>.

Rice, J. and Landis, E. (2016): Chemical Speciation Network (CSN) Summary of Precision from Six Collocated Sites [Poster presentation]. 2016 National Ambient Air Monitoring Conference, Portland, OR, United States, https://www.epa.gov/sites/production/files/2016-09/documents/summary_of_precision.pdf

Quality Assurance Guidance Document 2.12 – Monitoring PM_{2.5} in Ambient Air Using Designated Reference or Class I Equivalent Methods, January 2016. Available at
<https://www3.epa.gov/ttnamti1/files/ambient/pm25/qa/m212.pdf>