

Chemical Speciation Network (CSN)

Annual Quality Report

Samples Collected January 1, 2020 through December 31, 2020

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1. Executive Summary

1.1 Introduction

The University of California, Davis (UC Davis) Air Quality Research Center summarizes quality assurance (QA) annually in this report as a contract deliverable for the Chemical Speciation Network (CSN) program (contract #EP-D-15-020). The primary objectives of this report are:

1. Provide the U.S. Environmental Protection Agency (EPA) and other potential data users with graphical and tabular illustrations of quality control (QC) for species measured within the network.
2. Identify and highlight observations of interest that may have short- or long-term impact on data quality across the network or at particular sites.
3. Serve as a record and tool for ongoing UC Davis QA efforts.

Each standard network site includes two samplers: (1) URG 3000N carbon sampler (URG Corporation; Chapel Hill, NC) for collection of particulate matter on quartz filters; and (2) Met One SASS or SuperSASS (Met One Instruments, Inc.; Grants Pass, OR) for collection of particulate matter on polytetrafluoroethylene (PTFE) filters and nylon filters. The following analyses are performed:

- PTFE filters: filters are analyzed at UC Davis using energy dispersive X-ray fluorescence (EDXRF) for a suite of 33 elements.
- Nylon filters: filters are analyzed at Research Triangle Institute International (RTI) using ion chromatography (IC) for a suite of six ions.
- Quartz filters: filters are analyzed at UC Davis for organic and elemental carbon — including carbon fractions — using thermal optical analysis (TOA).

Unless otherwise noted, data and discussions included in this report cover samples collected during the time period January 1, 2020 through December 31, 2020 (batches 63-74, where each month corresponds with a single calendar month).

1.2 Data Quality Overview and Issues

Section 4 of this report provides laboratory performance details for each of the analytical measurement techniques. The laboratory performance is detailed in Section 4.1 (RTI Ion Chromatography Laboratory), Section 4.2 (UC Davis X-ray Fluorescence Laboratory), and Section 4.3 (UC Davis Thermal Optical Analysis Laboratory).

Across the network, completeness — determined by the total number of valid samples relative to the total number of scheduled samples — was 86.4% for PTFE filters, 86.8% for nylon filters, and 84.5% for quartz filters. Data from sites with non-standard sampler configurations are not included in the completeness calculations. The impact of COVID-19 related shutdowns on data completeness is discussed in Section 3.1.1.1.

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

2. Summary of Laboratory Operation Issues

2.1 RTI Ion Analysis Laboratory

2.1.1 Chloride Peak Interference

During this reporting period, RTI observed noticeable differences between total sulfur measured by ICP-OES and sulfate measured by IC in IMPROVE samples while conducting a collaborative research study exploring the prevalence of organic sulfur (OS) compounds and their impact on sulfur measurements. The differences were most substantial for samples collected in summer and less evident in winter-collected samples (RTI, 2020). RTI further investigated the possibility of chloride peak interference from organic sulfur in samples and their findings indicate that while there is an interference, the magnitude is generally comparable to, or lower than, the MDL, concluding that any interference will likely have minimal impact for most samples. However, it is hypothesized that the impact of the observed bias will vary seasonally and regionally as a function of the OS and chloride concentrations. RTI flag samples for reanalysis that have a measurable OS presence, specifically a 2-methyltetrol sulfate peak area of 0.005 or greater, and UCD continue to perform cross-module analysis to identify suspect results and request reanalysis where necessary. No flagging, invalidation, or other additional actions are taken on the data.

2.2 UC Davis X-ray Fluorescence Laboratory

2.2.1 COVID-19 Related Laboratory Shutdown

During this reporting period, the laboratory was shut down and inaccessible to laboratory staff beginning March 19, 2020 due to the University entering suspended operations in response to local shelter-in-place orders. Restricted access to the laboratory was restored in early May 2020 and routine CSN sample analysis resumed. Due to the limited laboratory access and cessation of routine analysis, there were fewer QC checks performed during this time with no monthly QC checks performed in the month of April 2020. All QC checks, including the monthly check, were performed prior to restarting routine sample analysis in May 2020. Other than the delay in analysis, this shutdown did not impact the sample results.

2.2.2 Laboratory Move

During this reporting period the AQRC Laboratory moved from Jungerman Hall on the main UC campus to a building less than three miles away in Davis, but not on the main campus. The new laboratory and office space are located at 1560 Drew Ave., Davis, CA 95618.

All five of the XRF instruments used by the AQRC laboratory were moved to the new laboratory location between October and November 2020. The instruments were moved in staggered groups to minimize any downtime due to unforeseen issues at the new location. The manufacturer was contracted to shut down, disconnect, and crate each instrument prior to transport to the new lab. University Special Services department handled the physical move of the palletted instruments to the new lab. The manufacturer then un-crated and reinstalled the instruments at the new location, testing environmental and electrical power requirements at the new lab to ensure proper operation. The manufacturer also ran their basic installation qualification tests.

Once the manufacturer signed off on the installations, the instruments were calibrated and ran all the normal calibration QC procedures as well as the daily, weekly, and monthly QC checks. All instruments passed these checks and routine analysis was started at the new location. There has been no indication of any impact to the sample analysis results related to the move.

2.3 UC Davis Thermal Optical Analysis Laboratory

2.3.1 COVID-19 Related Laboratory Shutdown

During this reporting period, the laboratory was shut down and inaccessible to laboratory staff beginning March 19, 2020 due to the University entering suspended operations in response to local shelter-in-place orders. Restricted access to the laboratory was restored in late April 2020 and routine CSN sample analysis was restarted on April 28, 2020. Due to the limited laboratory access and the cessation of routine analysis, there were no, or fewer, QC checks performed between March 19 and April 28, 2020. All QC checks were performed prior to restarting routine sample analysis in April 2020. Other than the delay in analysis, this shutdown did not impact the sample results.

2.3.2 Laboratory Move

As stated in Section 2.2.2, during this reporting period the AQRC Laboratory moved from Jungerman Hall on the main UC campus to an off-campus location. The new laboratory and office space is located at 1560 Drew Ave., Davis, CA 95618.

All five of the carbon analyzers (Alpha, Beta, Gamma, Delta, and Zeta) used by the AQRC laboratory were moved to the new laboratory location on November 23, 2020. Prior to this date, quartz filters sampled between January 1 and August 31, 2020 (e.g., batch 63 through batch 70) were analyzed for their carbon contents at the previous laboratory location between the dates March 10 and November 11, 2020. The remaining samples that were collected from September 1 to December 31, 2020 (e.g., batch 71 through 74) were analyzed in the new laboratory location starting from November 23, 2020 to March 9, 2021 (See Table 4.3-1).

Additionally, a new Sunset OCEC carbon analyzer (hereinafter referred to as Theta) was purchased prior to the laboratory move and was directly installed at the new location by the Sunset Laboratory technician during November 3-5, 2020.

After the relocation, multi-point sucrose standard checks were applied to all six instruments by running a complete set of calibration standards listed in Table 4.3-4 on November 23, 2020. Additionally, temperature calibration was applied to the new instrument, Theta, on November 24, 2020 and to Beta after replacing its main oven on December 1, 2020 (See Table 4.3-9).

Comparison of the QC checks before and after the relocation date of the carbon analyzers at the UC Davis TOA Laboratory can be found in Section 4.3 of this report (See Figures 4.3.1-4.3.5).

3. Quality Issues and Corrective Actions

3.1 Data Quality

3.1.1 Completeness

Completeness is evaluated network wide by filter type, and determined by the total number of valid samples relative to the total number of collected and scheduled samples (Table 3.1-1). Data from sites with non-standard sampler configurations are not included in the completeness calculations. Additionally, for completeness relative to the total number of collected samples, calculation results shown in Table 3.1-1 and Table 3.1-2 do not include placeholder records generated for samples that were scheduled but not collected (Section 3.2.4.5). The completeness is comparable for PTFE and nylon filters which are both collected by the Met One SASS / Super SASS sampler; however, the number of invalid samples is higher for quartz filters, which are collected by the URG sampler.

Table 3.1-1: Network sample completeness by filter type, January 1, 2020 through December 31, 2020. The total number of scheduled samples is calculated from the sampling schedule (does not include field blanks). The total number of collected samples is the actual number of samples collected in the field.

Filter Type	Total Number of Scheduled Samples	Total Number of Collected Samples	Number of Valid Samples	Number of Invalid Samples	% Valid (relative to # of collected samples)	% Valid (relative to # of scheduled samples)
PTFE	13,536	12,338	11,701	637	94.8	86.4
Nylon	13,536	12,338	11,743	595	95.2	86.8
Quartz	13,536	12,350	11,435	915	92.6	84.5

Across the network there were thirteen sites with completeness (relative to the number of collected samples, and determined for null codes applied at the filter level) less than 75% for at least one filter type (Table 3.1-2), considering samples collected January 1, 2020 through December 31, 2020.

Table 3.1-2: Network sites with less than 75% sample completeness (relative to the number of collected samples, and determined for null codes applied at the filter level) for at least one filter type, January 1, 2020 through December 31, 2020. For each filter type, the percentage of different null codes is listed relative to the total number of null codes per site. For null code definitions, see Table 3.1-3.

AQS ID #	Location	Completeness			Null Codes		
		PTFE	Nylon	Quartz	PTFE	Nylon	Quartz
10-003-2004-5	Wilmington - MLK	88.0%	88.0%	67.4%	AF (55%) Other (45%)	AF (55%) Other (45%)	AH (57%) AF (17%) Other (26%)
12-073-0012-5	Tallahassee Community College	73.8%	73.8%	96.7%	AH (94%) AF (6%)	AH (94%) AF (6%)	AF (50%) AV (50%)
13-069-0002-5	Douglas	73.8%	98.4%	100.0%	AH (94%) AF (6%)	BA (100%)	---

AQS ID #	Location	Completeness			Null Codes		
		PTFE	Nylon	Quartz	PTFE	Nylon	Quartz
17-031-0076-5	Chicago - Com Ed	72.0%	73.7%	52.9%	AB (33%) AF (30%) Other (36%)	AB (35%) AF (32%) Other (32%)	AN (53%) AB (18%) Other (29%)
25-013-0008-5	Westover AFB (Chicopee)	82.5%	82.5%	70.0%	AF (43%) BE (43%) BB (14%)	AF (43%) BE (43%) BB (14%)	AN (60%) AF (13%) Other (27%)
28-049-0020-5	Jackson Ncore	100.0%	100.0%	68.9%	---	---	AH (89%) SV (5%) Other (6%)
30-049-0004-5	Seiben Flats	97.5%	97.5%	73.0%	AN (100%)	AN (100%)	AN (97%) AH (3%)
32-003-0540-5	Jerome Mack Middle School	96.7%	96.7%	65.6%	AF (50%) BJ (50%)	AF (50%) BJ (50%)	AH (90%) AF (5%) Other (5%)
42-075-0100-5	Lebanon	16.7%	16.7%	16.7%	AV (60%) AF (40%)	AV (60%) AF (40%)	AV (60%) AF (40%)
46-099-0008-5	Sioux Falls School of Deaf	91.5%	90.7%	52.5%	AF (100%)	AF (91%) AH (9%)	AN (77%) AF (18%) Other (5%)
47-093-1020-5	Knoxville - Spring Hill Elementary School	93.4%	93.4%	62.0%	AH (100%)	AH (100%)	AH (63%) AN (32%) AS (5%)
53-077-0009-5	Yakima - 4th Ave	83.6%	83.6%	72.1%	BE (80%) AF (10%) AG (10%)	BE (80%) AF (10%) AG (10%)	AH (47%) BE (47%) AF (6%)
72-021-0010-5	Jail at Bayamon, PR	0.0%	0.0%	28.6%	AN (43%) AF (29%) AH (29%)	AN (43%) AF (29%) AH (29%)	AN (60%) AF (40%)

Samples can be invalidated for a variety of reasons, as detailed in the *UCD CSN TI 801C* and the *Data Validation for the Chemical Speciation Network* guide. Null codes indicate the reasons for invalidation (Table 3.1-3).

Table 3.1-3: Number and type of null codes applied at the filter level to SASS and URG samples from January 1, 2020 through December 31, 2020. Codes are ordered by frequency of occurrence.

Null Code	SASS PTFE	SASS Nylon	URG Quartz	Null Code Description
AF	138	138	130	Scheduled but not Collected
BB	91	91	93	Unable to Reach Site
AH	88	66	220	Sample Flow Rate or CV out of Limits
AN	83	80	223	Machine Malfunction
BJ	64	56	31	Operator Error
AB	38	38	33	Technician Unavailable
AV	36	36	51	Power Failure
BE	19	19	18	Building/Site Repair
AL	13	13	10	Voided by Operator
AG	13	13	20	Sample Time out of Limits
AJ	9	10	2	Filter Damage
AR	8	0	4	Lab Error
BI	6	6	6	Lost or damaged in transit
BA	5	5	8	Maintenance/Routine Repairs
AO	5	6	6	Bad Weather
SV	4	4	16	Sample Volume Out of Limits
AW	4	1	0	Wildlife Damage
AQ	3	3	3	Collection Error
AM	3	3	4	Miscellaneous Void
AI	3	3	0	Insufficient Data (cannot calculate)
SA	2	2	2	Storm Approaching
AU	1	1	1	Monitoring Waived
AC	1	1	0	Construction/Repairs in Area
AS	0	0	30	Poor Quality Assurance Results
AK	0	0	2	Filter Leak
DA	0	0	1	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)
AZ	0	0	1	Q C Audit

3.1.1.1 COVID-19 Related Sample Losses

Between March 16, 2020 and December 7, 2020, various sites across the network shutdown because of the COVID-19 pandemic. A total of 41 sites shutdown during this period, with a maximum of 27 sites with paused operations at the same time.

Filters the Sample Handling Laboratory (Wood PLC) had already shipped to impacted sites were not sampled and subsequently marked invalid. Filter shipments to impacted sites were subsequently paused and UC Davis created placeholder electronic filter records for expected sample filters for completeness purposes where physical filters and associated electronic records were not generated at the Sample Handling Laboratory (Section 3.2.4.5). These records are marked invalid with the ‘AF – Scheduled but not Collected’ null code flag automatically by UC

Davis when creating these records; the final reported null code flags for some records in AQS may differ. Note that placeholder electronic filter records are also created during this reporting period for other reasons including sites with sampler malfunctions or repairs.

A total of 2,918 placeholder electronic sample filter records during 2020 were created by UC Davis for completeness due to COVID-19 reasons only: 976 for each of the expected PTFE and nylon sample filters and 966 for the expected quartz sample filters. In April 2020, 75% of the expected number of filters were collected (Figure 3.1-1), with filter collection numbers returning to similar pre-COVID-19 levels in Fall 2020. Only a slight decrease in the fraction of collected to expected filters is observed in March 2020 because physical filters and associated electronic records were created by the Sample Handling Laboratory, however, many of these from March 16, 2020 through to the end of the month were marked invalid (Figure 3.1-2).

Figure 3.1-1: Time series of the fraction of number of filters collected compared to the number expected per month in 2020. The number of expected 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 but does not consider the filter validity.

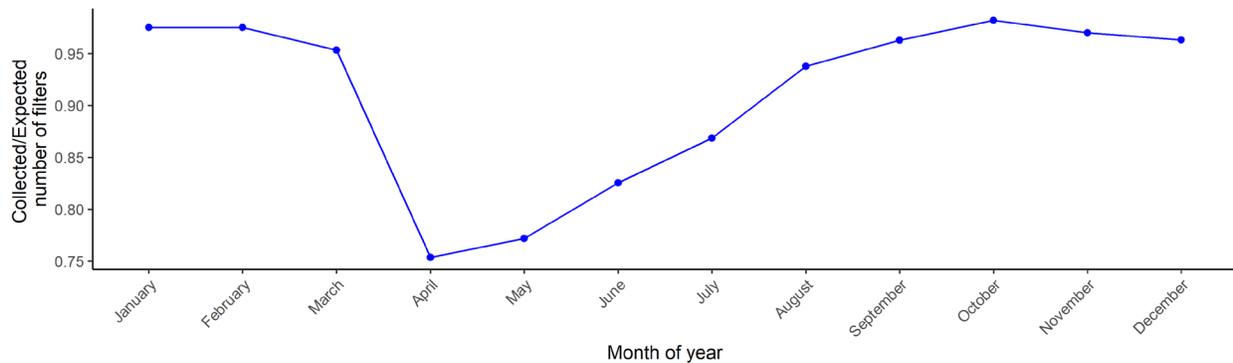
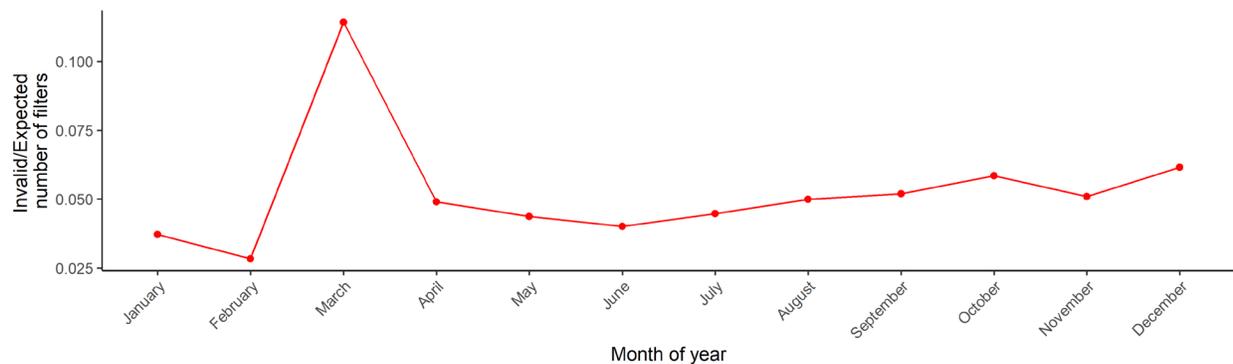


Figure 3.1-2: Time series of the fraction of number of invalid filters compared to the number filters expected to be collected per month in 2020. The number of expected samples is calculated from the sampling schedule (does not include field blanks). The total number of invalid samples is the number of physical samples marked invalid and does not include placeholder records generated for completeness.

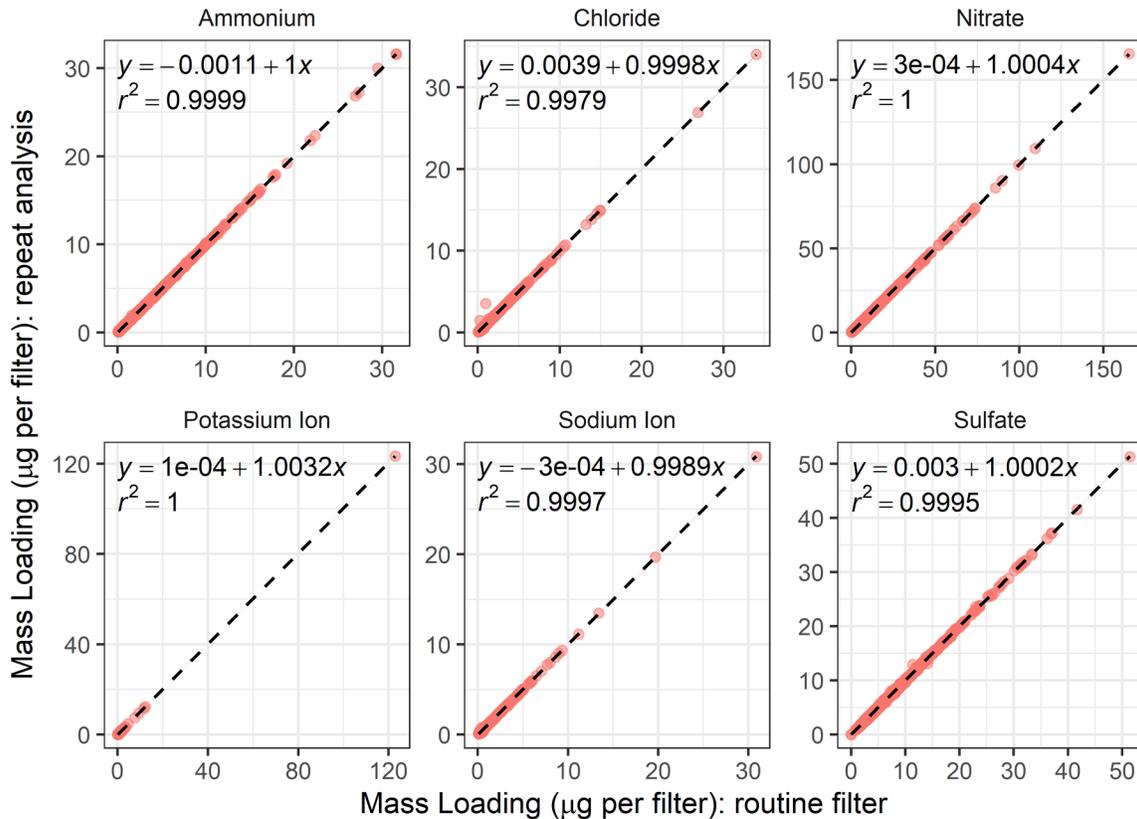


3.1.2 Comparability and Analytical Precision

Analytical precision is evaluated by comparing data from repeat analyses, where two analyses are performed on the same sample extract using either the same instrument (duplicate) or different instruments (replicate). Reliable laboratory measurements should be repeatable with good precision. Analytical precision includes only the uncertainties associated with the laboratory handling and analysis, whereas collocated precision (Section 6.5) also includes the uncertainties associated with sample preparation, field handling, and sample collection. Analytical precision is used internally as a QC tool.

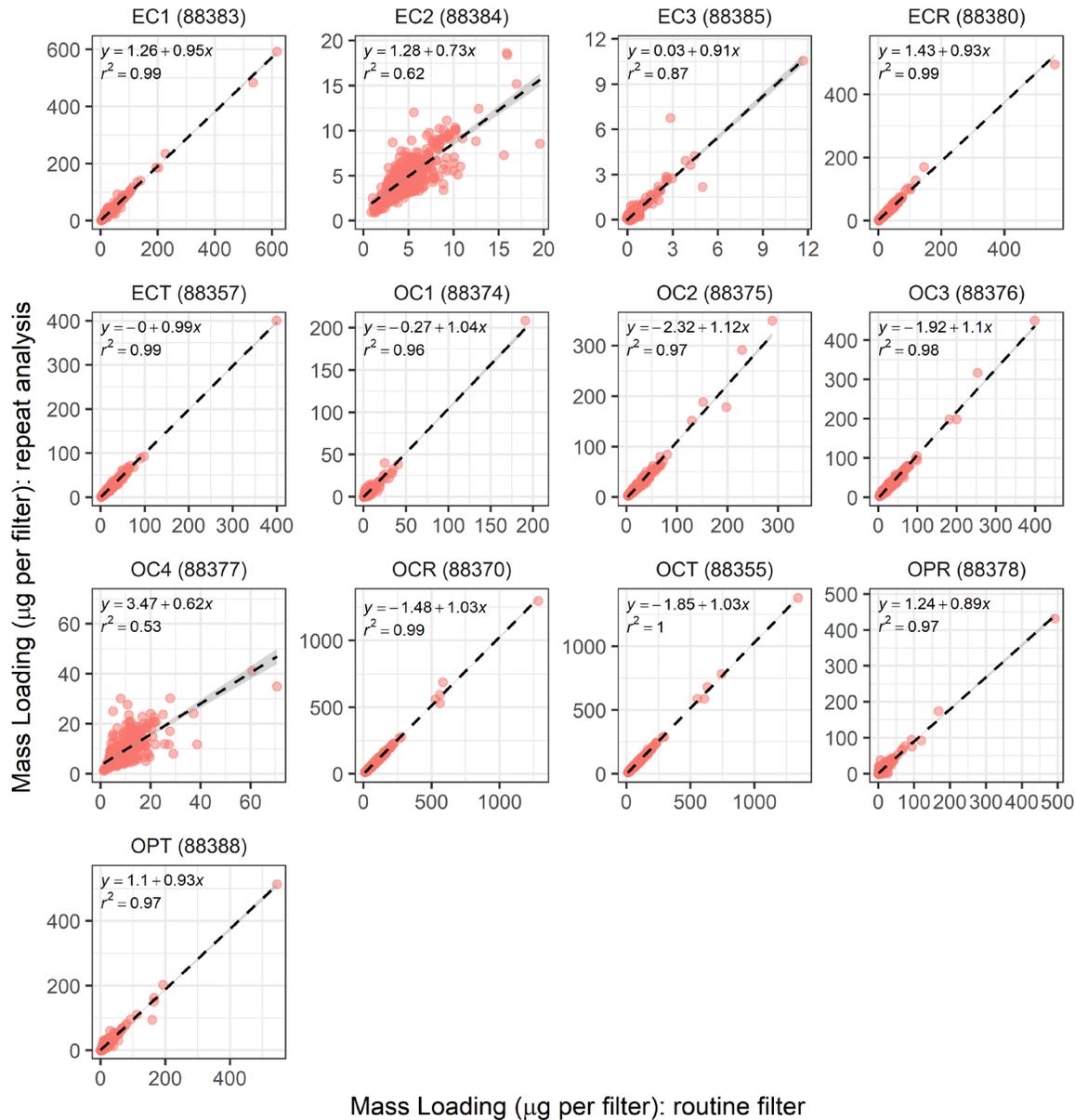
Comparisons of ion mass loadings from repeat analyses (replicates and/or duplicates) on nylon filters analyzed by IC show agreement (Figure 3.1-2). Nine different IC instruments were used for routine and repeat analyses where both replicate and duplicate analyses are performed using the same extract.

Figure 3.1-2: Ion repeat analysis (replicates and/or duplicates) results; data from valid samples collected January 1, 2020 through December 31, 2020.



Comparison of carbon mass loadings from repeat analyses (replicates and/or duplicates) on valid quartz filters analyzed by TOA generally show agreement (Figure 3.1-3), with agreement deteriorating for carbon fractions with lower mass loadings (e.g. EC2, EC3, OC4). Repeat analyses are performed on the same filter as the routine analyses; different punches are used for each analysis.

Figure 3.1-3: Carbon repeat analysis (replicates and/or duplicates) results; data from samples collected during January 1, 2020 through December 31, 2020. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T). AQS parameter codes indicated in parentheses.



Replicate EDXRF analyses of routine CSN samples were started on December 20, 2020, resulting in 32 replicate measurements during this reporting period. QC criteria are being developed for these replicate analyses, and the analytical precision will be evaluated in the next report. XRF replicates were previously not performed by EDXRF on routine CSN samples due to time limitations, as analyses take approximately 65 minutes per sample, and to preserve volatile elements like chlorine and bromine, and to a lesser extent sulfur, which are lost when the sample is analyzed under vacuum on the EDXRF. For this reporting period, EDXRF precision was evaluated by analyzing the same set of samples, which are UCD-made multi-element

reference materials (see Table 4.2.2), on a monthly basis to assess both the short- and long-term stability of the EDXRF measurements as described in UCD CSN SOP #302. See Section 4.2.2.4.

3.1.3 Blanks

Field blanks are an integral part of the QA process and field blank analysis results are used to artifact correct the sampled filters as part of the concentration calculation (see Section 3.1.3.1). Artifacts can result from initial contamination in the filter material, contamination during handling and analysis, and adsorption of gases during sampling and handling. Additionally, field blanks are used to calculate method detection limits (MDLs; see Section 3.1.3.2).

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

There is some variability in field blank mass loadings by species. The 10th percentile of network sample mass loadings, before artifact correction, is indicated in Figure 3.1-4 through Figure 3.1-18 to facilitate understanding of field blank mass loadings in context of network sample mass loadings; 90% of network sample mass loadings fall above the indicated 10th percentile. As part of the validation process (see Section 6), field blank outliers are investigated but are only invalidated if there is cause to do so. Artifact correction (Section 3.1.3.1) and MDL (Section 3.1.3.2) calculation methods are robust against influence from occasional outliers.

Field blank mass loadings for the ion species (Figure 3.1-4 through 3.1-9) are examined in an effort to identify changes that may be associated with the October 1, 2018 laboratory transition from DRI to RTI (see Section 2.1.1 of the CSN 2019 Annual Quality Report) or changes that may be occurring independently from the laboratory transition. The monthly 10th percentile ammonium mass loading of network samples increased in November 2017 and has become increasingly elevated relative to earlier years. Additionally, the monthly median ammonium mass loading of field blanks increased corresponding with the laboratory transition. This trend has continued through 2020. For potassium ion, the monthly 10th percentile mass loading of network samples – as well as the monthly field blank median mass loading and variability – increased corresponding with the laboratory transition. Both of these are also observed to be gradually increasing since the laboratory transition. Conversely, monthly median mass loadings of field blanks were generally lower for nitrate specifically April through August 2019 and sulfate following the laboratory transition. Median nitrate mass loadings of field blanks from June 2020 through December 2020 are more comparable to those measured prior to the laboratory transition.

Figure 3.1-4: Time series of ammonium measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no nylon filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Outlier points that are off scale are plotted at the 1 μg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

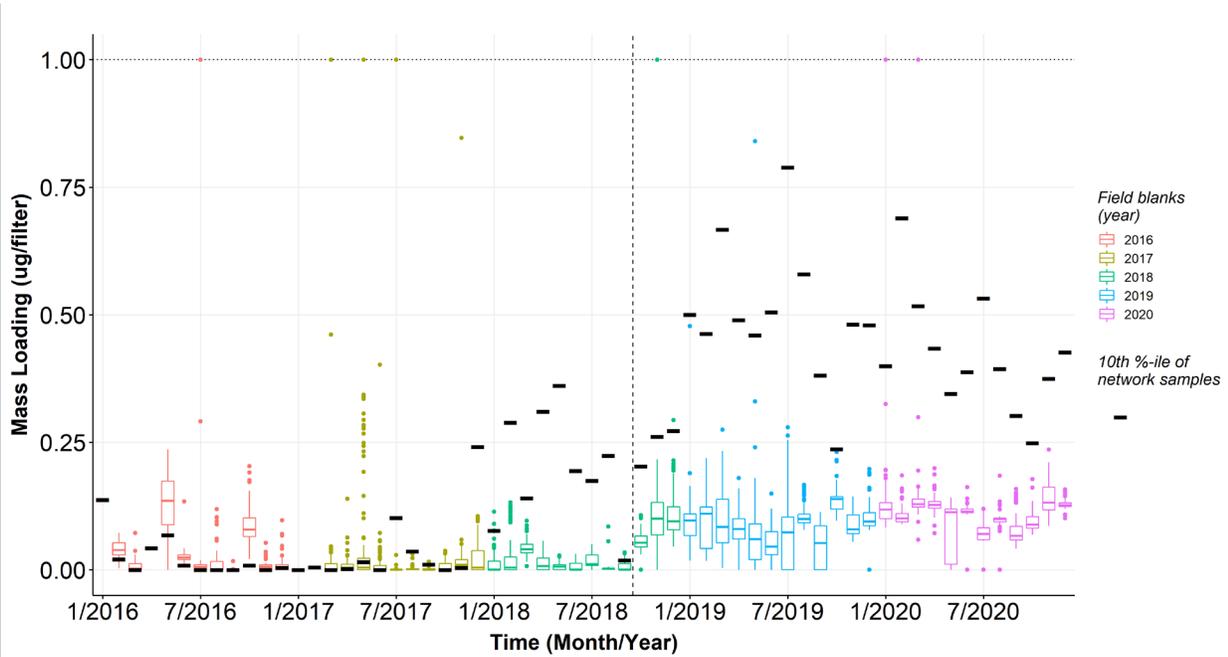


Figure 3.1-5: Time series of chloride measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no nylon filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

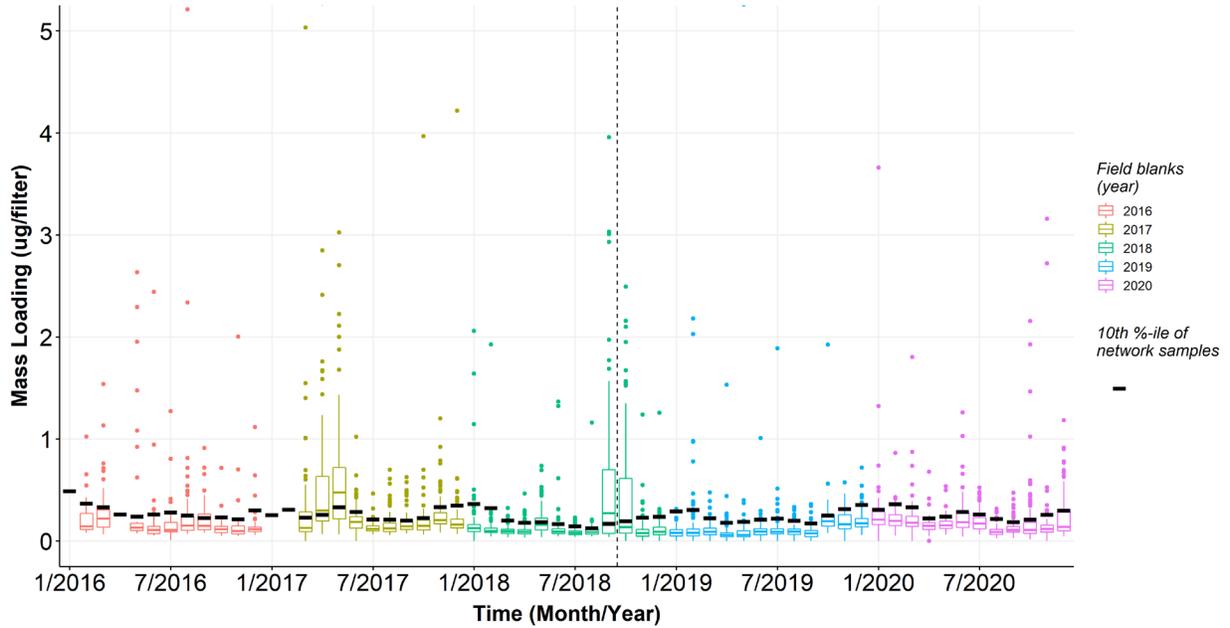


Figure 3.1-6: Time series of nitrate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no nylon filter field blanks were collected. The horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

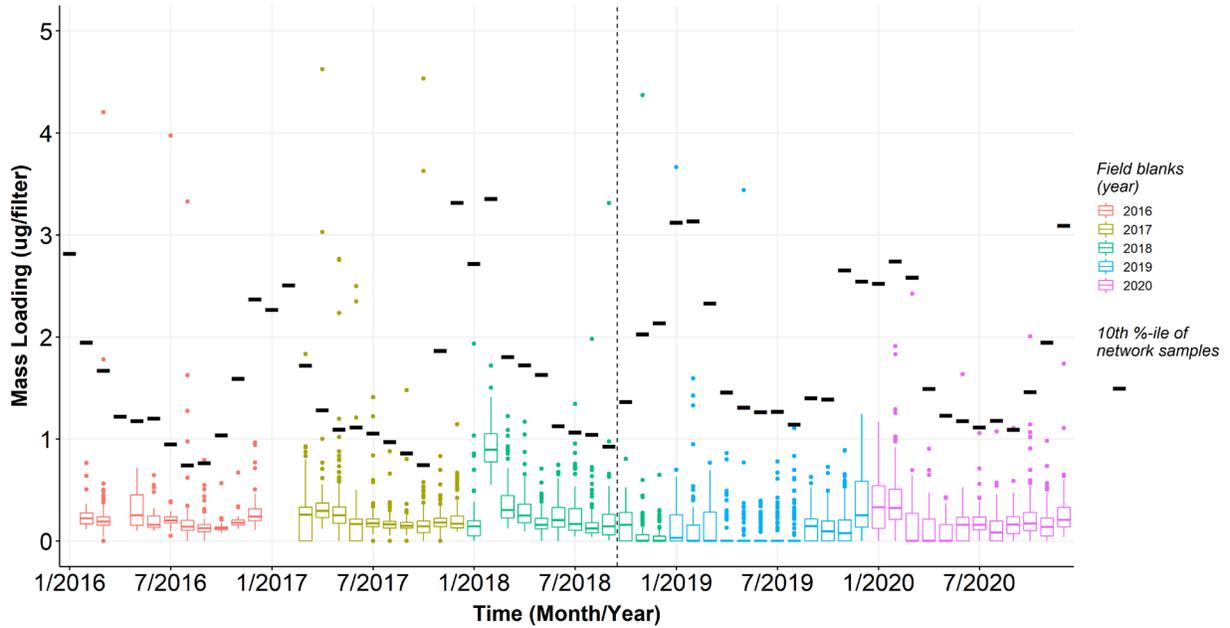


Figure 3.1-7: Time series of potassium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no nylon filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Outlier points that are off scale are plotted at the 0.5 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

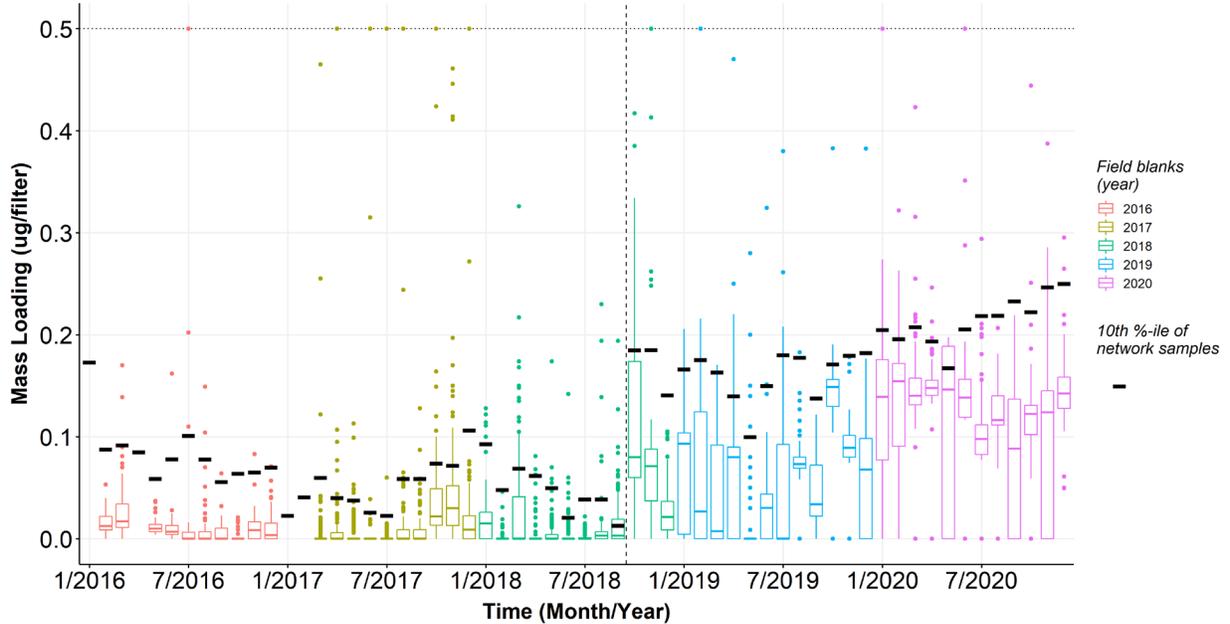


Figure 3.1-8: Time series of sodium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no nylon filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Outlier points that are off scale are plotted at the 2 μg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

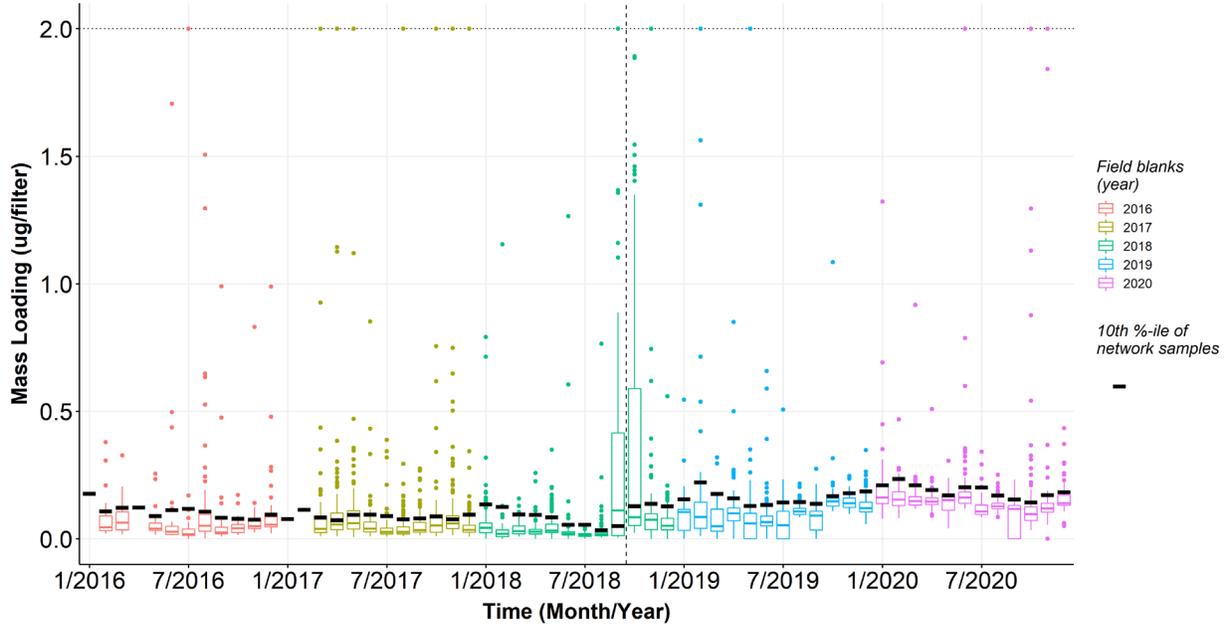
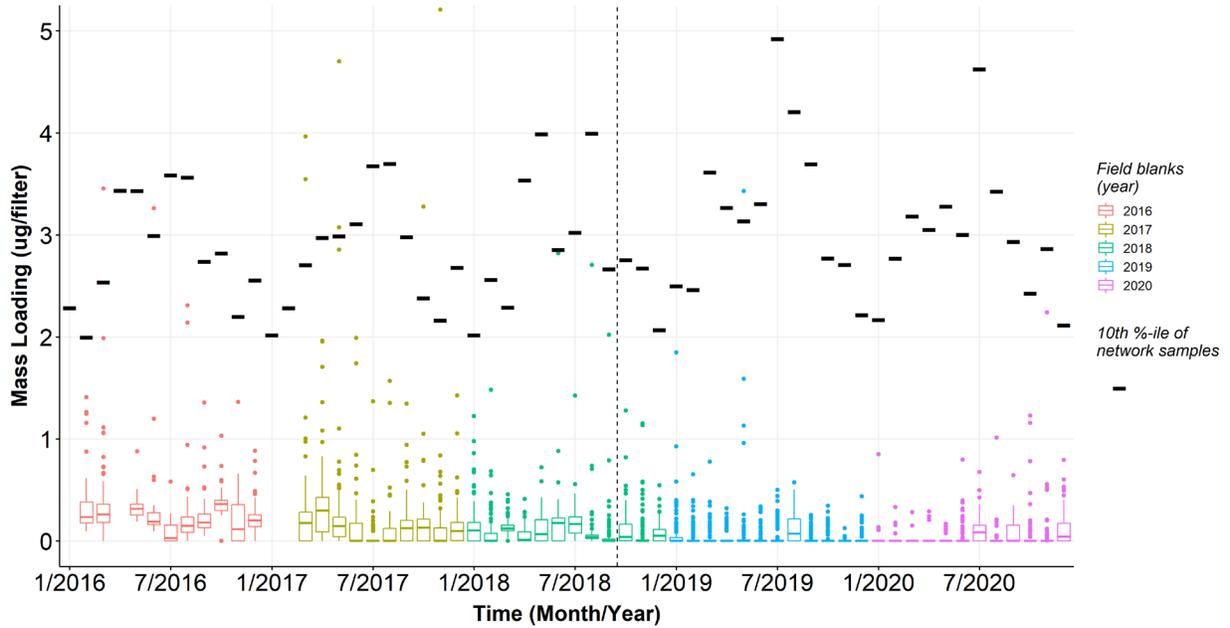


Figure 3.1-9: Time series of sulfate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no nylon filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.



Field blank mass loadings for organic carbon (Figure 3.1-10) and elemental carbon (Figure 3.1-11) are examined in an effort to identify changes that may be associated with the October 1, 2018 laboratory transition from DRI to UC Davis (see Section 2.3.1 of the CSN 2019 Annual Quality Report and the Carbon Analyzer Change Data Advisory available at <https://www.epa.gov/amtic/chemical-speciation-network-data-reporting-and-validation>) or changes that may be occurring independently from the laboratory transition.

Both the monthly 10th percentile organic carbon mass loading of network samples and the monthly median organic carbon mass loading of field blanks show some variability and increases during the time series, January 1, 2016 through December 31, 2020. As discussed in the CSN 2019 Annual Quality Report, corresponding with the October 1, 2018 laboratory transition, there is an increase in the monthly median organic carbon mass loading of field blanks, which is likely caused by the change in the signal integration threshold and other small differences between instrumentation and laboratory methods associated with the transition. Additionally, following the transition, and particularly for field blanks collected beginning November 2019, there are numerous cases of field blanks with elevated mass loadings; these cases are being investigated. No evidence of an analytical issue has been found. Laboratory blanks show low concentrations (see Section 4.3.5.2) suggesting the contamination is arising from sample handling in the laboratory or field. Investigations are on-going.

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

Figure 3.1-10: Time series of organic carbon by reflectance (OCR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no quartz filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to UC Davis. The black horizontal dashes indicate the 10th percentile of network samples.

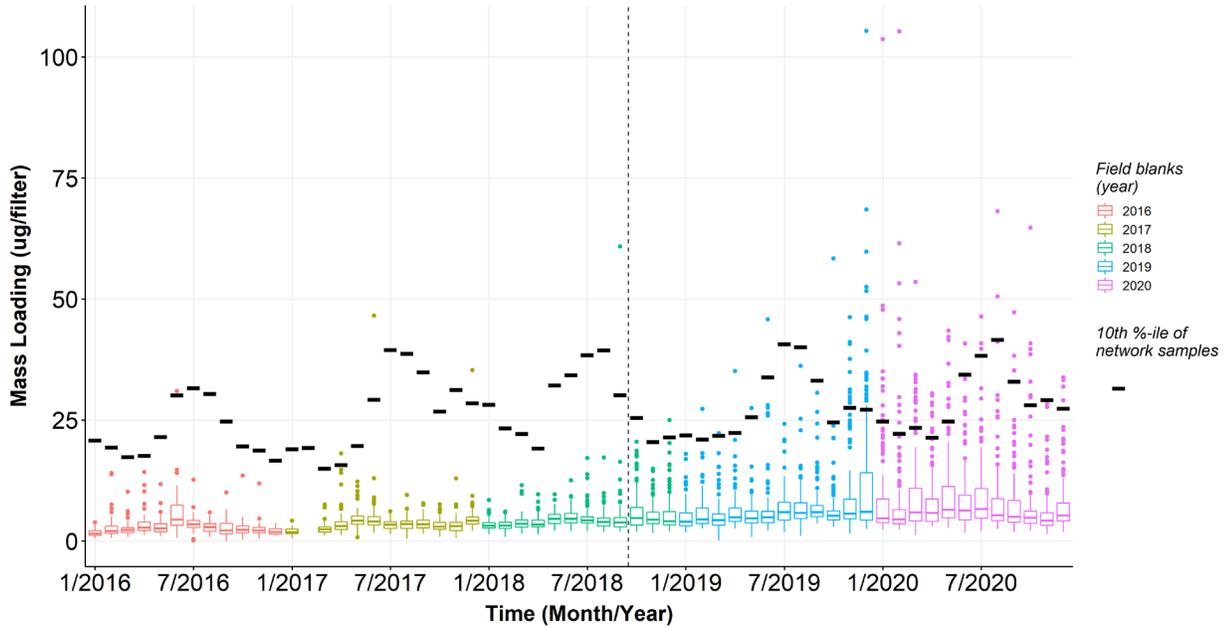
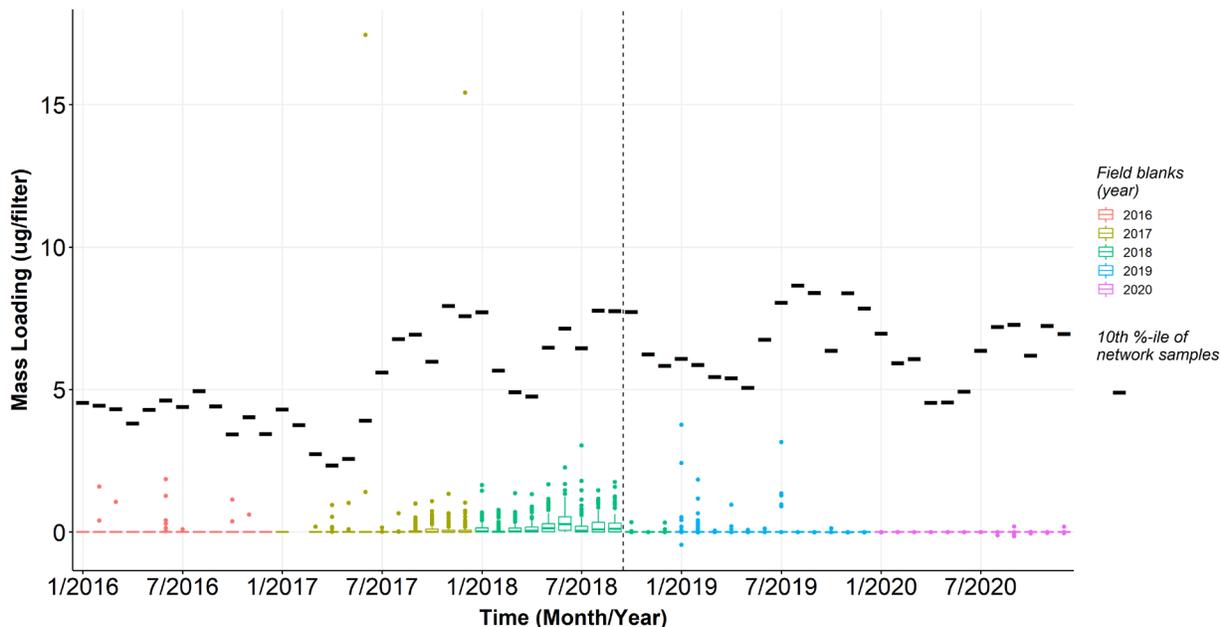


Figure 3.1-11: Time series of elemental carbon by reflectance (ECR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no quartz filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to UC Davis. The black horizontal dashes indicate the 10th percentile of network samples.



Time series of monthly median mass loading of field blanks and monthly 10th percentile mass loading of network samples are shown Figure 3.1-12 through 3.1-17 for select well-measured element species (species where at least 50% of the network sample concentrations are above the reported method detection limit, see Table 3.1-4). As discussed in the CSN 2018 Annual Quality Report, the EDXRF analysis conditions (including the secondary targets and integrations times, collectively referred to as the *application*) were changed in December 2018, and were implemented beginning with analysis of samples and field blanks collected October 2018. For further details see the XRF Protocol Change Data Advisory (available at <https://www.epa.gov/amtic/chemical-speciation-network-csn-data-reporting-and-validation-files>). There does not appear to be evidence of unexpected shifts or changes to the monthly median mass loading of field blanks or monthly 10th percentile mass loading of network samples for sulfur (S; Figure 3.1-13), potassium (K; Figure 3.1-14), calcium (Ca; Figure 3.1-15), titanium (Ti; Figure 3.1-16), iron (Fe; Figure 3.1-17), or zinc (Zn; Figure 3.1-18). However, silicon (Si; Figure 3.1-12) monthly median field blank mass loadings continue to show increased variability. The XRF application did not change for silicon, or any elements below Mn. The increased variability may instead be related to the change from analyzing filters on three instruments to five instruments beginning with February 2019 filters (analysis beginning May 2019; see Table 4.2-1 in the CSN 2019 Annual Quality Report).

Figure 3.1-12: Time series of silicon (Si) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

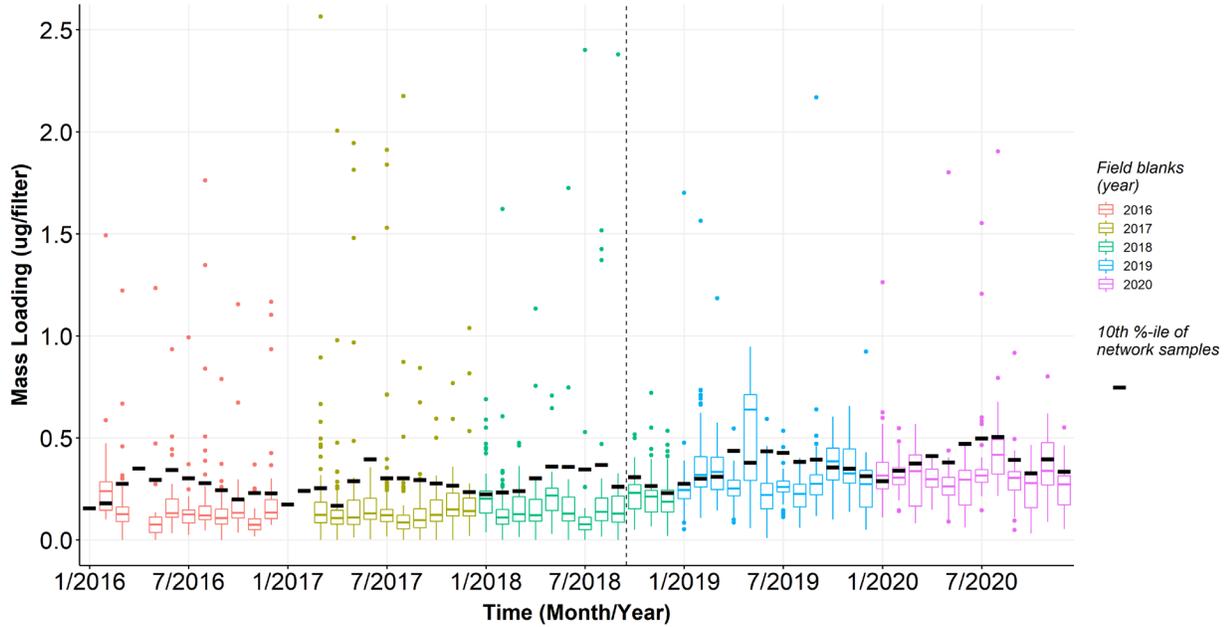


Figure 3.1-13: Time series of sulfur (S) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

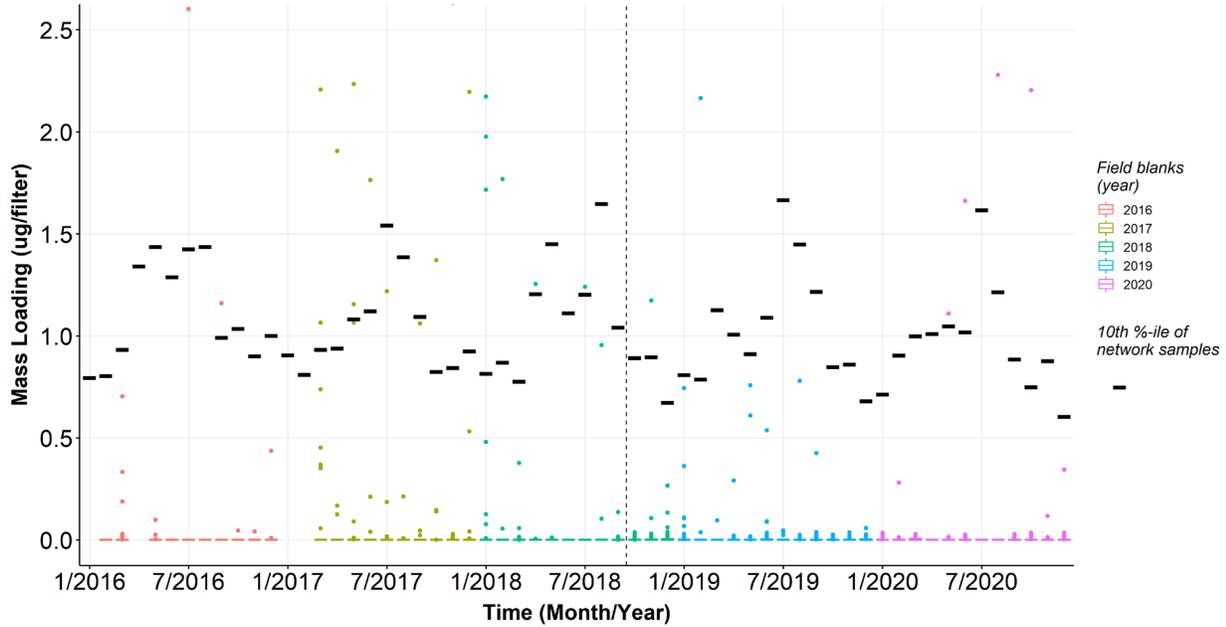


Figure 3.1-14: Time series of potassium (K) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

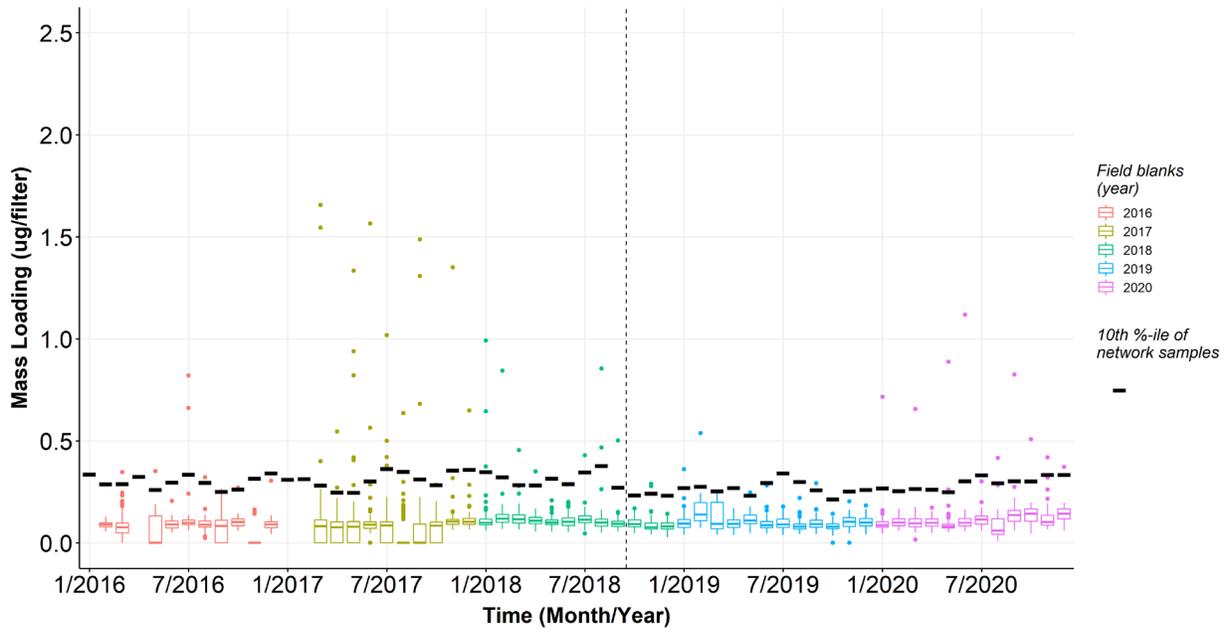


Figure 3.1-15: Time series of calcium (Ca) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

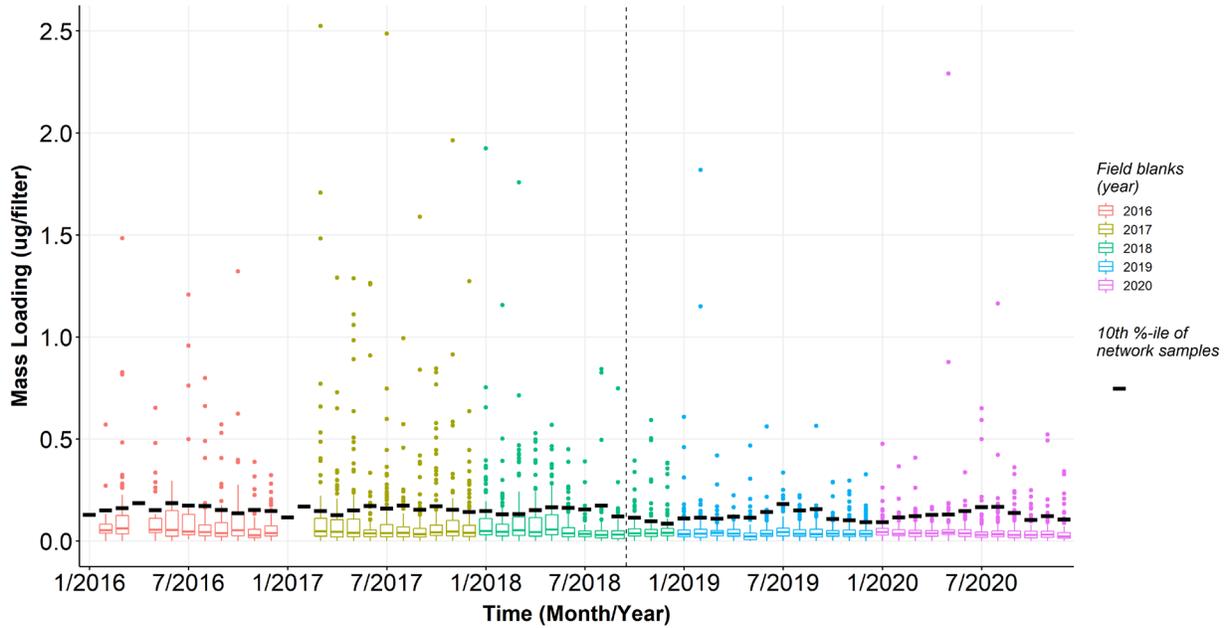


Figure 3.1-16: Time series of titanium (Ti) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Outlier points that are off scale are plotted at the 0.15 µg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

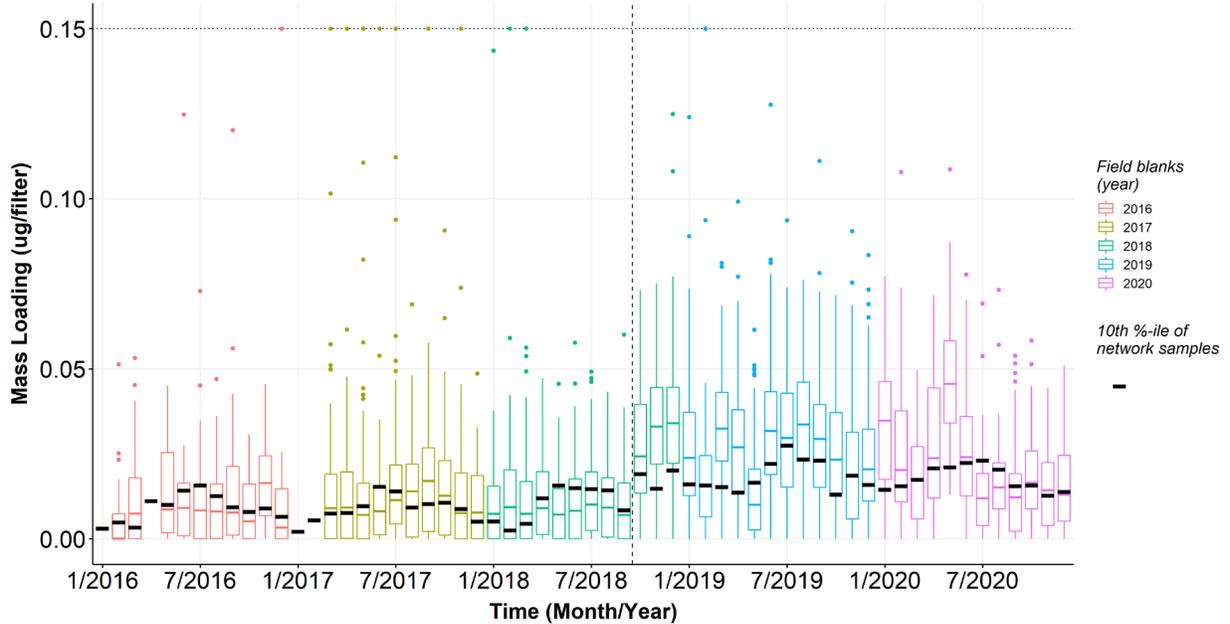


Figure 3.1-17: Time series of iron (Fe) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

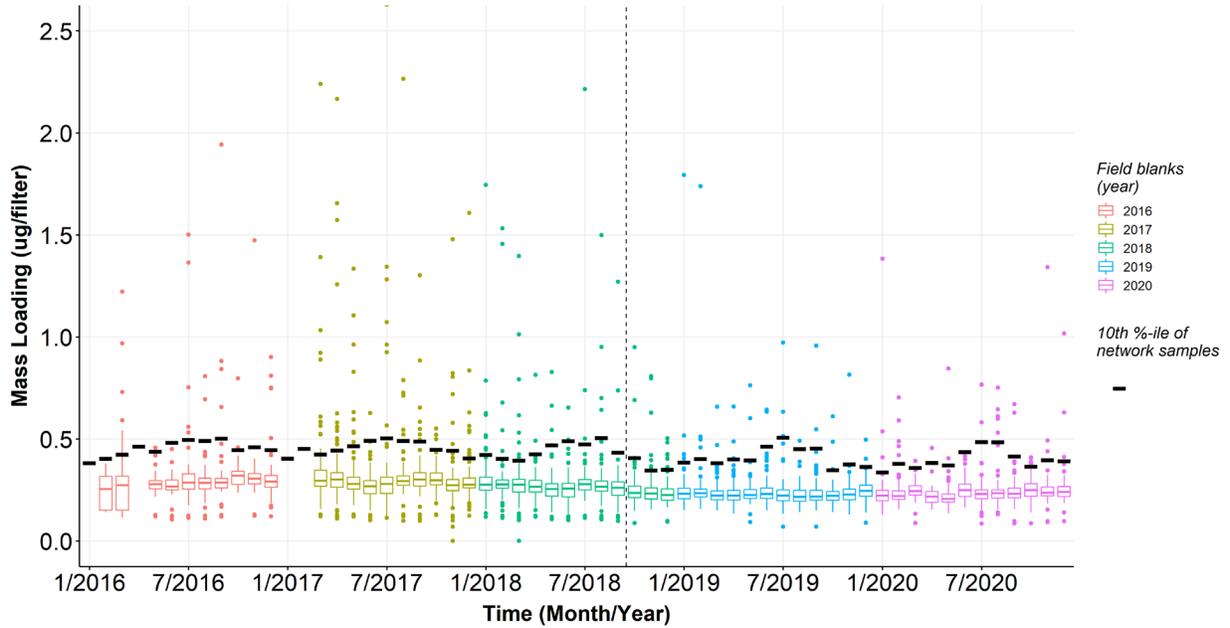
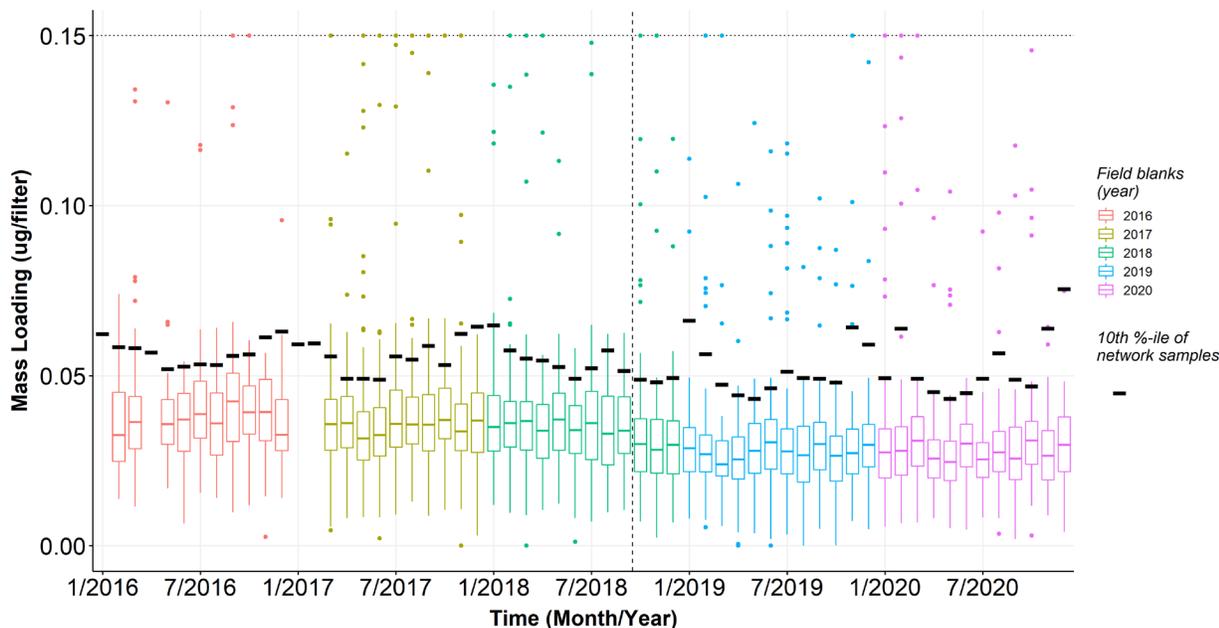


Figure 3.1-18: Time series of zinc (Zn) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2020. Gaps in time series are present when no PTFE filter field blanks were collected. The colored horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR. Outlier points that are off scale are plotted at the 0.15 μg/filter boundary shown by the horizontal dotted line. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.



Beginning with the shipment to UCD of filters collected in July 2020, the Sample Handling Laboratory, Wood PLC, included five laboratory blanks for each filter type (PTFE, nylon, and quartz) as part of the routine shipment. A total of 30 laboratory blanks of each filter type were analyzed during the current reporting period. Summaries of the analyses are in Section 4.1.6 (nylon), Section 4.2.6 (PTFE), and Section 4.3.6 (carbon).

3.1.3.1 *Blank Correction*

Blank correction is performed on data from all filter types (quartz, nylon, and PTFE) by subtracting a rolling median value from at least 50 field blanks collected in and closest to the sample month. Field blanks are collected once per month for each filter type per site since May 2017; the median value is typically calculated using field blanks from the sample month only.

3.1.3.2 *Method Detection Limits*

Network-wide method detection limits (MDLs) are updated monthly and are delivered to AQS for each species. The MDL calculation is harmonized for all analysis pathways, calculated as 95th percentile minus median of field blanks, using 50 field blanks collected in or closest to the sampling month for each respective filter type. Field blanks are collected once per month for each filter type per site since May 2017, allowing for a robust MDL calculation. Field blanks capture artifacts from both field and laboratory processes, thus it is expected that field blank mass loadings are generally higher than lab blanks, which have only been handled in a laboratory environment and have less opportunity for mishandling and contamination. When the MDL

determined from field blanks is lower than the analytical MDL (calculated by the laboratories using laboratory blanks, daily blank QC filters, or the lowest standard or spiked solution), the analytical MDL is assigned as a floor value.

The average MDLs calculated for this reporting period (samples collected January 1, 2020 through December 31, 2020) are compared to those calculated using the same method from the previous reporting period (samples collected January 1, 2019 through December 31, 2019) (Table 3.1-4). MDLs calculated during this reporting period compare well with those from the previous reporting period for many species. However, there are some cases where 2020 MDLs are lower (improved) or higher (degraded): (1) all elemental species except calcium (Ca) have lower 2020 MDLs relative to their 2019 MDLs or have not changed; (2) ions species potassium ion MDL in 2020 is lower relative to their 2019 MDL; (3) elemental carbon species (ECR, ECT) and organic carbon fraction (OC3) 2020 MDLs are lower and higher, respectively, relative to their 2019 MDLs.

Table 3.1-4: Average method detection limits (MDLs) and percentage of reported data above the MDLs for all species, calculated for data from samples collected January 1, 2019 through December 31, 2019 (previous reporting period) and January 1, 2020 through December 31, 2020 (current reporting period). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T). Species shown in bold have differences $\geq 50\%$ between those reported for the previous reporting period (2019) and the current reporting period (2020). Typical MDLs are from the CSN laboratory analysis contract's statement of work.

Species	EPA Attachment D	2019 (previous reporting period)		2020 (current reporting period)	
	Typical MDL, ng/m ³	Average MDL, ng/m ³	% Above MDL	Average MDL, ng/m ³	% Above MDL
Ag	37.5	16.4	4.1	12.9	9.3
Al	25.0	32.2	31.2	23.1	48.0
As	2.7	1.9	0.1	0.1	6.5
Ba	59.4	80.1	0.2	28.3	13.3
Br	2.3	4.5	2.7	0.1	31.2
Ca	7.6	8.9	89.7	9.9	88.5
Cd	22.9	15.8	5.4	13.9	7.8
Ce	87.5	95.3	0.1	36.2	8.2
Cl	11.5	4.3	41.9	4.0	45.0
Co	2.0	3.3	0.6	1.6	6.8
Cr	2.6	2.8	24.8	2.3	24.8
Cs	45.8	53.8	0.3	27.1	9.4
Cu	2.5	11.4	6.3	4.3	22.6
Fe	3.3	17.5	90.5	8.5	96.9
In	33.3	38.1	0.1	14.9	11.5
K	11.5	6.3	98.1	5.4	99.1
Mg	18.8	46.2	16.0	45.1	17.2
Mn	2.9	6.4	10.1	3.0	28.0
Na	55.2	91.6	26.5	80.6	30.8
Ni	1.9	1.9	15.0	1.2	22.9
P	15.6	2.6	5.4	1.9	9.0

Species	EPA Attachment D	2019 (previous reporting period)		2020 (current reporting period)	
	Typical MDL, ng/m ³	Average MDL, ng/m ³	% Above MDL	Average MDL, ng/m ³	% Above MDL
Pb	6.4	12.2	5.3	6.7	22.6
Rb	2.6	8.9	0.1	3.2	8.8
S	9.9	3.7	99.6	1.1	99.7
Sb	52.1	38.8	0.1	16.1	8.6
Se	2.6	5.3	0.4	2.5	10.6
Si	18.8	17.6	73.8	13.9	79.5
Sn	36.5	48.8	0.0	15.6	9.4
Sr	3.5	7.2	0.9	2.9	14.0
Ti	5.3	3.5	39.1	2.9	51.3
V	3.9	1.3	3.5	0.7	9.2
Zn	3.5	3.2	86.1	1.7	93.1
Zr	22.9	35.9	0.1	14.0	7.8
Ammonium	25.0	6.9	98.4	12.9	95.1
Chloride	27.1	15.3	89.0	25.4	75.9
Nitrate	21.9	39.3	99.5	38.7	99.3
Potassium Ion	24.0	60.6	13.9	12.9	79.2
Sodium Ion	30.2	8.8	85.0	14.1	65.3
Sulfate	35.4	21.8	99.8	29.4	99.7
Elemental Carbon (EC1)	94.6	29.3	99.9	33.7	99.8
Elemental Carbon (EC2)	63.1	23.2	99.5	30.8	98.8
Elemental Carbon (EC3)	63.1	4.1	80.3	5.7	71.9
Elemental Carbon (ECR)	63.1	11.7	99.9	2.8	99.8
Elemental Carbon (ECT)	63.1	11.7	99.8	0.3	99.8
Organic Carbon (OC1)	63.1	15.7	77.4	14.6	69.2
Organic Carbon (OC2)	63.1	45.8	99.5	37.6	99.6
Organic Carbon (OC3)	94.6	224.7	85.8	494.0	56.1
Organic Carbon (OC4)	94.6	73.5	89.5	95.9	86.5
Organic Carbon (OCR)	63.1	349.6	95.6	643.6	89.8
Organic Carbon (OCT)	63.1	354.1	96.4	643.6	91.5
Organic Pyrolyzed (OPR)	94.6	52.2	91.1	66.2	89.8
Organic Pyrolyzed (OPT)	63.1	52.0	94.4	66.2	94.9

3.2 Corrective Actions

To ensure ongoing quality work, UC Davis reacts as quickly and decisively as possible to unacceptable changes in data quality. These reactions are usually in the form of investigations, and, if necessary, corrective actions. The following subsections describe significant corrective actions undertaken for data from samples collected during 2020.

3.2.1 Elemental Analysis

3.2.1.1 *Detector Issue on XRF-4*

On March 10, 2020, XRF-4's detector entered forced heat-up, a condition which normally occurs when the detector's liquid nitrogen runs low and the detector temperature begins to rise. After contacting the manufacturer, they concluded there was no issue and they reset the forced heat-up condition and instructed us to refill the liquid nitrogen and continue operation, which we did. Over the course of the next few days it was obvious that the aluminum (Al) and silicon (Si) values for the daily multi-element reference material (ME-RM) QC sample had risen and were failing QC acceptance. Due to the rapidly evolving COVID-19 situation the laboratory quickly assessed, by reanalyzing 16 samples on another instrument, that the Al and Si results of the samples were not impacted by the QC results (the Al concentration on the QC sample is one to two orders of magnitude higher than those seen on the samples). Therefore, analysis continued on the instrument (in anticipation of an impending laboratory shutdown due to the pandemic).

The manufacturer was contacted about the QC issue. After additional review of temperature logs, they concluded that the detector had warmed slightly on 3/10/2020 and the recommendation was to allow the detector to warm completely to room temperature and then cool it back down to liquid nitrogen temperature again. This was performed from 3/25/2020 to 4/2/2020 and resolved the QC issue. The reanalysis of 16 samples on another instrument showed agreement with the original results obtained during the QC failure, therefore, the original results for all 181 samples analyzed on XRF-4 during the QC failure for Al and Si were reported. No impact on the sample results is expected based on the results of the 16 reanalyzed samples.

Additional details can be found in Section 4.2.2.1.

3.2.1.2 *XRF-1 S, Ca, and Ni Contamination*

During review of the results from the March 2020 sampling month the validation team reported to the laboratory that there were 17 samples with anomalously high sulfur (S), calcium (Ca), and nickel (Ni) concentrations. All 17 samples had been analyzed on XRF-1 between 6/17/2020 and 6/22/2020. This XRF instrument had stopped analyzing just before this time period because of mechanical issues with the beamstop not fully opening. The manufacturer was called out to repair it and sample analysis resumed on 6/17/2020. On 6/22/2020 the same error occurred again and the instrument stopped analyzing. The manufacturer had to replace the motor that opens and closes the beamstop to correct the issue this second time. The issue with these 17 samples reported by validation was likely that the beamstop did not fully open and part of the X-ray beam was hitting the edge of the beamstop and reading higher S, Ca, and Ni from it. This must have been an intermittent issue as the QC results did not show this contamination. Therefore, it was assumed that the 17 samples discovered by the validation team may not have been the only affected samples.

Therefore, a test was constructed to identify any other sample results possibly affected by the beamstop issue. The ratio of Si/Ca was analyzed for all samples measured on XRF-1 during the period between the two beamstop issues, 6/17 – 6/22/2020. It was determined that 27 samples total had low Si/Ca ratios indicating possible issues during their analysis. All 27 samples along with two samples which did not meet the Si/Ca ratio criteria were reanalyzed. The two samples not meeting the Si/Ca ratio criteria were found to have reanalysis results which confirmed the original results (so the original results were reported). The other 27 samples had their original

results for all elements invalidated and the reanalysis results for all elements were reported. All elements were handled in this way, not just S, Ca, and Ni, because of the methods used for data transfer from the XRF instruments to the UCD database.

3.2.1.3 XRF-3 Detector Issue

On July 27, 2020 QC checks of both the daily and weekly ME-RM samples indicated rising concentrations for multiple elements, though none were failing QC criteria. The detector was known to be in need of replacement after a previous intervention by the manufacturer indicating possible future failure. This knowledge together with the changing QC results prompted the decision to stop analysis on the instrument.

Analysis was halted on XRF-3 on July 27, 2020. In addition, a selection of 16 samples analyzed between 7/17/2020 and 7/24/2020 were reanalyzed on another instrument. The reanalysis results confirmed the original results so there was no impact on sample results due to the change in the detector. All original sample results were reported.

The manufacturer was contacted about the possible detector issue and they installed a new detector between 8/11/2020 and 8/20/2020. After the detector replacement, XRF-3 was calibrated and passed all QC checks. Routine sample analysis restarted on this instrument on 9/2/2020 and CSN samples were analyzed again beginning 10/26/2020.

3.2.1.4 XRF-5 X-ray Intensity Loss

On September 14, 2020, a Monday, the daily ME-RM QC sample was found to have lower intensity on multiple elements beginning with the results from 9/11/2020, the previous Friday. This was a small drop in intensity and did not fail QC criteria, however, it was noted and watched. The daily QC check on 9/15/2020 showed no issues and analysis on XRF-5 continued. However, the daily QC check on 9/16/2020 also showed similar low intensities to the results on 9/14/2020. This indicated some kind of issue, so sample analysis was stopped on 9/16/2020.

All samples analyzed since the last good QC check on 9/10/2020 were reanalyzed on another instrument and the reanalysis results were reported. In total there were 65 CSN samples which were reanalyzed.

The manufacturer was contacted about the issue and it was determined that the instrument needed a new X-ray tube and high voltage generator. The installation of these parts was put on hold until the instrument was moved to the new lab location in October, 2020. Once moved the new X-ray tube and generator were installed and the system underwent calibration and all QC checks. Analysis was restored on 11/7/2020 and CSN sample analysis resumed on 11/17/2020.

On 2/4/2021 a similar drop in X-ray intensity was noticed and all sample analysis was again stopped. All samples analyzed since the last good QC check on 2/3/2021 were reanalyzed on another instrument and the reanalysis results were reported. This included 15 CSN samples. The manufacturer's investigation also linked this to the high voltage generator. However, due to a quality issue with the supplier of the generators, multiple replacements also failed and XRF-5 remained unusable for the remainder of this reporting period.

Additional details can be found in Section 4.2.2.4.

3.2.2 Ion Analysis

During this reporting period nineteen samples were flagged for re-analysis due to suspected contamination. Re-analysis confirmed contamination during the original analysis for three samples; reanalysis results were reported for these three samples.

3.2.3 Carbon Analysis

During the report period, there were three exceedances of the laser reflectance signal of Gamma (9/4/2020, 9/8/2020, and 9/14/2020), which resulted in a laser source and optical detector replacement. Similarly Beta had three exceedances of laser reflectance values after the relocation of the UC Davis TOA Laboratory (11/25/2020, 11/30/2020, and 12/1/2020), which resulted in laser fine-tuning and signal optimization performed on 12/1/2020 (see Figure 4.3-5 of Section 4.3.2.4 for details). No network samples were analyzed by Beta or Gamma during the exceedance days.

3.2.4 Data Processing

3.2.4.1 *Data Flagging Modifications*

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

3.2.4.2 *Chromium and Nickel Contamination*

As discussed in the CSN 2018 Annual Quality Report (Section 3.2.1.3), UC Davis identified a potential chromium and nickel contamination issue that impacts data from both prior to the contract transition (November 20, 2015) and beyond. Per direction from the EPA, UC Davis coordinated with the Sample Handling Laboratory (Wood PLC) to investigate this issue. The source of the contamination has not been identified, but is likely related to the Met One SASS / Super SASS samplers. As discussed in the Intermittent Contamination of Chromium and Nickel Data Advisory (available at <https://www.epa.gov/amtic/chemical-speciation-network-data-reporting-and-validation>), species associated with the contamination (chromium, nickel, iron, cobalt, and copper) are assigned the SC null data qualifier (SC – sampler contamination) prior to delivery to DART, beginning with samples collected January 2020.

A total of 132 filters met the contamination criteria during 2020; 123 sample filters and 9 field blank filters. However, four of these filters were already invalidated at the filter level prior to analysis; these data were not assigned the SC null data qualifier as only one null data qualifier is permitted per data record. Table 3.2-1 details the resulting number of filters per month that met the contamination criteria during 2020 and relevant species were invalidated.

Table 3.2-1: Number of filters per month that met the contamination criteria during 2020. The chromium, nickel, iron, cobalt, and copper species were assigned the SC null data qualifier in these cases.

Month	Number of filters
January	15
February	9
March	11
April	6
May	8
June	11
July	16
August	17
September	5
October	9
November	9
December	12

3.2.4.3 Delivery of Composite Variables

Beginning with data from samples collected June 1, 2019, UC Davis began calculating and delivering composite variables for reconstructed mass (RCM) and soil to DART and AQS (see *UCD CSN TI #801B* for further information and equations for calculation of RCM and soil). Subsequently, UCD retroactively delivered RCM and soil results for samples collected January 1, 2018 through May 31, 2019. For composite variable results, if any of the contributing species are invalid, the composite variable is delivered as invalid with the AI null code (AI – Insufficient Data, Cannot Calculate). Beginning with samples collected October 1, 2020 the new method of calculating MDLs for RCM and soil was implemented. The new method involves first calculating RCM and soil for each field blank, then applying the 95th percentile minus median approach for calculating monthly MDLs for these calculated parameters. The average MDLs for RCM and soil for the 2021 reporting period will be included in Table 3.1-4 in the next report once a full year of data has been reported using this method.

3.2.4.4 Delivery of Field Blank Gravimetric Mass

Gravimetric mass analysis results from Wood PLC for a select subset of field blanks and special studies are delivered to UC Davis. Beginning with field blanks collected in July 2020, 16 sites collect PTFE filters which are routinely analyzed for gravimetric mass by Wood PLC before being shipped to UC Davis for EDXRF analysis. Using a nominal sample volume of 9.6 m³, the results are reported to AQS as nominal concentrations.

3.2.4.5 Reporting Invalid Records for Completeness

Beginning with sample filters intended to be collected in the field from September 1, 2017, UC Davis adds placeholder electronic records for samples that were scheduled but not collected for completeness purposes. Physical filters and associated electronic records were not generated at the Sample Handling Laboratory for these scheduled samples because, for example, a sampler at a given site was out for repairs or the site was temporarily closed such as was the case for many sites during the COVID-19 pandemic (see Section 3.1.1.1). Only sample filters are considered; placeholder records are not created for field blank filters. The placeholder records are created per filter i.e., records for all parameters associated with a given filter type are created, for each

sample filter that was expected to have been collected per scheduled sampling date. The placeholder records are marked invalid with the 'AF – Scheduled but not Collected' null code flag automatically by UC Davis when creating the records; the final reported null code flags for some records in AQS may differ.

Beginning with sample filters intended to be collected in the field from July 1, 2020, UC Davis also adds placeholder electronic records for samples to complete a sampling event, where a sampling event is defined as all three filter types (PTFE, nylon, and quartz) with the same sampling date. Records are created for every sampling date for a given site, where the sampling date may not be the intended use date or any other scheduled sampling date. This ensures records are reported for all parameters for every date. For example, placeholder electronic records are created for quartz sample filters to complete the sampling event if the PTFE and nylon sample filters are sampled in the field on a day different to the intended use date. Placeholder electronic records would also be created to complete the sampling event for the day that the quartz filter was sampled, which was on the scheduled sampling date i.e., the intended use date. If samples for all three filter types are sampled on a date other than the intended use date, placeholder electronic records would be created for the sampling event with the intended use date. As with the scheduled but not collected cases, only sample filters are considered, all parameters for a given filter type are created, and the placeholder records are marked invalid with the 'AF – Scheduled but not Collected' null code flag.

3.2.5 Technical System Audit

The EPA conducted a Technical Systems Audit (TSA) of UC Davis laboratory and data handling operations on August 18 & 19, 2019; on-site audit activities were performed by Battelle (Columbus, OH) as an EPA contractor. Audit findings were detailed in a report from the EPA delivered to UC Davis on January 16, 2020. Discussion and resolution of the corrective action findings are documented in a corrective action report (CAR) prepared by UC Davis and delivered to the EPA (initially on February 13, 2020, and with revisions on March 31, 2020). The EPA sent a close-out letter to UC Davis on May 7, 2021.

3.2.6 System Audits

UCD performed an internal audit on December 17, 2020. A third party auditor, T&B Systems, was contracted to perform the audit. The auditors were provided with a tour of the data processing and validation tools. No issues were noted for correction.

4. Laboratory Quality Control Summaries

4.1 RTI Ion Chromatography Laboratory

The RTI Ion Chromatography Laboratory, as a subcontractor to UC Davis, received and analyzed extracts from nylon filters for batches 63 through 74, covering the sampling period January 1, 2020 through December 31, 2020. Routine analysis of these samples was performed March 9, 2020 through March 9, 2021. Both routine analysis and reanalysis was performed March 9, 2020 through April 16, 2021. Using ion chromatography, RTI analyzed for both anions (chloride [Cl⁻], nitrate [NO₃⁻], and sulfate [SO₄²⁻]) and cations (sodium [Na⁺], ammonium [NH₄⁺], and potassium [K⁺]) using five Thermo Dionex ICS systems and four Thermo Dionex Aquion systems (five anion systems: A11, A12, A9, A10, and A8; four cation systems: C9, C10,

C3, and C6) and reported the results of those analyses to UC Davis. Table 4.1-1 details the analysis dates for each batch of data, including both routine analysis and reanalysis.

Table 4.1-1: Sampling dates and corresponding IC analysis dates covered in this reporting period. Analysis dates include reanalysis – as requested during QA level 0 and level 1 validation – of any samples within the sampling year and month.

Sampling Month (2020)	Analysis Batch #	IC Analysis Dates
January	63	3/9/2020- 6/18/2020
February	64	4/13/2020- 7/10/2020
March	65	5/11/2020 – 8/11/2020
April	66	6/9/2020 – 9/14/2020
May	67	7/13/2020 – 9/14/2020
June	68	8/7/2020 – 10/29/2020
July	69	9/10/2020 – 11/12/2020
August	70	10/13/2020 – 12/14/2020
September	71	11/9/2020 – 1/19/2021
October	72	12/14/2020 – 2/10/2021
November	73	1/15/2021 – 2/11/2021
December	74	2/12/2021 – 4/16/2021

4.1.1 Summary of QC Checks and Statistics

Samples are received by the RTI Ion Chromatography Laboratory following the chain-of-custody procedures specified in *RTI SOP #Ions1*. Samples are analyzed using Thermo Dionex ICS-2000, ICS-3000, and Aquion systems following *RTI SOP #Ions1*. Extraction procedures are documented on worksheets which are maintained with the associated analysis files. The QC measures for the RTI ion analysis are summarized in Table 4.1-2. The table details the frequency and standards required for the specified checks, along with the acceptance criteria and corrective actions. Stated acceptance criteria are verified and documented on review worksheets, and reviewers document acceptance criteria not met, corrective actions, samples flagged for reanalysis, and subsequent reanalysis dates.

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

Activity	Frequency	Acceptance Criteria	Corrective Action
Calibration regression	Daily	$R^2 \geq 0.999$	Investigate; repeat calibration
Continuing calibration verification (CCV) check standard; RTI dilution of a commercially prepared, NIST-traceable QC sample	Daily, immediately after calibration and at every 10 samples	Measured concentrations < 0.050 ppm: within 35% of known values. Measured concentrations >0.050 ppm: within 10% of known values.	Investigate; reanalyze samples

Activity	Frequency	Acceptance Criteria	Corrective Action
Duplicate sample	3 per set of 50 samples	Relative % Difference = 10% at 10x MDL Relative % Difference = 200% at MDL	Investigate; reanalyze
Spiked sample extract	2 per set of 50 samples	Recoveries within 90 to 110% of target values	Investigate; reanalyze
Reagent blanks	One reagent blank per reagent used (DI H ₂ O and/or eluent); at least one per day	No limit set; the data is compiled for comparability studies; < 10 times MDL	Investigate; reanalyze
Round Robin (External QA by USGS)	4 per month	Not applicable; data reported and compared annually	Investigate
Reanalysis	5% per of all samples, reanalyzed on different day and as requested	MDL to 10 times MDL: RPD up to 200%, 10 to 100 times MDL: RPD < 20%, >100 times MDL: differences within 10%	Investigate and reanalyze samples if needed

4.1.2 Summary of QC Results

RTI followed the acceptance criteria stated in Table 4.1-2. Instruments were recalibrated when calibration failed to meet the criteria. For cases where CCV failures occurred during analyses, samples bracketed by the CCV failure were reanalyzed. When duplicate precision or spiked sample recoveries failed to meet the criteria, the duplicated samples or matrix spike sample plus additional samples (5% of all samples) were reanalyzed. The original data were only replaced with reanalysis data in cases where precision between the reanalysis and original result failed to meet the criteria. For cases where check samples failed to meet the reanalysis criteria, the remaining samples not already reanalyzed from the set of 50 samples were reanalyzed.

4.1.2.1 Calibration regression

Ion chromatographs are calibrated daily with calibration standards prepared as serial dilutions of a NIST-traceable stock standard. Anion instruments are calibrated from 10 to 2,000 parts per billion (ppb) for chloride and from 50 to 10,000 ppb for nitrate and sulfate. A high calibration standard at 5,000 ppb for chloride and 25,000 ppb for sulfate and nitrate are used in the calibration curve only for samples exceeding 2,000 and 10,000 ppb, respectively. Cation instruments are calibrated from 10 to 1,000 ppb for sodium, ammonium, and potassium. A high calibration standard at 3,000 ppb is used only for samples whose concentrations exceed 1,000 ppb. The correlation coefficients for the daily calibration must be at least 0.999. If the criterion is not met, the curve is investigated. A calibration standard or standards that are suspect are removed from the curve and not used for calculations. If the calibration still fails to meet the stated acceptance criteria, the situation is further investigated until it has been confirmed that the instrument is performing correctly.

After calibration, an analytical sequence is assigned to an instrument and includes 50 samples, extraction QC checks, three sets of replicate samples, two matrix spikes, and continuing calibration verification (CCV) standards analyzed at a frequency of every 10 samples.

4.1.2.2 Continuing calibration verification (CCV) check standard

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

Table 4.1-3: Target concentrations of anion CCV check standards for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

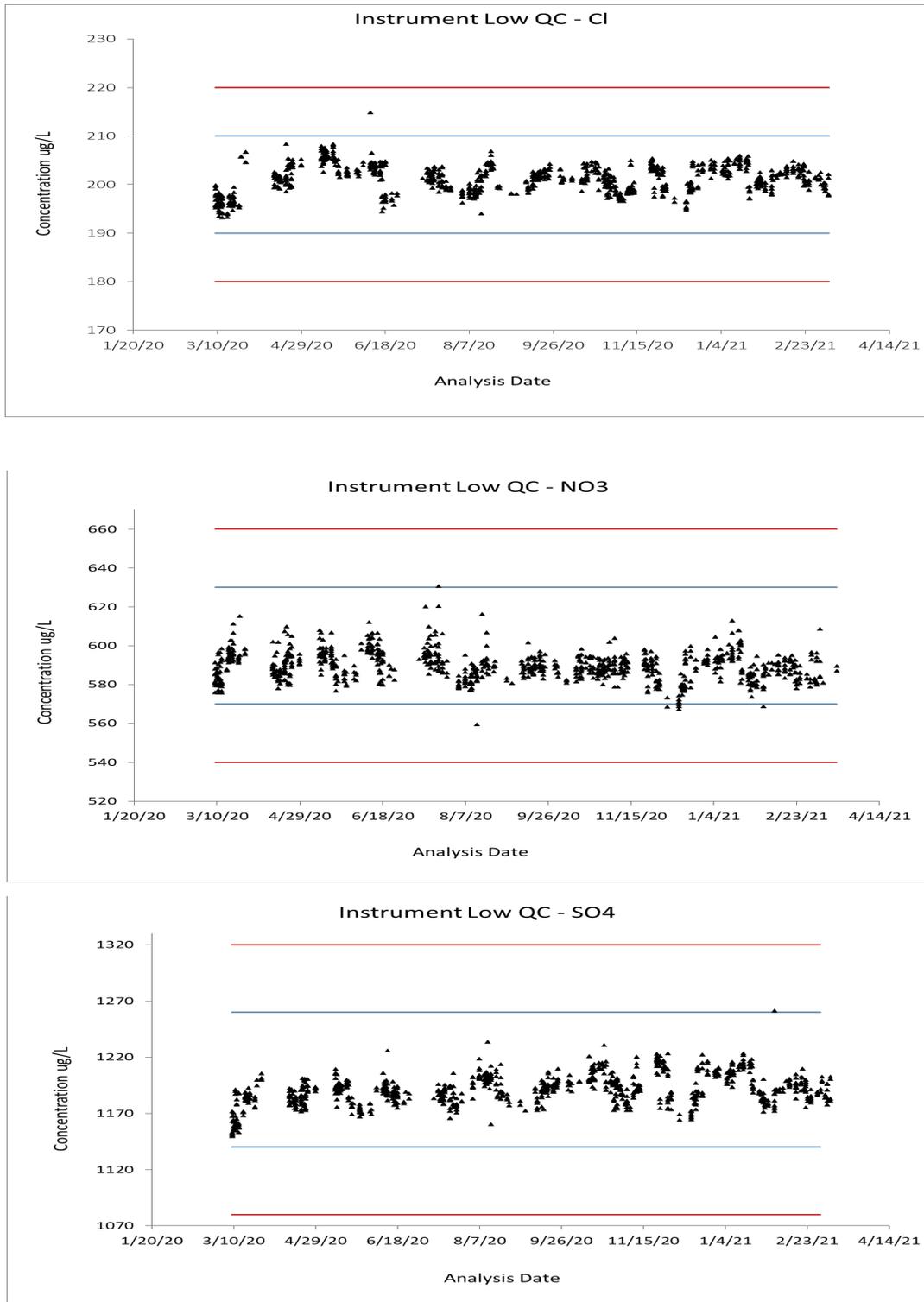
QC Sample	Cl ⁻ (ppb)	NO ₃ ⁻ (ppb)	SO ₄ ²⁻ (ppb)
Instrument Low QC	200	600	1200
Instrument Medium QC	500	1500	3000
Instrument Medium-High QC	1000	3000	6000
Instrument High QC	2000	6000	12000

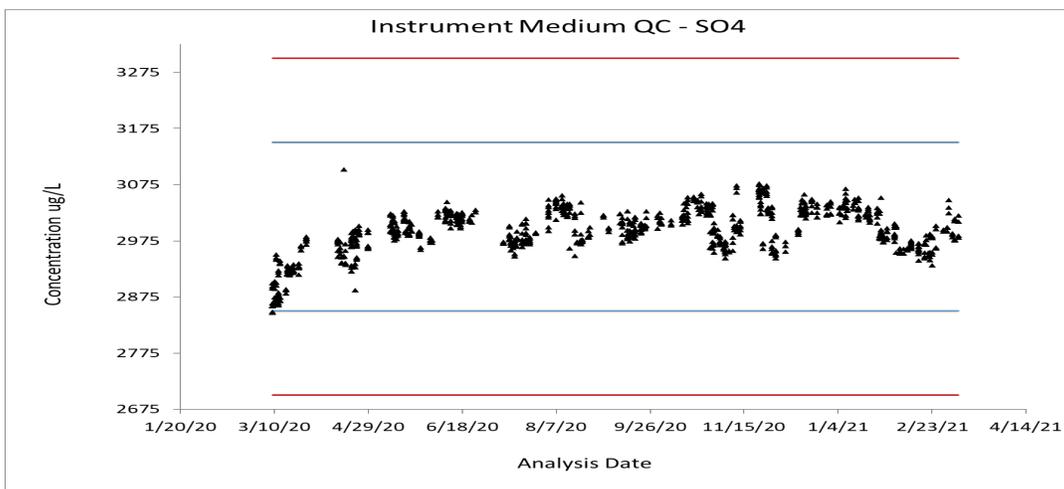
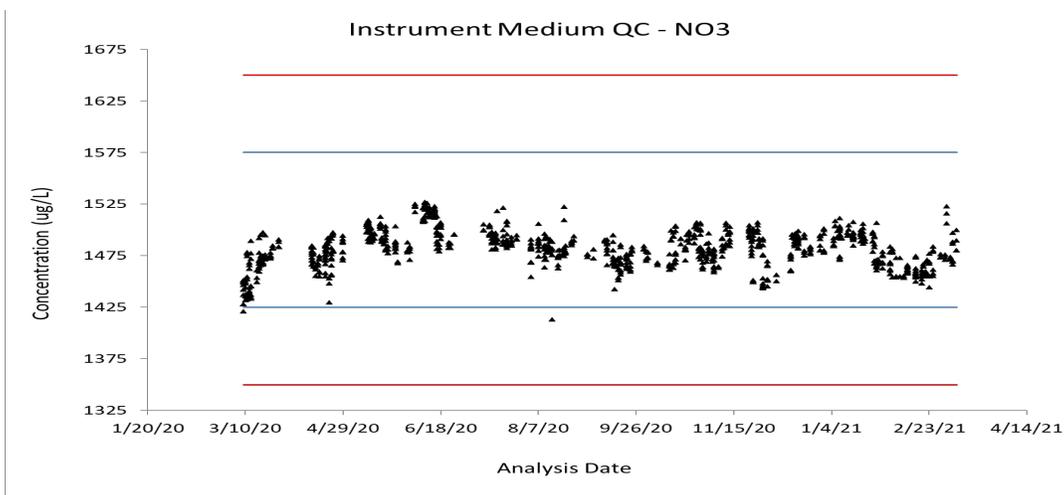
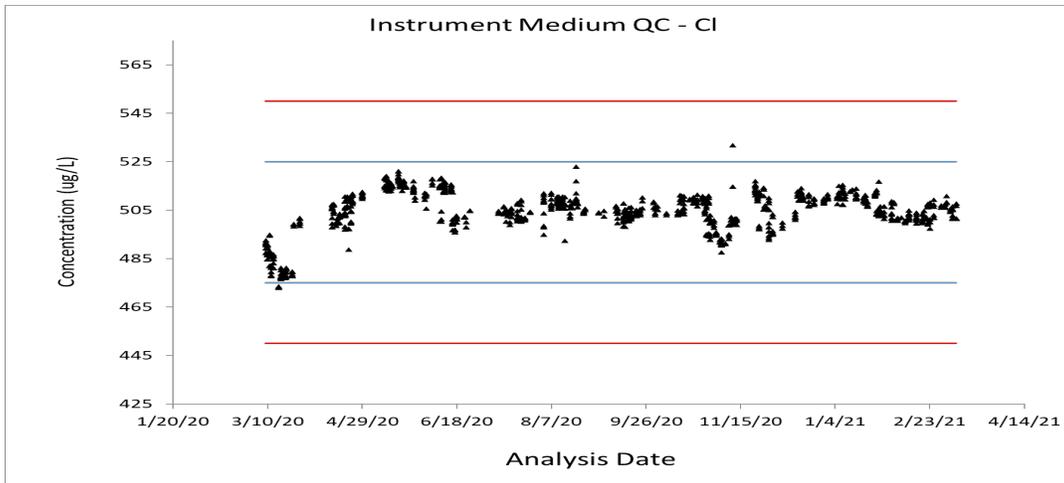
Table 4.1-4: Target concentrations of cation CCV check standards for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

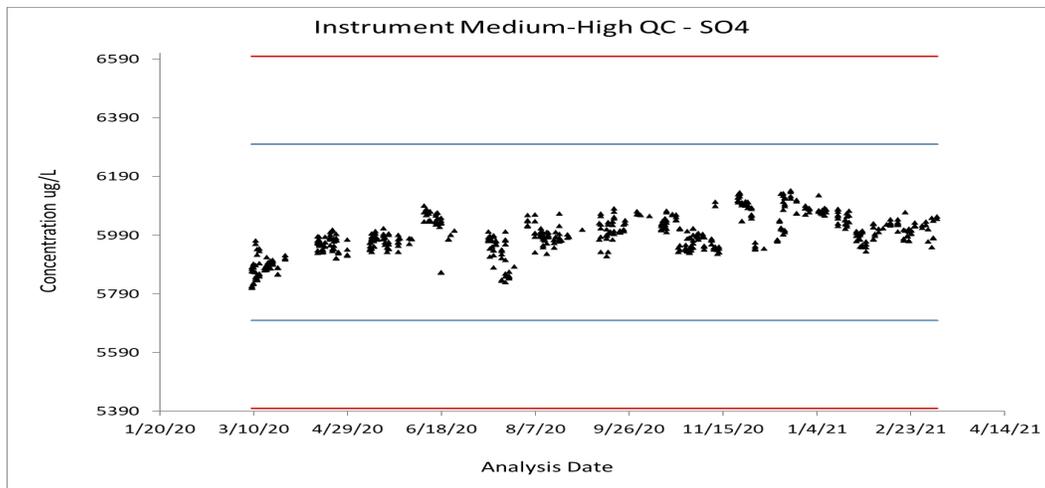
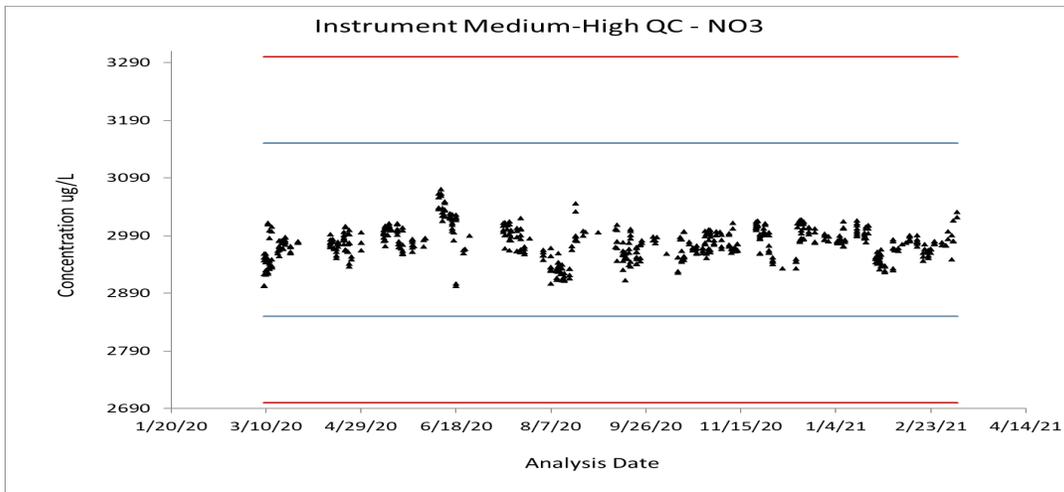
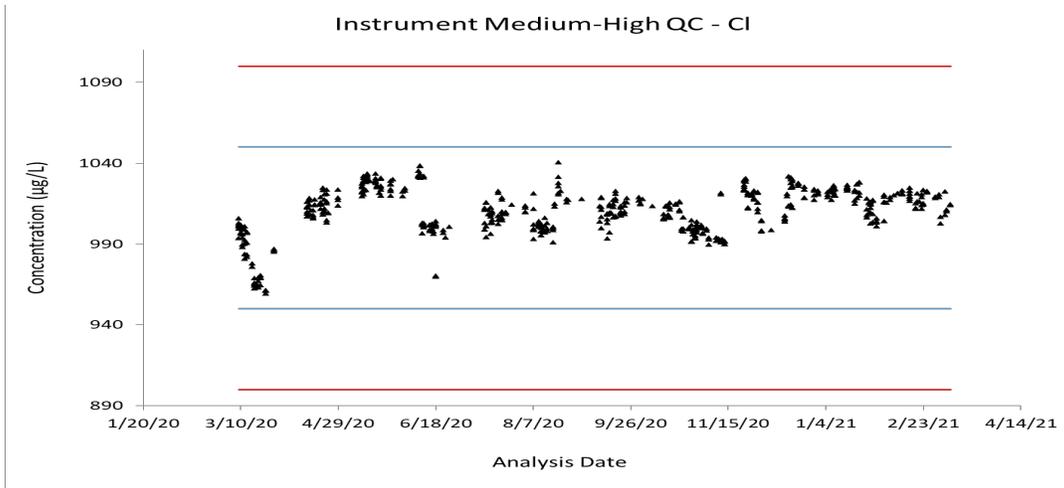
QC Sample	Na ⁺ (ppb)	NH ₄ ⁺ (ppb)	K ⁺ (ppb)
Instrument Low QC	20	20	20
Instrument Medium QC	250	250	250
Instrument Medium-High QC	750	750	750
Instrument High QC	2000	2000	2000

At least two CCV check standards are analyzed immediately after the calibration standards and a single CCV check standard is analyzed after every ten samples. When an instrument CCV check standard fails the acceptance criteria by falling outside of the control limits, impacted samples are reanalyzed. If a CCV check standard fails, and there is a second CCV check standard measured immediately following the failure which passes, samples are not reanalyzed. The failed CCV check standard, samples flagged for reanalysis, and date of reanalysis are documented on the review worksheet and maintained with the analysis records for each set of 50 samples analyzed. Control charts were prepared for anion (Figure 4.1-1) and cation (Figure 4.1-2) CCV check standards. Failures occurred at a rate less than 1% for all check standards and data obtained during failures were not reported. Only data with check standards within limits were reported.

Figure 4.1-1: Control charts for anion CCV check standards at low, medium, medium-high, and high concentrations measured in units of $\mu\text{g/L}$ (see Table 4.1-3) for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Red lines show upper and lower control limits set at $\pm 10\%$ of the nominal concentrations for the low, medium, medium-high, and high standards. Blue lines show upper and lower warning limits.







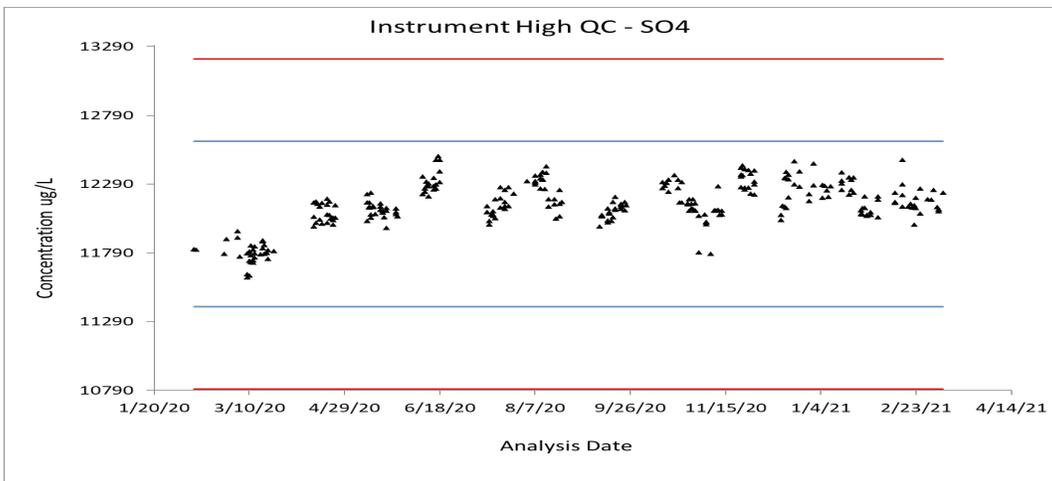
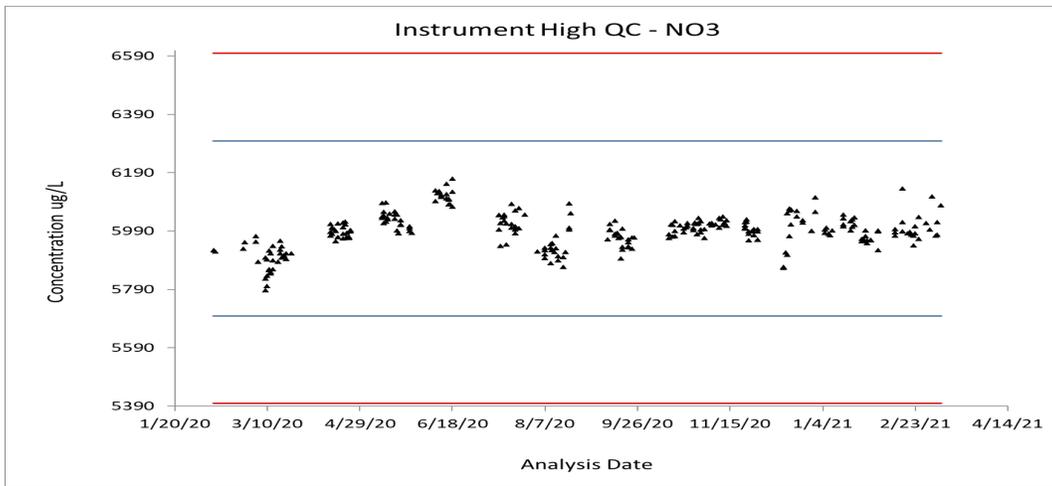
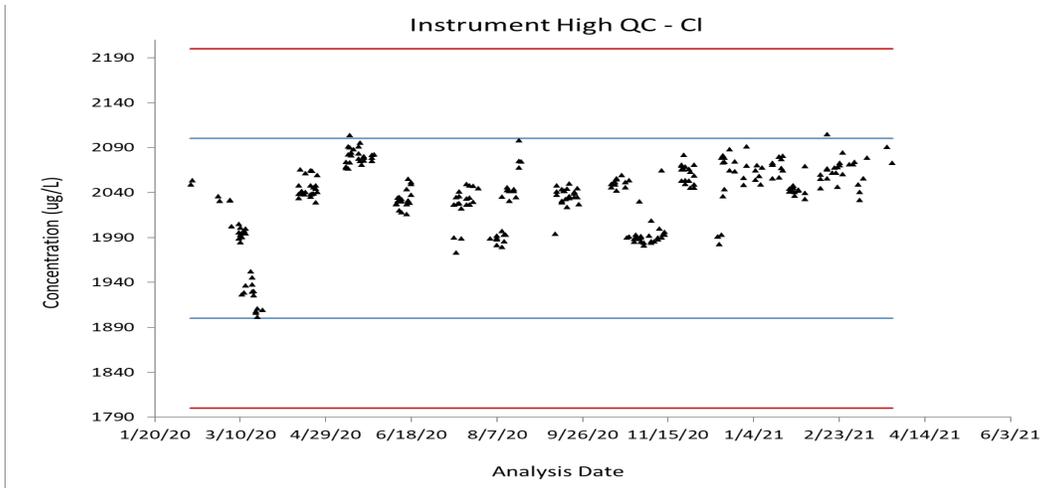
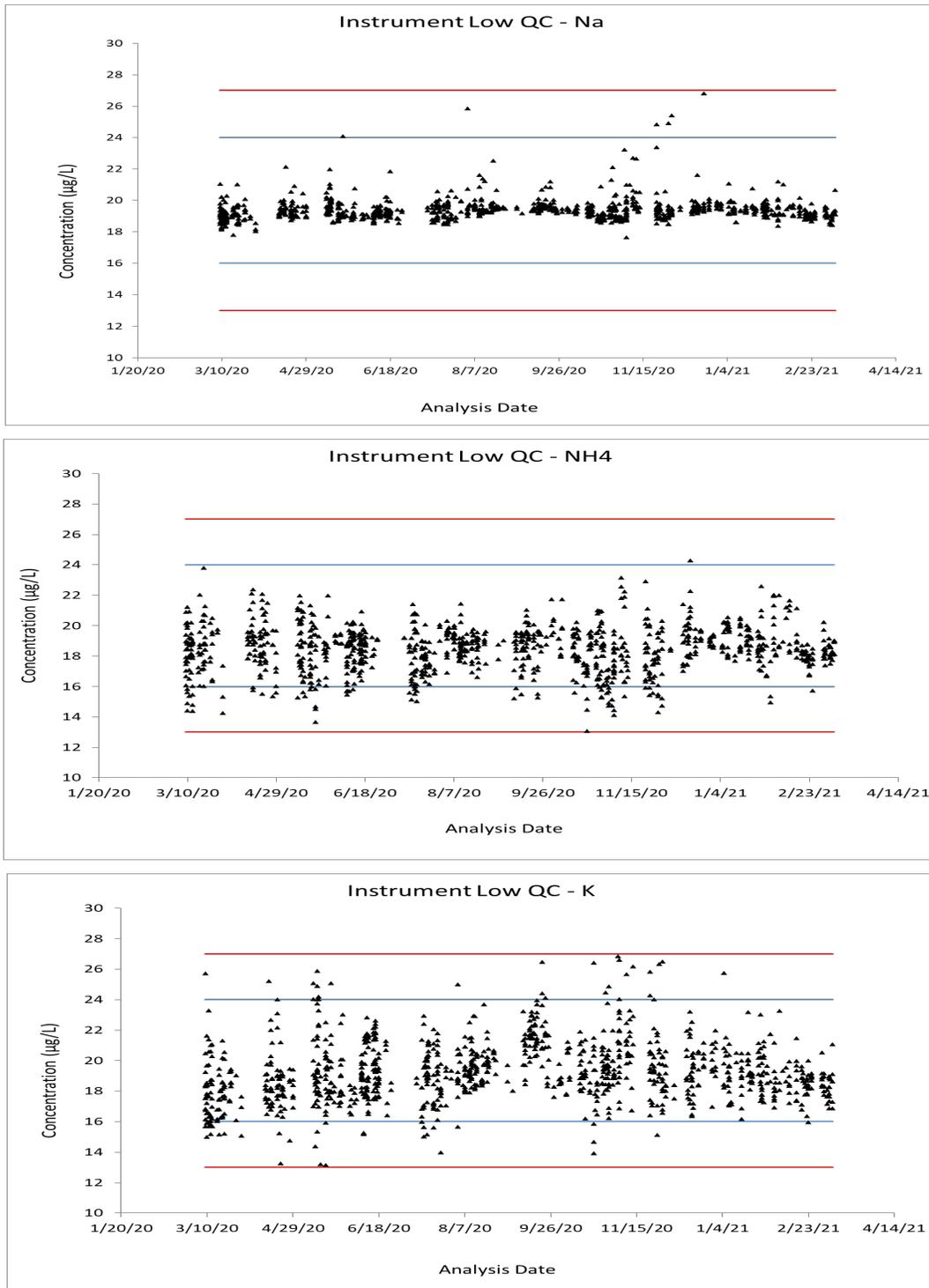
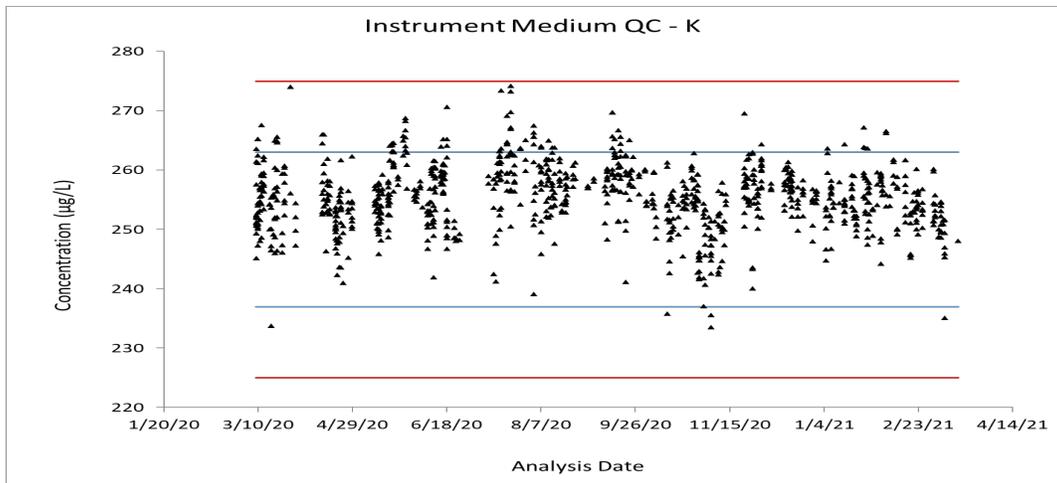
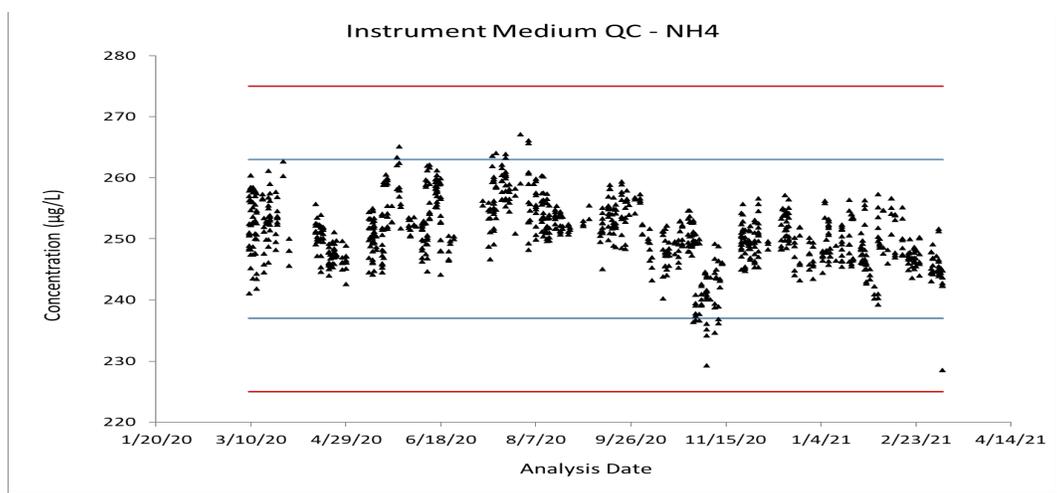
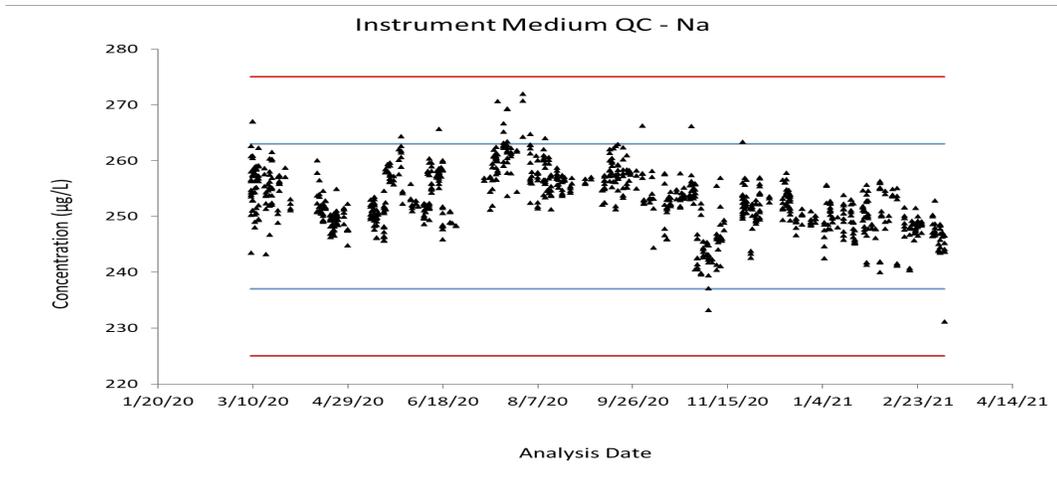
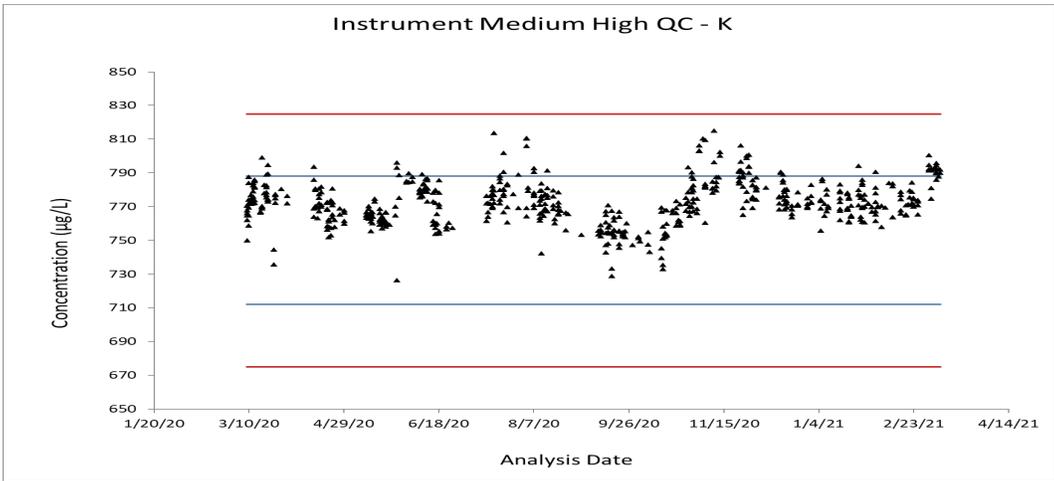
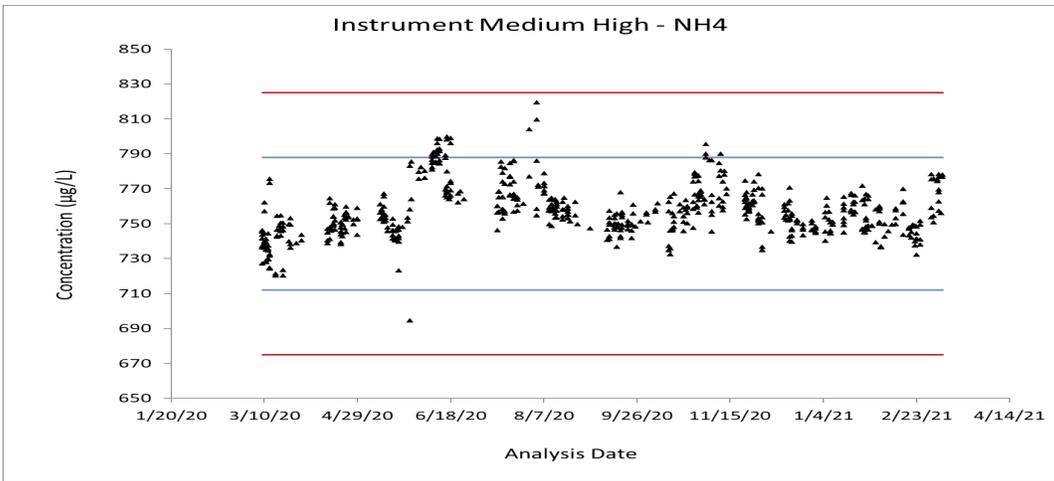
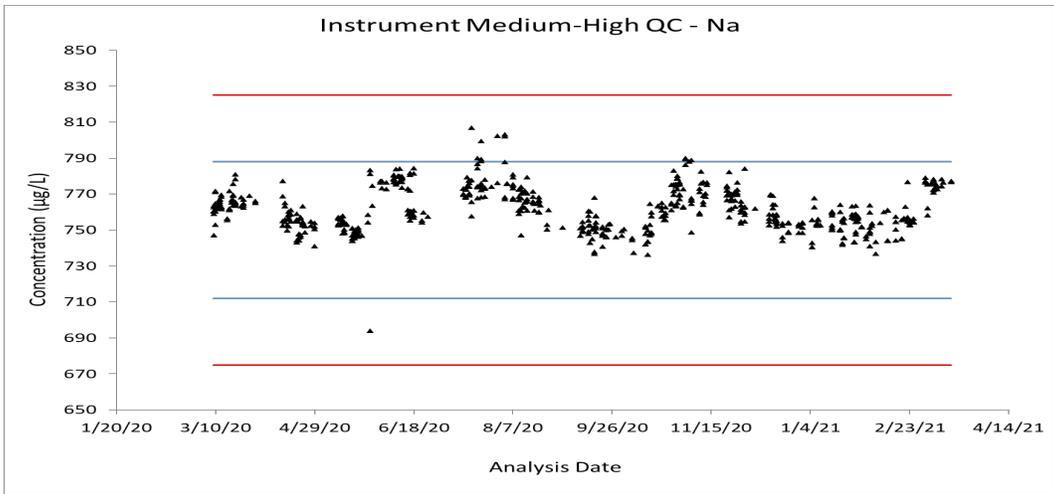
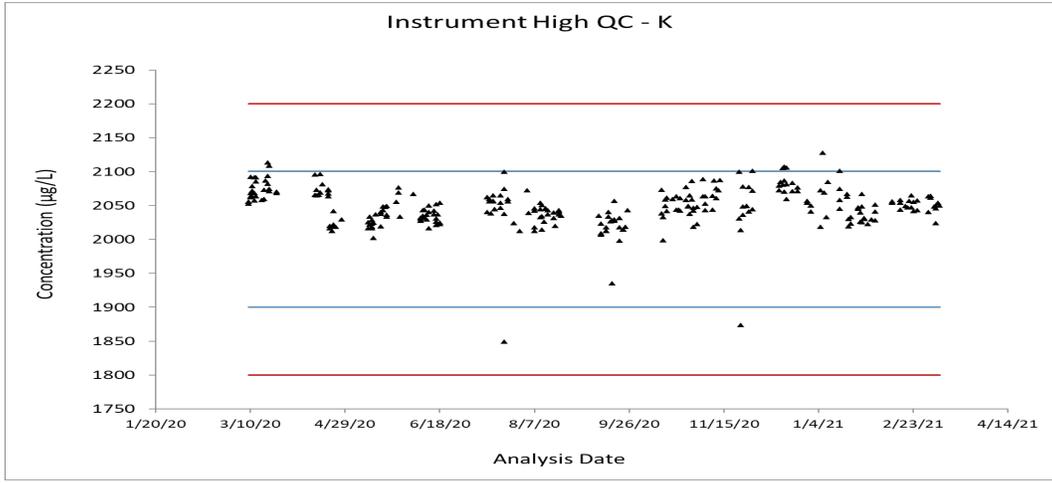
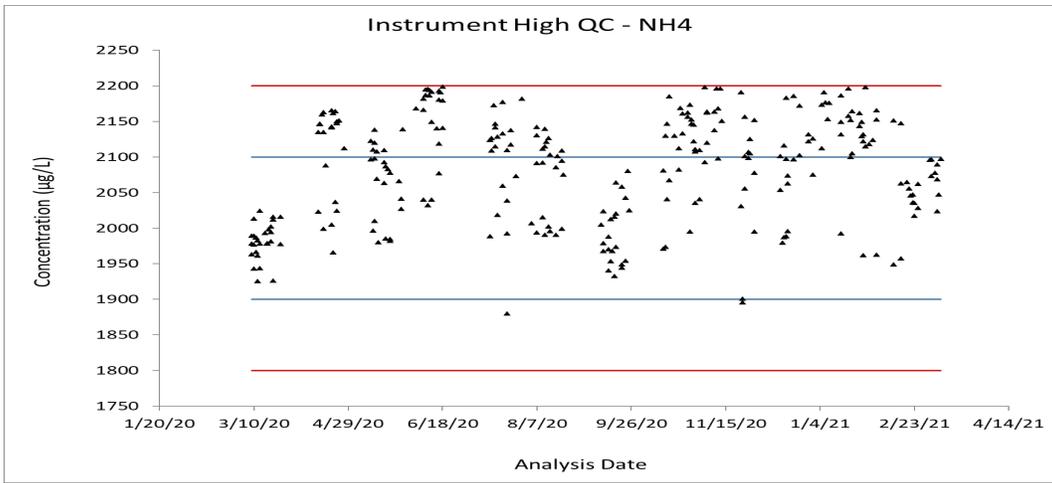
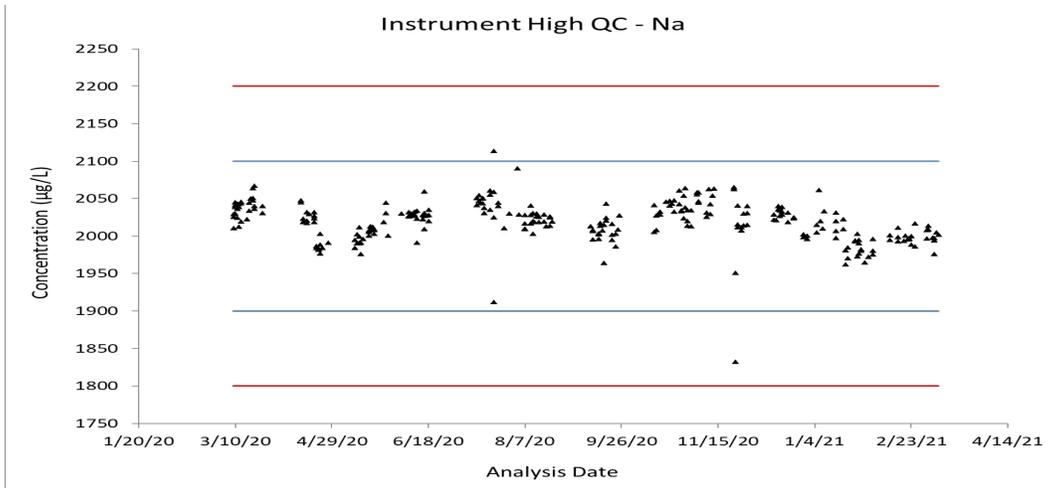


Figure 4.1-2: Control charts for cation CCV check standards at low, medium, medium-high, and high concentrations measured in units of $\mu\text{g/L}$ (see Table 4.1-4) for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Red lines show upper and lower control limits set at $\pm 35\%$ of the nominal concentrations for the low standards and $\pm 10\%$ of the nominal concentrations for the medium, medium-high, and high standards. Blue lines show upper and lower warning limits.



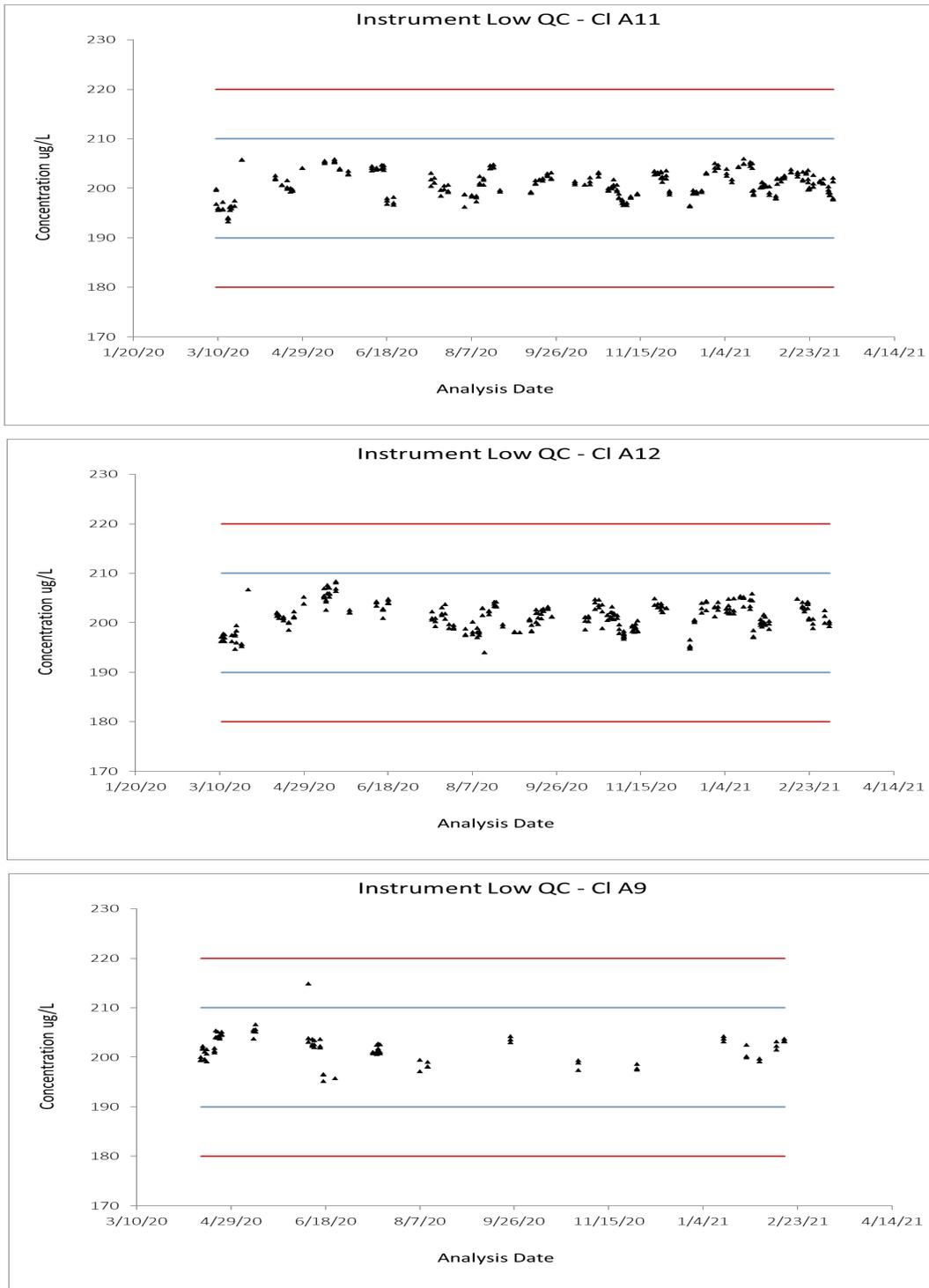


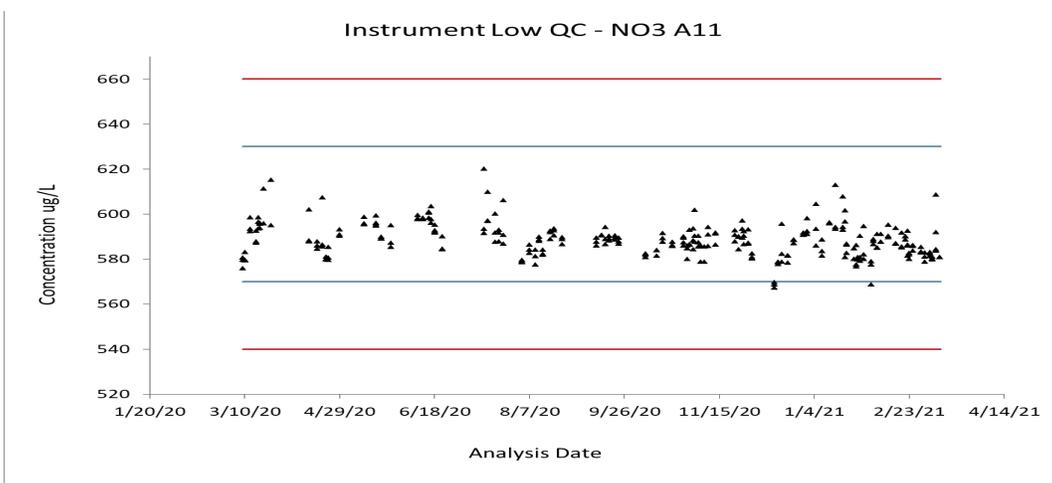
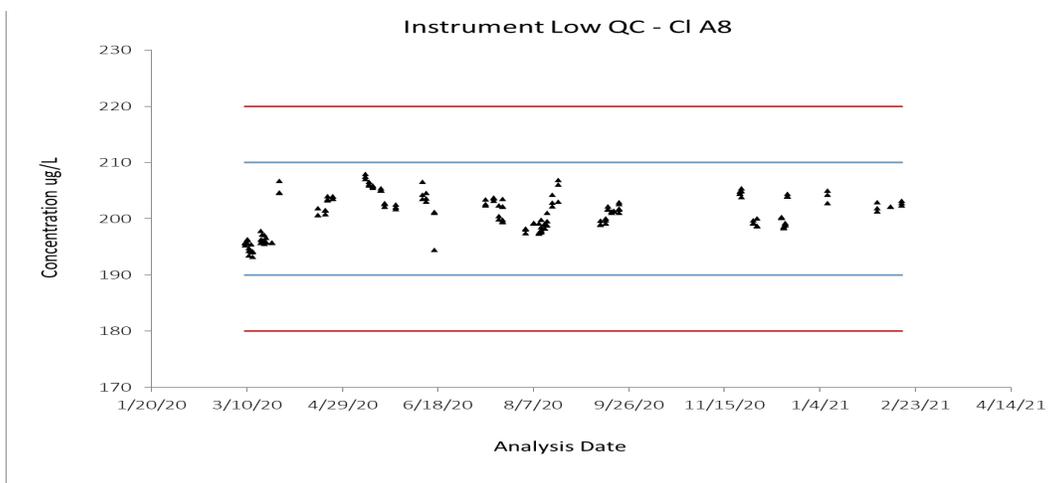
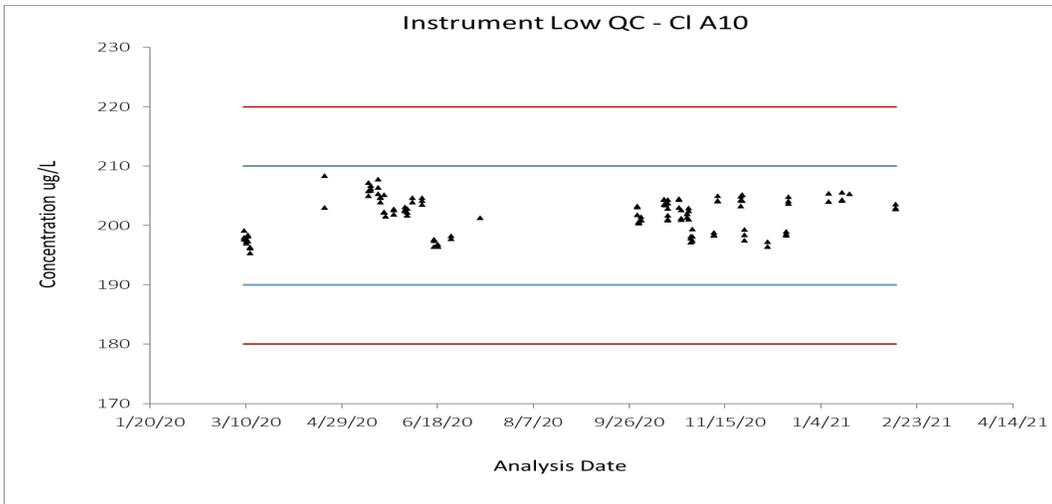


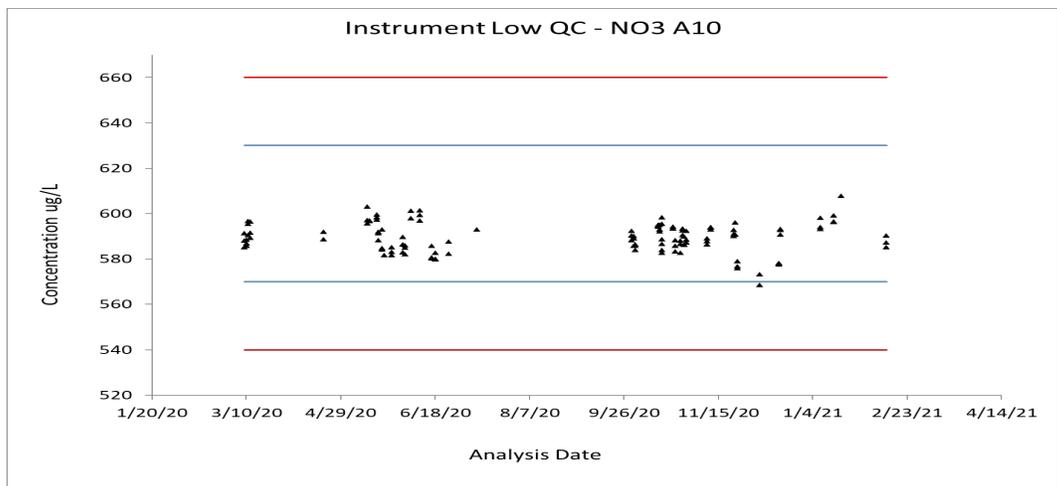
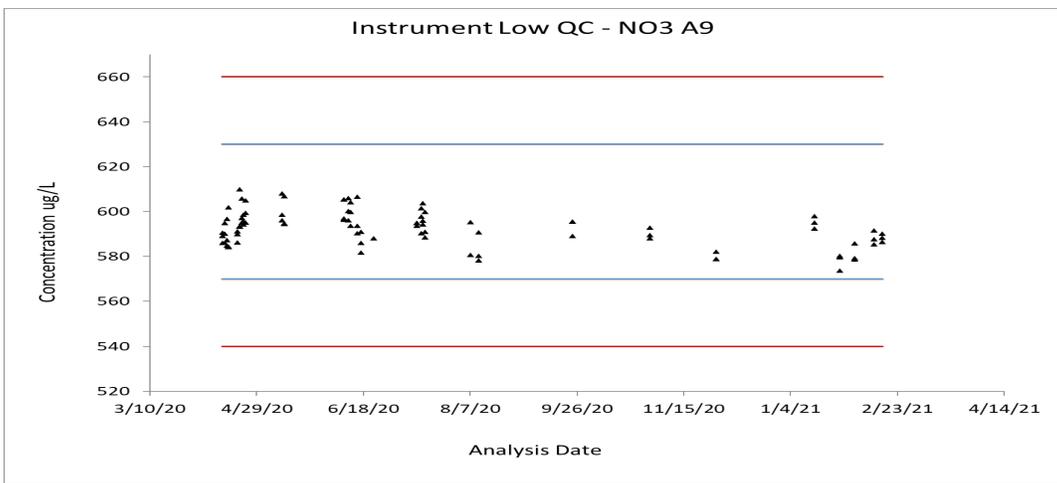
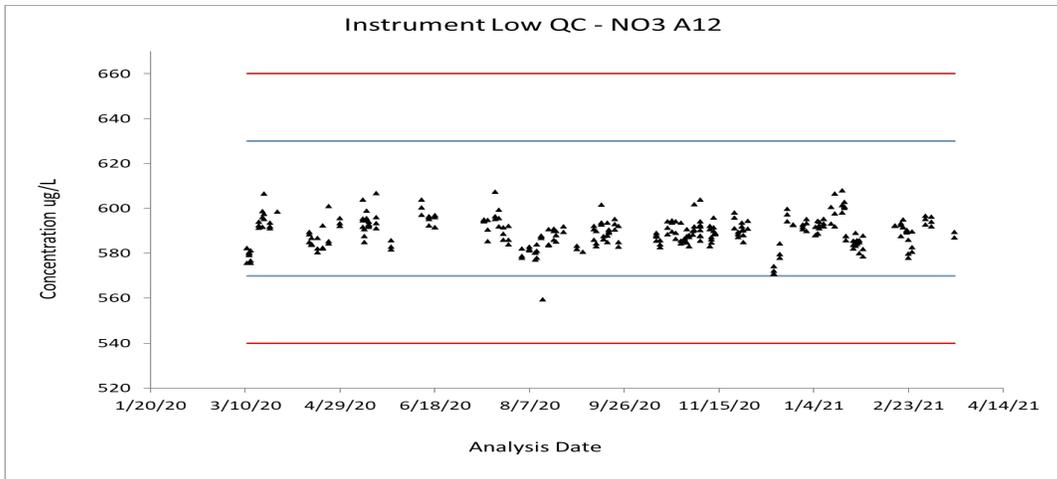


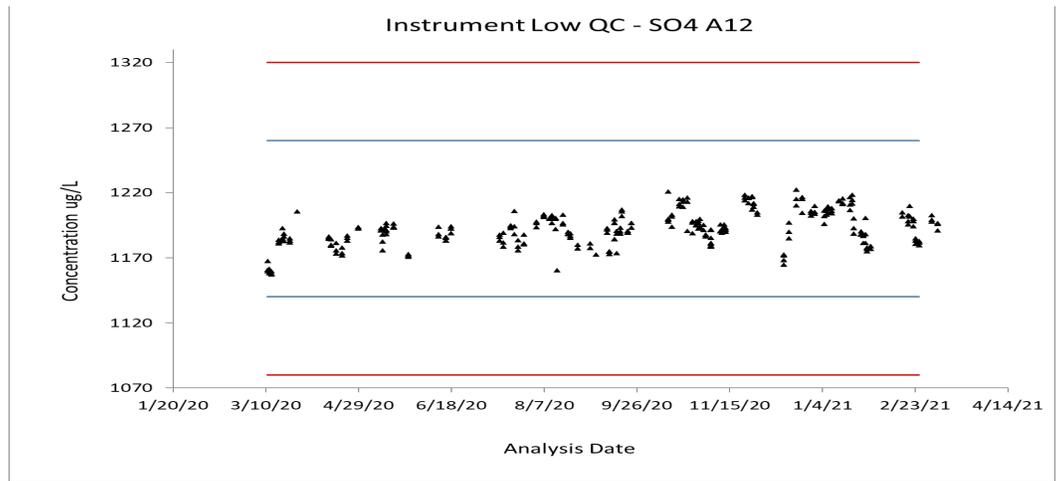
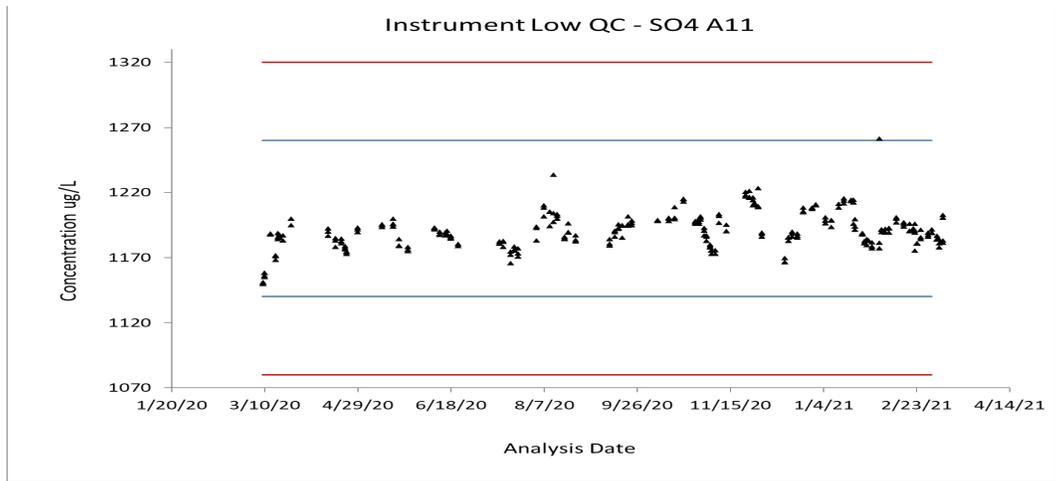
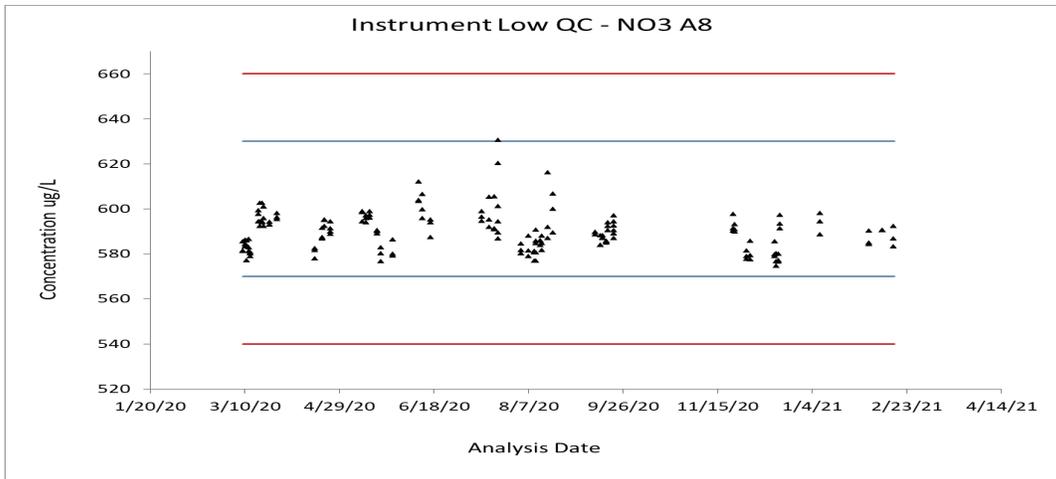
For the purpose of demonstrating instrument-to-instrument performance, control charts for the lowest CCV check standards were generated, where instruments A11, A12, A9, A10, and A8 are compared for anions (Figure 4.1-3) and instruments C9, C10, C3, and C6 are compared for cations (Figure 4.1-4). The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

Figure 4.1-3: Control charts for anion CCV check standards showing comparability between instruments (A11 and A12, Thermo Dionex Aquion systems; A9, A10, and A8 Thermo Dionex ICS-3000 systems) at low concentrations (see Table 4.1-3) for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Red lines show upper and lower control limits set at $\pm 10\%$ of the nominal concentrations. Blue lines show upper and lower warning limits.









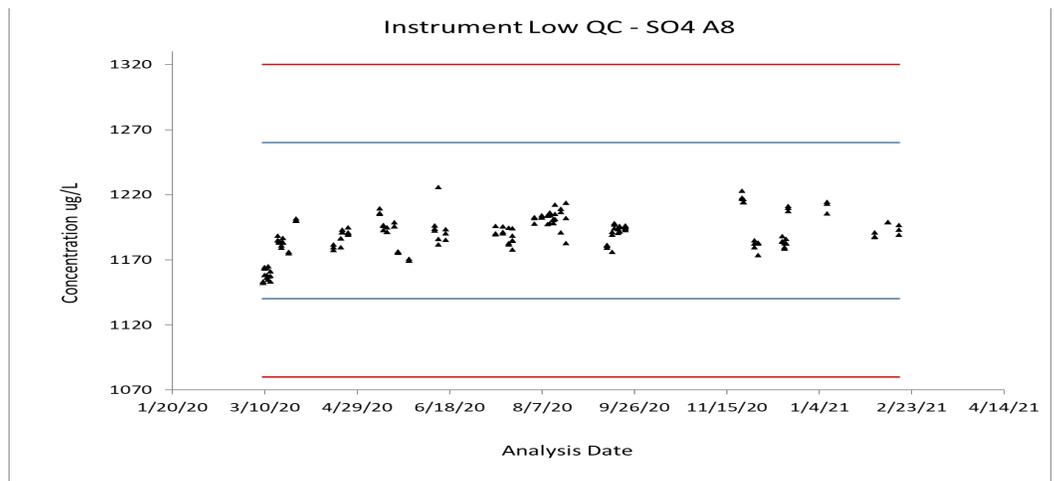
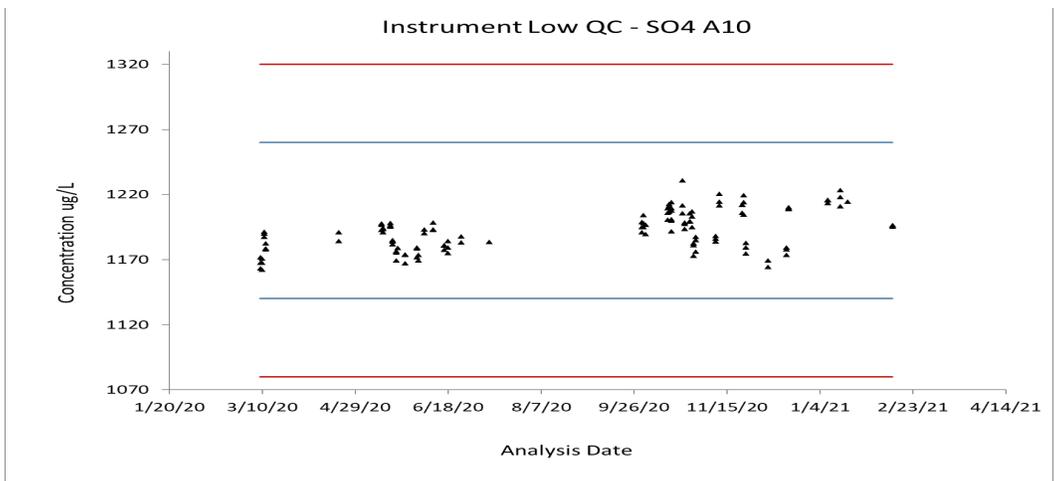
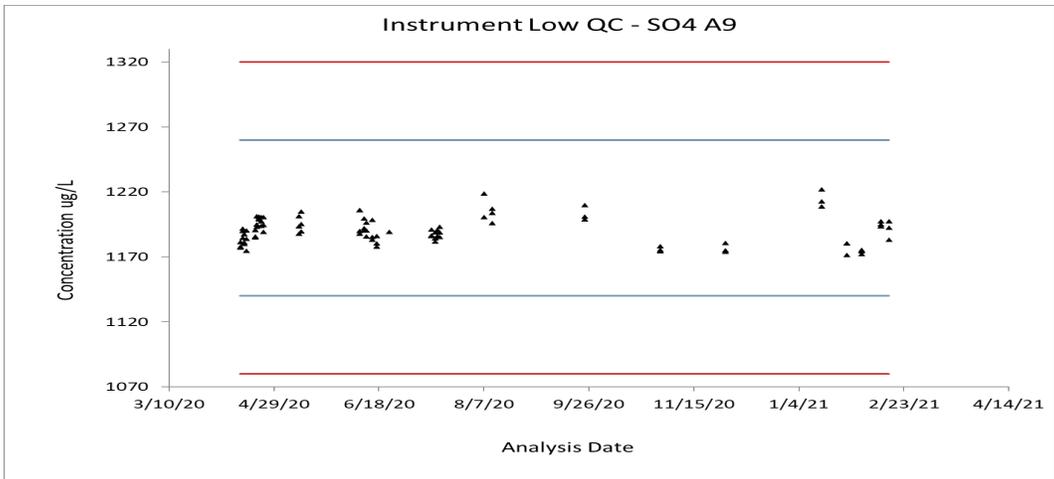
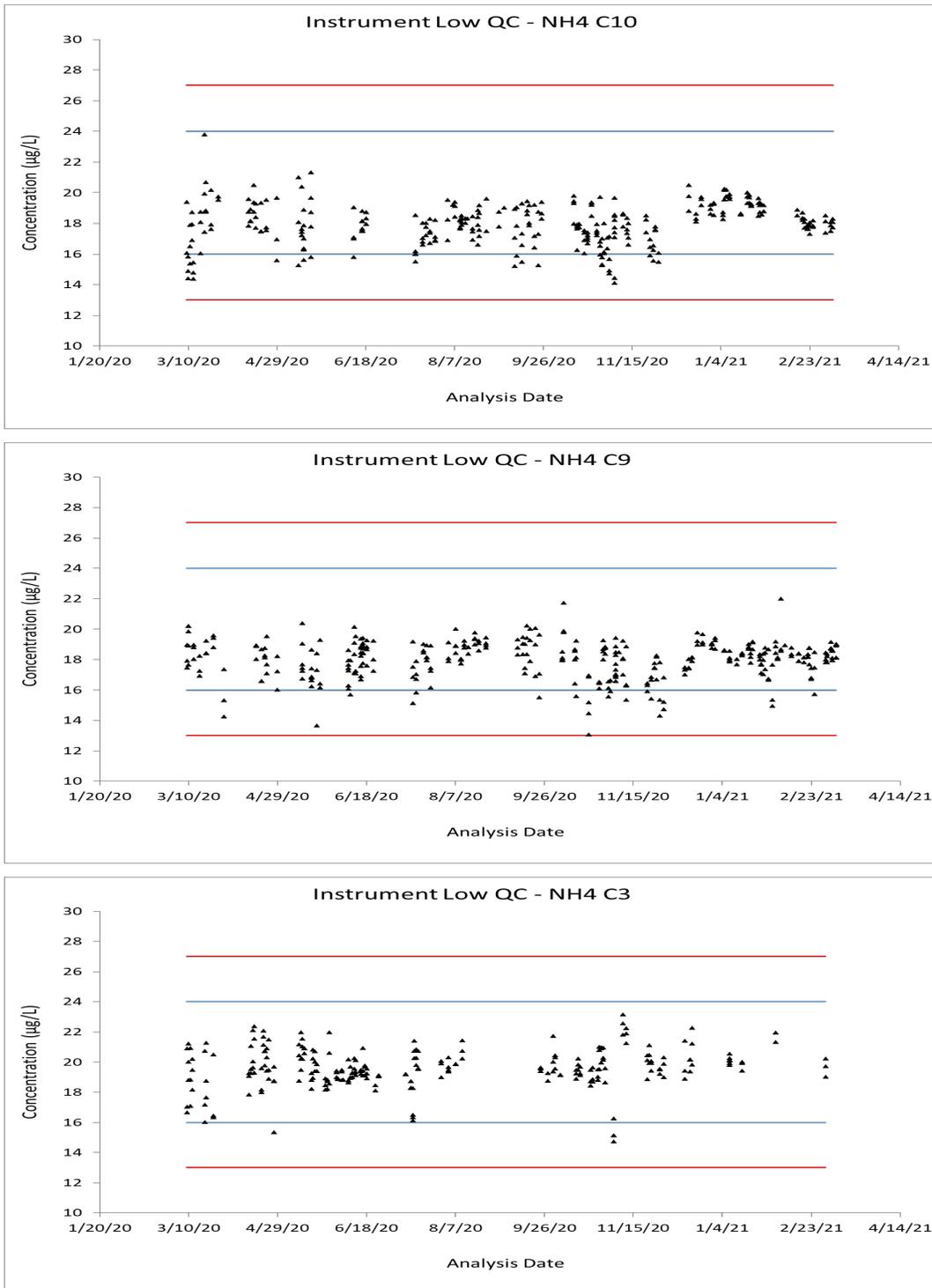
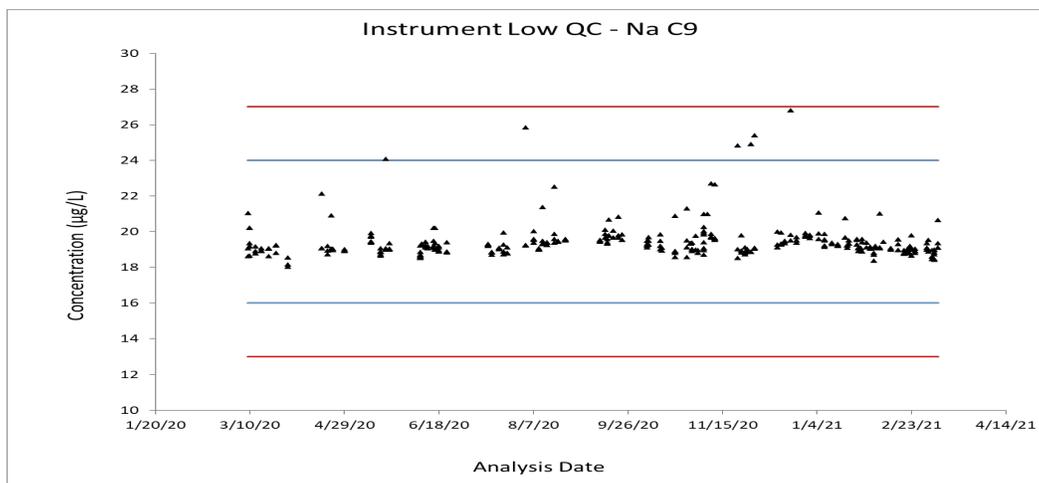
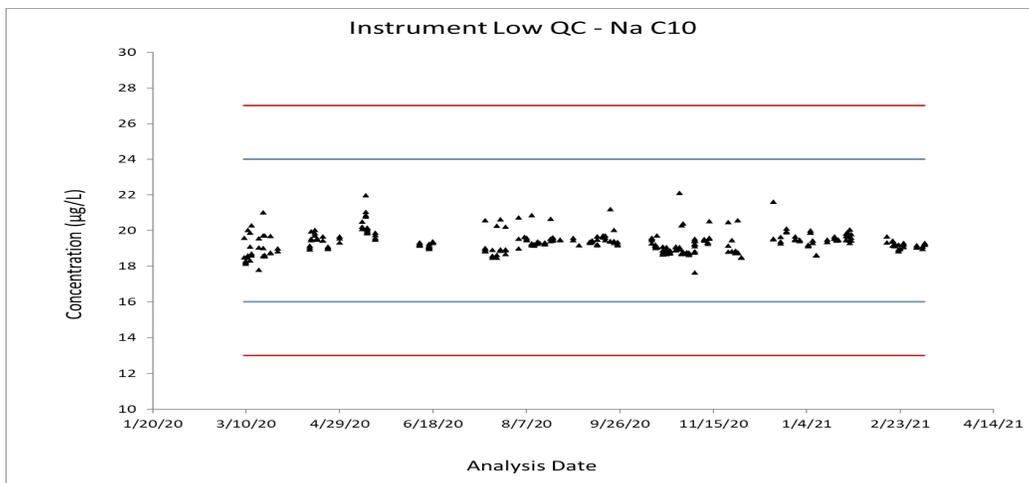
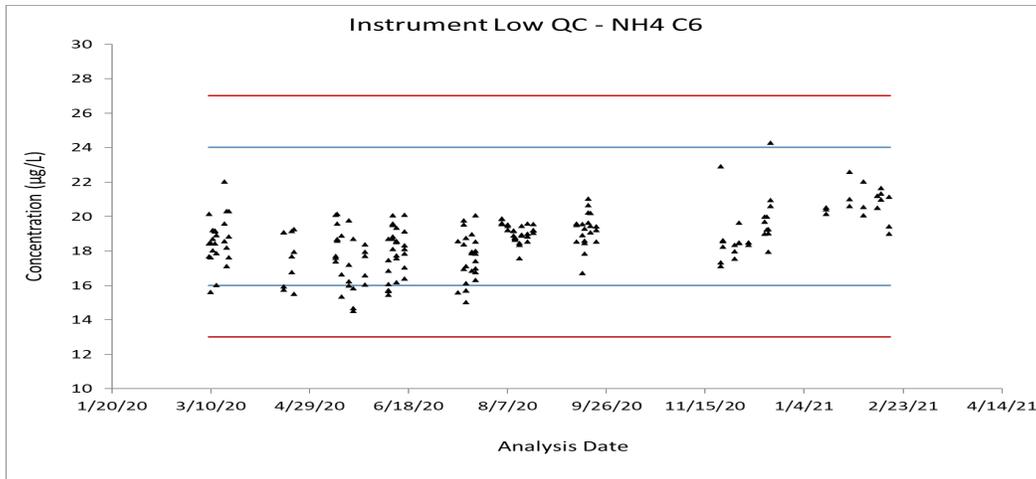
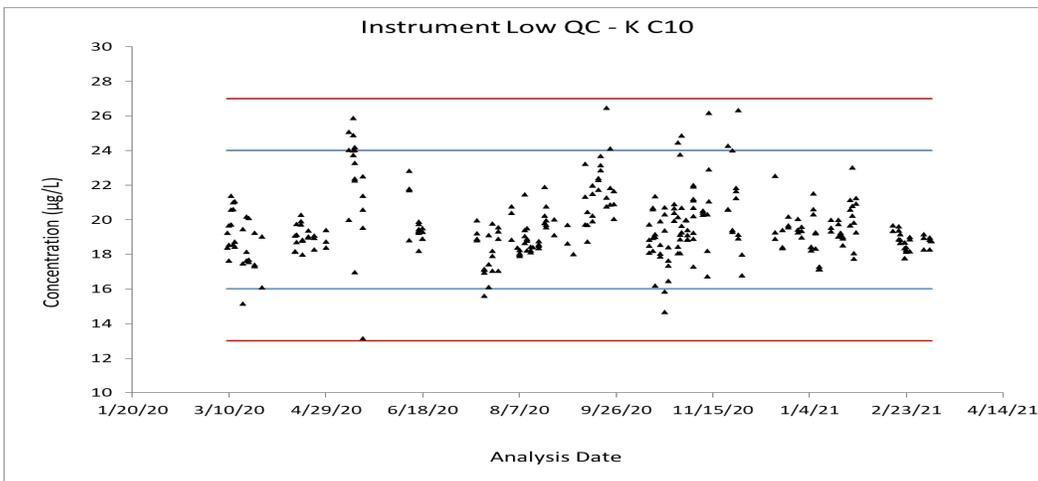
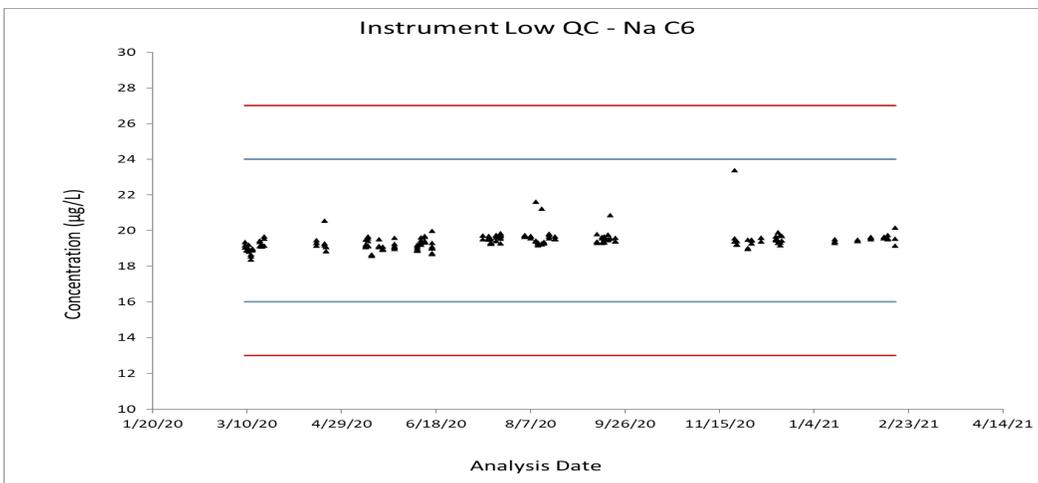
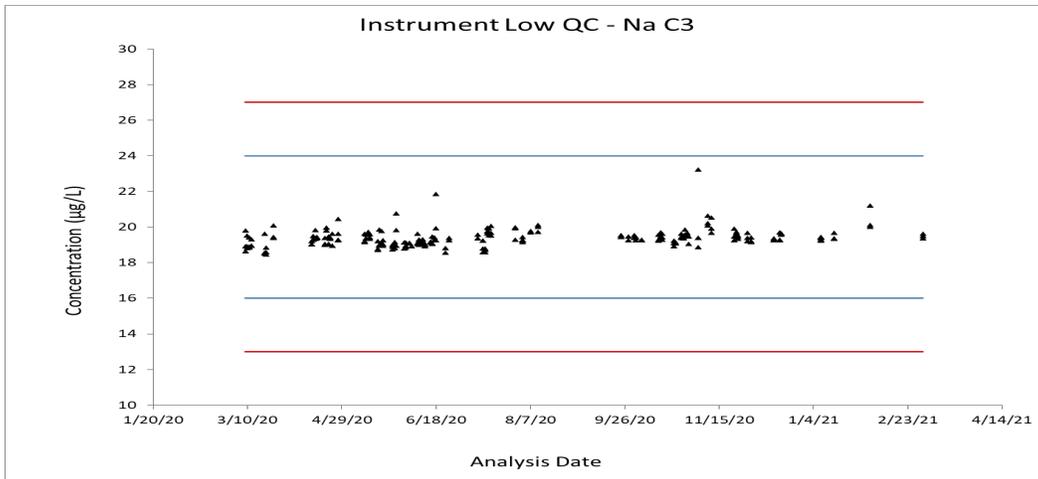
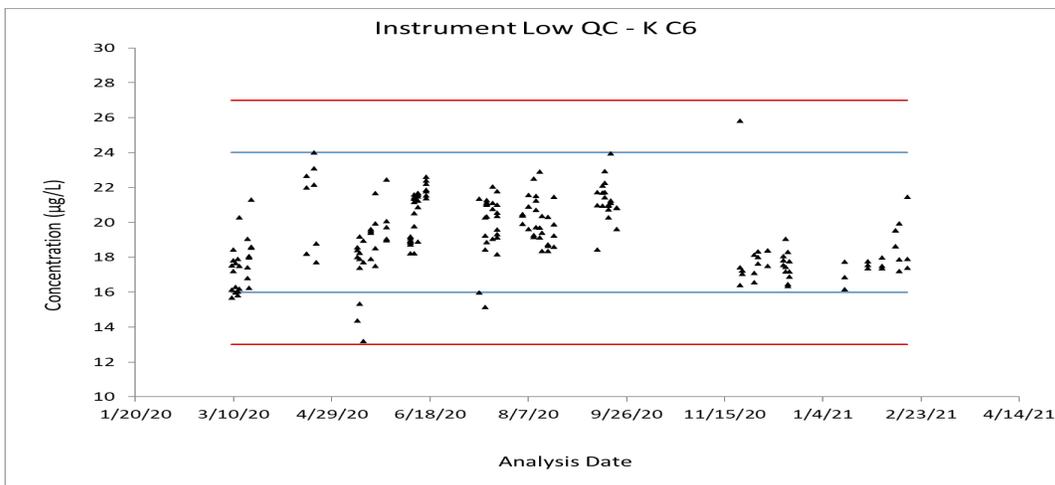
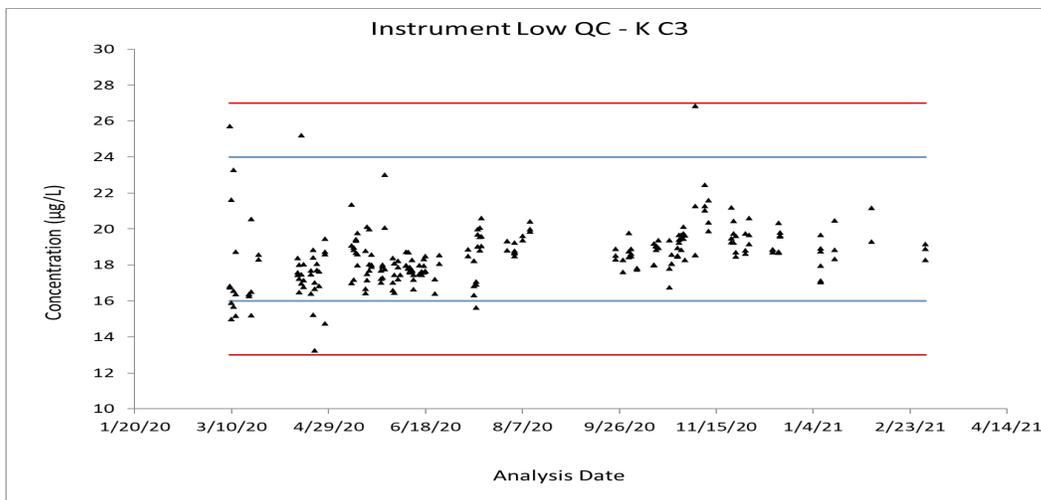
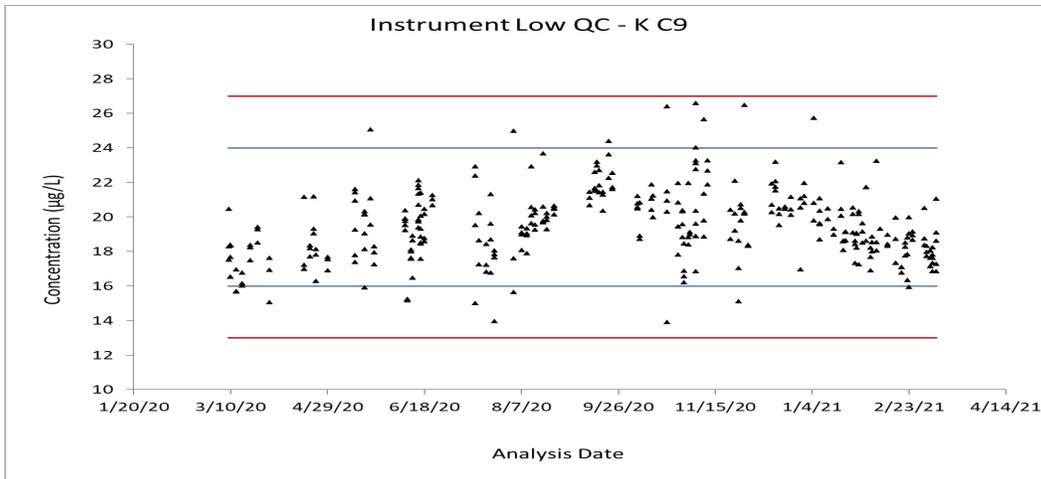


Figure 4.1-4: Control charts for cation CCV check standards showing comparability between instruments (C9 and C10, Thermo Dionex Aquion systems; C3 and C6, Thermo Dionex ICS-3000 systems) at low concentrations (see Table 4.1-4) for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2021). Red lines show upper and lower control limits set at $\pm 35\%$ of the nominal concentrations. Blue lines show upper and lower warning limits.







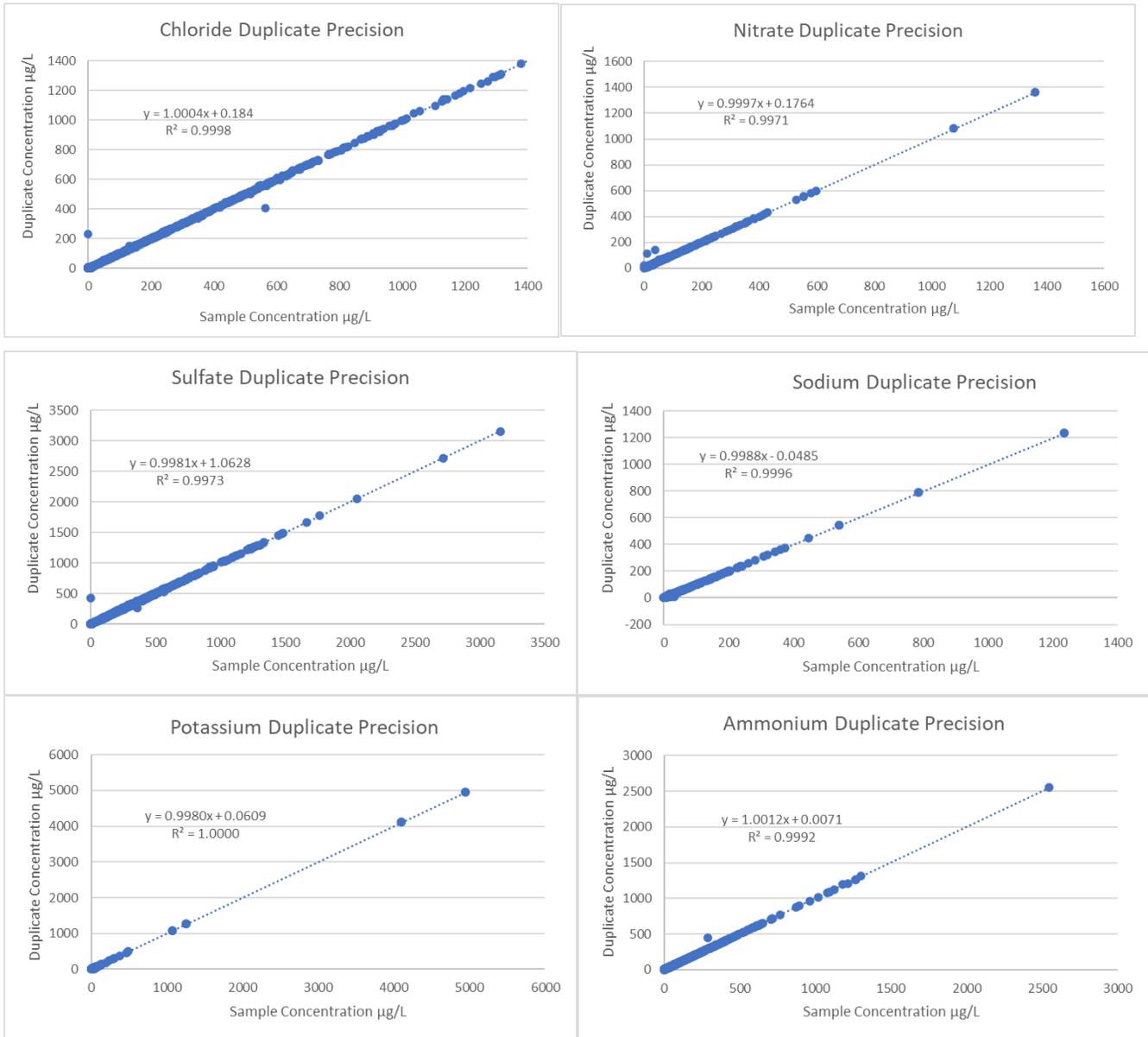


4.1.2.3 Duplicate Samples

Duplicate analysis results are obtained from two different aliquots of the same filter sample extract run on the same instrument sequentially; there are three sets of duplicate samples for every 50 samples analyzed. The relative percent difference (RPD) for duplicate samples must be

within $\pm 10\%$ when sample concentrations are greater than ten times the analytical MDL and within $\pm 100\%$ when sample concentrations are at or up to ten times the analytical MDL. During the analysis period when samples collected during 2020 were analyzed (March 9, 2020 through March 9, 2021), there were a total of 905 duplicate samples analyzed for anions (Figure 4.1-5), with five cases where the RPD did not meet the acceptance criteria for chloride and two cases for nitrate and one case for sulfate. Also during this analysis period, there were a total of 900 duplicate samples analyzed for cations (Figure 4.1-5), with one case each where the RPD did not meet the acceptance criteria for ammonium and sodium; and two cases where RPD did not meet the acceptance criteria for potassium. In all cases when duplicate precision failed to meet the acceptance criteria, five samples were reanalyzed (one duplicate aliquot plus four randomly selected network samples) were performed from the analysis set. If any of the reanalyses failed to meet the acceptance criteria, the entire set of 50 samples was reanalyzed.

Figure 4.1-5: Ion duplicate analysis results for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Cases that did not meet the acceptance criteria, as described in Section 4.1.2.3, are included in these figures.

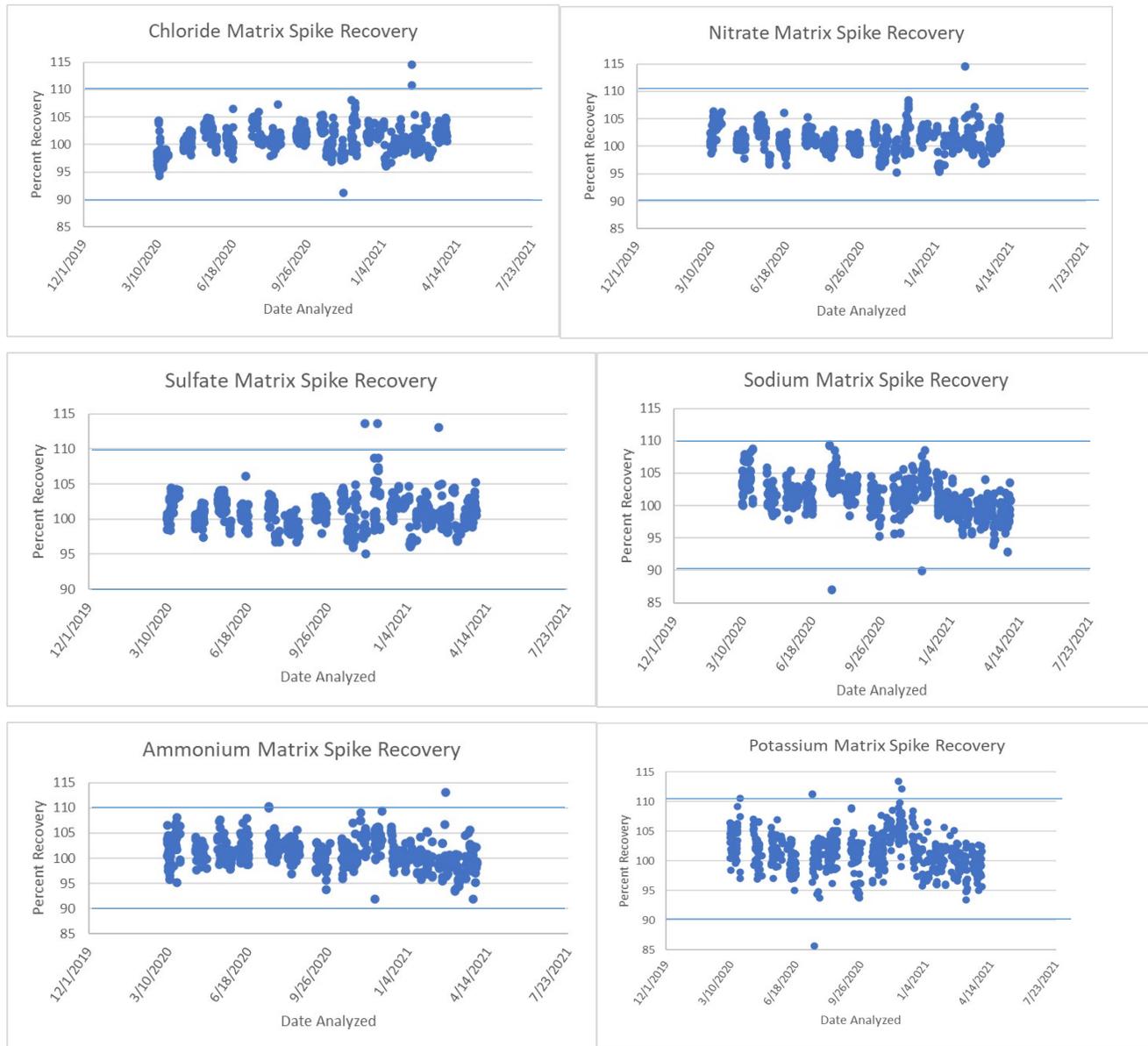


4.1.2.4 *Spiked Sample Extracts*

Matrix spikes are performed on 4% (two per set of 50 samples) of the samples analyzed. The matrix is deionized (DI) water, and spike samples typically meet the acceptance criteria with failures most likely resulting from introduced contamination. A total of 599 matrix spikes were analyzed for anions. There were six cases where either chloride, nitrate, or sulfate failed spike recovery criteria (Figure 4.1-6); samples were reanalyzed for all six cases. A total of 605 matrix spikes were analyzed for cations. There were seven cases where spiked samples failed to meet

recovery criteria of 90-100% for either sodium, ammonium, or potassium spiked samples (Figure 4.1-6); samples were reanalyzed for all cases.

Figure 4.1-6: Time series of recovery (%) for anion and cation of matrix spikes for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). The blue lines are drawn to indicate the acceptable recovery limits of 90% to 110%.

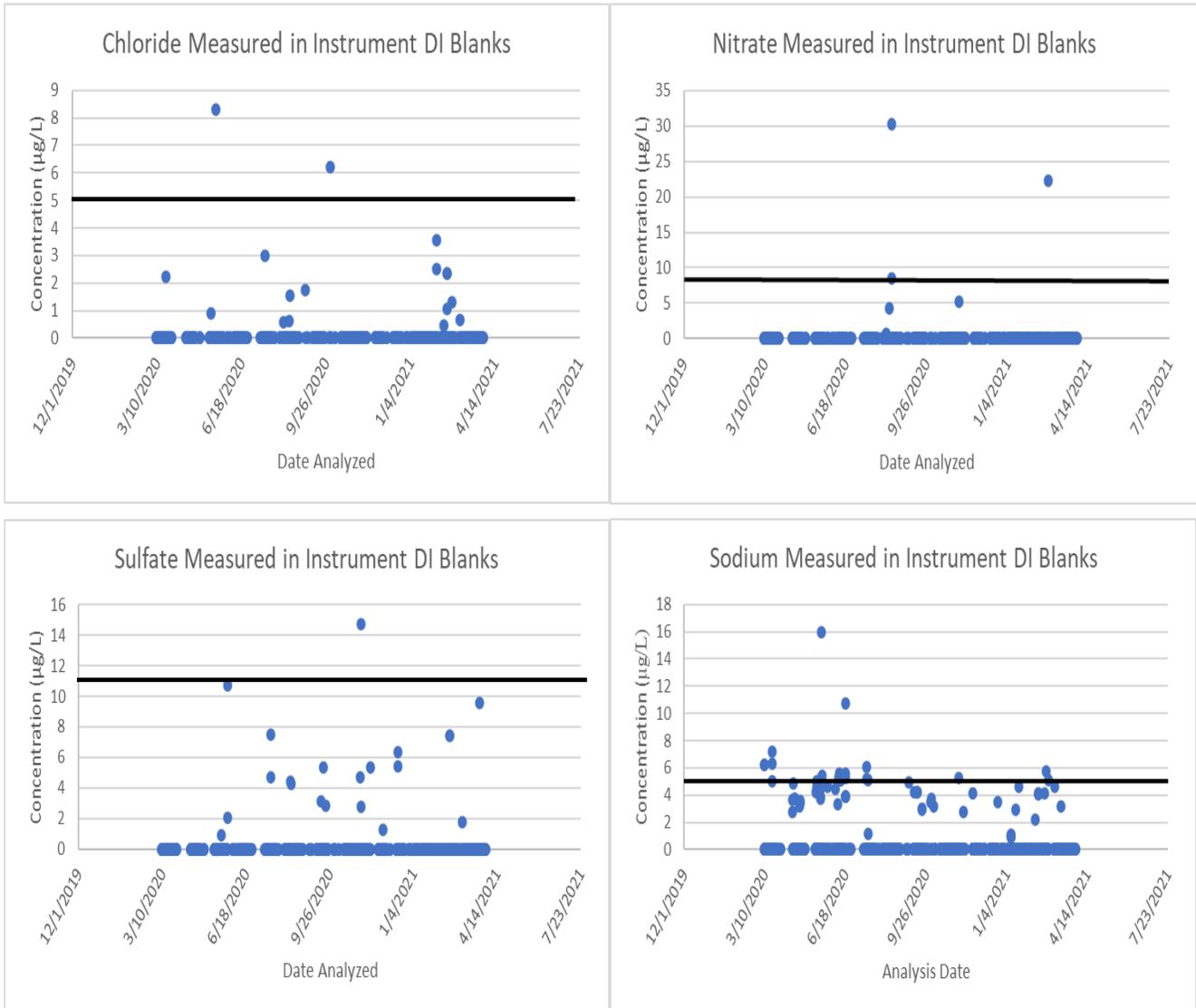


4.1.2.5 Reagent Blanks and Spikes

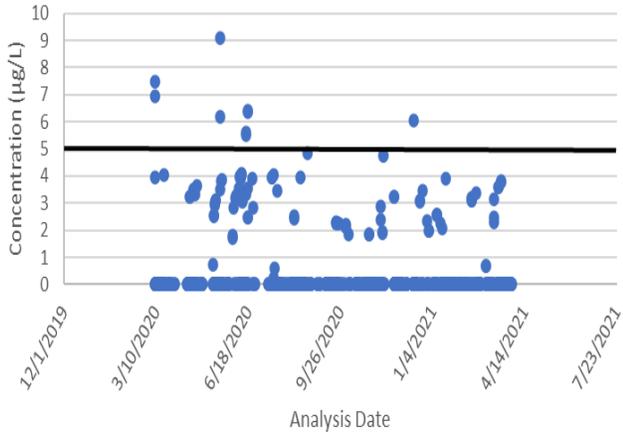
All analyses begin with the injection of two DI water instrument blanks which clean the sample loop prior to injection of calibration standards. Method blanks and laboratory control spikes (LCS) are used to measure the background contamination that could be introduced during the extraction, sample handling, or analysis processes. At the time of filter extraction, an empty extraction vial is included as a method blank at a rate of 1 for every 50 samples. Empty

extraction vials are also spiked with exact volumes of concentrated solutions for both anions and cations a rate of 1 for every 25 samples for LCS analysis. The same volume of water (25.0 mL) is added to the method blank and LCS vials as is added to the vials with the filter samples to be extracted.

Figure 4.1-7: Concentrations of anions and cations in DI water blanks for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Black line indicates the analytical method detection limit.



Ammonium Measured in Instrumental DI Blanks



Potassium Measured in Instrumental DI Blanks

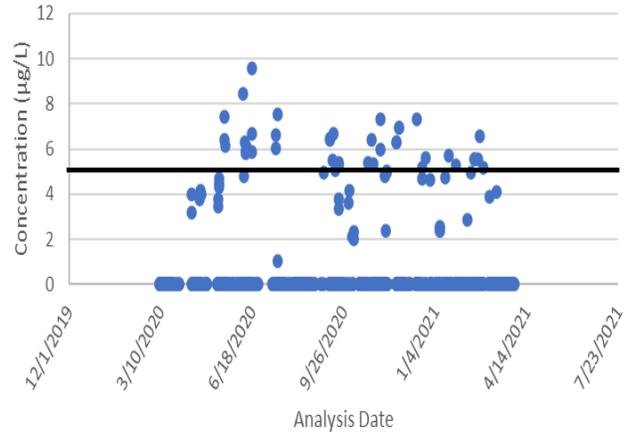
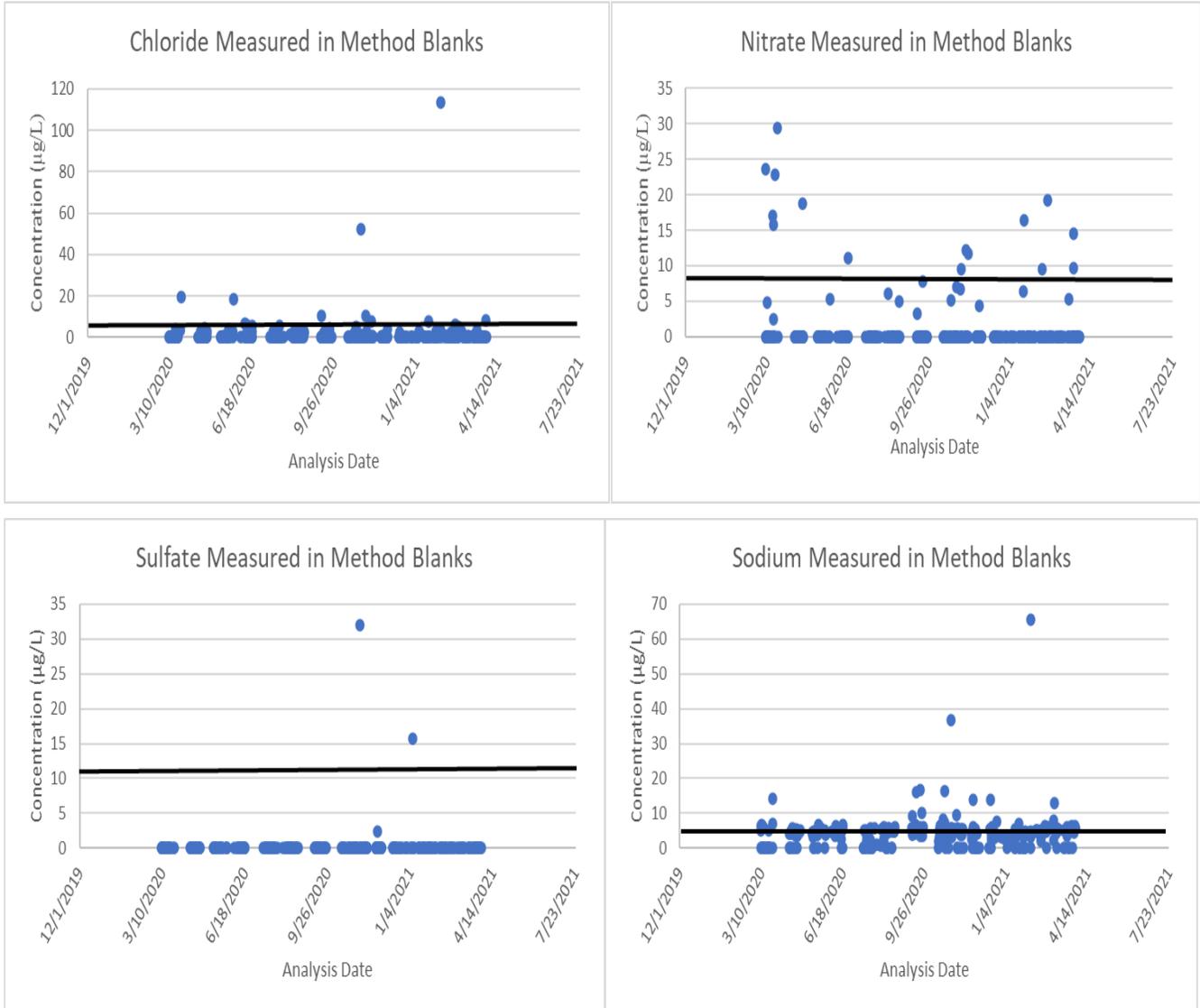
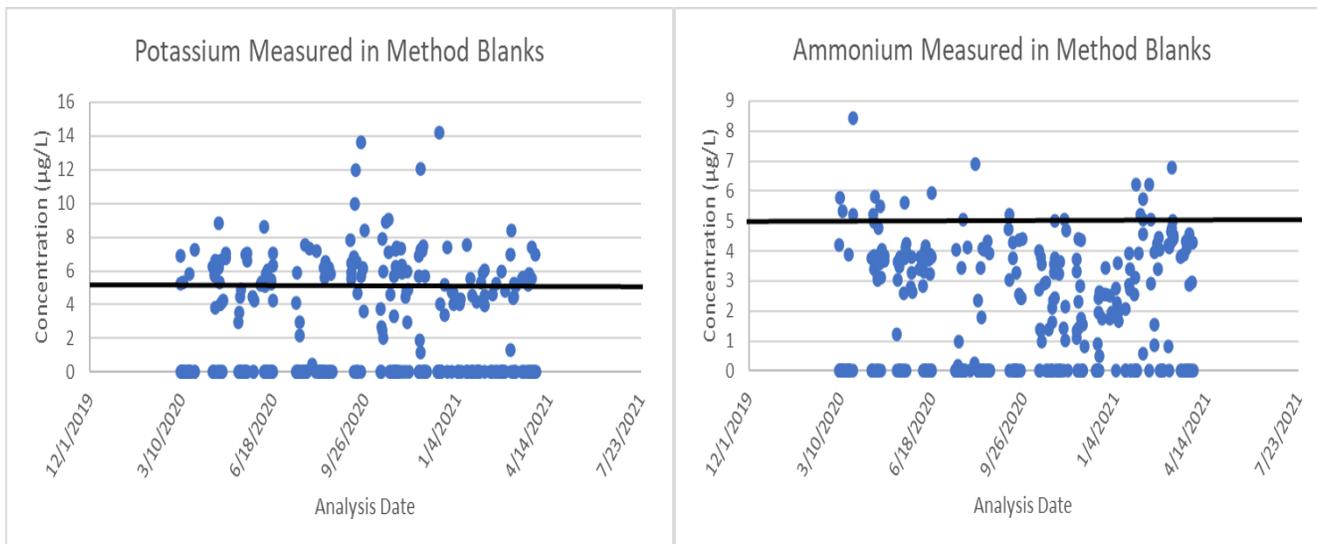


Figure 4.1-8: Concentrations of anions and cations in method blanks for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2021). Black line indicates the analytical method detection limit.





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

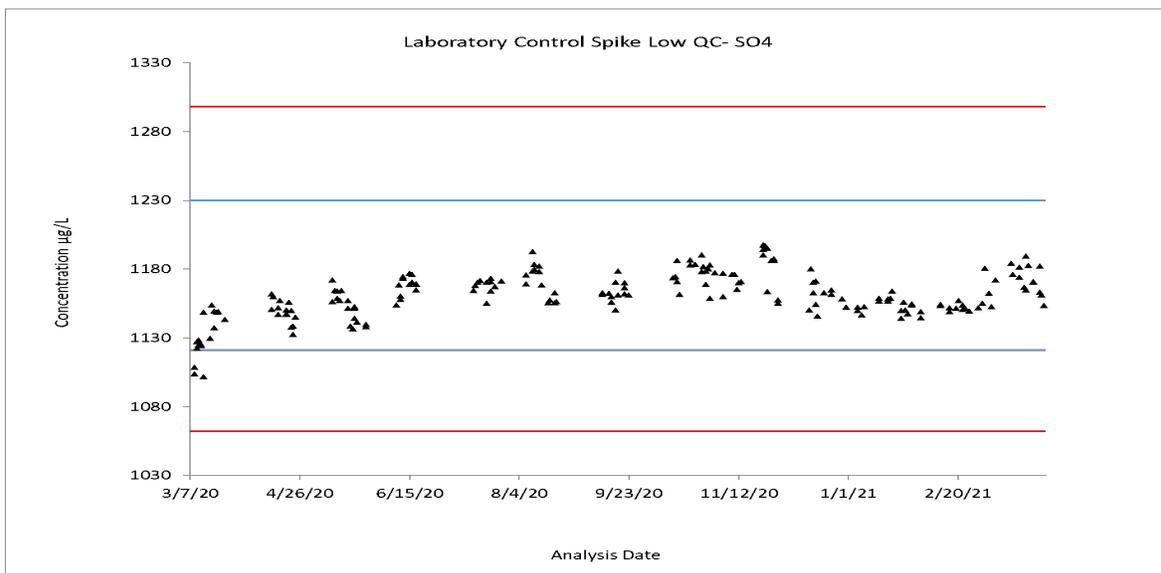
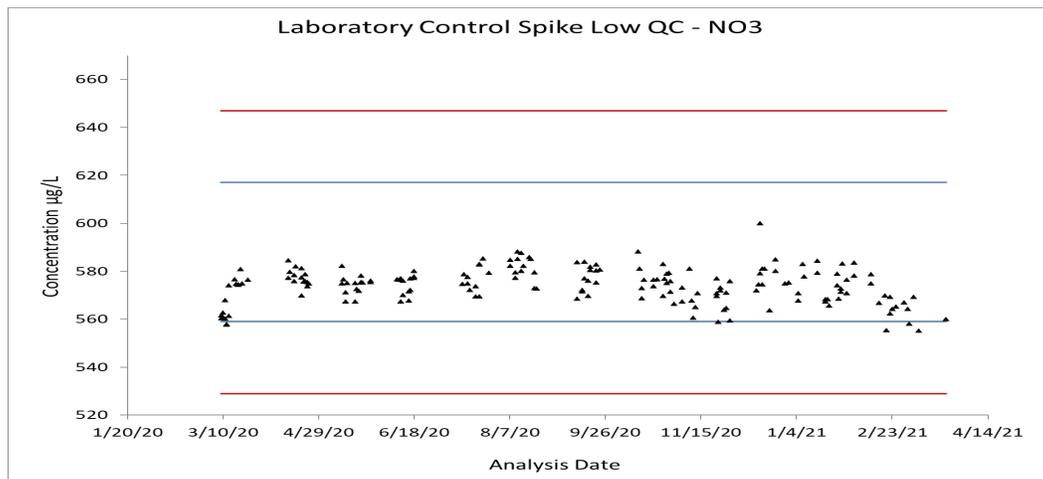
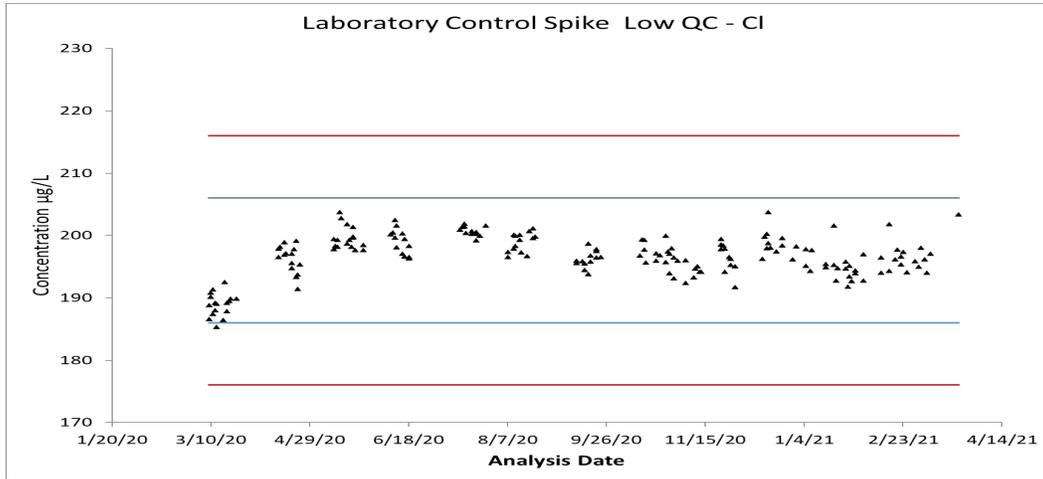
Table 4.1-5: Target concentrations for anion LCS for the analysis period 03/9/2020 through 03/9/2021 (samples collected 1/1/2020 through 12/31/2020).

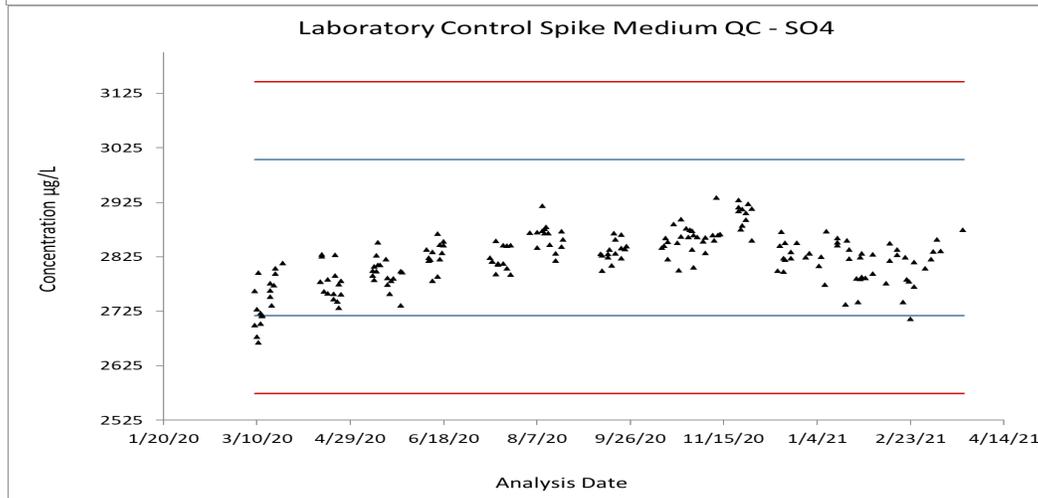
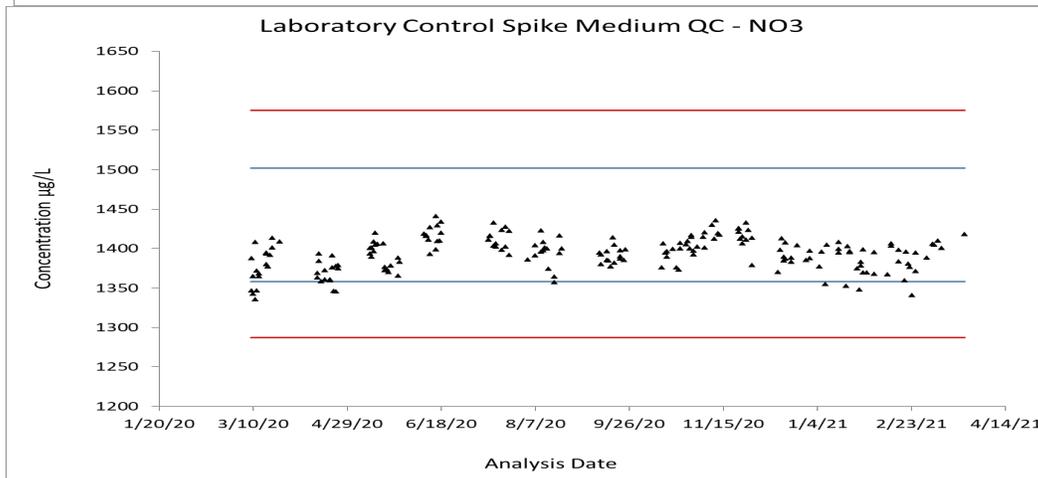
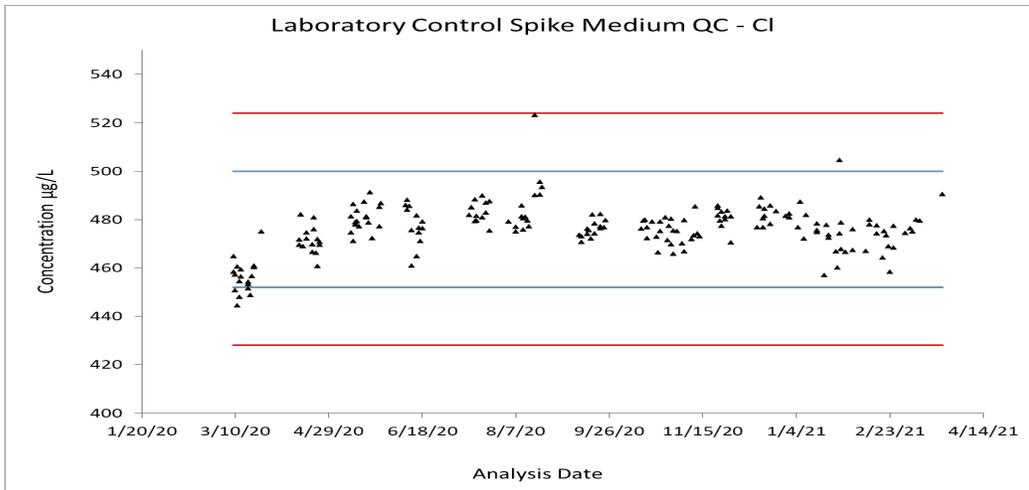
QC Sample	Cl ⁻ (ppb)	NO ₃ ⁻ (ppb)	SO ₄ ²⁻ (ppb)
LCS Low	196	588	1180
LCS Medium	476	1430	2860
LCS High	2000	6000	12000

Table 4.1-6: Target concentrations for cation LCS for the analysis period 3/9/2019 through 03/9/2020 (samples collected 1/1/2020 through 12/31/2020).

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

Figure 4.1-9: Control charts for anion LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Red lines show upper and lower control limits per the CCV check standard acceptance criteria. Blue lines show upper and lower warning limits.





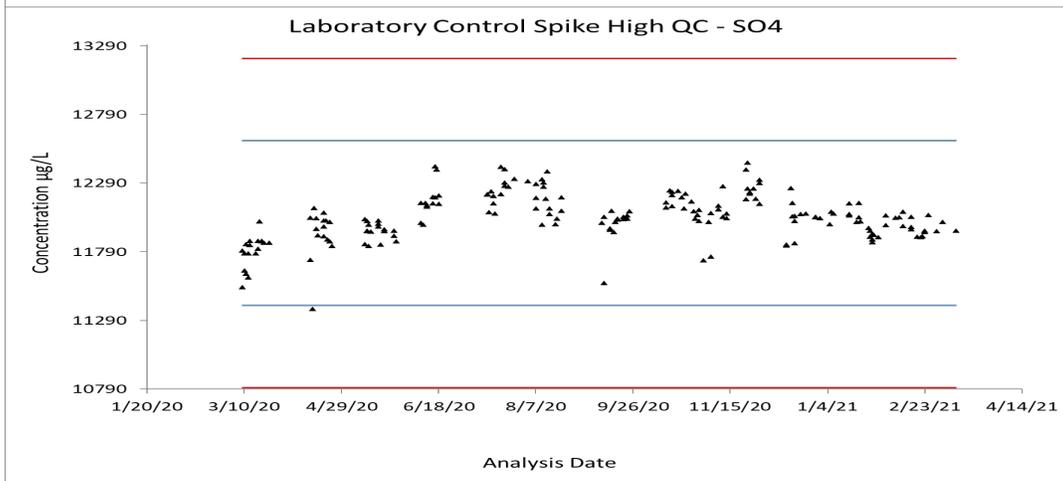
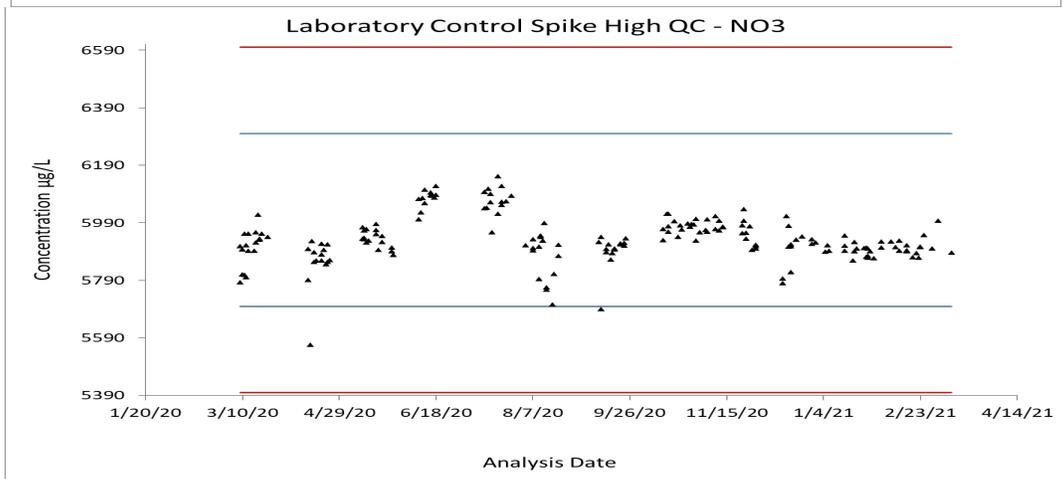
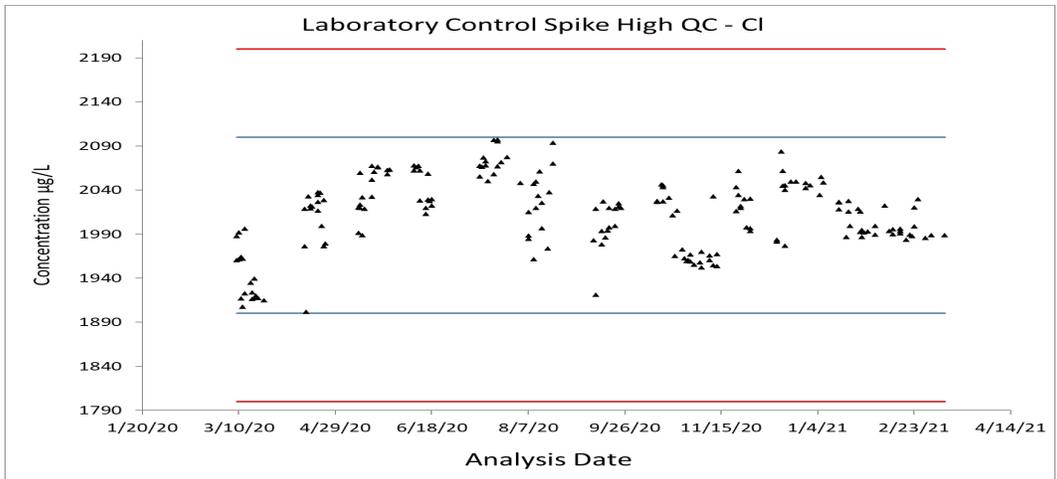
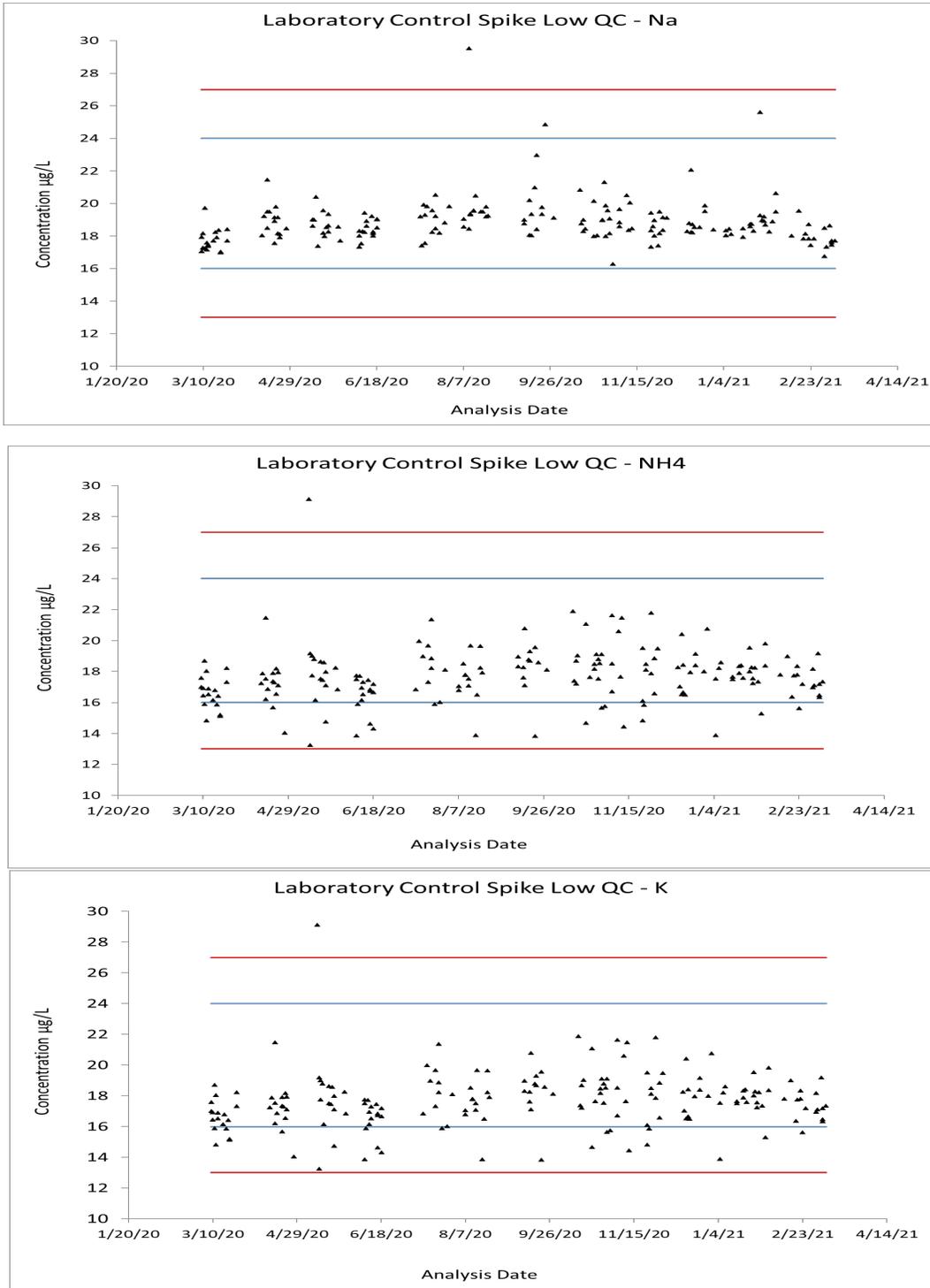
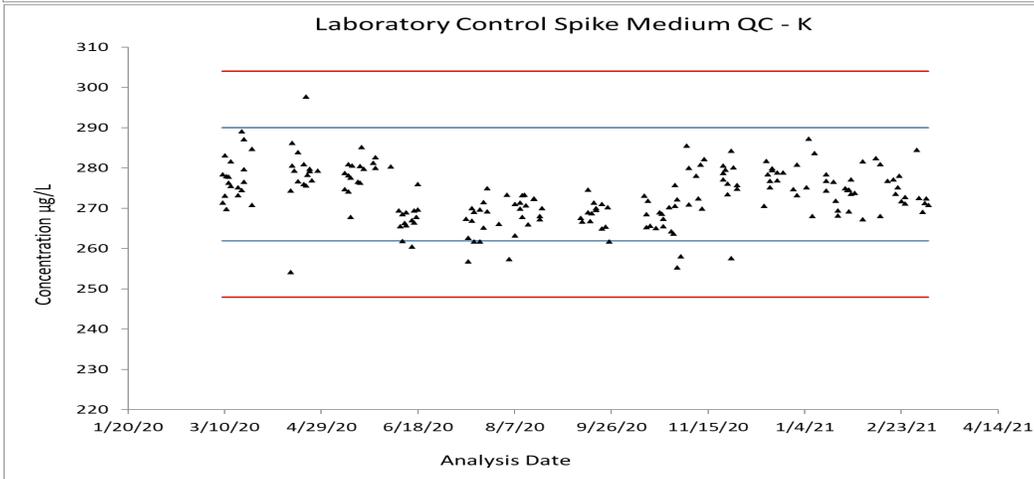
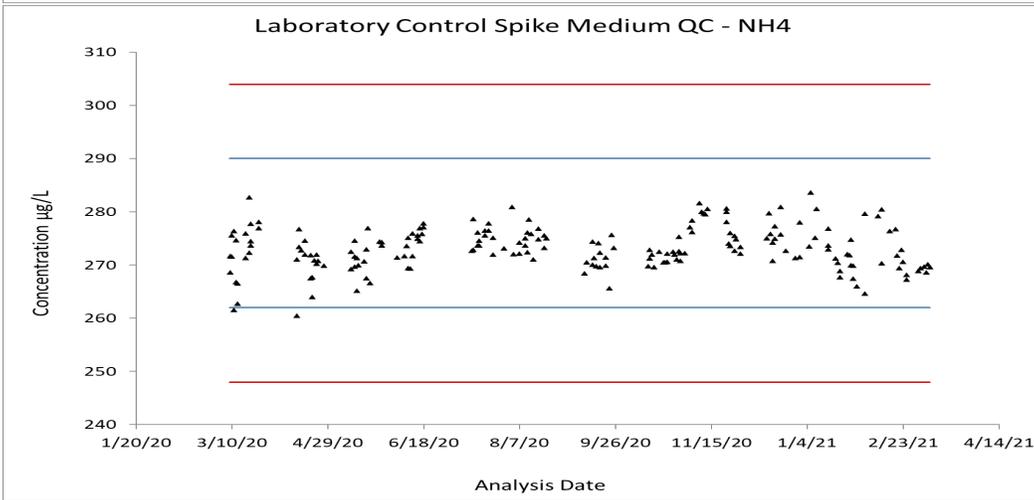
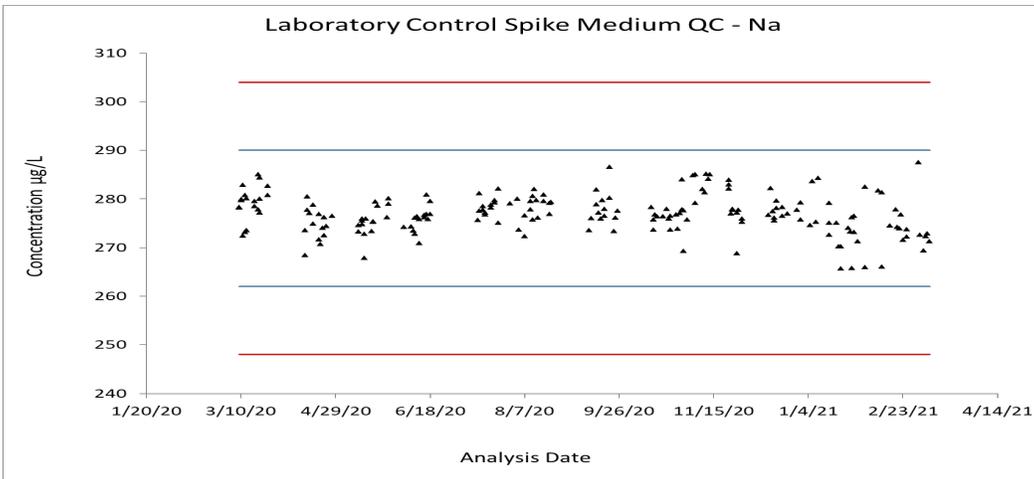
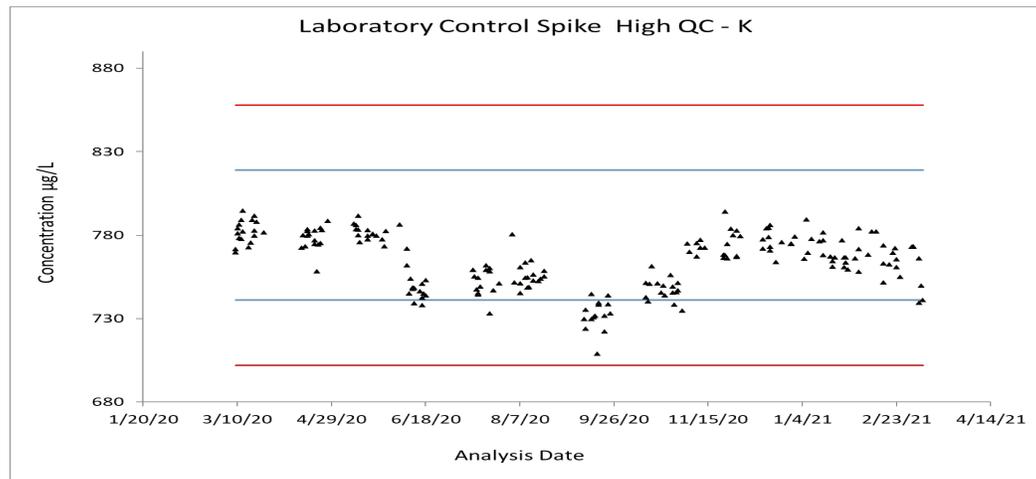
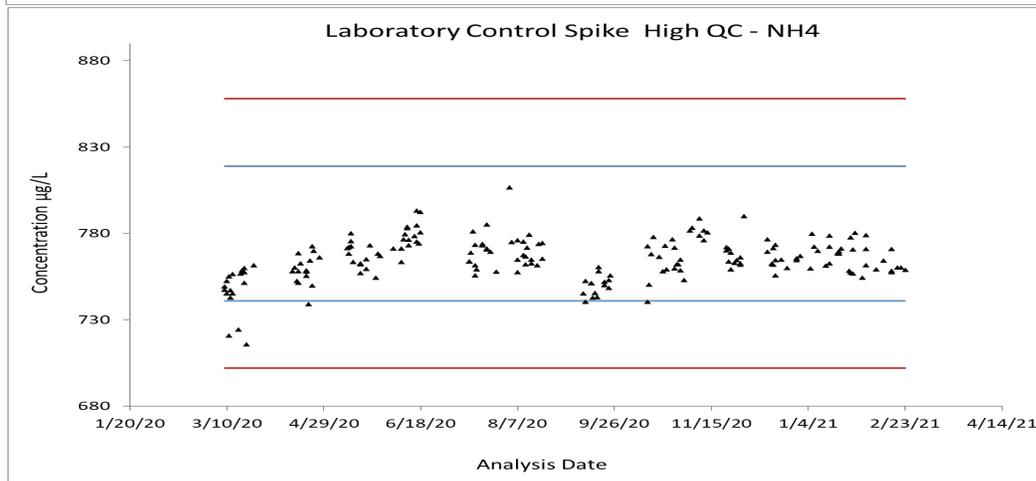
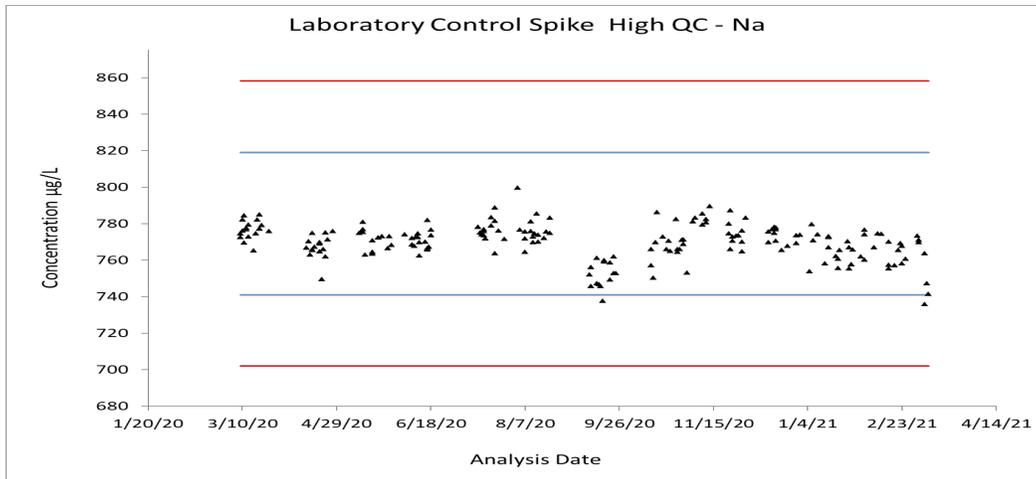


Figure 4.1-10: Control charts for cation LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Red lines show upper and lower control limits per the CCV check standard acceptance criteria. Blue lines show upper and lower warning limits.







4.1.2.6 Round robin (USGS)

The RTI Ions Chromatography Laboratory participated in the National Atmospheric Deposition Program/Mercury Deposition Network Interlaboratory Comparison Program. The program is administered by the United States Geological Survey (USGS) Branch of Quality Systems. Four samples per month were sent to participating laboratories for analysis. A website reporting participant results is currently in development; a report for the 2020 results is available upon

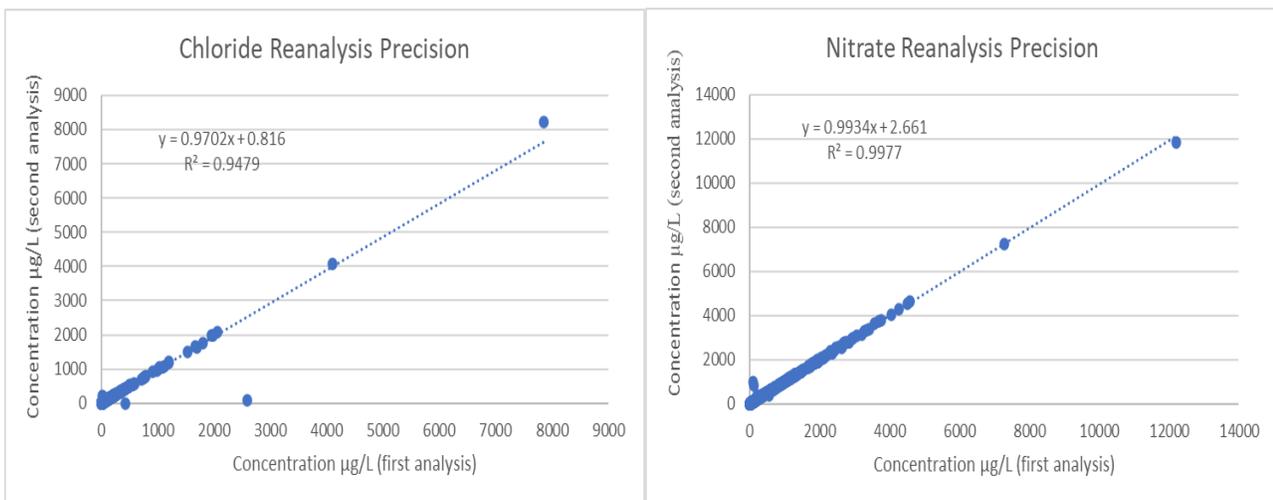
request. Reports from prior years are available online and conclude that RTI had comparable, low overall variability among the participating laboratories for chloride, nitrate, sulfate, sodium, potassium, and ammonium (Wetherbee and Martin, 2020).

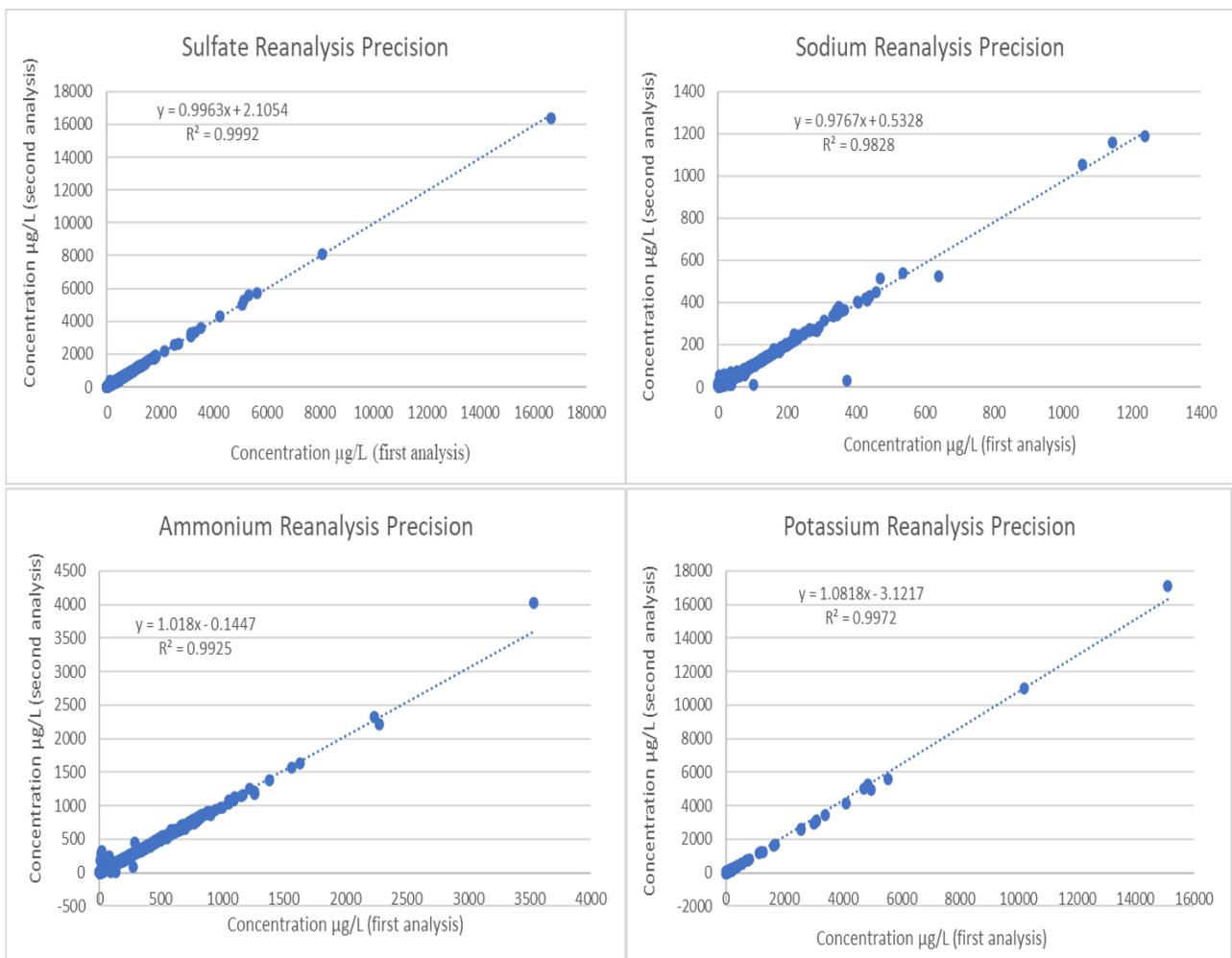
4.1.2.7 *Reanalysis*

Replicate analyses are reanalyses where two analyses are performed on the same sample extract using different instruments. Five percent of all samples are reanalyzed using different instruments and different calibration curves (these reanalyses are specific to the analytical acceptance criteria described in Table 4.1-2, distinct from additional reanalyses that may be requested later during the UC Davis Level 0 or Level 1 validation process described in Section 6). Samples are flagged for reanalysis during analyst review of analytical results, and reasons include poorly integrated peaks and cases where one peak is significantly higher than the other peaks in the chromatograph (particularly for cations peaks, which elute very close together). In these cases, the sample may be diluted for reanalysis. Samples are also flagged if the acceptance criteria for reanalysis samples are not met. When more than one analysis within an analysis set fails to meet the acceptance criteria as outlined in Table 4.1-2, the whole set of samples is reanalyzed. The majority of reanalyzed samples are from acceptance criteria failure for background contamination from sodium, chloride, and/or potassium detected in either the original or reanalysis result. In cases where the entire set of samples were reanalyzed, background contamination did not propagate through the whole set.

During this reporting period, there were 1,741 samples reanalyzed for anions and 2,048 samples reanalyzed for cations (Figure 4.1-11). Less than 0.4% and 1.9% of samples reanalyzed for anions and cations, respectively, failed to meet the acceptance criteria for precision between the original and reanalysis result. For cases that failed, a third analysis was performed. The reanalysis result was reported only for the impacted ion species. Typically, a sample only fails the acceptance criteria for one ion species, and these failures are usually caused by contamination introduced during the analysis.

Figure 4.1-11: Ion reanalysis results for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).





4.1.3 Determination of Uncertainties and Method Detection Limits

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

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

4.1.4 Audits, Performance Evaluations, Training, and Accreditations

4.1.4.1 System Audits

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

4.1.4.2 Performance Evaluations

No performance evaluations were conducted during this reporting period.

4.1.4.3 Training

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

4.1.4.4 *Accreditations*

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

4.1.5 **Summary of Filter Blanks**

4.1.5.1 *Field Blanks*

Over the sampling period (January 1, 2020 through December 31, 2020) there were 1,500 valid nylon filter field blanks. Table 4.1-7a and Table 4.1-7b summarize the field blank statistics.

Table 4.1-7a: Nylon filter field blank statistics in µg/mL for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl ⁻	1,500	0.006	0.008	0.000	0.359	0.015
NO ₃ ⁻	1,500	0.006	0.009	0.000	1.721	0.045
SO ₄ ²⁻	1,500	0.000	0.003	0.000	0.754	0.024
Na ⁺	1,500	0.005	0.006	0.000	0.203	0.008
NH ₄ ⁺	1,500	0.004	0.005	0.000	0.519	0.014
K ⁺	1,500	0.005	0.005	0.000	0.035	0.003

Table 4.1-7b: Nylon filter field blank statistics in µg/filter (extraction volume 25 mL) for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl ⁻	1,500	0.146	0.198	0.000	8.963	0.367
NO ₃ ⁻	1,500	0.159	0.230	0.000	43.030	1.130
SO ₄ ²⁻	1,500	0.000	0.064	0.000	18.838	0.602
Na ⁺	1,500	0.136	0.151	0.000	5.071	0.208
NH ₄ ⁺	1,500	0.112	0.119	0.000	12.972	0.359
K ⁺	1,500	0.132	0.120	0.000	0.871	0.064

4.1.5.2 *Laboratory Blanks*

As described in Section 3.1.3, beginning with filters from the sampling period July 1, 2020, five nylon laboratory blanks are shipped with each batch of routine filters to the analysis laboratory and analyzed. A total of 30 nylon laboratory blanks were analyzed during the current reporting period, where each set of laboratory blanks were analyzed either before or straight after the routine analysis of the associated batch. Table 4.1-8a and Table 4.1-8b summarize the laboratory blank statistics.

Table 4.1-8a: Nylon filter laboratory blank statistics in $\mu\text{g/mL}$ for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

Ions	Count	Median ($\mu\text{g/mL}$)	Average ($\mu\text{g/mL}$)	Min ($\mu\text{g/mL}$)	Max ($\mu\text{g/mL}$)	St. Dev. ($\mu\text{g/mL}$)
Cl^-	30	0.002	0.002	0.000	0.007	0.002
NO_3^-	30	0.004	0.004	0.000	0.011	0.004
SO_4^{2-}	30	0.000	0.001	0.000	0.009	0.002
Na^+	30	0.005	0.005	0.002	0.019	0.003
NH_4^+	30	0.004	0.004	0.001	0.006	0.001
K^+	30	0.005	0.005	0.000	0.013	0.002

Table 4.1-8b: Nylon filter laboratory blank statistics in $\mu\text{g/filter}$ (extraction volume 25 mL) for the analysis period 3/9/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

Ions	Count	Median ($\mu\text{g/filter}$)	Average ($\mu\text{g/filter}$)	Min ($\mu\text{g/filter}$)	Max ($\mu\text{g/filter}$)	St. Dev. ($\mu\text{g/filter}$)
Cl^-	30	0.054	0.060	0.000	0.167	0.044
NO_3^-	30	0.097	0.104	0.000	0.277	0.101
SO_4^{2-}	30	0.000	0.019	0.000	0.237	0.052
Na^+	30	0.119	0.118	0.050	0.484	0.076
NH_4^+	30	0.111	0.102	0.035	0.138	0.034
K^+	30	0.119	0.124	0.000	0.317	0.056

4.2 UC Davis X-ray Fluorescence Laboratory

The UC Davis X-ray Fluorescence Laboratory received and analyzed PTFE filters from samples collected January 1, 2020 through December 31, 2020. 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 12, 2020 through April, 21, 2021, including both routine analysis and reanalysis. Five EDXRF instruments — XRF-1, XRF-2, XRF-3, XRF-4, and XRF-5 — performed all of the analyses during this period; see Table 4.2-1 for details.

Table 4.2-1: Sampling months during 2020 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	63	3/13/2020 – 5/21/2020	N/A	5/11/2020 – 5/16/2020	3/12/2020 – 5/23/2020	3/12/2020 – 5/23/2020
February	64	5/23/2020 – 7/15/2020	N/A	5/22/2020 – 6/8/2020	5/23/2020 – 6/8/2020	5/23/2020 – 6/8/2020
March	65	6/8/2020 – 7/17/2020	N/A	6/12/2020 – 6/30/2020	6/8/2020 – 8/16/2020	6/8/2020 – 8/15/2020
April	66	6/30/2020 – 7/16/2020	N/A	N/A	6/30/2020 – 7/17/2020	6/30/2020 – 7/17/2020
May	67	7/17/2020 – 7/20/2020	N/A	N/A	7/17/2020 – 9/21/2020	7/17/2020 – 8/9/2020
June	68	8/19/2020 – 9/4/2020	N/A	N/A	8/15/2020 – 10/15/2020	8/15/2020 – 9/5/2020
July	69	9/17/2020 – 11/13/2020	N/A	N/A	9/11/2020 – 10/16/2020	N/A
August	70	10/15/2020 – 12/17/2020	N/A	10/26/2020 – 11/12/2020	10/16/2020 – 11/12/2020	N/A
September	71	11/27/2020 – 1/20/2021	11/17/2020 – 12/11/2020	N/A	12/01/2020 – 12/11/2020	11/17/2020 – 12/11/2020
October	72	12/19/2020 – 2/12/2021	1/7/2021 – 1/14/2021	N/A	12/18/2020 – 1/15/2021	12/19/2020 – 1/6/2021
November	73	1/29/2021 – 3/22/2021	2/2/2021 – 2/17/2021	1/29/2021 – 2/17/2021	1/30/2021 – 2/17/2021	1/29/2021 – 2/3/2021
December	74	2/19/2021 – 4/21/2021	2/26/2021 – 3/10/2021	2/25/2021 – 3/11/2021	2/19/2021 – 3/11/2021	N/A
All Months	63-74	3/13/2020 – 4/21/2021	11/17/2020 – 3/10/2021	5/11/2020 – 3/11/2021	3/12/2020 – 3/11/2021	3/12/2020 – 2/3/2021

4.2.1 Summary of QC Checks and Statistics

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

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

Activity	Frequency	Acceptance Criteria	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	<ul style="list-style-type: none"> XRF software automatically adjusts the energy channels
PTFE Blank	Daily	≤ acceptance limits (see Section 4.2.2.1 below) with exceedance of a single element not to occur in more than two consecutive days	<ul style="list-style-type: none"> Change/clean blank if contaminated/damaged Clean the diaphragm, if necessary Further cross-instrumental testing
UC Davis Multi-element reference material (ME-RM)	Daily	±10% of reference mass loadings for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb with exceedance of a single element not to occur in more than two consecutive days	<ul style="list-style-type: none"> Check sample for damage/contamination Further cross-instrumental testing Replace sample if necessary
UC Davis Multi-element reference material (ME-RM)	Weekly	±10% of reference mass loadings for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb with exceedance of a single element not to occur in more than two consecutive days	
Reanalysis samples	Monthly	z-score between ±1 for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb	
SRM 2783	Monthly	Bias between ±1 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	

Daily QC checks include a laboratory blank (PTFE blank) and a multi-elemental reference material (ME-RM) to monitor contamination and stability/performance of the instruments. A UC Davis-made ME-RM is also analyzed weekly to check the instrument performance. Inter-instrumental comparability is monitored by analyzing the bias and precision between instruments of the weekly UC Davis ME-RM. Long-term inter-instrumental comparability is monitored using a set of reanalysis filters which are reanalyzed monthly on each instrument. Long-term reproducibility is monitored using the reanalysis filters and by analyzing a NIST SRM 2783 standard monthly and comparing the EDXRF error from the certified/reference mass loadings to acceptance limits.

4.2.2 Summary of QC Results

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

Random occasional zinc contamination was observed on daily PTFE blank filters for all XRF analyzers. This intermittent contamination appears to be related to the design of the instrument and is unavoidable. Samples analyzed during this period were monitored closely for any contamination and were reanalyzed if there was any question of contamination. The reported data were not impacted.

QC failures and issues and the corrective actions taken are reported in section 3.2.1. All QC issues during this reporting period were found and acted upon quickly. In all cases sample results

were not impacted because the samples were either reanalyzed or a subset of samples was reanalyzed to indicate the original results were valid. A summary of the QC performance of the instruments is presented below.

4.2.2.1 Results of Daily QC Checks

Possible contamination and instability issues are monitored by analyzing a daily PTFE blank. The EDXRF results are compared to acceptance criteria, which are calculated as three times the standard deviation plus the mean of a set of the PTFE blanks. Figure 4.2-1a and Figure 4.2-1b show the results of daily analyses of PTFE blanks for each instrument. If the mass loading exceeds the acceptance criteria for more than two consecutive days, the blank is replaced to distinguish between contamination on the blank and instrument contamination. Some occasional exceedances of the acceptance criteria are expected but not continuous or repeated exceedances. In all cases of exceedance, the other QC filters are checked to determine if the problem is instrumental or strictly contamination of the PTFE blank. Sample analysis results are reviewed and elements associated with occasional contamination (e.g. zinc, copper) are monitored closely. When contamination is suspected, filters are reanalyzed and the reanalysis result is reported if contamination was present in the original analysis. A total of eleven samples from 2020 were reanalyzed for suspected zinc contamination. Of those, four were found to have zinc contamination and the reanalysis result was reported. For the rest the original valid result was reported.

All XRF instruments had intermittent elevated measurements of zinc on the daily PTFE blank throughout the analysis period. These elevated levels were not measured over consecutive days thus did not fail the acceptance criteria; however, these occurrences are monitored closely. Zinc contamination likely comes from wear on the sample changer; zinc is a common contaminant in elemental analysis systems.

XRF-1, XRF-3, and XRF-4 all had single elevated iron measurements above the acceptance criteria on 10/22/2020, 12/5/2020, and 12/2/2020, respectively. These incidents were corrected by cleaning the daily PTFE blank filters for each instrument and did not impact instrument responses or network sample results.

XRF-3 had regular exceedances of the daily PTFE blank acceptance criteria for aluminum after the annual calibration on 12/27/2019 which lasted until 8/8/2020 when the detector was replaced. There was no acceptance criteria failure as the exceedances did not occur on more than two consecutive days. The exceedances appear to be caused by a shift of the background level of aluminum associated with the calibration. Network sample results are background corrected so the delivered data was not impacted by this slight shift.

As was reported in the 2019 Annual Report, XRF-2 exceeded and failed the daily PTFE blank acceptance criteria for silicon. The acceptance criteria exceedances began in late 2019 and continued to get worse; the first acceptance criteria failure occurred on 12/12/2019 just before the annual calibration. CSN sample analysis was halted on 1/9/2020 which was before the 2020 sampling year samples were analyzed. No CSN samples were analyzed on XRF-2 until after the Si issue was resolved and the instrument was installed and calibrated at the new Drew Ave. laboratory in late October 2020. CSN analysis resumed on 11/17/2020 after the Si issue was corrected, so this had no impact on the sample results from this reporting period.

Lastly, there were a few chlorine exceedances of the daily PTFE blank acceptance criteria on all instruments in August 2020. On 8/28/2020 the QC blanks were replaced on all instruments which resolved the high Cl blank signal. The cause of the chlorine exceedances is unknown; as a volatile element, chlorine has a highly variable signal from QC filters. These exceedances are caused by variability in the chlorine measurement and possible contamination of the QC blank filters due to their prolonged exposure to the environment, not contamination in the EDXRF instruments. In addition, XRF-4 also experienced some chlorine exceedances, but no failures, for the blank from 3/15/2020 to 3/23/2020. These were caused by the detector issue on this instrument which is detailed in section 3.2.1.1 and was resolved after the detector was replaced.

Figure 4.2-1a: Analysis results from daily PTFE blanks for the analysis period 3/12/2020 through 4/21/2021 (see Table 4.2-1 for corresponding sampling dates). Elements Na through Zn shown.

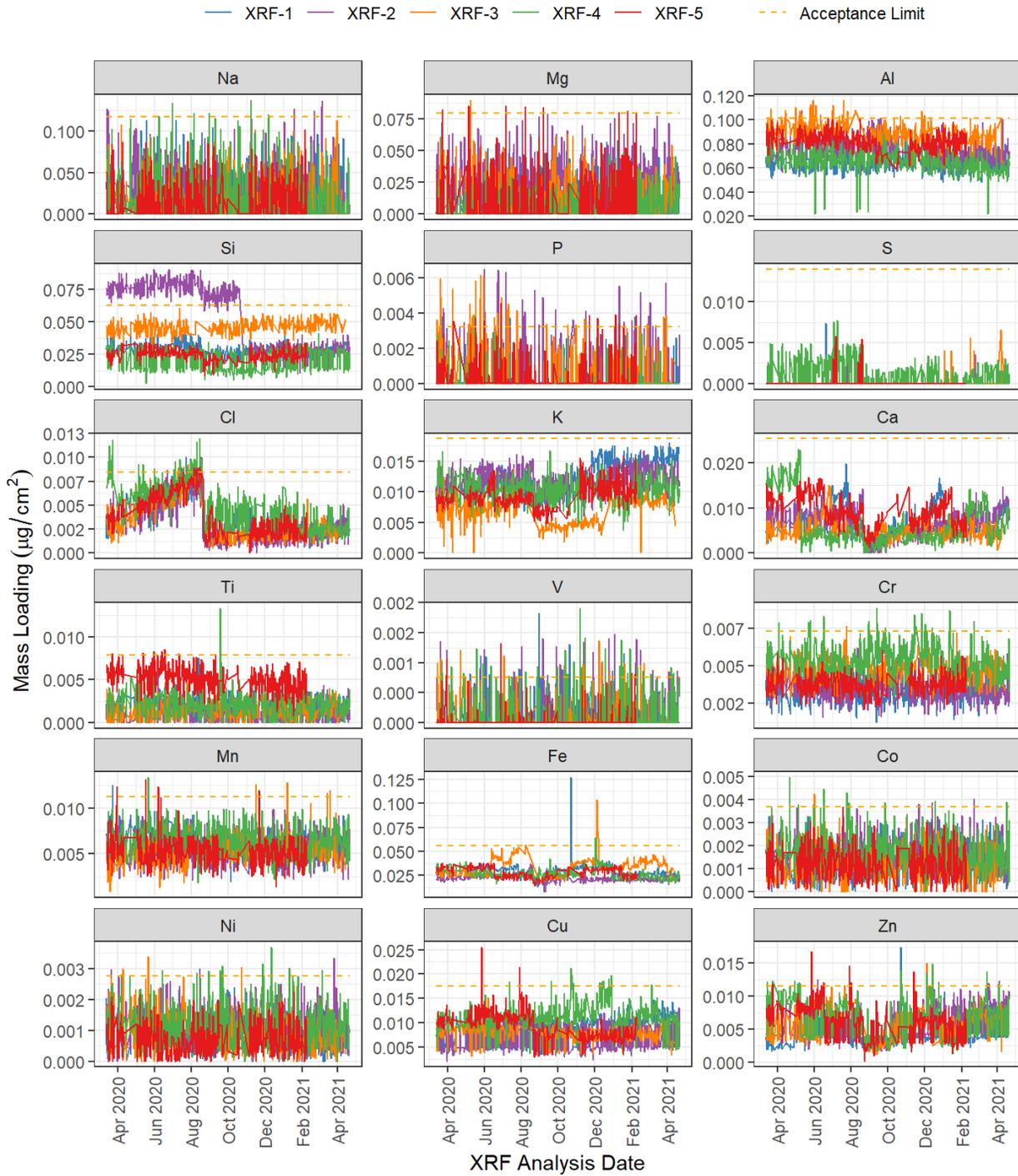
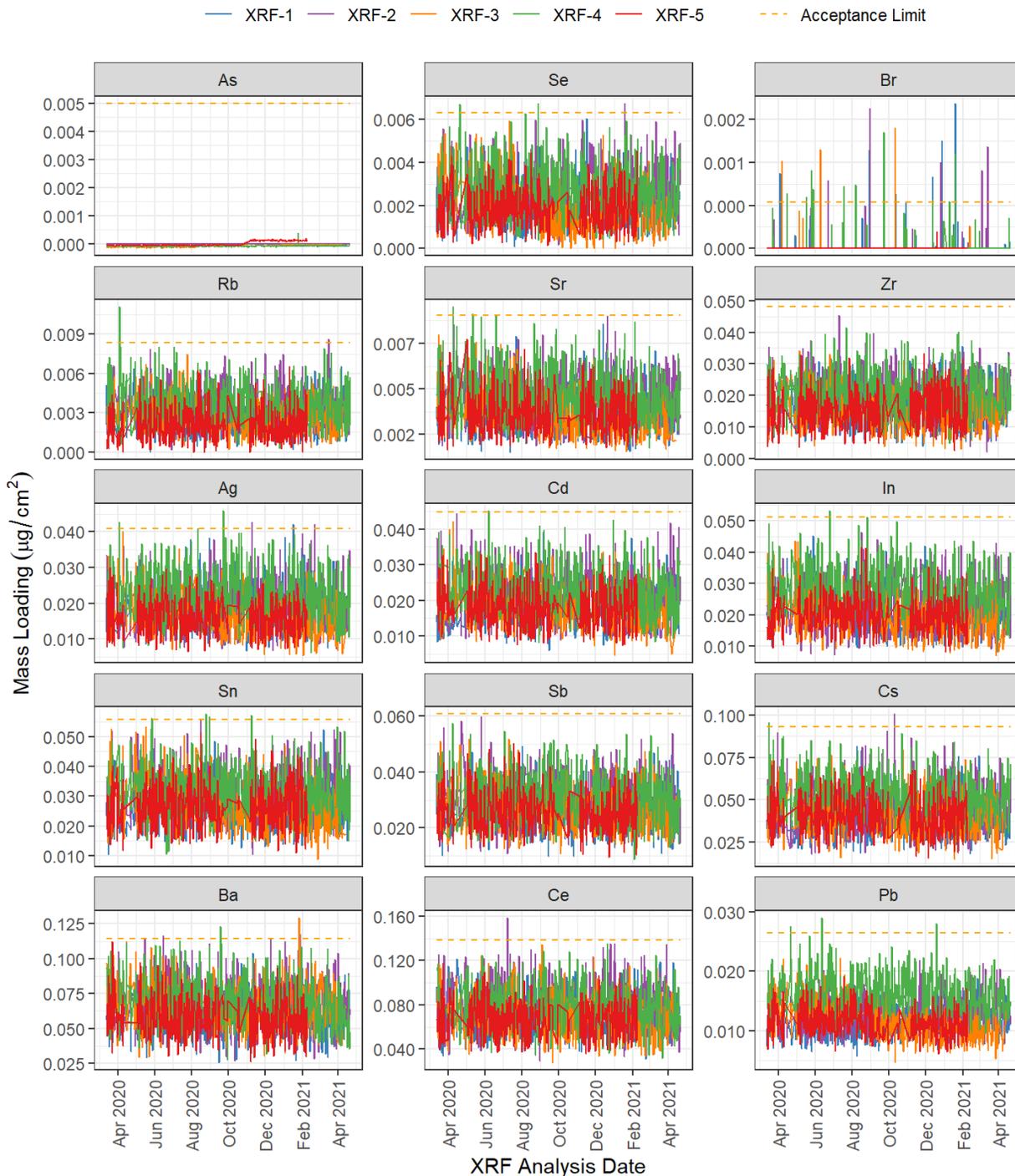


Figure 4.2-1b: Analysis results from daily PTFE blanks for the analysis period 3/12/2020 through 4/21/2021 (see Table 4.2-1 for corresponding sampling dates). Elements As through Pb shown.



Daily operational performance of the instruments is monitored using UC Davis produced ME-RM (different than the weekly ME-RM); each instrument had its own daily ME-RM. The acceptance criteria are +/- 10% of the reference values for the relevant elements, as listed in Table 4.2-2. When more than two consecutive measurements exceed these limits, the results are marked unacceptable. Corrective actions for unacceptable QC results include checking the

sample for damage or contamination, checking the results for the affected element on other QC samples, cross-instrumental testing if necessary to determine if the unacceptable result is due to the instrument or the QC sample, and further investigations as necessary. Sample analysis is halted or samples analyzed after the unacceptable QC result are noted for possible reanalysis depending on the outcome of the investigation. When a problem with the instrument is found the affected samples are reanalyzed on a different instrument or the same instrument after the issue is corrected and once it has been demonstrated to be within control again. QC samples which have been found to be damaged or contaminated will be replaced (*UCD CSN TI 302D*).

Tables 4.2-3 through 4.2-7 show the results of the UC Davis ME-RMs. A small number of criteria exceedances are expected statistically, but not more than a few percent of the total number of measurements. Investigations of other QC filters and laboratory blanks following these exceedances did not show any contamination or instrumental issues, so no corrective actions were taken. Also, note that the Lower Limit and Upper Limit columns do not represent exact $\pm 10\%$ limits. Over the course of this analysis period there were changes in the reference values and limits for the UC Davis ME-RM filters due to changes in instrument calibration or replacement of the ME-RM filter. The listed lower and upper limits are averages of the different lower and upper limits used during the entire analysis period.

Table 4.2-3: Descriptive statistics of XRF-1 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 3/12/2020 through 4/20/2021 (see Table 4.2-1 for corresponding sampling dates), N = 551.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	2.032	1.613	2.359	0	0	3.4
Si	0.827	0.679	1.115	0	0	2.1
S	16.74	15.073	18.423	0	0	0.9
K	2.343	2.13	2.603	0	0	0.5
Ca	2.333	2.085	2.549	0	0	0.8
Cr	0.96	0.861	1.053	0	0	0.8
Fe	2.767	2.46	3.006	0	0	0.8
Zn	0.336	0.299	0.366	0	0	1.1
As	0.656	0.589	0.72	0	0	0.9
Se	0.469	0.423	0.517	0	0	1.0
Rb	0.227	0.202	0.247	0	0	1.5
Sr	0.219	0.196	0.24	0	0	1.6
Cd	0.291	0.26	0.324	1.1	0	4.2
Sn	0.342	0.309	0.383	1.3	0	3.8
Pb	0.086	0.065	0.106	0.2	0	7.6

Table 4.2-4: Descriptive statistics of XRF-2 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 11/17/2020 through 4/20/2021 (see Table 4.2-1 for corresponding sampling dates), N = 96.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.859	1.549	2.146	0	0	1.8
Si	0.855	0.657	1.044	0	0	1.9
S	15.589	13.924	17.018	0	0	0.5
K	2.197	1.985	2.426	0	0	0.4
Ca	2.158	1.933	2.362	1.0	0	1.4
Cr	0.883	0.791	0.967	0	0	0.7
Fe	2.488	2.235	2.731	0	0	0.5
Zn	0.275	0.246	0.300	0	0	1.3
As	0.606	0.547	0.668	0	0	1.3
Se	0.429	0.382	0.467	0	0	1.1
Rb	0.210	0.189	0.231	0	0	1.6
Sr	0.206	0.183	0.224	0	0	1.8
Cd	0.276	0.230	0.319	0	0	4.2
Sn	0.320	0.278	0.360	1.0	0	5.0
Pb	0.097	0.081	0.118	5.2	0	9.8

Table 4.2-5: Descriptive statistics of XRF-3 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 3/12/2020 through 4/7/2021 (see Table 4.2-1 for corresponding sampling dates), N = 169.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.918	1.455	2.089	4.1	0	2.4
Si	0.827	0.646	0.999	0	0	3.4
S	14.935	13.290	16.243	0	0	2.0
K	2.134	1.898	2.320	0	0	0.7
Ca	2.096	1.895	2.317	0	0	1.4
Cr	0.871	0.787	0.961	0	0	1.1
Fe	2.478	2.261	2.763	0	0	0.8
Zn	0.335	0.309	0.377	0	0	1.4
As	0.607	0.546	0.667	0	0	1.0
Se	0.429	0.390	0.477	0	0	1.3
Rb	0.209	0.188	0.230	0	0	2.4
Sr	0.203	0.184	0.224	0	0	2.1
Cd	0.273	0.239	0.307	0	0	4.0
Sn	0.315	0.283	0.356	1.8	0	4.0
Pb	0.089	0.065	0.108	1.8	0	8.3

Table 4.2-6: Descriptive statistics of XRF-4 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 3/12/2020 through 4/20/2021 (see Table 4.2-1 for corresponding sampling dates), N = 469.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.909	1.640	2.215	6.4	0	3.3
Si	1.017	0.646	1.161	1.1	0	3.7
S	16.605	14.663	17.922	0	0	0.9
K	2.359	2.101	2.567	0	0	0.6
Ca	2.390	2.111	2.580	0	0	0.9
Cr	0.979	0.871	1.064	0	0	0.8
Fe	2.735	2.457	3.003	0	0	0.6
Zn	0.366	0.335	0.410	0	0	1.4
As	0.671	0.597	0.730	0	0	1.0
Se	0.485	0.432	0.528	0	0	1.0
Rb	0.232	0.205	0.251	0	0	1.9
Sr	0.222	0.198	0.242	0	0	1.7
Cd	0.299	0.253	0.340	0	0	4.1
Sn	0.351	0.305	0.385	1.9	0	4.1
Pb	0.082	0.070	0.101	15.6	0	9.6

Table 4.2-7: Descriptive statistics of XRF-5 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 3/12/2020 through 3/22/2021 (see Table 4.2-1 for corresponding sampling dates), N = 344.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	2.161	1.697	2.382	0	0	2.3
Si	0.782	0.643	1.044	0	0	2.7
S	17.083	14.965	18.291	0.3	0	1.9
K	2.398	2.149	2.627	0.3	0	1.7
Ca	2.295	2.101	2.568	0	0	1.3
Cr	0.955	0.854	1.044	0	0	1.0
Fe	2.657	2.402	2.936	0	0	0.8
Zn	0.378	0.340	0.416	0	0	1.4
As	0.649	0.580	0.709	0	0	1.0
Se	0.474	0.423	0.518	0	0	1.0
Rb	0.223	0.199	0.243	0	0	1.5
Sr	0.214	0.192	0.235	0	0	1.7
Cd	0.290	0.255	0.321	0	0	3.6
Sn	0.339	0.301	0.367	0.9	0	3.6
Pb	0.075	0.064	0.095	2.6	0	8.2

4.2.2.2 *Results of Weekly QC Checks*

Weekly QC checks include analysis of a UC Davis produced ME-RM (different than the daily ME-RM). The UC Davis weekly ME-RM was replaced in December 2018. Weekly results are

compared to acceptance criteria of +/- 10% of the reference values for the relevant elements, as listed in Table 4.2-2. When more than two consecutive measurements exceed these limits, the results are marked unacceptable. Corrective actions for unacceptable results are described in section 4.2.2.1 and can be found in the *UCD XRF SOP 302* and *UCD CSN TI 302D*. A weekly QC report is generated internally, which includes checks of the laboratory blanks and the daily and weekly ME-RMs. Also, note that the Lower Limit and Upper Limit columns do not represent exact $\pm 10\%$ limits. Over the course of this analysis period there were changes in the reference values and limits for the UC Davis ME-RM filters due to changes in instrument calibration or replacement of the ME-RM filter. The listed lower and upper limits are averages of the different lower and upper limits used during the entire analysis period.

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

Table 4.2-8: Descriptive statistics of XRF-1 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/18/2020 through 4/15/2021 (see Table 4.2-1 for corresponding sampling dates), N = 52.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.156	0.862	1.360	0	0	3.2
Si	1.169	1.094	1.360	0	0	1.4
S	8.981	8.063	9.855	0	0	1.5
K	1.274	1.174	1.434	0	0	0.7
Ca	1.185	1.062	1.297	0	0	1.1
Cr	0.461	0.418	0.511	0	0	1.2
Fe	1.335	1.201	1.468	0	0	1.1
Zn	0.365	0.327	0.400	0	0	1.8
As	0.321	0.288	0.352	0	0	1.8
Se	0.230	0.208	0.254	0	0	1.3
Rb	0.112	0.100	0.123	0	0	2.1
Sr	0.115	0.103	0.126	0	0	2.4
Cd	0.155	0.127	0.184	0	0	6.3
Pb	0.235	0.210	0.256	0	0	2.8

Table 4.2-9: Descriptive statistics of XRF-2 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/17/2020 through 4/20/2021 (see Table 4.2-1 for corresponding sampling dates), N = 55.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.170	0.862	1.360	0	0	5.0
Si	1.173	1.094	1.360	7.3	0	4.9
S	9.048	8.063	9.855	0	0	1.5
K	1.274	1.174	1.434	0	0	1.0
Ca	1.177	1.062	1.297	0	0	1.5
Cr	0.458	0.418	0.511	0	0	1.2
Fe	1.323	1.201	1.468	0	0	1.4
Zn	0.361	0.327	0.400	0	0	2.1
As	0.316	0.288	0.352	0	0	2.0
Se	0.230	0.208	0.254	0	0	1.9
Rb	0.112	0.100	0.123	0	0	2.7
Sr	0.115	0.103	0.126	0	0	3.1
Cd	0.158	0.127	0.184	0	0	7.4
Pb	0.232	0.210	0.256	3.6	0	4.5

Table 4.2-10: Descriptive statistics of XRF-3 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/17/2020 through 3/30/2021 (see Table 4.2-1 for corresponding sampling dates), N = 45.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.210	0.862	1.360	0	0	3.6
Si	1.220	1.094	1.360	4.4	0	4.2
S	9.294	8.063	9.855	2.2	0	3.9
K	1.315	1.174	1.434	0	0	2.0
Ca	1.191	1.062	1.297	0	0	2.3
Cr	0.465	0.418	0.511	0	0	2.1
Fe	1.319	1.201	1.468	0	0	1.7
Zn	0.360	0.327	0.400	0	0	1.9
As	0.321	0.288	0.352	0	0	2.2
Se	0.229	0.208	0.254	0	0	1.9
Rb	0.114	0.100	0.123	4.4	0	4.3
Sr	0.117	0.103	0.126	0	0	3.1
Cd	0.157	0.127	0.184	2.2	0	6.0
Pb	0.238	0.210	0.256	0	0	3.4

Table 4.2-11: Descriptive statistics of XRF-4 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/12/2020 through 4/14/2021 (see Table 4.2-1 for corresponding sampling dates), N = 54.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.028	0.862	1.360	0	0	4.6
Si	1.253	1.094	1.360	1.9	0	2.8
S	9.178	8.063	9.855	0	0	2.5
K	1.318	1.174	1.434	0	0	1.0
Ca	1.207	1.062	1.297	0	0	1.4
Cr	0.470	0.418	0.511	0	0	1.6
Fe	1.343	1.201	1.468	0	0	1.1
Zn	0.367	0.327	0.400	0	0	1.1
As	0.327	0.288	0.352	0	0	2.3
Se	0.232	0.208	0.254	0	0	1.6
Rb	0.114	0.100	0.123	1.9	0	3.2
Sr	0.115	0.103	0.126	0	0	2.5
Cd	0.160	0.127	0.184	0	0	5.9
Pb	0.236	0.210	0.256	0	0	3.5

Table 4.2-12: Descriptive statistics of XRF-5 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 3/13/2020 through 2/8/2021 (see Table 4.2-1 for corresponding sampling dates), N = 47.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.168	0.862	1.360	0	0	4.6
Si	1.176	1.094	1.360	4.7	0	3.7
S	9.252	8.063	9.855	2.3	0	3.3
K	1.305	1.174	1.434	2.3	0	2.9
Ca	1.173	1.062	1.297	0	0	1.1
Cr	0.467	0.418	0.511	0	0	1.0
Fe	1.328	1.201	1.468	0	0	1.1
Zn	0.365	0.327	0.400	0	0	1.2
As	0.322	0.288	0.352	0	0	1.8
Se	0.230	0.208	0.254	0	0	1.4
Rb	0.112	0.100	0.123	0	0	2.2
Sr	0.115	0.103	0.126	0	0	1.8
Cd	0.157	0.127	0.184	0	0	5.5
Pb	0.231	0.210	0.256	0	0	2.5

4.2.2.3 *Reproducibility and Inter-instrument Performance Tests*

The weekly ME-RM is also used as an inter-instrument comparison, with the same sample analyzed by all EDXRF instruments. Figure 4.2-2 plots the elemental concentrations for the weekly UC Davis ME-RM sample used during this analysis. The following approach is used to

quantify the differences observed in the plots. A reference value for the weekly ME-RM is calculated as the mean of all the instrument results:

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

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

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

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

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

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

The precision is estimated by,

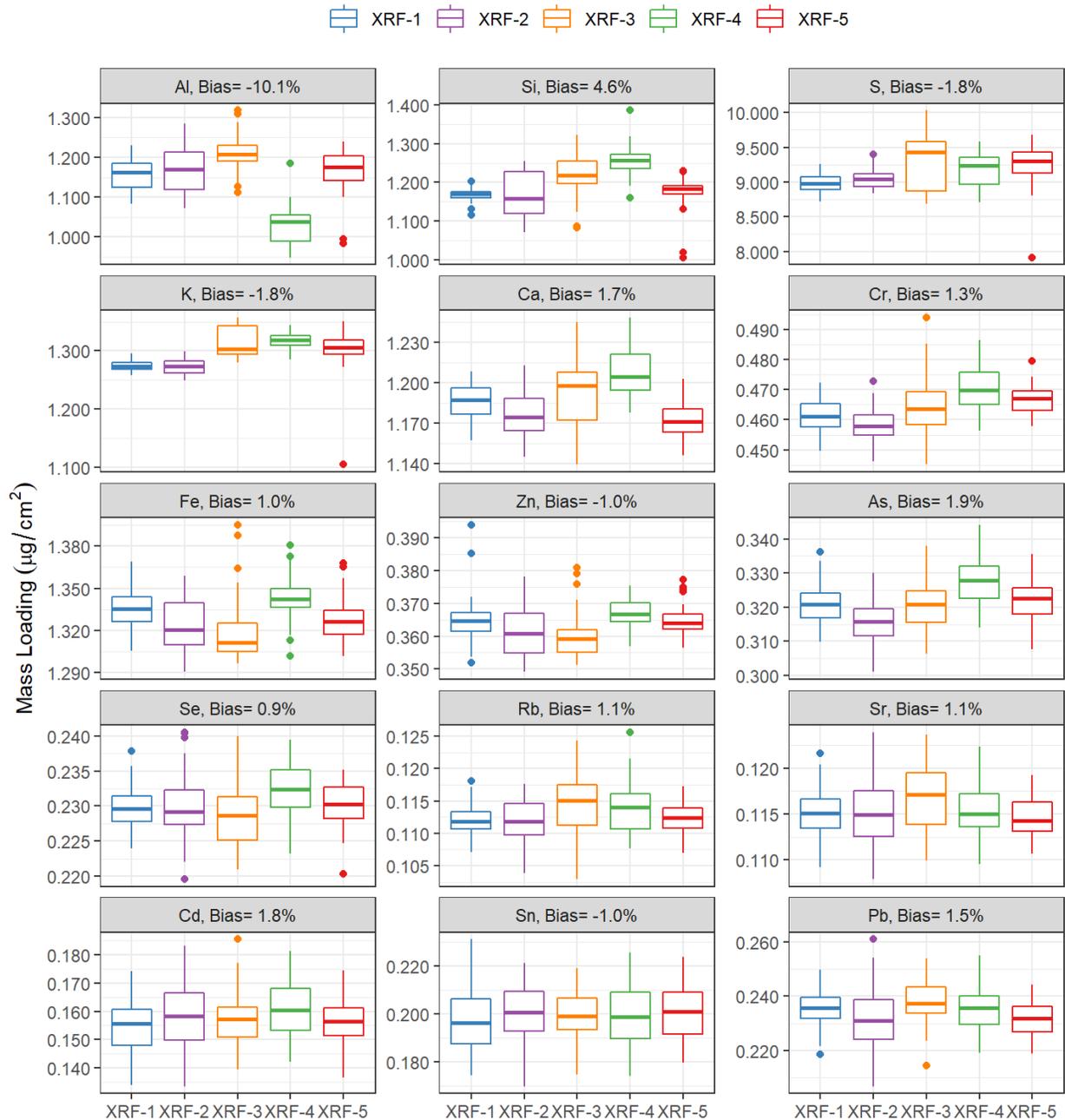
$$Precision_i = \sqrt{\frac{n \sum_{j=1}^n d_{i,j}^2 - (\sum_{j=1}^n d_{i,j})^2}{n(n-1)}}$$

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

Table 4.2-13: Precision and bias of all EDXRF instruments from the weekly UC Davis ME-RM calculated for the analysis period 3/31/2019 through 3/12/2020 (see Table 4.2-1 for corresponding sampling dates). Only elements listed in Table 4.2-2 for the weekly UC ME-RM are evaluated.

Element	XRF-1 Bias %	XRF-2 Bias %	XRF-3 Bias %	XRF-4 Bias %	XRF-5 Bias %	XRF-1 Prec. %	XRF-2 Prec. %	XRF-3 Prec. %	XRF-4 Prec. %	XRF-5 Prec. %
Al	1.1	2.3	5.8	-10.1	2.2	3.2	5.1	3.8	4.1	4.7
Si	-2.4	-2.1	1.8	4.6	-1.9	1.4	4.8	4.2	3.0	3.6
S	-1.8	-1.0	1.7	0.4	1.2	1.5	1.5	4.0	2.5	3.3
K	-1.7	-1.8	1.5	1.7	0.7	0.7	1.0	2.0	1.0	2.9
Ca	-0.2	-0.9	0.3	1.7	-1.2	1.1	1.4	2.3	1.5	1.1
Cr	-0.6	-1.3	0.1	1.3	0.6	1.2	1.2	2.1	1.6	1.0
Fe	0.4	-0.5	-0.8	1.0	-0.2	-0.1	1.4	1.6	1.1	1.1
Zn	0.3	-0.6	-1.0	1.0	0.3	1.8	2.1	1.9	1.1	1.2
As	-0.1	-1.8	-0.2	1.9	0.2	1.8	2.0	2.2	2.3	1.8
Se	-0.3	-0.1	-0.7	0.9	0.0	1.3	1.9	1.9	1.6	1.4
Rb	-0.5	-0.8	1.1	0.9	-0.6	2.1	2.7	4.4	3.2	2.2
Sr	-0.2	-0.2	1.1	0.0	-0.6	2.4	3.1	3.1	6.4	1.8
Cd	-1.7	0.3	-0.4	1.8	-0.2	6.2	7.4	6.0	6.0	5.4
Sn	-1.0	0.6	-0.2	0.0	0.6	5.9	5.4	5.0	6.4	5.7
Pb	0.4	-1.2	1.5	0.6	-1.3	2.8	4.4	3.4	3.5	2.5

Figure 4.2-2: Instrumental comparison using the weekly UC Davis ME-RM. Bias shown in plot labels is the maximum bias between any two instruments. The thick horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). Dots indicate individual data points beyond 1.5×IQR.



4.2.2.4 Long-term Stability, Reproducibility, and Inter-instrument Performance

A set of filters are reanalyzed monthly to monitor the long-term instrument performance. The set consists of 16 UC Davis produced ME-RMs and covers a range of mass loadings simulating the range of real CSN samples. In order to compare multiple filters with different mass loadings, the

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

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

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

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

Every month, two different reference values are used to calculate z-scores: (1) one reference value is only based on the average response from the one instrument for which the z-score is being calculated, and (2) the other reference value is based on the average response from all instruments. The first z-score serves as long-term reproducibility of each instrument while the second z-score is an inter-instrumental comparison. These two z-scores are plotted and checked to be within -1 to 1 for elements which have mass loadings above the MDL (Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se, and Sr). For further detail see *UCD CSN TI 302D*.

Figure 4.2-3 shows the mean z-score plots during the analysis period. Issues observed include increasing mean z-scores for iron and zinc which are most likely indicative of environmental contamination build up on the monthly reanalysis samples. Additionally, the silicon z-score for XRF-2 exceeded the acceptance criteria from March to September 2020. This increase is coincident with an increase in silicon on the daily PTFE blank, as discussed in Section 4.2.2.1. Analysis of CSN samples on XRF-2 was halted beginning 1/9/2020 and no CSN samples from this reporting period were analyzed on XRF-2 until the issue was resolved in November 2020. Finally, XRF-5 showed a drop in the mean z-score for Al, Si, S, and K in September 2020. While the z-scores remained acceptable, the decrease is remarkable. This decrease is due to the intensity loss of the X-ray tube for the instrument. Further explanation and the corrective actions taken are described in section 3.2.1.4.

Figure 4.2-3: Inter-instrument comparison by z-score of monthly reanalysis sample set. The orange dashed lines indicate the mean z-score acceptance criteria of ± 1 . Note there is no result for April 2020 due to the pandemic related shutdown.



4.2.2.5 Calibration Verification with NIST SRM 2783

The EDXRF measurement of NIST SRM 2783 certified/reference mass loadings is monitored monthly for selected elements with loadings at least three times higher than the EDXRF analytical method detection limits. The error, calculated as the difference between the measured and certified/reference mass loading relative to the certified/reference mass loading, is plotted for each instrument and provides a measure of instrument stability and accuracy. The error is compared to element specific acceptance criteria calculated as \pm the root-mean-squared-relative error plus three times the standard deviation for a set of monthly measurements ($n=44$); see *UCD CSN TI 302D* for further detail.

The NIST SRM 2783 results from this analysis period (3/12/2020 through 4/21/2021) are shown in Figure 4.2-4, and Table 4.2-14 summarizes the calibrations performed during this analysis period. All EDXRF instruments underwent routine annual calibrations in December 2019/January 2020 except XRF-2 which was not in use due to the silicon blank issue discussed in Section 4.2.2.1. Annual calibrations were also performed in conjunction with the move to the new laboratory in November and December 2020. XRF-3 also underwent calibration in August 2020 because of replacement of the detector. The results from the monthly NIST SRM 2783 analyses indicate that calibrations for all instruments were stable over the calibration periods.

Figure 4.2-4: Error of each EDXRF instrument from the NIST SRM 2783 standard run monthly for the analysis period 3/12/2020 through 4/21/2021.

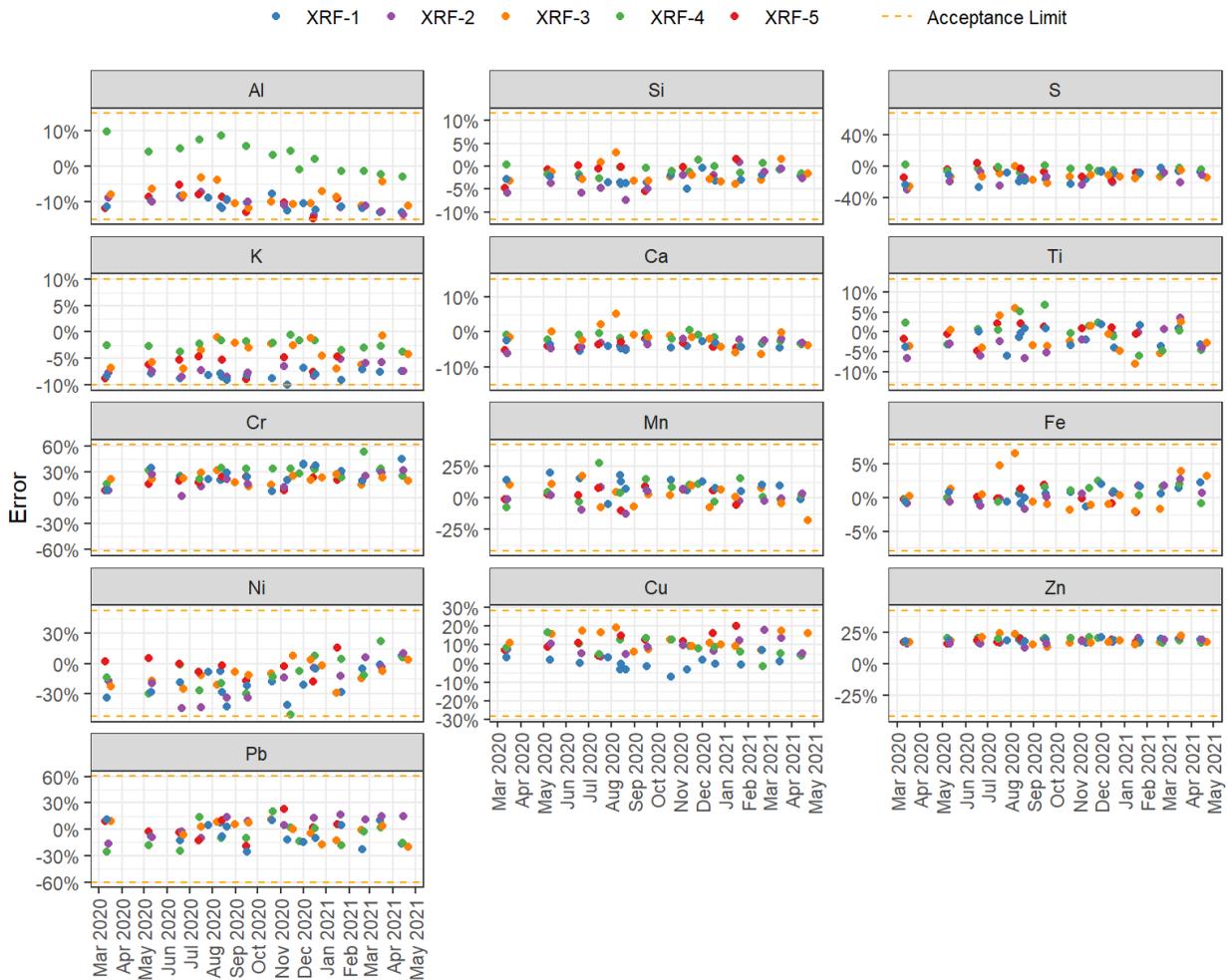


Table 4.2-14: Dates for calibrations performed on each EDXRF instrument during this analysis period (March 31, 2019 through March, 12, 2020).

EDXRF Instrument	Calibration Date	Reason for Calibration	Range of Sample Dates Analyzed
XRF-5	12/17/2019	Annual calibration	1/1/2020 – 6/29/2020
XRF-4	12/21/2019	Annual calibration	1/4/2020 – 8/31/2020
XRF-3	12/27/2019	Annual calibration	1/28/2020 – 3/31/2020
XRF-1	1/29/2020	Annual calibration	1/10/2020 – 8/31/2020
XRF-3	8/29/2020	New Detector	8/16/2020 – 8/31/2020
XRF-5	11/4/2020	Move, X-ray tube	9/3/2020 – 11/2/2020
XRF-2	11/4/2020	Move, CaF2 target	9/1/2020 – 12/29/2020
XRF-1	11/25/2020	Move	8/25/2020 – 12/29/2020
XRF-4	11/25/2020	Move	9/24/2020 – 12/29/2020
XRF-3	12/22/2020	Move	11/2/2020 – 12/29/2020

4.2.3 Determination of Uncertainties and Method Detection Limits

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

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

4.2.4 Audits, Performance Evaluations, Training, and Accreditations

4.2.4.1 System Audits

UCD performed an internal audit on December 16, 2020. A third party auditor, T&B Systems, was contracted to perform the audit. Findings from the audit included the blank silicon issue on XRF-2 which is discussed in Section 4.2.2.1, but this issue does not affect the samples from this reporting period. The audit also reiterated the lack of replicate analyses for determining measurement precision. As described in Section 3.1.2, replicate EDXRF analysis started in December 2020 and QC criteria are being developed. EDXRF analytical precision will be evaluated in the next report.

4.2.4.2 Performance Evaluations

No performance evaluations were conducted during this reporting period.

4.2.4.3 Training

Training of all personnel who assist with or operate the EDXRF instruments is mandatory through UC Davis. Personnel in the XRF laboratory are required to take the following UC Davis safety trainings: UC Laboratory Safety Fundamentals, Radiation Safety for Users of Radiation Producing Machines, Analytical X-ray Quiz, and Cryogen Safety.

Only personnel listed in *UC Davis CSN Quality Assurance Project Plan (QAPP)*, trained on the appropriate SOPs and Technical Instructions (*CSN SOP 302* and *CSN TI 302A-D*), and authorized by the Laboratory Manager can perform EDXRF analysis on CSN samples.

4.2.4.4 *Accreditations*

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

4.2.5 **Summary of Filter Blanks**

4.2.5.1 *Field Blanks*

Over the sampling period (January 1, 2020 through December 31, 2020) there were 1,498 valid PTFE filter field blanks. Table 4.2-15 summarizes the field blank statistics.

Table 4.2-15: PTFE filter field blank statistics for the analysis period March 12, 2020 through April 21, 2021 (samples collected 1/1/2020 through 12/31/2020).

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	1,498	0.018	0.019	0.006	0.042	0.006
Al	1,498	0.076	0.076	0.024	0.147	0.013
As	1,498	0.000	0.000	0.000	0.000	0.000
Ba	1,498	0.064	0.064	0.024	0.120	0.015
Br	1,498	0.000	0.000	0.000	0.002	0.000
Ca	1,498	0.003	0.004	0.000	0.193	0.007
Cd	1,498	0.019	0.019	0.006	0.042	0.006
Ce	1,498	0.073	0.074	0.025	0.140	0.017
Cl	1,498	0.002	0.003	0.000	0.527	0.015
Co	1,498	0.001	0.001	0.000	0.005	0.001
Cr	1,498	0.004	0.004	0.001	0.020	0.001
Cs	1,498	0.042	0.044	0.013	0.095	0.012
Cu	1,498	0.008	0.007	0.002	0.019	0.003
Fe	1,498	0.020	0.020	0.007	0.117	0.007
In	1,498	0.021	0.022	0.007	0.052	0.007
K	1,498	0.009	0.009	0.001	0.094	0.005
Mg	1,498	0.005	0.013	0.000	0.126	0.016
Mn	1,498	0.006	0.006	0.001	0.017	0.002
Na	1,498	0.000	0.018	0.000	0.345	0.027
Ni	1,498	0.001	0.001	0.000	0.006	0.001
P	1,498	0.000	0.000	0.000	0.023	0.001
Pb	1,498	0.012	0.013	0.005	0.027	0.003
Rb	1,498	0.003	0.003	0.000	0.008	0.001
S	1,498	0.000	0.002	0.000	0.566	0.022
Sb	1,498	0.027	0.028	0.010	0.066	0.007
Se	1,498	0.002	0.002	0.000	0.007	0.001
Si	1,498	0.026	0.026	0.003	0.161	0.011
Sn	1,498	0.028	0.029	0.010	0.058	0.007
Sr	1,498	0.004	0.004	0.002	0.009	0.001
Ti	1,498	0.002	0.002	0.000	0.009	0.002
V	1,498	0.000	0.000	0.000	0.002	0.000
Zn	1,498	0.002	0.002	0.000	0.028	0.001
Zr	1,498	0.016	0.017	0.003	0.043	0.006

4.2.5.2 Laboratory Blanks

As described in Section 3.1.3, beginning with filters from the sampling period July 1, 2020, five PTFE laboratory blanks are shipped with each batch of routine filters to the analysis laboratory and analyzed. A total of 30 PTFE laboratory blanks were analyzed during the current reporting period. Table 4.1-16 summarizes the laboratory blank statistics.

Table 4.2-16: PTFE filter laboratory blank statistics for the analysis period March 12, 2020 through April 21, 2021 (samples collected 1/1/2020 through 12/31/2020).

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	30	0.019	0.020	0.010	0.036	0.006
Al	30	0.068	0.069	0.053	0.087	0.009
As	30	0.000	0.000	0.000	0.000	0.000
Ba	30	0.063	0.065	0.035	0.122	0.020
Br	30	0.000	0.000	0.000	0.000	0.000
Ca	30	0.002	0.004	0.000	0.057	0.010
Cd	30	0.017	0.018	0.006	0.034	0.006
Ce	30	0.073	0.073	0.046	0.113	0.017
Cl	30	0.001	0.002	0.000	0.008	0.002
Co	30	0.001	0.001	0.000	0.003	0.001
Cr	30	0.004	0.004	0.002	0.006	0.001
Cs	30	0.044	0.045	0.019	0.063	0.011
Cu	30	0.005	0.007	0.004	0.013	0.003
Fe	30	0.020	0.020	0.014	0.045	0.005
In	30	0.022	0.023	0.010	0.039	0.008
K	30	0.011	0.011	0.006	0.019	0.003
Mg	30	0.016	0.017	0.000	0.063	0.017
Mn	30	0.006	0.006	0.004	0.009	0.002
Na	30	0.001	0.015	0.000	0.059	0.019
Ni	30	0.001	0.001	0.000	0.003	0.001
P	30	0.000	0.000	0.000	0.003	0.001
Pb	30	0.012	0.013	0.007	0.022	0.004
Rb	30	0.003	0.003	0.001	0.006	0.001
S	30	0.000	0.000	0.000	0.000	0.000
Sb	30	0.032	0.031	0.014	0.047	0.007
Se	30	0.002	0.002	0.001	0.005	0.001
Si	30	0.025	0.022	0.006	0.033	0.008
Sn	30	0.033	0.033	0.021	0.050	0.007
Sr	30	0.004	0.004	0.002	0.007	0.001
Ti	30	0.001	0.001	0.000	0.004	0.001
V	30	0.000	0.000	0.000	0.001	0.000
Zn	30	0.002	0.002	0.001	0.004	0.001
Zr	30	0.021	0.019	0.004	0.035	0.006

4.3 UC Davis Thermal Optical Analysis Laboratory

The UC Davis Thermal Optical Analysis (TOA) Laboratory received and analyzed quartz filters from batches 63 through 74, covering the field sampling period beginning from January 1, 2020 through December 31, 2020. Analyses of these samples were performed March 10, 2020 through March 9, 2021. Five existing Thermal Optical Carbon Analyzers (Sunset Laboratory Model 5L; designated as Alpha, Beta, Delta, Gamma, and Zeta) were used for analysis during the whole period using the IMPROVE_A temperature protocol, and a sixth Sunset analyzer, Theta, was put in use to analyze network samples beginning November 24, 2020.

Table 4.3-1: Sampling months in 2020 and corresponding TOA analysis dates covered in this reporting period. Analysis dates include reanalysis – as requested during QA level 0 and level 1 validation – of any samples within the sampling year and month.

Sampling Month (2019)	Analysis Batch #	TOA Analysis Dates
January	63	3/10/2020 – 5/20/2020
February	64	5/20/2020 – 6/8/2020
March	65	6/8/2020 – 6/30/2020
April	66	6/29/2020 – 7/15/2020
May	67	7/15/2020 – 7/31/2020
June	68	8/7/2020 – 8/27/2020
July	69	9/10/2020 – 10/6/2020
August	70	10/8/2020 – 11/13/2020
September	71	11/23/2020 – 12/23/2020
October	72	12/28/2020 – 1/22/2021
November	73	1/22/2021 – 2/16/2021
December	74	2/16/2021 – 3/9/2021
All month	63-74	3/10/2020 – 3/9/2021

4.3.1 Summary of QC Checks and Statistics

Samples are received by the UC Davis Thermal Optical Analysis Laboratory following the chain-of-custody procedures specified in the *UCD CSN TI 402A*. Samples are analyzed using Sunset Laboratory Model 5L OCEC analyzers following *UCD CSN SOP #402*. Daily and weekly QC checks are implemented to ensure data quality. Calibrations of the analyzers are performed semi-annually or as needed (e.g., when the CH₄/He mixture gas cylinder is replaced or a consistent one-side bias is observed with the daily single-point sucrose standard check, whichever comes first). Maintenance is performed as needed by trained laboratory staff. Quality control procedures are described in *UCD CSN SOP #402* and are summarized in Table 4.3-2.

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

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

^a NA: Not Applicable.

4.3.2 Summary of QC Results

Detailed results from the TOA QC checks are presented in the subsections below. In addition to performing routine daily and weekly QC activities, readings of oven pressure, back oven temperature, methanator oven temperature, FID baseline, and initial laser transmittance/reflectance are verified to be within the acceptable range specified for each analyzer before starting sample analysis. After analysis, each thermogram is reviewed for the following: 1) correct peak identification and integration, 2) correct laser response, 3) system pressure stability, and 4) FID baseline stability to ensure data quality objectives are met. Individual samples with unusual laser response, baseline shift, low system pressure, erroneous split point, or samples impacted by failure to meet acceptance criteria outlined in Table 4.3-2 are reanalyzed.

4.3.2.1 Laboratory and Instrument Blanks

At the beginning of the analysis day, following the clean oven procedure, a quartz filter laboratory blank and an instrument blank are analyzed to check for system contamination and evaluate laser response. These blanks are purchased by UC Davis and are not necessarily the same as the quartz filters used for sampling. The filters are pre-fired by UC Davis to remove contaminant carbon according to SOP #402. Results are reviewed immediately upon analysis completion and are compared against the acceptance criteria. Table 4.3-3 lists the number of blanks analyzed during the report period and their areal density statistics.

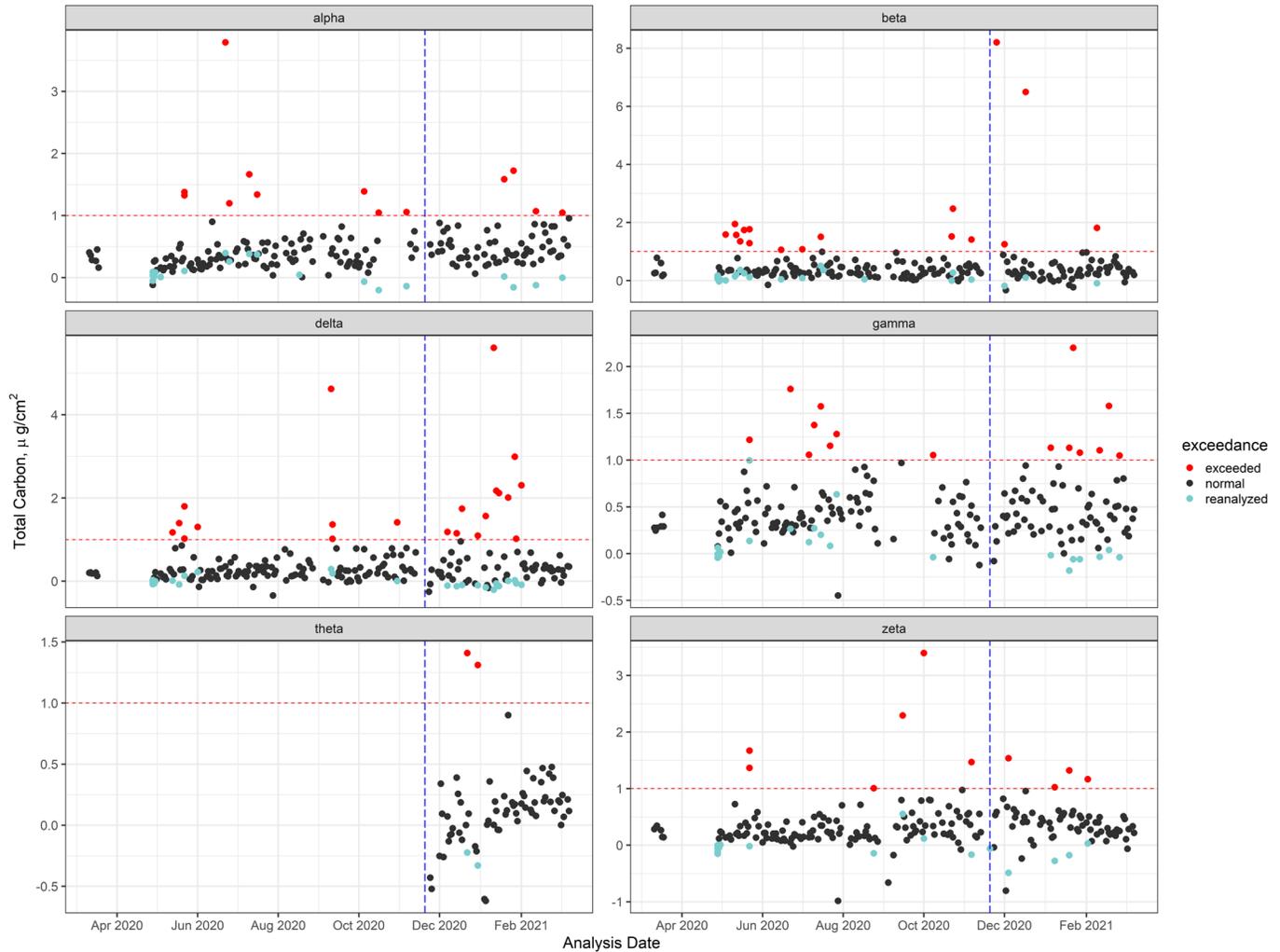
Table 4.3-3: Statistics of daily quartz filter laboratory blank and instrument blank analyses on all carbon analyzers for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

Blank Type	Count	Median ($\mu\text{g}/\text{cm}^2$)	Average ($\mu\text{g}/\text{cm}^2$)	Min ($\mu\text{g}/\text{cm}^2$)	Max ($\mu\text{g}/\text{cm}^2$)	St.Dev. ($\mu\text{g}/\text{cm}^2$)	# Exceedance
Laboratory Blank	1,019	0.308	0.422	-0.984	8.206	0.554	73
Laboratory Blank – R*	111	0.010	0.100	-0.488	1.767	0.344	5
Instrument Blank	1,040	-0.058	-0.071	-1.254	0.329	0.113	32
Instrument Blank – R*	36	-0.221	-0.135	-0.354	1.672	0.330	7

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

For laboratory blanks, if the TC areal density exceeds $1.0 \mu\text{g C}/\text{cm}^2$, a second punch taken from the same blank filter lot is analyzed (Laboratory Blank-R). Usually, the exceedances can result from contamination on the filter blanks, on the punching device, or in the system. If the original and repeated blank analyses on more than one instrument exceeds the acceptance criteria, or if the Laboratory Blank-R analysis still exceeds the limit (five cases during the report period), a new lot of quartz blank filters is used to determine the source of contamination. Occasionally, exceedances result from unstable FID baseline, which is distinguishable from contamination. On April 28, 2020, the carbon analyzers were brought back online after being down for over a month due to COVID-19. The laboratory blanks were repeated 5 times on each analyzer to achieve an operable and stable baseline. Figure 4.3-1 and Figure 4.3-2 show the results of daily laboratory and instrument blanks, respectively, analyzed by each instrument during this reporting period. Importantly, the daily blank analysis results before and after the relocation of the carbon analyzers to the new laboratory site (i.e., November 23, 2020) were separated with a dashed vertical line in dark blue color in the related figures for comparison purpose.

Figure 4.3-1: Results of daily quartz filter laboratory blanks from each analyzer for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Red dashed horizontal line indicates the acceptance criteria of $1.0 \mu\text{g C}/\text{cm}^2$ for total carbon areal density. Dark blue vertical line refers to the date (11/23/2020) when a new analyzer, Theta, began operation and the other five analyzers were moved to the new laboratory location. For cases when the acceptance criteria was exceeded (red points), a repeat analysis (blue points) was performed.

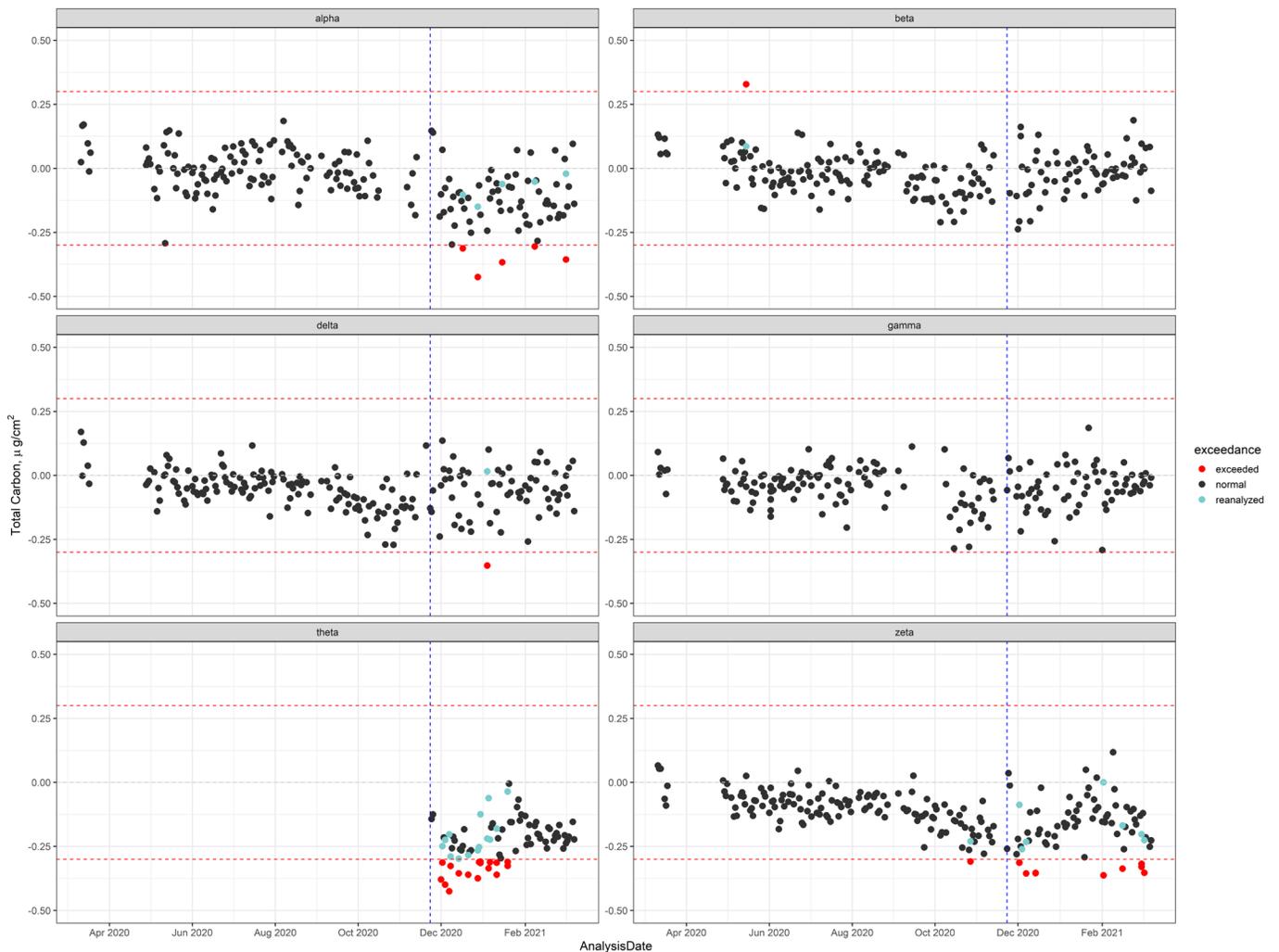


Instrument blank analysis is performed following the laboratory blank analysis by reusing the sample punch. The instrument blank acceptance criteria is TC (total carbon) within $\pm 0.3 \mu\text{g}/\text{cm}^2$. When the instrument blank fails to meet the QC criteria (red points in Figure 4.3-2), analysis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

Figure 4.3-2 shows the results of daily analyses of instrument blanks by each instrument. Most of the IB results were within criteria prior to the laboratory move, although a mild decreasing trend

in TC concentration was observed for Delta and Zeta. After the move, there was a considerable increase in instrument blank exceedances for Alpha and Zeta. The reason is the FID baseline drift (below 0) due to small change in the system pressure. In most cases the repeated IB analysis is satisfactory. In addition, 16 of 32 Instrument Blank exceedances (and 4 of 7 Instrument Blank – R exceedances) listed in Table 4.3-3 were from Theta, the newly-built instrument that requires longer warm-up time for baseline stabilization at the beginning of each analysis day.

Figure 4.3-2: Results of daily instrument blanks from each analyzer for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Horizontal dash lines in red color indicate the acceptance criteria of $\pm 0.3 \mu\text{g C}/\text{cm}^2$ for total carbon areal density. Dark blue vertical line refers to the date (11/23/2020) when the new analyzer, Theta, began operation and the other five analyzers were moved to the new laboratory location. For cases when the acceptance criteria was exceeded (red points), a repeated analysis (blue points) was performed.



4.3.2.2 *Single-Point Sucrose Standard Check*

Following the daily blank analyses, a single-point sucrose calibration check is performed to evaluate FID response by injecting 10 µL of sucrose standard solution onto a clean filter punch and analyzing for its total carbon content. Table 4.3-4 summarizes the concentrations of all sucrose standard solutions generated for calibrating the carbon analyzers on a semi-annual basis (or as needed). Sucrose calibration standards cover a wide range of the TC levels from 2.11 µg C/cm² through 210.5 µg C/cm², typically seen from the CSN network samples. Among these standards, Sucrose #15 is chosen for daily single-point calibration check as its concentration is most comparable to the CSN median TC value.

Table 4.3-4: Sucrose solution standard concentrations in µgC/cm².

Sucrose ID	Concentration (µg C/cm ²)
Sucrose 11	210.50
Sucrose 12	105.25
Sucrose 13	42.10
Sucrose 14	21.05
Sucrose 15	10.53
Sucrose 16	2.11
Sucrose 17*	36.38

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

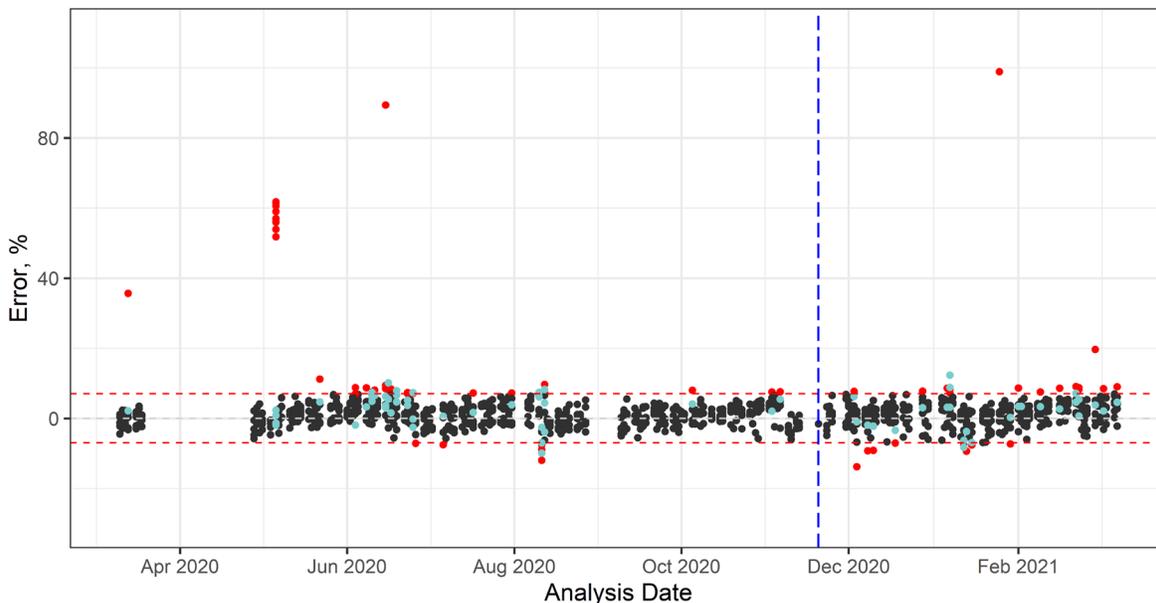
Upon completion of the sucrose analysis, the measured TC is compared against the true value (i.e. calculated TC) provided in Table 4.3-4. The % error between the measured and calculated TC is derived using Equation 4.3-1. If the error exceeds the ± 7% acceptance criteria, a second analysis is performed before any network samples are analyzed on that instrument. If the second analysis still exceeds the acceptance criteria, or if a consistent one-sided bias (with error within ± 7%) is observed on multiple instruments, a different sucrose solution is analyzed to determine if the problem is with the solution or with the instrument. If the former, a new sucrose solution is made and verified; if the latter, a full five-point calibration is performed to determine the new calibration constant for that instrument. Table 4.3-5 summarizes the statistics of the daily sucrose check. There were 74 exceedances out of the 1,100 sucrose runs during the report period. All repeat-analyses of the sucrose solution showed acceptable results (Figure 4.3-3). Note that on May 6, 2020, a pipetting error caused multiple sucrose QC failures on all five instruments. No network samples were analyzed before the issue was resolved and all repeated sucrose analyses met the QC criteria.

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

Table 4.3-5: Statistics of daily single-point sucrose standard analyses on all carbon analyzers for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
1,100	1.425	1.900	-33.581	98.898	7.612	74

Figure 4.3-3: Results of daily single-point sucrose calibration standard check for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Red dashed lines indicate the acceptance criteria of $\pm 7\%$ error. Dark blue vertical line refers to the date (11/23/2020) when a new analyzer, Theta, began operation and the other five analyzers have been moved to the new laboratory location. For cases when original measured sucrose value (red points) exceeded the acceptance criteria, a repeated analysis was performed (blue points).



4.3.2.3 Calibration Peak Area Check

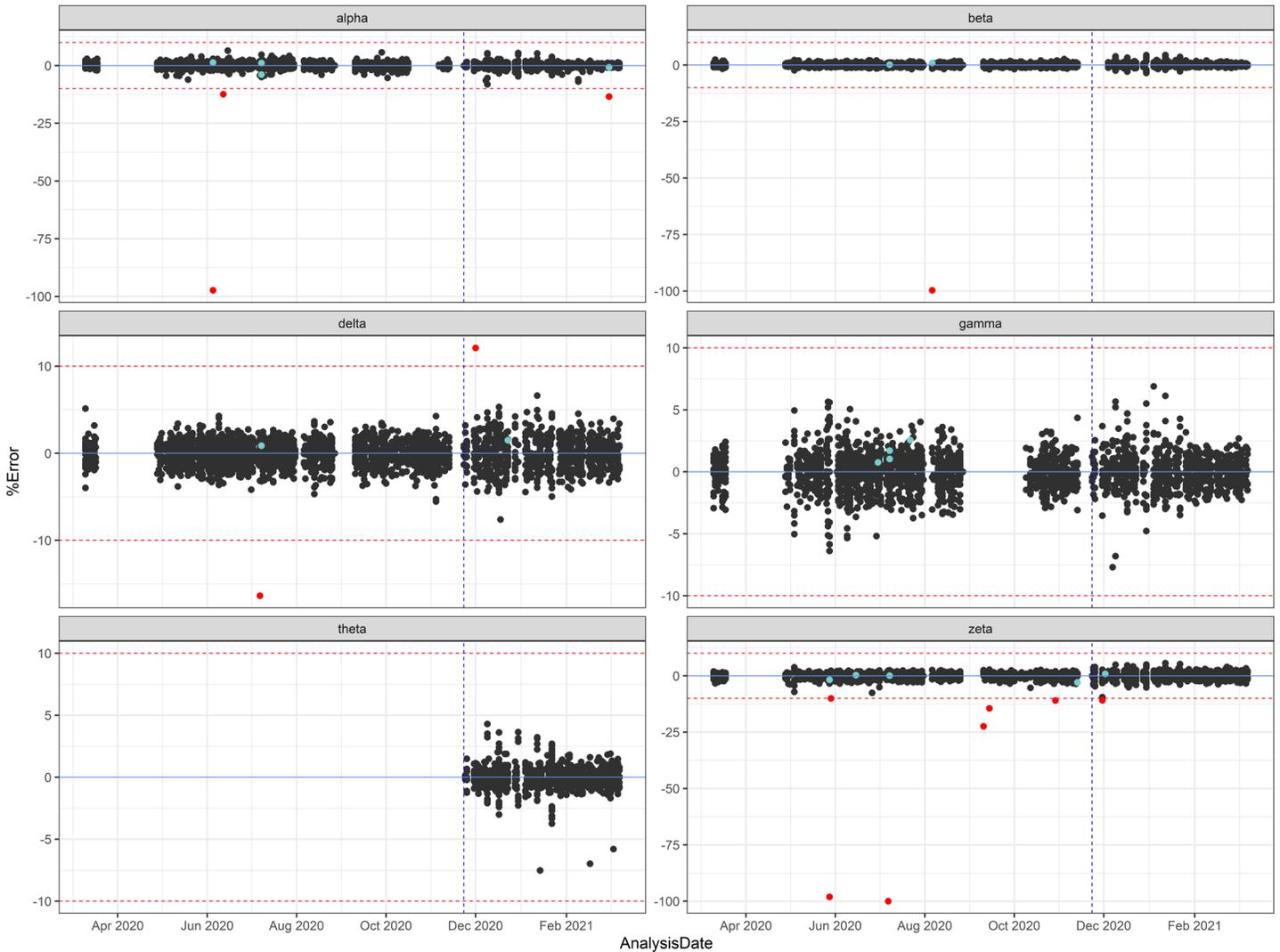
At the end of each analysis, a fixed amount of methane (CH_4) from a cylinder containing 5% CH_4 in helium is injected into the system as an internal gaseous standard. The CH_4 peak area is quantified and compared to the average peak area of all analyses performed on that instrument on that day. If the error (calculated using Equation 4.3-2) exceeds $\pm 10\%$ acceptance criteria, the analysis result is voided; the flowrate of the calibration gas and sample oven pressure are verified; corrective actions (if applicable) are taken immediately after the problem is identified; and the analysis is repeated using a second filter punch analyzed on the original analyzer (or on a different analyzer if the original analyzer is not available). For samples in CSN batches 63 through 70 (analyzed between 3/10/2020 and 11/12/2020), repeat analyses for calibration area exceedances were performed after completing analysis of the whole batch. For samples in CSN batches 71 to 74 (analyzed between 11/23/2020 and 3/9/2021), the repeat analyses were performed on the same day as the exceedances. Table 4.3-6 summarizes the statistics of the calibration peak area checks. There were 19 exceedances during this reporting period. Nine of the 19 exceedances occurred when the clamp that connects the oven ball joint was not sufficiently tightened, resulting in a leak in the system. The other ten exceedances occurred due to FID ignition being off during the analysis. Seven of ten calibration peak area exceedances due to the FID error were performed by the carbon analyzer, Zeta, on July 7, 2020; Zeta's FID igniter battery was replaced on July 9, 2020, to fix this problem. All repeat analyses of the affected samples had acceptable results. No corrective action was performed for the two samples, i.e., F210449 and F212066 that were analyzed by Zeta on 9/10/2020 and 9/14/2020 respectively with the calibration area failures (See Figure 4.3-4). The carbon data of F210449 and F212066 were consequently invalidated with the AQS Null Code "AS – Poor Quality Assurance Results".

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

Table 4.3-6: Statistics of internal calibration peak area check on all carbon analyzers for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2021).

Analyzer	Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
Alpha	2469	-0.003	-0.050	-97.343	6.486	2.329	3
Beta	2724	-0.038	-0.038	-99.650	4.446	2.040	1
Delta	2862	0.076	-0.001	-16.361	12.106	1.521	2
Gamma	2353	0.037	-0.002	-7.691	6.895	1.407	0
Zeta	2766	0.113	-0.308	-99.993	5.673	5.553	13
Theta	979	0.010	0.000	-7.524	4.297	0.919	0

Figure 4.3-4: Results of internal calibration area check for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Red dashed lines indicate the acceptance criteria of $\pm 10\%$ error from the mean value. Dark blue vertical line refers to the date (11/23/2020) when a new analyzer, Theta, began operation and the other five analyzers have been moved to the new laboratory location. For cases when calibration area exceeded the acceptance criteria, a repeated analysis (blue points) was performed and the original analysis was voided (red points).

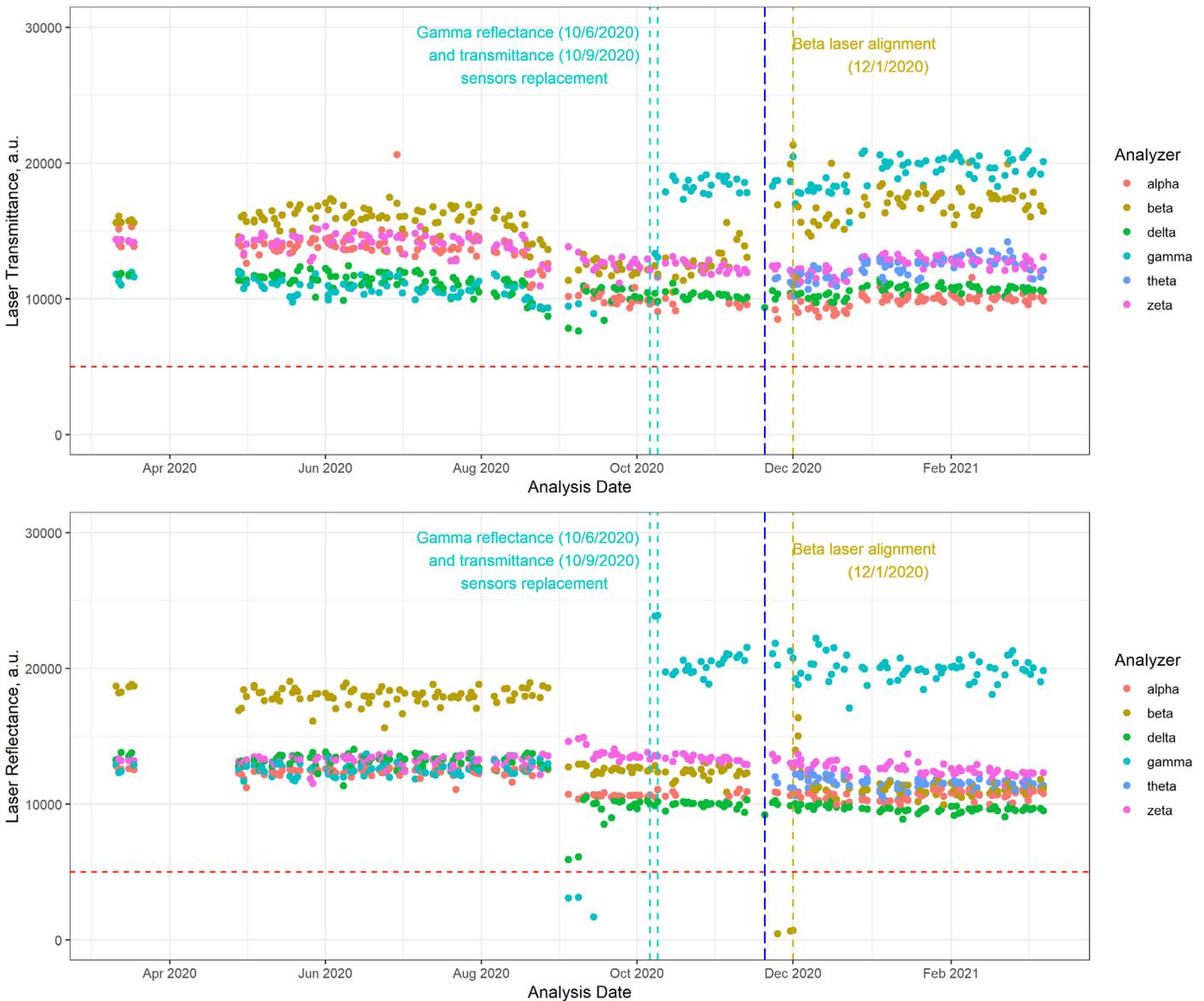


4.3.2.4 Laser Performance Check

Laser signals (both reflectance and transmittance) are monitored throughout the TOA analysis and are examined for stability during post-analysis thermogram review. Any unusual laser response, caused by either weak/non-functioning laser or laser-sample-detector misalignment, results in corrective actions (if applicable) and reanalysis of the sample. In addition, before starting the instrument blank analysis each day, the readings of clean filter reflectance and transmittance are checked to make sure they are above the initial laser acceptance criterion (i.e. 5000 a.u.). Figure 4.3-5 shows the filter reflectance and transmittance initial readings for all instrument blank analyses during the report period. There were three exceedances of the laser

reflectance signal of Gamma on 9/4/2020, 9/8/2020, and 9/14/2020, which resulted in a laser source replacement. Similarly, Beta had three exceedances of laser reflectance values after the relocation of the UC Davis TOA Laboratory on 11/25/2020, 11/30/2020, and 12/1/2020, which resulted in laser fine-tuning and signal optimization performed on 12/1/2020. No network samples were analyzed by Beta or Gamma during the exceedance days.

Figure 4.3-5: Laser initial readings (top: Transmittance; bottom: Reflectance) of the instrumental blank analysis for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Red dashed line indicates the acceptance criteria of 5000 a.u. of the laser signal. Dark blue vertical line refers to the date (11/23/2020) when a new analyzer, Theta, began operation and the other five analyzers have been moved to the new laboratory location. Other vertical lines indicate dates of related maintenance on the instrument optical components. Different analyzers are indicated by data point color.



4.3.2.5 Network Sample Replicates

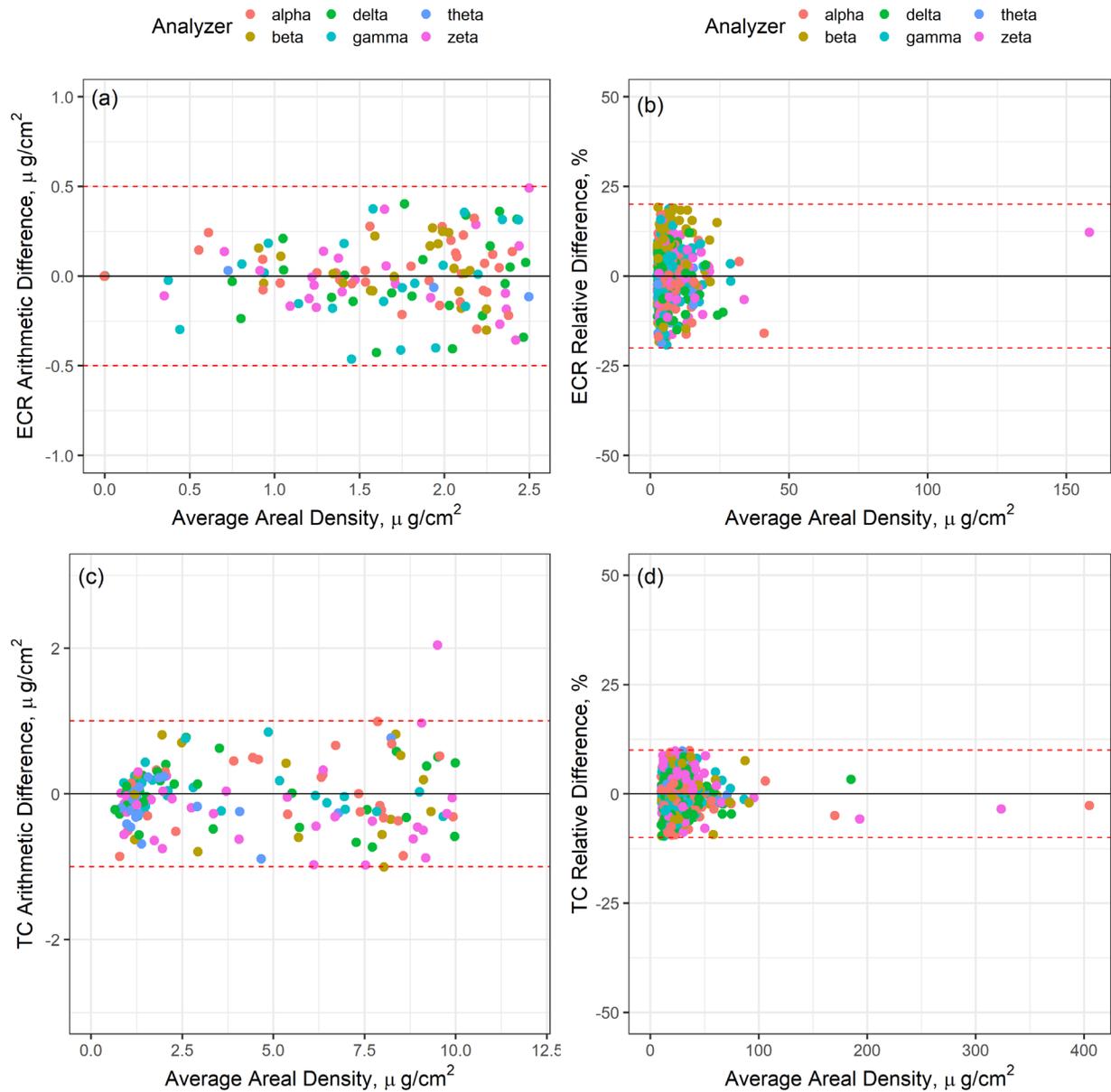
Replicate analyses are performed on every 20th CSN filter (samples and field blanks), where replicate analysis results are obtained from a second punch from the same filter analyzed on a randomly selected analyzer. Table 4.3-7 lists the acceptance criteria for replicate analysis and the summary statistics from this reporting period. A total of 671 replicate analyses were performed out of the 14,314 samples and field blanks. For cases that exceeded the acceptance criteria, a third punch (if available) was analyzed on a different analyzer, and all three sets of results (routine, replicate, and reanalysis) from the same filter are compared to determine analysis validity. Instrument anomaly and/or deposit inhomogeneity are also examined. Figure 4.3-6 shows the results of the replicate analyses. There were a total of 55 TC exceedances and 51 ECR exceedances during this reporting period. Samples with exceedances were reanalyzed on a third analyzer. One sample (barcode ID# F197432) failed the replicate analysis criteria for TC but was not reanalyzed because the sample deposit was determined to be inhomogeneous by visual inspection (see Figure 4.3-6, panel c). All other reanalyses had satisfactory results.

Table 4.3-7: Acceptance criteria and the summary statistics of the replicate analyses for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

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	671	55	54
ECR	*RPD < ±20% when EC > 2.5 µg /cm ² or Absolute difference <±0.5 µg/cm ² when EC ≤2.5 µg/cm ²	671	51	51

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

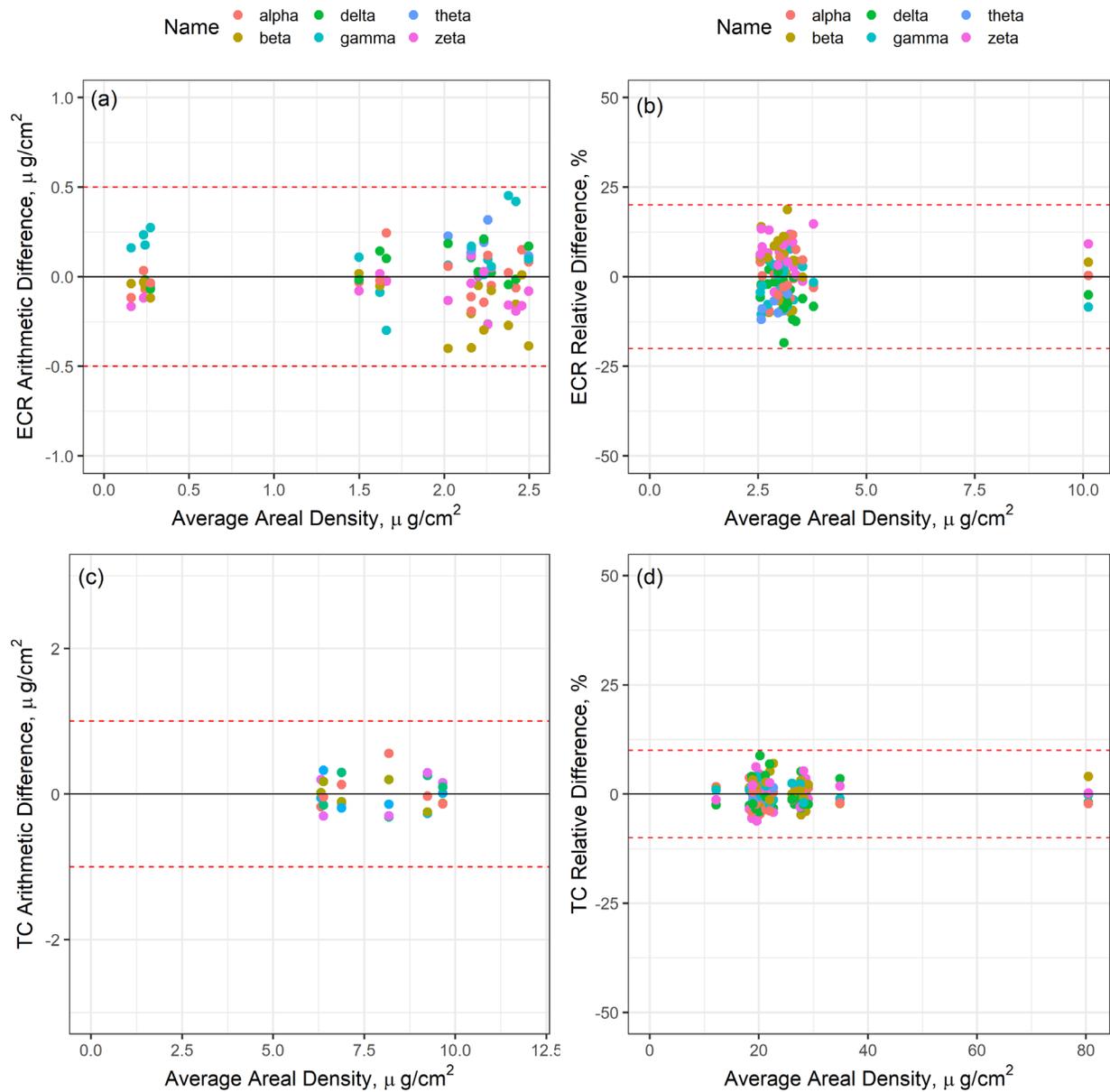
Figure 4.3-6: Results of CSN replicate analysis for ECR (Panel a and b) and TC (Panel c and d) for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). The red dashed lines in each panel represents the acceptance criteria.



4.3.2.6 Inter-instrument Comparison Check

Instrument inter-comparison is evaluated weekly by analyzing performance check (PC) samples collected at UC Davis. Pre-fired quartz filters with 37 mm diameter are used to provide enough deposit area for at least seven 0.6 cm^2 punches. A total of 39 weekly PC samples were analyzed during this reporting period. Six 0.6 cm^2 punches were taken from the same PC sample, one was analyzed by each instrument. Figure 4.3-7 shows the results of the weekly PC samples for each analyzer.

Figure 4.3-7: Results of the weekly performance check samples by each analyzer for ECR (Panel a and b) and TC (Panel c and d) for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). The red dashed lines in each panel represent the acceptance criteria.



The measured carbon areal density from each analyzer (A_X) is compared against the average value derived from measurements by all available analyzers on the same performance check sample. Acceptance criteria at higher filter loadings (TC > 10 $\mu\text{g C}/\text{cm}^2$ and ECR > 2.5 $\mu\text{g C}/\text{cm}^2$) are based on the relative difference (%) by dividing the difference between the measurement of a given analyzer (i) and the average value for the same PC sample obtained from all analyzers used in comparison by the average value using the equation as follows:

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

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 is the same as that for the network sample replicates (See Table 4.3-2 for details). Exceeding the acceptance criteria results in further investigation of the instrument, and reanalysis of the performance check sample. Table 4.3-8 summarizes the statistics of the instrument bias for ECR and TC. There were no exceedances during this reporting period.

Table 4.3-8: Statistics (median, mean, and standard deviation) of the relative (%) and arithmetic difference values from the weekly inter-instrument comparison analysis of high and low PC filter loadings, respectively. Analysis period covers the dates starting from 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

Analyzer	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 > $10 \mu\text{g/cm}^2$			
	Count	Median	Mean	St.Dev.	Count	Median	Mean	St.Dev.
Alpha	18	0.260	1.022	5.746	30	-0.876	-1.031	2.083
Beta	21	4.571	2.920	8.125	32	0.419	0.614	2.696
Delta	21	-3.856	-5.012	5.009	32	-0.824	0.031	3.205
Gamma	18	-1.790	-1.629	5.228	29	0.228	0.243	1.799
Zeta	21	6.646	5.826	5.618	33	0.238	0.058	2.962
Theta	8	-9.206	-8.437	2.434	14	-0.859	0.096	2.050
Analyzer	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 - $10 \mu\text{g/cm}^2$			
	Count	Median	Mean	St.Dev.	Count	Median	Mean	St.Dev.
Alpha	18	-0.026	-0.006	0.110	6	-0.034	0.051	0.270
Beta	17	-0.077	-0.148	0.148	6	-0.045	-0.016	0.176
Delta	17	0.026	0.043	0.127	6	0.056	0.033	0.236
Gamma	17	0.109	0.120	0.176	6	-0.099	-0.054	0.210
Zeta	18	-0.065	-0.072	0.098	6	0.014	-0.014	0.262
Theta	6	0.170	0.189	0.075	NA	NA	NA	NA

NA: Not available.

4.3.2.7 Multi-point Sucrose Standard Check

A multi-point calibration is performed every six months, when the calibration gas cylinder or instrument main oven is replaced, or if a consistent one-sided bias is observed with the daily single-point sucrose standard check, whichever comes first. The calibration uses sucrose standards with at least six different concentration levels that cover a wide range of TC

concentrations typically seen on the CSN samples (See Table 4.3-4 for details). The least-square correlation coefficient (r^2) of measured versus calculated mass of carbon, force-fit through the origin (0, 0), should be higher than 0.995. The new calibration constant for each analyzer is calculated by taking the ratio of the current constant and the calibration slope. The calibration constant is automatically updated in the database after the calibration is completed. Table 4.3-9 summarizes the multi-point sucrose calibrations performed during this reporting period.

Table 4.3-9: Summary of multi-point sucrose standard checks performed for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020).

Analyzer	Calibration Date	Slope	r^2	Calibration Constant
Alpha	3/9/2020	0.9890	0.9998	20.9274
Alpha ¹	6/19/2020	1.0265	0.9994	20.3871
Alpha	9/9/2020	0.9727	0.9999	20.9593
Alpha ²	11/23/2020	1.0031	1.0000	20.7259
Beta	3/10/2020	0.9715	0.9999	21.3938
Beta ¹	6/19/2020	1.0159	0.9999	20.0746
Beta	9/9/2020	0.9419	0.9998	21.3129
Beta	10/9/2020	1.0133	0.9999	21.0332
Beta ³	12/3/2020	0.9840	1.0000	21.3752
Gamma	3/9/2020	0.9847	1.0000	20.6414
Gamma ¹	6/19/2020	1.0218	0.9999	20.2010
Gamma	9/9/2020	0.9975	0.9999	20.2516
Gamma ⁴	10/8/2020	1.0003	1.0000	20.2455
Gamma ²	11/23/2020	0.9947	1.0000	20.4674
Delta	3/9/2020	1.0226	0.9990	20.5100
Delta ¹	6/19/2020	0.9787	0.9997	20.9564
Delta	9/9/2020	1.0112	0.9997	20.7243
Delta ²	11/23/2020	0.9600	1.0000	21.2040
Zeta	3/9/2020	1.0180	0.9991	20.7828
Zeta ¹	6/19/2020	0.9706	0.9997	21.4123
Zeta	9/9/2020	1.0000	0.9999	21.4123
Zeta ²	11/23/2020	1.0341	0.9999	20.0192
Zeta ⁵	1/25/2021	0.9474	0.9999	21.1307
Theta ²	11/12/2020	1.0000	1.0000	20.1190
Theta ²	11/23/2020	0.9644	0.9999	20.8617

¹ Calibration gas cylinder was replaced on 6/11/2020.

² Theta was purchased and all other instruments were moved to the new laboratory location.

³ Beta's main oven and heating coils were replaced on 11/24/2020 and 12/1/2020.

⁴ Gamma's main oven and heating coils were replaced on 9/12/2020

⁵ Zeta's daily sucrose check results were approaching to the upper acceptance limit.

4.3.2.8 Temperature Calibration

A temperature calibration is performed every six months (usually along with a multi-point sucrose calibration) or after a major instrument repair (e.g., replacement of main oven or heating coils). The difference (i.e. offset) between the oven temperature and sample temperature at each IMPROVE_A protocol temperature set point is determined using a manufacturer-provided temperature calibration device, inserted into the sample oven so that the external temperature probe sits where a sample punch would be during routine analysis. The oven temperature cycles through the IMPROVE_A protocol temperature set points (from 140 °C to 840 °C). The differences in temperature readings by the calibration probe and oven temperature probe (i.e. temperature offsets) are calculated and updated in the IMPROVE_A protocol parameter file. The system then goes through the IMPROVE_A protocol temperature cycle again to verify that the temperature readings from the two probes are within 10 °C at all temperature steps. Table 4.3-10 summarizes the temperature calibrations performed on each analyzer during this reporting period.

Table 4.3-10: Summary of the temperature calibrations performed on each analyzer for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Oven re-wrap refers to adjustment or replacement of heating coils that are wrapped around the sample oven.

Analyzer	Calibration Date	Oven Re-Wrapped?	Temperature Offsets (°C)					
			140°C	280°C	480°C	580°C	740°C	840°C
Alpha ¹	3/5/2020	No	16	29	34	28	-5	-19
Alpha	9/3/2020	No	13	26	26	21	-6	-18
Beta ¹	3/5/2020	No	-26	-50	-58	-56	-16	-23
Beta	9/3/2020	No	-25	-49	-58	-54	-14	-20
Beta ²	11/24/2020	Yes	6	0	-21	-29	-29	-40
	12/2/2020	Yes	12	24	20	15	-16	-30
Gamma ¹	3/5/2020	No	-15	-33	-44	-48	-29	-38
Gamma	9/3/2020	No	-19	-40	-50	-53	-34	-42
Gamma ³	9/15/2020	Yes	15	26	26	26	-7	-14
Delta ¹	3/5/2020	No	3	-1	-11	-17	1	-5
Delta	9/3/2020	No	4	0	-8	-16	-2	-6
Zeta ¹	3/5/2020	No	-26	-43	-50	-44	0	-12
Zeta	9/3/2020	No	-23	-39	-32	-30	5	-6
Theta ⁴	11/3/2020	No	32	44	35	28	6	3

¹ On 3/5/2020 all instruments were calibrated before starting analysis of 2020 CSN samples.

² Beta's main oven was replaced on 11/24/2020 and 12/1/2020.

³ Gamma's main oven was replaced on 9/12/2020.

⁴ Theta's purchase.

4.3.3 Determination of Uncertainties and Method Detection Limits

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

For uncertainty estimates see Section 6.5.

4.3.4 Audits, Performance Evaluations, Training, and Accreditations

4.3.4.1 *System Audits*

An internal audit was conducted at the UC Davis TOA Laboratory on December 18, 2020. A third party auditor, T&B Systems, was contracted to perform the audit. The audit found that the deionized water used for analysis is purchased from a vendor but is not tested for purity. The auditors recommended performing water spike tests and also possibly employing a conductivity meter to routinely verify the deionized water purity. The laboratory has a plan for exploring the usefulness of an additional point on the calibration solutions, i.e. a zero spike solution. It is expected that any carbonaceous impurities in the water would be detectable in the lowest calibration standard; UC Davis will perform testing to better understand.

4.3.4.2 *Performance Evaluations*

The UC Davis Thermal Optical Analysis Laboratory participated in an inter-laboratory comparison study organized by the European Center for Aerosol Calibration (ECAC) in March 2020. Eight quartz filter samples and one aqueous solution of phthalic acid were received and analyzed for OC, EC and TC. UC Davis passed the evaluation with good data repeatability and overall small systematic bias for measurement of TC, OC and EC. The full report is downloadable via <https://www.actris-ecac.eu/january-to-june--ocec-2020-1-.html>.

4.3.4.3 *Training*

All new laboratory staff and student assistants working in the UC Davis Thermal Optical Analysis Laboratory receive mandatory UC Laboratory Safety Fundamentals training. Personnel who operate the TOA analyzers receive additional training on the *CSN SOP 402* and relevant Technical Instructions.

4.3.4.4 *Accreditations*

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

4.3.5 Summary of Filter Blanks

4.3.5.1 *Field Blanks*

Over the sampling period (January 1, 2020 through December 31, 2020) there were 1,486 valid quartz filter field blanks. Table 4.3-11 summarizes the field blank statistics.

Table 4.3-11: Quartz filter field blank statistics for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).

Species	Count	Median (µg/cm ²)	Average (µg/cm ²)	Min (µg/cm ²)	Max (µg/cm ²)	St.Dev. (µg/cm ²)
EC1	1,486	0.046	0.091	-0.077	1.599	0.155
EC2	1,486	0.063	0.105	-0.020	1.399	0.127
EC3	1,486	0.000	0.002	-0.042	0.512	0.024
ECR	1,486	0.000	0.000	-0.042	0.054	0.003
ECT	1,486	0.000	0.000	-0.004	0.029	0.001
OC1	1,486	0.193	0.189	-0.017	1.317	0.105
OC2	1,486	0.374	0.416	-0.009	1.967	0.187
OC3	1,486	0.548	1.269	-0.003	25.159	1.977
OC4	1,486	0.165	0.320	-0.047	2.581	0.352
OCR	1,486	1.465	2.391	0.335	29.827	2.528
OCT	1,486	1.465	2.391	0.335	29.827	2.528
OPR	1,486	0.116	0.198	-0.081	2.539	0.276
OPT	1,486	0.116	0.198	-0.081	2.539	0.276

4.3.5.2 Laboratory Blanks Supplied by Wood PLC

As described in Section 3.1.3, beginning with filters from the sampling period July 1, 2020, five quartz laboratory blanks are shipped from the Sample Handling Laboratory (Wood PLC) with each batch of routine filters to the analysis laboratory and analyzed. These filters are different than those used for daily QC as described in section 4.3.2.1. These filters are from the same filter lots as the sample filters and are pre-fired by Desert Research Institute (Reno, NV) and delivered to Wood PLC along with the quartz filters to be used for sampling. There are no QC criteria for these laboratory blanks. A total of 30 quartz laboratory blanks were analyzed during the current reporting period, with four runs of analysis per filter using different analyzers for each run. Table 4.1-12 summarizes the laboratory blank statistics.

Table 4.3-11: Quartz filter laboratory blank statistics for the analysis period 3/10/2020 through 3/9/2021 (samples collected 1/1/2020 through 12/31/2020). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).

Species	Count	Median (µg/cm ²)	Average (µg/cm ²)	Min (µg/cm ²)	Max (µg/cm ²)	St.Dev. (µg/cm ²)
EC1	30	-0.010	-0.004	-0.086	0.424	0.060
EC2	30	0.004	0.008	-0.045	0.149	0.031
EC3	30	0.006	0.009	-0.036	0.060	0.022
ECR	30	0.000	0.000	-0.002	0.001	0.000
ECT	30	0.000	0.000	-0.002	0.001	0.000

Species	Count	Median (µg/cm ²)	Average (µg/cm ²)	Min (µg/cm ²)	Max (µg/cm ²)	St.Dev. (µg/cm ²)
OC1	30	0.056	0.058	-0.020	0.119	0.028
OC2	30	0.045	0.047	-0.037	0.143	0.024
OC3	30	0.109	0.162	0.001	1.461	0.203
OC4	30	0.006	0.009	-0.168	0.367	0.075
OCR	30	0.202	0.288	-0.162	2.457	0.358
OCT	30	0.202	0.288	-0.162	2.455	0.358
OPR	30	0.009	0.013	-0.149	0.450	0.096
OPT	30	0.009	0.013	-0.149	0.449	0.096

5. Data Management and Reporting

5.1 Number of Events Posted to AQS

Table 5.1-1 summarizes dates that data were delivered to AQS for samples collected January 1, 2020 through December 31, 2020. Data are expected to be delivered to AQS within 120 days of receipt of filters by the analytical laboratories.

Table 5.1-1: Summary of data deliveries to AQS for samples collected January 1, 2020 through December 31, 2020.

Sampling Month (2020)	Analysis Batch #	Filter Receipt Date	AQS Delivery Date	Days
January	63	March 4, 2020	August 6, 2020	155
February	64	April 9, 2020*	August 26, 2020	139
March	65	May 6, 2020**	October 5, 2020	152
April	66	June 3, 2020***	November 5, 2020	155
May	67	July 8, 2020	November 5, 2020	120
June	68	August 5, 2020	December 2, 2020	119
July	69	September 2, 2020	January 7, 2021	127
August	70	October 7, 2020	February 4, 2021	120
September	71	November 4, 2020	March 3, 2021	119
October	72	December 9, 2020	April 8, 2021	120
November	73	January 13, 2021	May 13, 2021	120
December	74	February 10, 2021	June 10, 2021	120

* Nylon filters delivered to RTI; PTFE and quartz filters held at Wood PLC and delivered to UCD on 5/12/2020.

** Nylon filters delivered to RTI; PTFE and quartz filters held at Wood PLC and delivered to UCD on 5/19/2020.

*** Nylon filters delivered to RTI; PTFE and quartz filters held at Wood PLC and delivered to UCD on 6/17/2020.

As noted in Section 2.2.2 and Section 2.3.2, UCD suspended laboratory operations effective beginning March 19, 2020 in response to the COVID-19 guidance from state, county, and

university officials. February 2020, March 2020, and April 2020 filters shipments to UCD were subsequently delayed and January through April 2020 data deliveries were delayed.

6. Quality Assurance and Data Validation

6.1 QAPP Revisions

The UC Davis Quality Assurance Project Plan (QAPP) for Laboratory Analysis and Data Processing/Validation for Chemical Speciation of PM_{2.5} Filter Samples is reviewed and updated annually; the UC Davis 2020 QAPP was delivered to the EPA for review on August 21, 2020. The revised QAPP was delivered to the EPA for review on July 30, 2021, titled the UC Davis 2021 QAPP, revised again on August 31, 2021, and accepted by the EPA on September 15, 2021.

6.2 SOP Revisions

The UC Davis Standard Operating Procedures (SOPs) and Technical Information (TI) material for Laboratory Analysis and Data Processing/Validation for Chemical Speciation of PM_{2.5} Filter Samples are reviewed and updated annually; the UC Davis 2020 SOPs and TIs were delivered to the EPA on August 21, 2020. A subset of the UC Davis 2021 SOPs and TIs were delivered to the EPA on July 30, 2021 and the laboratory SOPs and TIs were delivered on August 31, 2021 so the incorporation of replicate analyses could be included in the 2021 documents.

6.3 Summary of Internal QA Activities

Following laboratory analysis all analytical results are assembled by UC Davis for processing and initial validation. Data processing involves calculating ambient concentration, uncertainty, and MDL for each analyte using the laboratory result plus the sample volume determined from the field data. The calculated concentrations undergo two levels of validation at UC Davis: (1) Level 0 validation to examine the fundamental information associated with each measured variable, such as chain of custody, shipping integrity, sample identification, and damaged samples, and (2) Level 1 review for technical acceptability and reasonableness based on information such as routine QC sample results, data quality indicator calculations, performance evaluation samples, internal and external audits, statistical screening, internal consistency checks, and value range checks. Further detail regarding the UC Davis data processing and validation can be found in *UCD CSN SOP #801: Processing and Validating Raw Data*, and in the associated Technical Information (TI) documents as follows:

- 1) *UCD CSN TI 801A, Data Ingest*: Sample event information (including filter IDs, flow rates, qualifier and null code flags, and comments) are received from the Sample Handling Laboratory (Wood PLC) via email and uploaded to the UC Davis CSN database. UC Davis EDXRF and TOA analysis results are transferred into the UC Davis CSN database through an automated service. RTI IC analysis result files are received via email from RTI and are ingested to the UC Davis CSN database. Additionally, for a select subset of field blanks and special studies, Wood PLC gravimetric mass result files are received via email from Wood PLC and are ingested to the UC Davis CSN database.

- 2) *UCD CSN TI 801C, Level 0 Validation*: Data and metadata are reviewed through several visualizations to identify oddities such as inconsistent dates that appear to be data transcription and/or data entry errors. These are resolved through communication with the Sample Handling Laboratory.
- 3) *UCD CSN TI 801B, Data Processing*: Sample volume and analysis results are combined to calculate concentrations. Field blank values are used to derive MDLs. MDLs and concentrations are used to estimate uncertainty.
- 4) *UCD CSN TI 801C, Level 1 Data Validation*: Several statistical and visual checks are applied and examined. Laboratory reanalyses are requested as needed. Data are flagged with qualifier or null codes.
- 5) *UCD CSN TI 801D, Data Posting*: Initially validated concentration data and metadata are posted to DART for SLT (State, Local, and Tribal) agency review. After the specified 30-day review period, changed or unchanged data are re-ingested to the UC Davis CSN database.
- 6) *UCD CSN TI 801E, AQS Delivery*: SLT initiated changes and comments are reviewed and resolved. Data are formatted for delivery to AQS and posted.

6.4 Data Validation and Review

The validation graphics shown in this section are a small subset of the many QC evaluations that UC Davis performs on a routine basis. They are selected to illustrate the nature and use of the QC tools, and provide an overview of the review process.

Additional information and detail regarding analytical and validation procedures can be found in the standard operation procedure (SOP) documents, *UC Davis CSN Quality Assurance Project Plan* (QAPP), and the *Data Validation for the Chemical Speciation Network* guide, all available at the UC Davis CSN site: <https://aqrc.ucdavis.edu/csn-documentation>.

6.4.1 Summary of Monthly Data Validation Review Results

6.4.1.1 Comparisons Across Years

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

Figures 6.4-1 and 6.4-2 show time series for the network-wide 90th percentile, median (50th percentile), and 10th percentile concentrations of organic carbon by reflectance (OCR) and elemental carbon by reflectance (ECR). These figures show raw data without blank correction to enable comparison across a wider timeframe. The carbon fractions OCR and ECR are determined by thermal optical analysis (TOA) with a correction for pyrolysis based on optical monitoring as the sample is heated. Measurements for samples collected from 2005 through 2015 were performed at DRI using DRI Model 2001 analyzers; samples collected from January 2016 through September 2018 were analyzed at DRI using DRI Model 2015 analyzers; and, beginning with samples collected from October 2018 analysis was performed at UC Davis using the Sunset Laboratory Model 5L analyzer.

Figure 6.4-1: Multi-year time series of network-wide organic carbon by reflectance concentrations (OCR; raw data without blank correction). Symbols denote laboratory and type of analyzer: DRI Model 2001 (circle), DRI Model 2015 (triangle), and UCD Sunset Laboratory Model 5L (square).

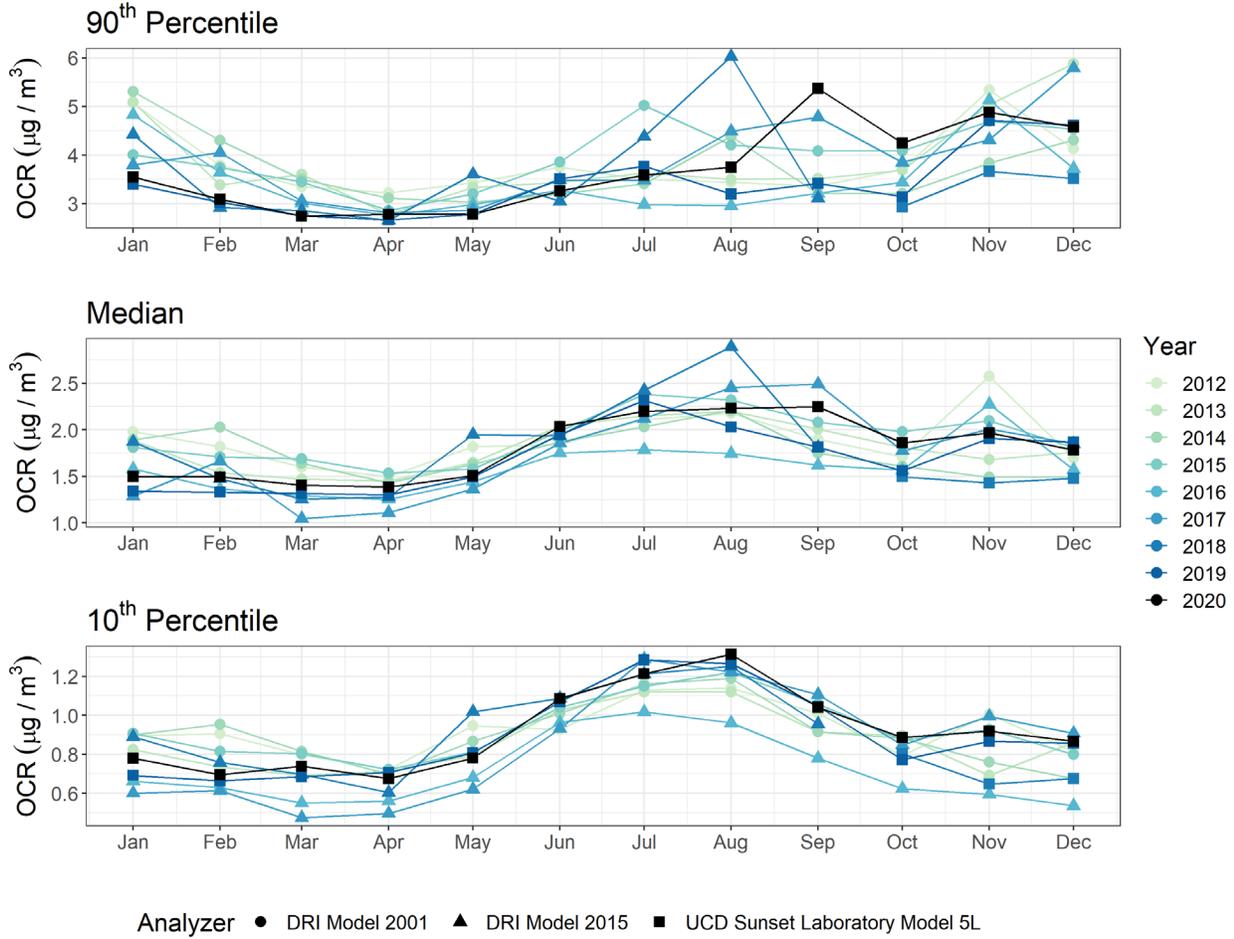
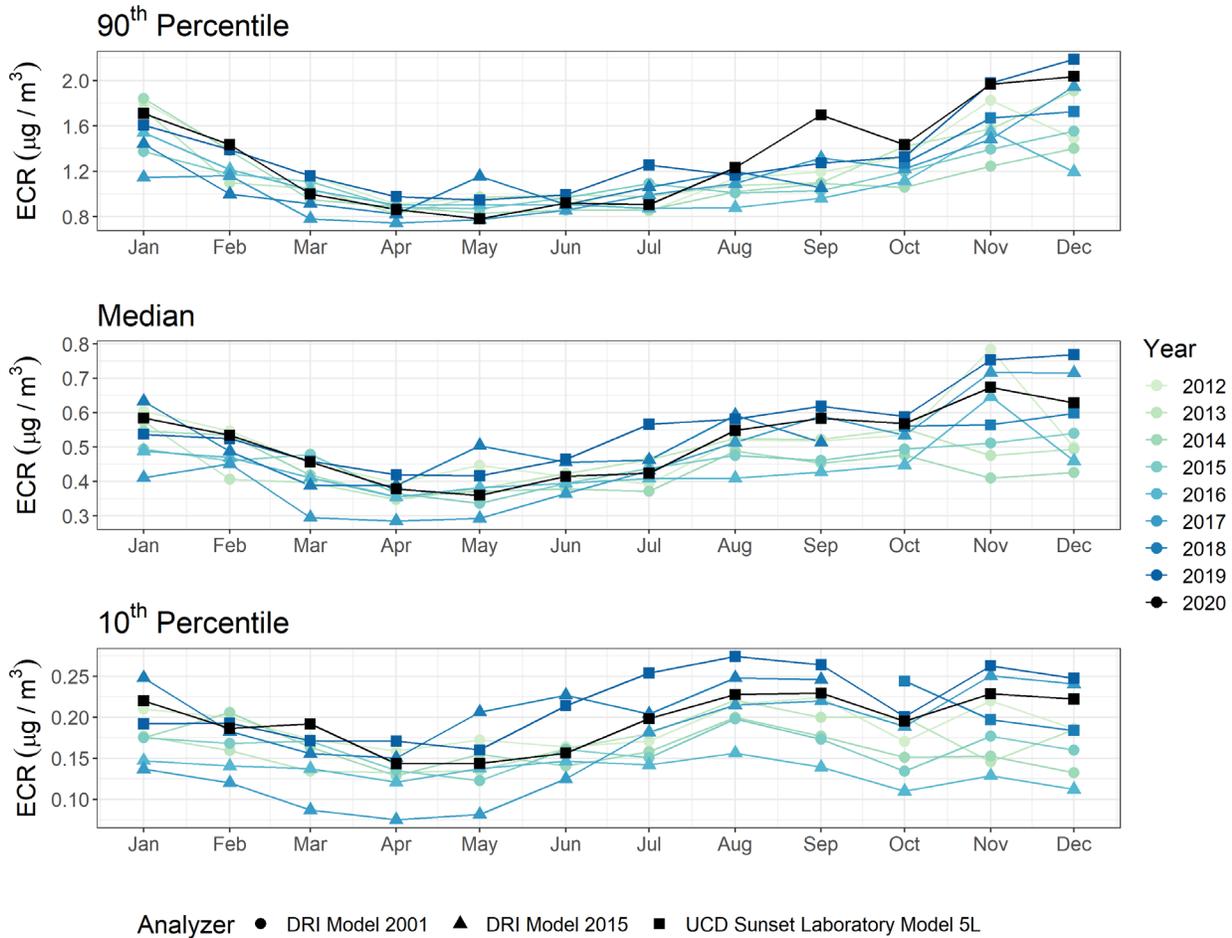


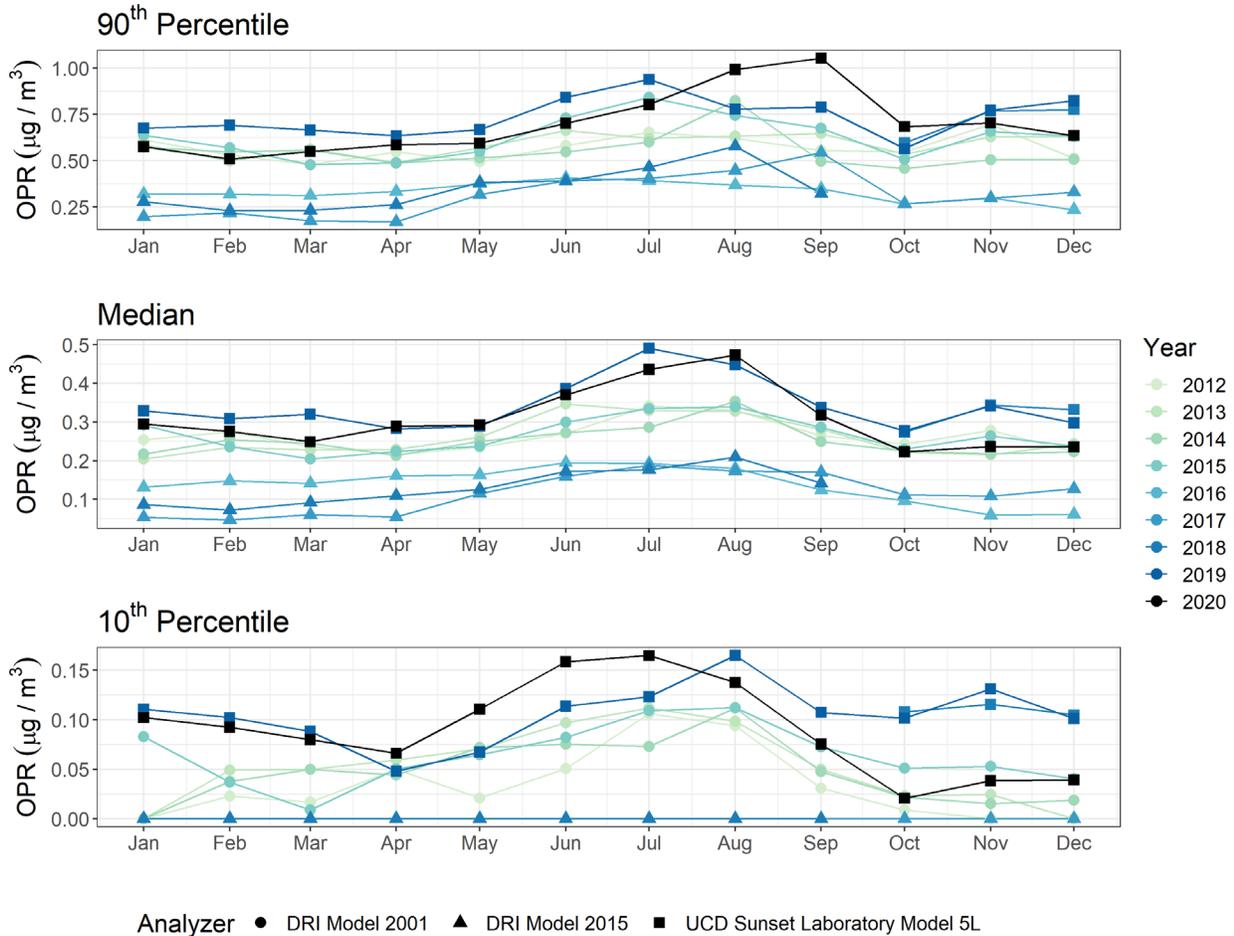
Figure 6.4-2: Multi-year time series of network-wide elemental carbon by reflectance concentrations (ECR; raw data without blank correction). Symbols denote laboratory and type of analyzer: DRI Model 2001 (circle), DRI Model 2015 (triangle), and UCD Sunset Laboratory Model 5L (square).



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

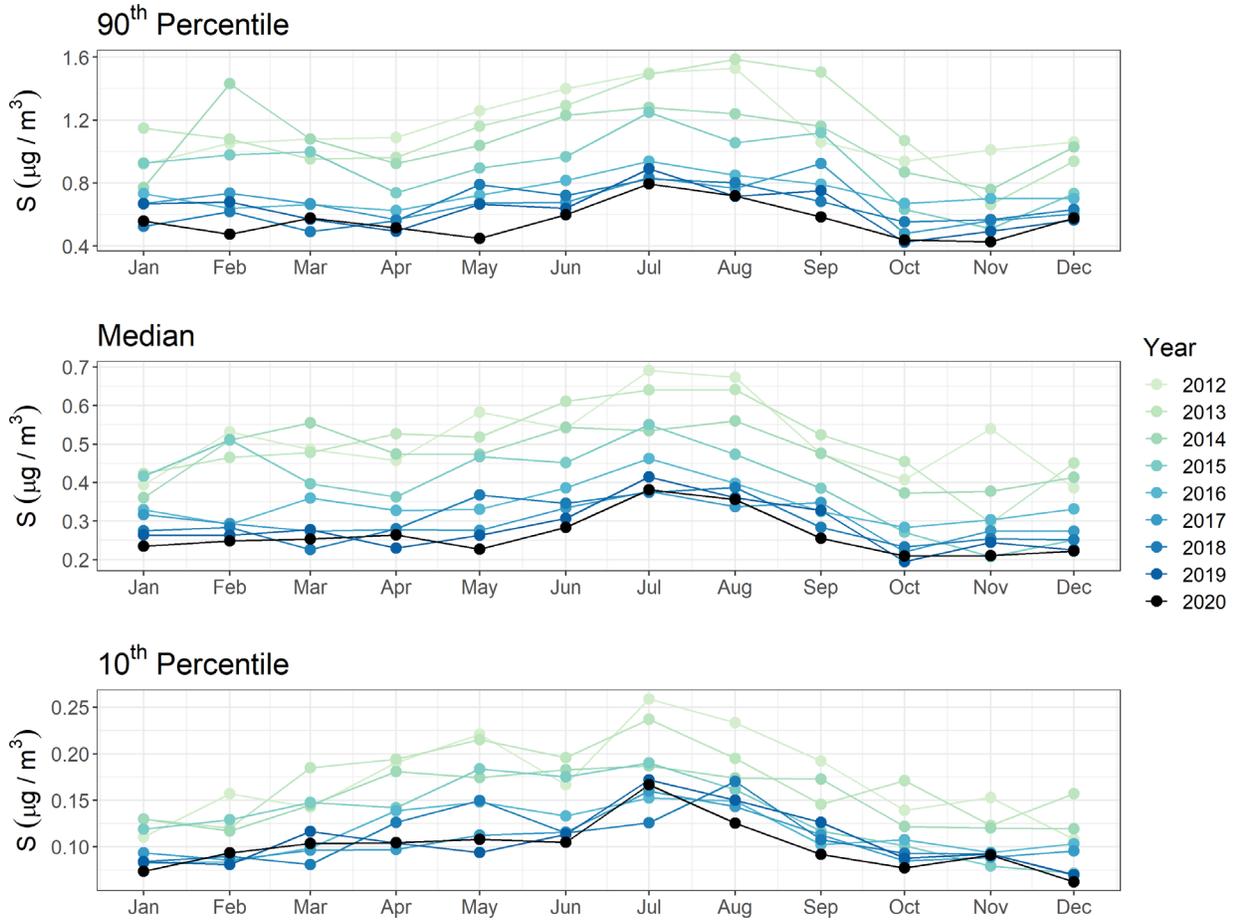
transition, see the Carbon Analyzer Change Data Advisory (available at <https://www.epa.gov/amtic/chemical-speciation-network-data-reporting-and-validation>).

Figure 6.4-3: Multi-year time series of network-wide organic pyrolyzed carbon by reflectance concentrations (OPR; raw data without blank correction). Symbols denote laboratory and type of analyzer: DRI Model 2001 (circle), DRI Model 2015 (triangle), and UCD Sunset Laboratory Model 5L (square).



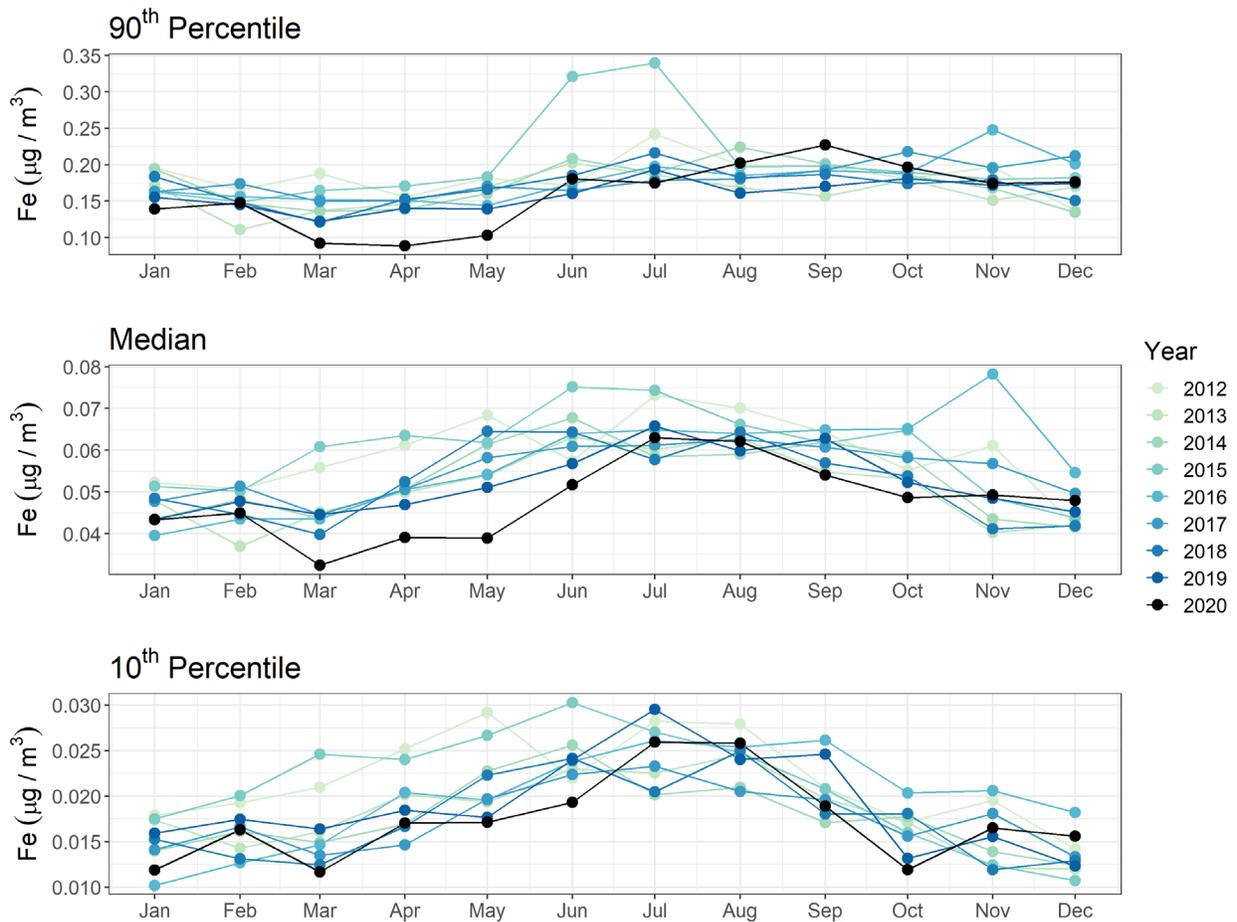
Similar to recent years, the 2020 sulfur concentrations generally continue to be low (Figure 6.4-4), with reduced seasonal variability.

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



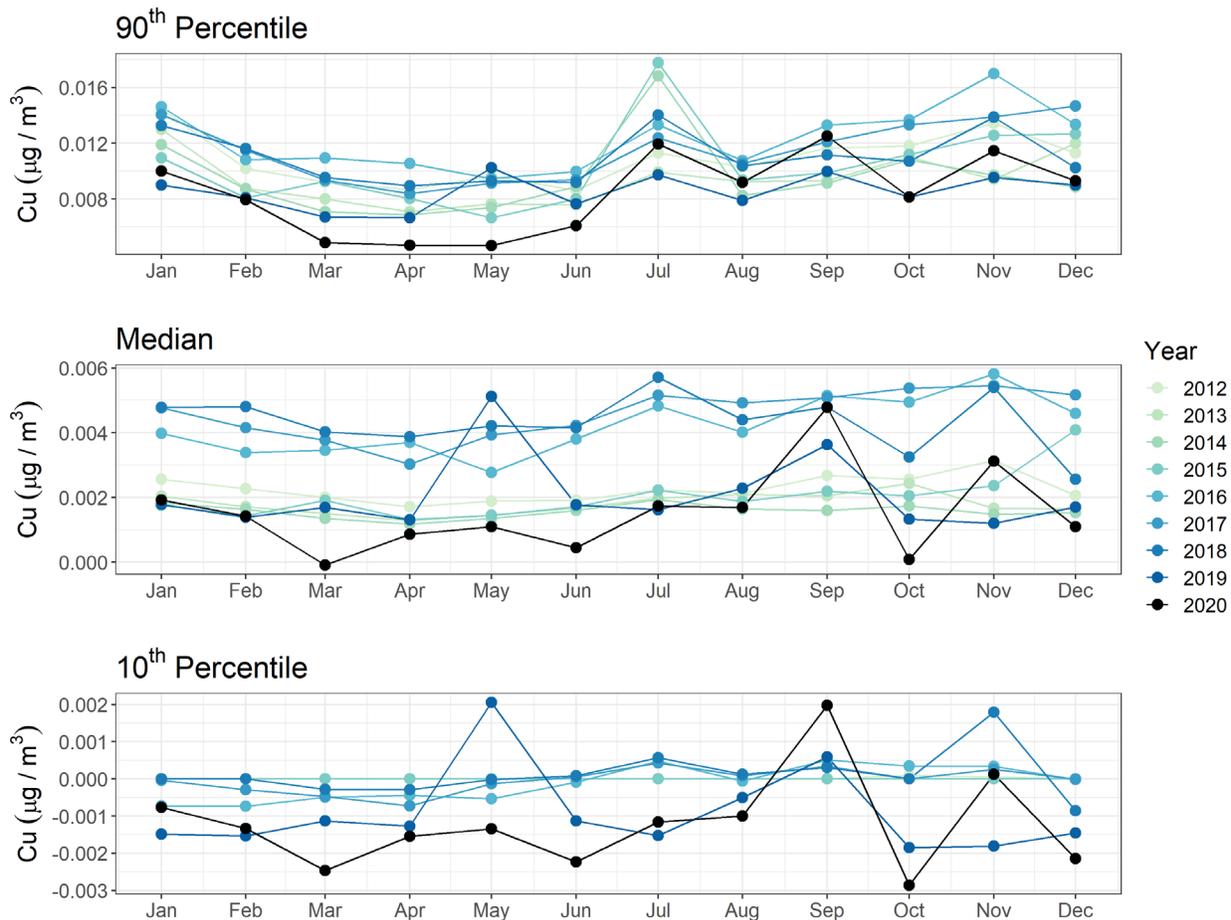
The 2020 iron concentrations are similar to previous years with the median peaking in the summer months (Figure 6.4-5). However, the median and 90th percentile concentrations are lower than previous years in March, April, and May. As described in Section 3.1.1.1, because of COVID-19 related site closures many samples from the second half of March 2020 were invalid and in April 2020 there was a decrease of nearly 25% in the number of filters collected compared to the number of expected samples. The closure of certain sites or reductions in human activity during this time may have resulted in the observed decreases in iron concentrations in spring 2020.

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



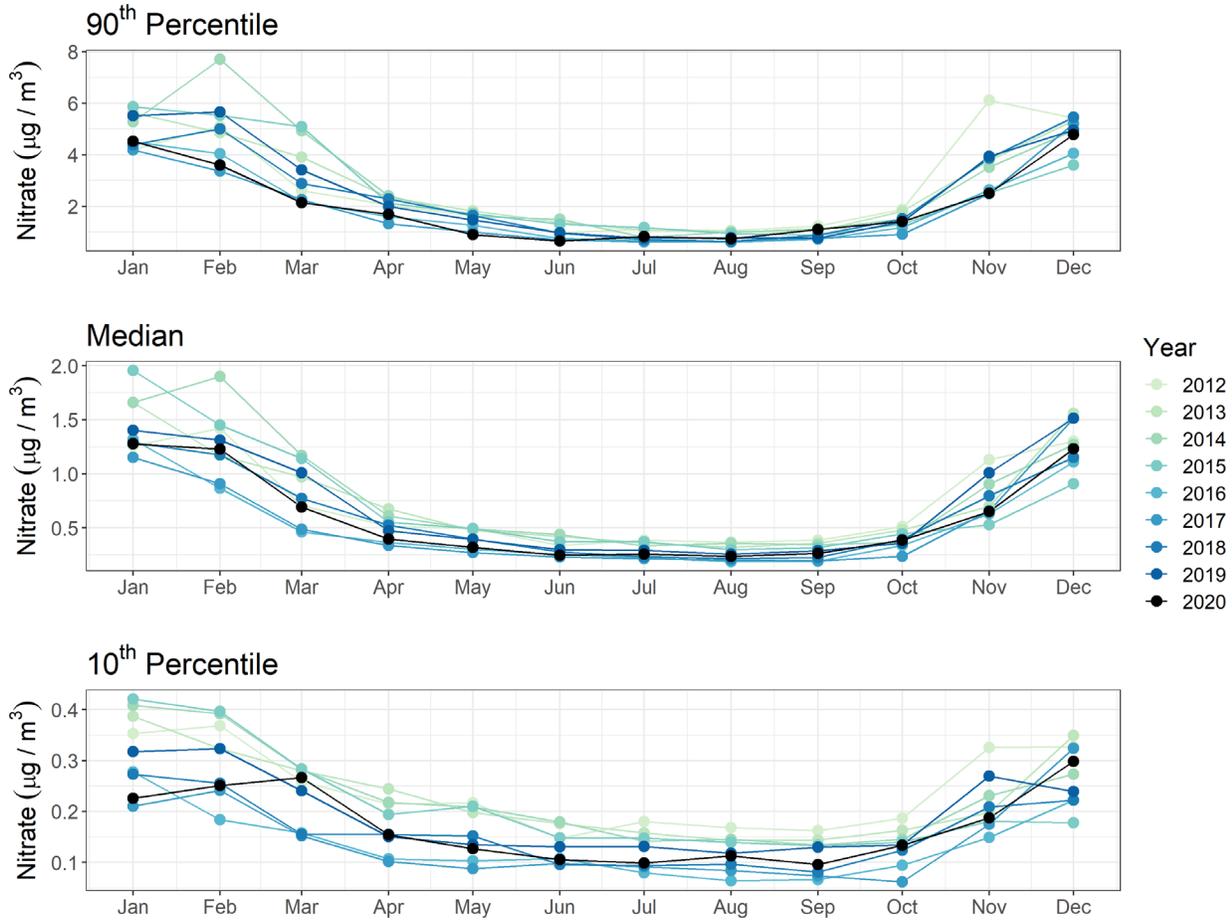
The median concentrations of copper exhibit two regimes with higher median concentrations observed in 2015-2018 and lower median concentrations in 2012-2015 and 2019-2020 (Figure 6.4-6). Between 2012 and November 2015, RTI performed XRF analysis. From November 2015 onward, UC Davis performs XRF analysis. In October 2018 the XRF analytical protocol for CSN samples changed, as documented in the XRF Protocol Change Data Advisory (available at <https://www.epa.gov/amtic/chemical-speciation-network-csn-data-reporting-and-validation-files>). The copper concentrations since the change in XRF analytical protocol are more comparable to those reported from the XRF instruments used by RTI, likely reflecting the lower detection limits achieved by the updated protocol.

Figure 6.4-6: Multi-year time series of network-wide copper (Cu) concentrations.



The 2020 nitrate concentrations continue to show strong seasonality with elevated winter concentrations (Figure 6.4-7).

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



As discussed in Section 3.2.4.3, UC Davis calculated and delivered composite variables for reconstructed mass (RCM) and soil back to January 1, 2018; beginning with data for samples collected June 1, 2019, data for these parameters are included with routine data deliveries to DART and AQS. The 2018, 2019, and 2020 RCM and soil results are shown in Figure 6.4-8 and 6.4-9, respectively.

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

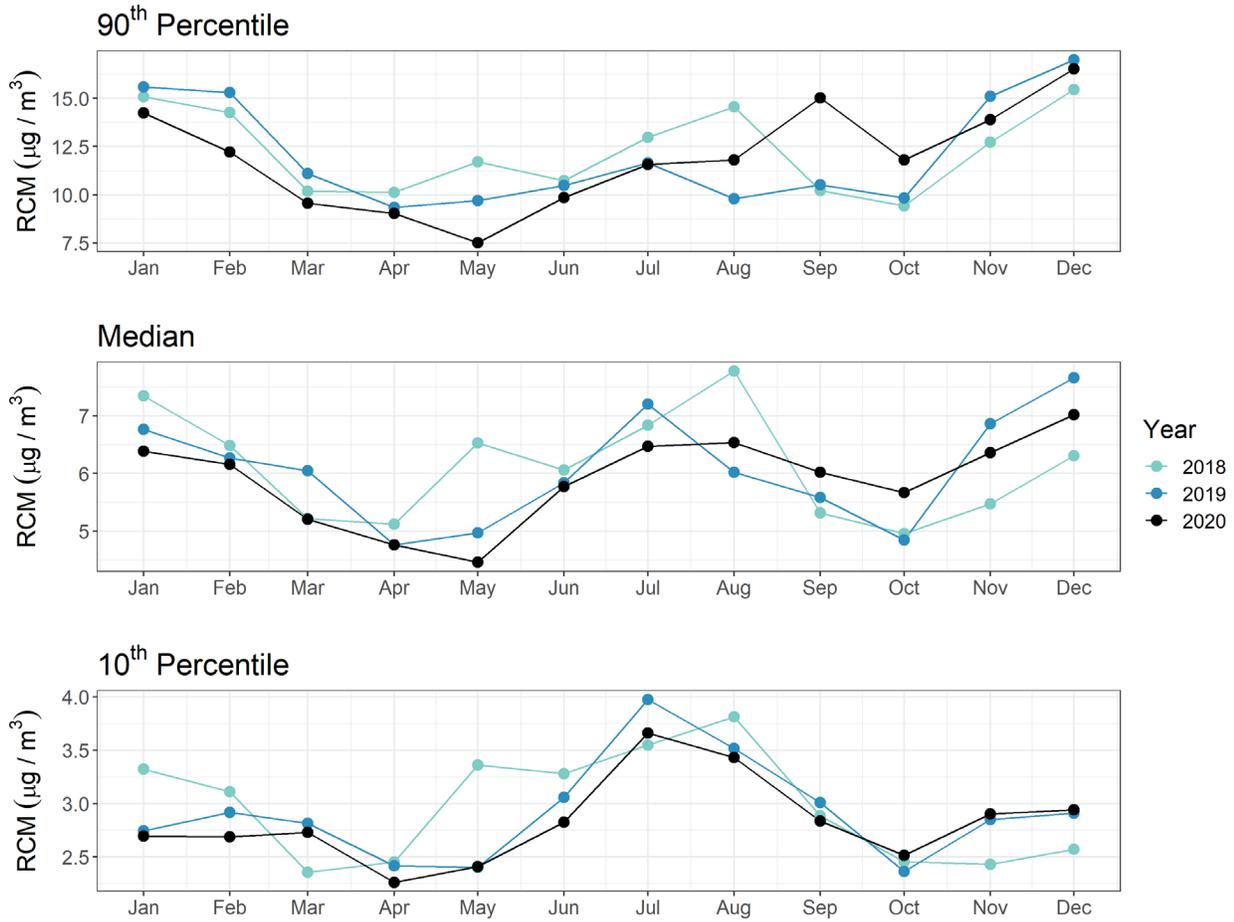
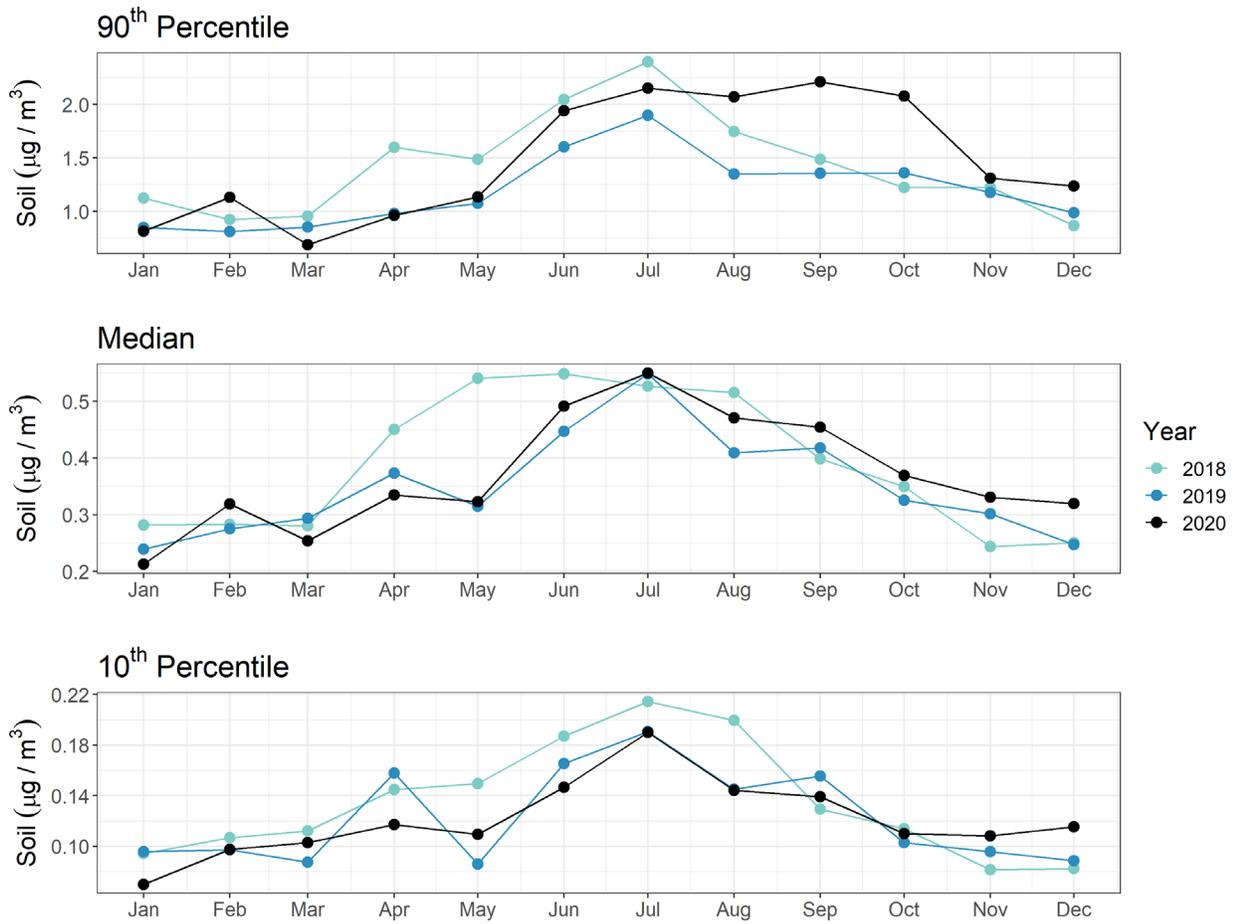


Figure 6.4-9: Multi-year time series of network-wide composite variable soil concentrations.



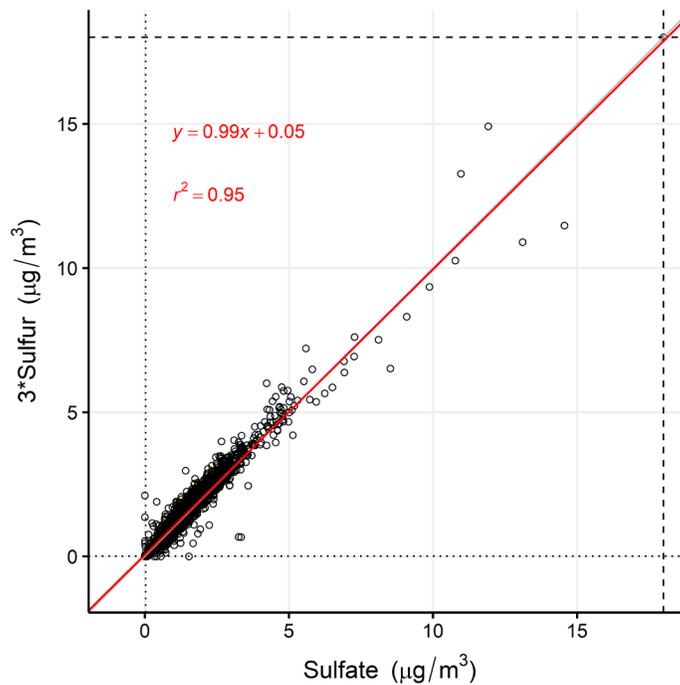
6.4.1.2 Comparisons Between Modules

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

Sulfur versus Sulfate

PTFE filters are analyzed for elemental sulfur using EDXRF, and nylon filters are analyzed for sulfate (SO_4) using IC. The molecular weight of SO_4 (96 g/mol) is three times the atomic weight of S (32 g/mol), so the concentration ratio $(3 \times \text{S})/\text{SO}_4$ should be one if all particulate sulfur is present as water-soluble sulfate. In practice, real measurements routinely yield a ratio greater than one, as was the case in 2018 and 2019 suggesting the presence of some sulfur in a non-water soluble form of sulfate or in a chemical compound other than sulfate. In 2020, there is good agreement between S and SO_4 (Figure 6.4-8).

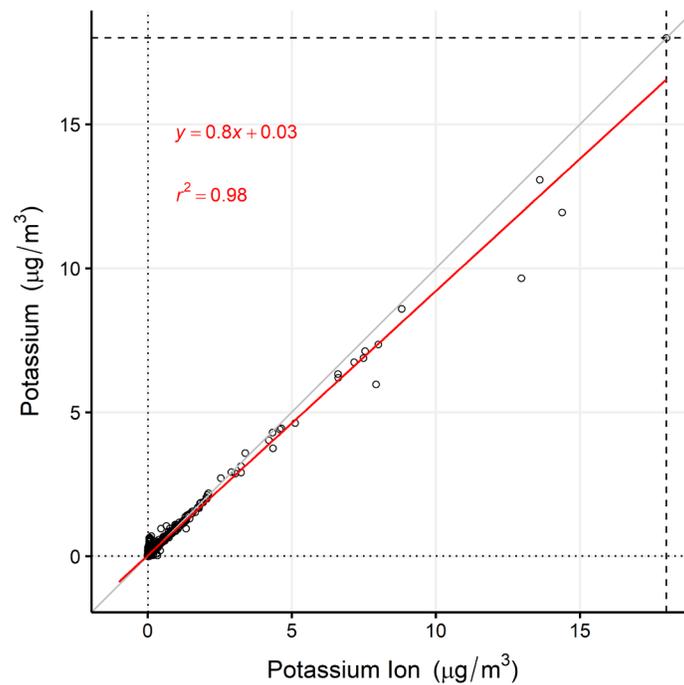
Figure 6.4-8: Scatter plot of $(3 \times \text{S})$ versus SO_4 , samples collected January 1, 2020 through December 31, 2020. Number of observations (complete pairs) is 11,669. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression. Outlier points that are off scale are plotted at the $18 \mu\text{g}/\text{m}^3$ boundaries shown by the dashed lines.



Potassium versus Potassium Ion

PTFE filters are analyzed for elemental potassium using EDXRF, and nylon filters are analyzed for potassium ion using IC. Similar to the S/SO₄ ratio relationship, the potassium/potassium ion ratio can be used to identify outliers as well as atmospherically unusual events. In a scenario where all the particulate potassium is present as water-soluble potassium ion, the potassium/potassium ion ratio is expected to be near one (Figure 6.4-9).

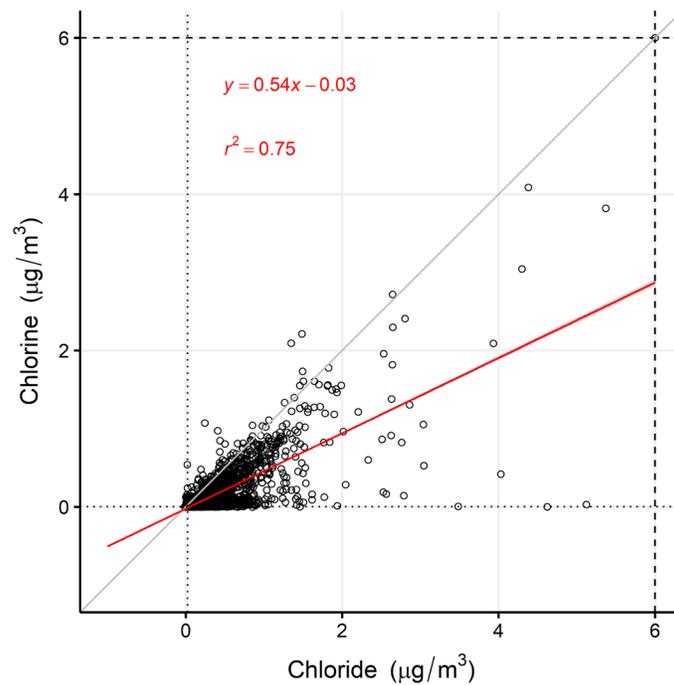
Figure 6.4-9: Scatter plot of potassium versus potassium ion, samples collected January 1, 2020 through December 31, 2020. Number of observations (complete pairs) is 11,669. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression. Outlier points that are off scale are plotted at the 18 $\mu\text{g}/\text{m}^3$ boundaries shown by the dashed lines.



Chlorine versus Chloride

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

Figure 6.4-10: Scatter plot of chlorine versus chloride ion, samples collected January 1, 2020 through December 31, 2020. Number of observations (complete pairs) is 11,669. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression. Outlier points that are off scale are plotted at the 6 $\mu\text{g}/\text{m}^3$ boundaries shown by the dashed lines.



PM_{2.5} versus Reconstructed Mass (RCM)

Gravimetric data are compared to composite variable reconstructed mass (RCM), where the RCM composite variable is estimated from chemical speciation measurements, to test many different aspects of overall data quality. The formulas used to estimate the mass contributions from various chemical species are detailed in *UCD CSN TI 801B*. In the simple case where valid measurements are available for all needed variables, reconstructed mass is the following sum:

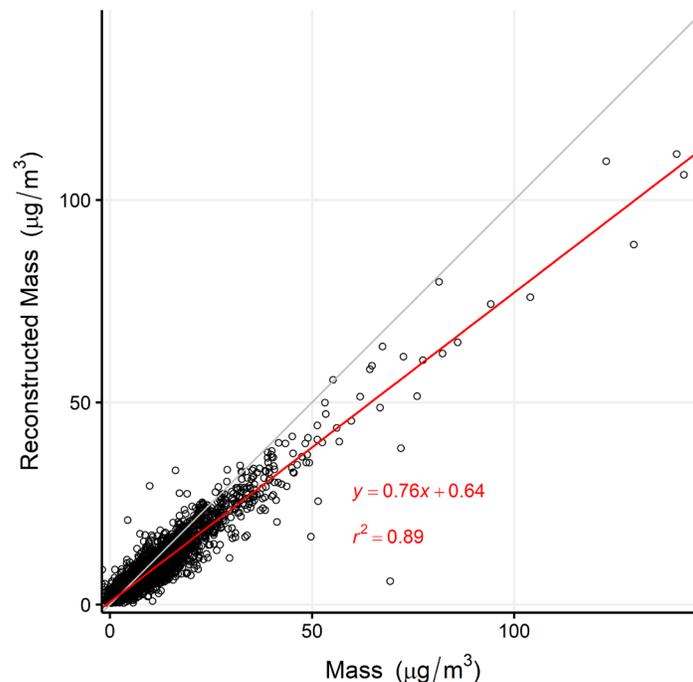
$$\text{RCM} = (4.125 \times \text{S}) + (1.29 \times \text{NO}_3^-) + (1.4 \times \text{OC}) + (\text{EC}) + \\ (2.2 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} + 2.42 \times \text{Fe} + 1.94 \times \text{Ti}) + (1.8 \times \text{chloride})$$

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

Gravimetric analysis is not routinely performed using CSN filters. Thus, for comparison purposes 24-hour average gravimetric PM_{2.5} mass data from AirNow Tech is used as part of the validation process in DART. The data provided by AirNow Tech is not final, so the data used here is a snapshot, downloaded at the time the plots were generated.

If the RCM completely captures and accurately estimates the different mass components, the RCM to AirNow Tech mass ratio is expected to be near one. The RCM and AirNow Tech mass generally correlate (Figure 6.4-11), but RCM tends to underestimate AirNow Tech mass.

Figure 6.4-11: Scatter plot of reconstructed mass (RCM) versus AirNow Tech PM_{2.5} mass data (Mass), samples collected January 1, 2020 through December 31, 2020. Number of observations (complete pairs) is 8,443. Solid gray line indicates 1:1. Solid red line indicates regression.



6.5 Uncertainty Estimates and Collocated Precision Summary Statistics

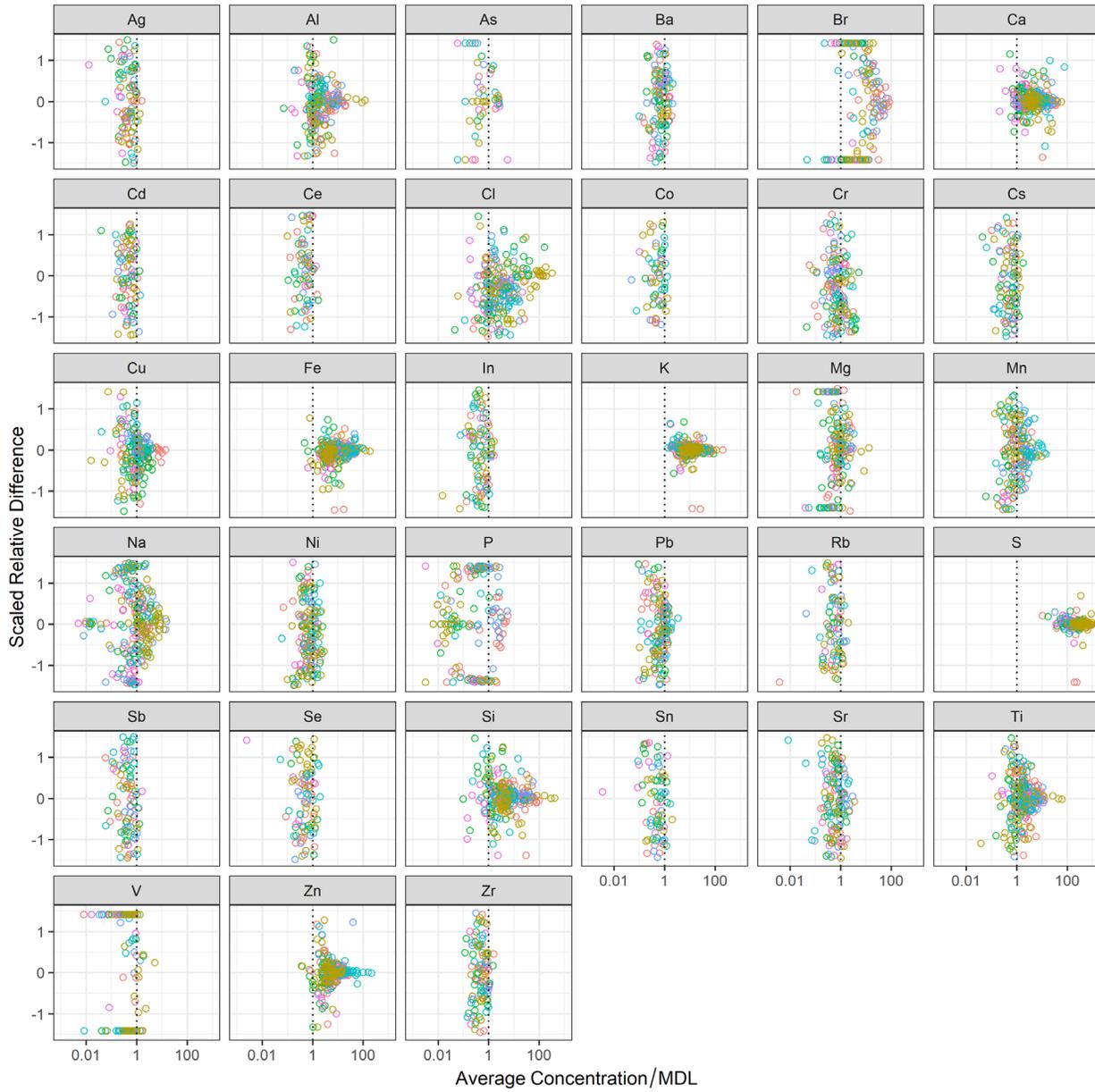
Several network sites are equipped with collocated samplers, where simultaneous samples are collected on independent samplers and analyzed using the same analytical protocols. Differences between the resulting data provide a measure of the total uncertainty associated with filter substrates, sampling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

Scaled relative difference between sample pairs collected at CSN collocated sites is calculated as shown in Equation 6.5-1 and used to evaluate collocated precision (Figure 6.5.1, elements; Figure 6.5-2, ions; Figure 6.5-3, carbon).

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

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

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



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

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

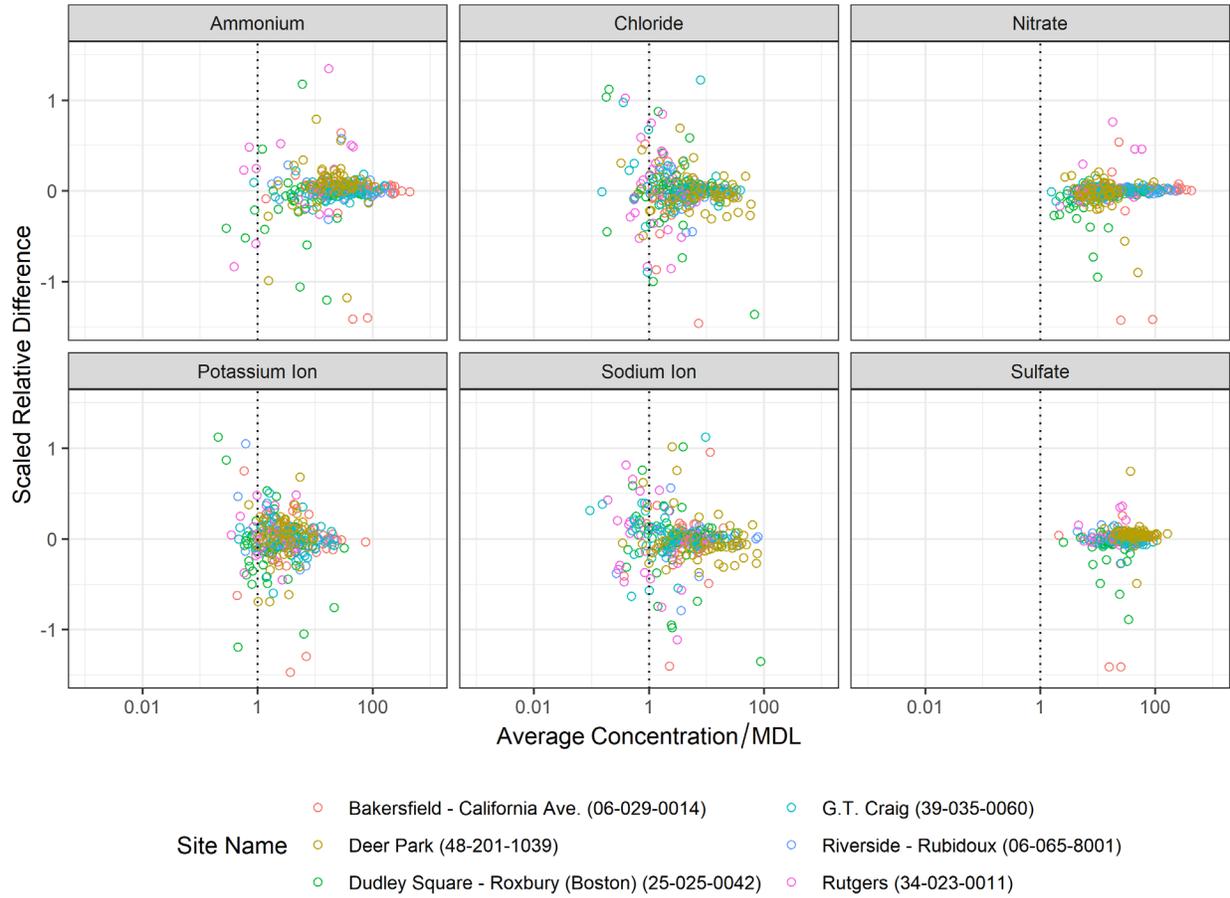
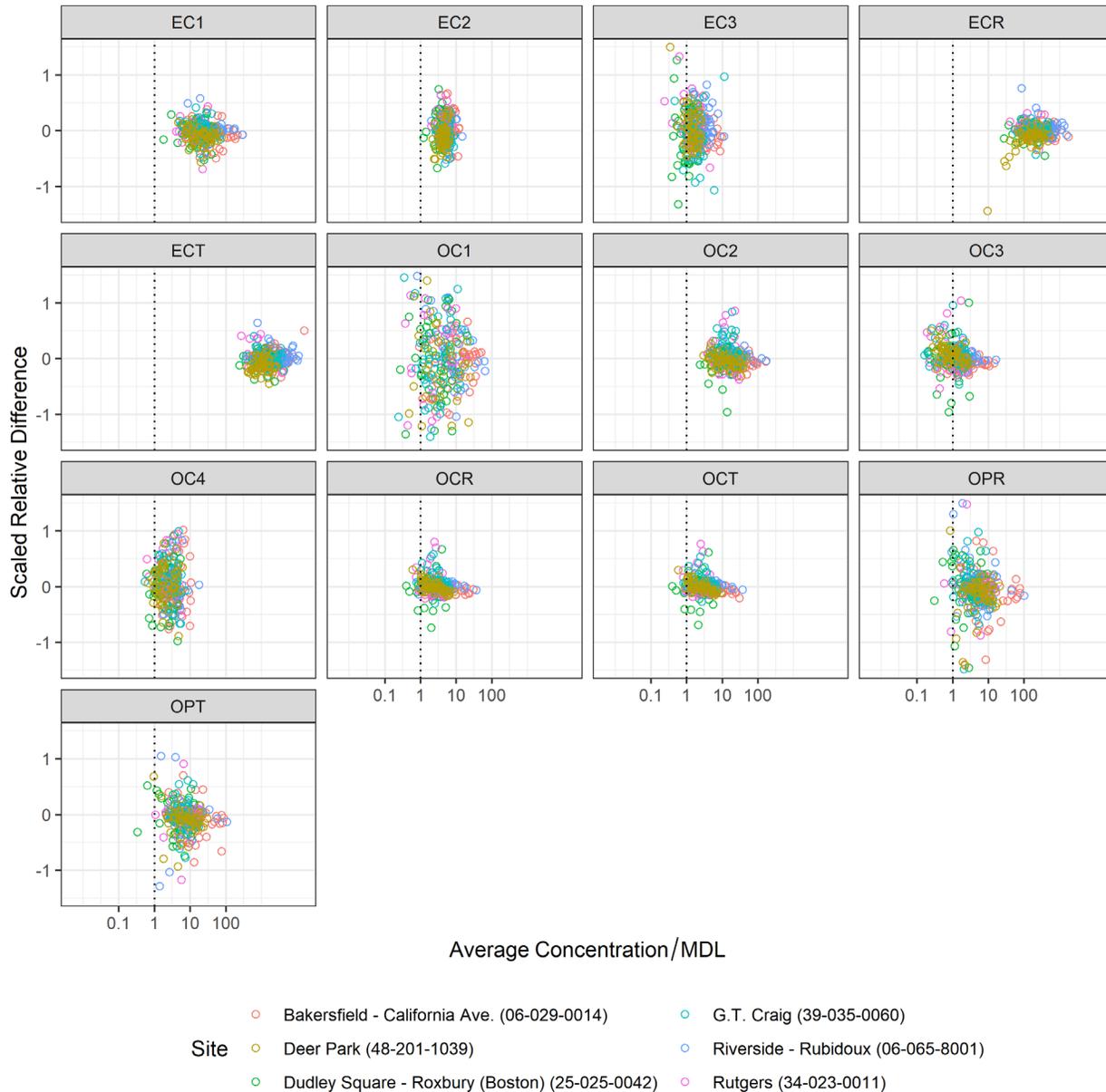


Figure 6.5-3: Scaled relative differences for carbon measurements at sites with collocated samplers across the network (January 1, 2020 through December 31, 2020). Dotted vertical lines indicate MDL. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated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



Collocated precision is reported for CSN data as fractional uncertainty. Fractional uncertainty is calculated from scaled relative differences (Equation 6.5-1) between sample pairs collected at CSN collocated sites, using the subset of observations with concentrations at least three times the MDL. Beginning with samples collected January 1, 2019 through December 31, 2019, fractional uncertainty is updated annually and calculated using collocated data from the previous two years. For this reporting period (samples collected January 1, 2020 through December 31, 2020) the

fractional uncertainty is calculated from sample pairs collected at CSN collocated sites June 1, 2017 through May 31, 2019, with a minimum of 60 collocated pairs. For cases where the total number of valid collocated pairs over the two-year period is less than 60, a value of 0.25 is adopted as the fractional uncertainty. The calculation for fractional uncertainty is documented in *UCD CSN TI 801B*, and summarized in Equation 6.5-1 and Equation 6.5-2.

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

Table 6.5-1 (elements), Table 6.5-2 (ions), and Table 6.5-3 (carbon) list fractional uncertainties calculated for this reporting period. Since many species are routinely measured at or below the MDL, there are numerous instances where a fractional uncertainty of 0.25 is assigned.

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

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

Where f is fractional uncertainty and C is ambient concentration.

The network measurement quality objectives (MQOs) are based on the coefficient of variation (CV) between collocated measurements, and are defined as CV of 10% for ions, 20% for elements, and 15% for total carbon.

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

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

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

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

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

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

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

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

Table 6.5-1 (elements), Table 6.5-2 (ions), and Table 6.5-3 (carbon) list median CV calculated using Equations 6.5-4 and 6.5-5 from collocated samples collected during 2020 (current reporting period) as well as 2019 (previous reporting period). The CFR CV calculated using Equations 6.5-4 and 6.5-6 from collocated samples collected during 2020 (current reporting period) is also included.

Table 6.5-1: Fractional uncertainty (f), median coefficient of variation (CV), and CFR coefficient of variation for element species. For the previous reporting period, f is calculated from samples collected June 1, 2016 through May 31, 2018 and applied to samples between January 1, 2019 through December 31, 2019 and CV is calculated from samples collected January 1, 2019 through December 31, 2019. For the current reporting period, f is calculated from samples collected June 1, 2017 through May 31, 2019 and applied to samples between January 1, 2020 through December 31, 2020 and CV is calculated from samples collected January 1, 2020 through December 31, 2020. For both reporting periods, f and CV values are not calculated for species with less than 60 collocated pairs with concentrations at least three times the MDL.

Species	2019 (previous reporting period)				2020 (current reporting period)					
	Fractional Uncertainty (%)	Pairs	Median Coefficient of Variation (%)	Pairs	Fractional Uncertainty (%)	Pairs	Median Coefficient of Variation (%)	Pairs	CFR Coefficient of Variation (%)	Pairs
Na	18.5	67	---	33	17.6	68	---	25	---	25
Mg	---	6	---	4	---	10	---	4	---	4
Al	13.2	79	---	36	15.3	91	---	58	---	58
Si	14.1	326	9.1	156	14.2	329	9.8	170	24.6	170
P	---	10	---	0	---	7	---	15	---	15
S	5.6	633	3.6	346	5.7	654	3.0	292	8.7	292
Cl	36.4	166	19.4	76	35.1	179	25.5	85	43.3	85
K	8.1	476	5.0	301	8.4	567	5.0	271	10.8	271
Ca	11.5	128	8.3	195	13.4	263	6.9	174	23.8	174
Ti	18.0	97	---	40	15.5	98	8.0	62	16.6	62
V	---	0	---	0	---	0	---	1	---	1
Cr	---	3	---	0	---	1	---	0	---	0
Mn	---	9	---	5	---	16	---	19	---	19
Fe	14.4	305	5.8	183	13.2	328	6.1	237	16.6	237
Co	---	0	---	0	---	0	---	0	---	0
Ni	---	1	---	0	---	0	---	0	---	0
Cu	---	12	---	0	---	6	---	17	---	17

Zn	11.0	244	5.9	127	9.8	245	6.2	223	16.7	223
As	---	0	---	0	---	0	---	0	---	0
Se	---	0	---	0	---	0	---	0	---	0
Br	---	1	---	0	---	1	35.6	70	57.6	70
Rb	---	0	---	0	---	0	---	0	---	0
Sr	---	1	---	0	---	0	---	1	---	1
Zr	---	0	---	0	---	0	---	0	---	0
Ag	---	0	---	0	---	0	---	0	---	0
Cd	---	0	---	0	---	0	---	0	---	0
In	---	0	---	0	---	0	---	0	---	0
Sn	---	0	---	0	---	0	---	0	---	0
Sb	---	0	---	0	---	0	---	0	---	0
Cs	---	0	---	0	---	0	---	0	---	0
Ba	---	1	---	0	---	0	---	0	---	0
Ce	---	0	---	0	---	0	---	0	---	0
Pb	---	0	---	0	---	0	---	0	---	0

Table 6.5-2: Fractional uncertainty (f), median coefficient of variation (CV), and CFR coefficient of variation for ion species. For the previous reporting period, f is calculated from samples collected June 1, 2016 through May 31, 2018 and applied to samples between January 1, 2019 through December 31, 2019 and CV is calculated from samples collected January 1, 2019 through December 31, 2019. For the current reporting period, f is calculated from samples collected June 1, 2017 through May 31, 2019 and applied to samples between January 1, 2020 through December 31, 2020 and CV is calculated from samples collected January 1, 2020 through December 31, 2020. For both reporting periods, f and CV values are not calculated for species with less than 60 collocated pairs with concentrations at least three times the MDL.

Species	2019 (previous reporting period)				2020 (current reporting period)					
	Fractional Uncertainty (%)	Pairs	Median Coefficient of Variation (%)	Pairs	Fractional Uncertainty (%)	Pairs	Median Coefficient of Variation (%)	Pairs	CFR Coefficient of Variation (%)	Pairs
Ammonium	20.9	486	6.2	336	15.9	591	4.6	263	14.0	263
Chloride*	12.2	232	5.8	253	11.4	403	5.4	173	17.5	173
Nitrate	10.8	581	3.1	337	7.9	628	3.1	284	13.4	284
Potassium Ion	17.9	174	---	5	---	11	7.7	126	16.8	126
Sodium Ion	16.3	317	7.2	241	14.1	411	5.0	163	19.2	163
Sulfate	8.5	612	2.6	347	5.8	654	2.9	292	11.2	292

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

Table 6.5-3: Fractional uncertainty (f), median coefficient of variation (CV), and CFR coefficient of variation for carbon species. For the previous reporting period, f is calculated from samples collected June 1, 2016 through May 31, 2018 and applied to samples between January 1, 2019 through December 31, 2019 and CV is calculated from samples collected January 1, 2019 through December 31, 2019. For the current reporting period, f is calculated from samples collected June 1, 2017 through May 31, 2019 and applied to samples between January 1, 2020 through December 31, 2020 and CV is calculated from samples collected January 1, 2020 through December 31, 2020. For both reporting periods, f and CV values are not calculated for species with less than 60 collocated pairs with concentrations at least three times the MDL. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).

Species	2019 (previous reporting period)				2020 (current reporting period)					
	Fractional Uncertainty (%)	Pairs	Median Coefficient of Variation (%)	Pairs	Fractional Uncertainty (%)	Pairs	Median Coefficient of Variation (%)	Pairs	CFR Coefficient of Variation (%)	Pairs
Elemental Carbon (EC1)	15.2	595	5.4	335	12.1	653	7.9	292	17.7	292
Elemental Carbon (EC2)	32.0	380	14.5	304	27.4	509	13.1	243	22.7	243
Elemental Carbon (EC3)	---	0	15.5	63	---	18	---	32	---	32
Elemental Carbon (ECR)	16.9	591	7.1	336	13.5	650	6.5	293	14.3	293
Elemental Carbon (ECT)	18.3	587	7.4	336	15.4	649	8.0	294	15.6	294
Organic Carbon (OC1)	33.5	357	21.7	131	32.5	399	24.1	124	40.5	124
Organic Carbon (OC2)	12.5	577	8.2	326	11.6	643	7.9	286	18.5	286
Organic Carbon (OC3)	15.1	530	7.3	162	12.2	530	---	34	---	34
Organic Carbon (OC4)	19.4	584	---	41	19.1	461	12.7	101	27.5	101
Organic Carbon (OCR)	10.3	580	5.5	265	8.5	614	5.7	141	8.8	141

Organic Carbon (OCT)	9.4	580	4.5	272	7.4	619	4.9	154	8.1	154
Organic Pyrolyzed (OPR)	37.7	291	10.0	255	23.7	421	15.7	183	24.3	183
Organic Pyrolyzed (OPT)	25.4	529	7.6	301	20.1	597	9.6	238	21.5	238

7. References

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