

Chemical Speciation Network (CSN)

Annual Quality Report

Samples Collected January 1, 2017 through December 31, 2017

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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 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 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: analyzed at UC Davis using energy dispersive X-ray fluorescence (EDXRF) for a suite of 33 elements.
- Nylon filters: analyzed at the Desert Research Institute (DRI) using ion chromatography (IC) for a suite of six ions.
- Quartz filters: analyzed at the Desert Research Institute (DRI) 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, 2017 through December 31, 2017.

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 (DRI Ion Analysis Laboratory), Section 4.2 (UC Davis X-Ray Fluorescence Laboratory), and Section 4.3 (DRI 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 96.3% for PTFE filters, 96.2% for nylon filters, and 93.1% for quartz filters. As detailed in Section 3.1.1, there were nine sites with less than 75% completeness.

No Technical Systems Audit (TSA) of UC Davis was performed by the EPA in 2017.

2. Summary of Laboratory Operation Issues

2.1 DRI Ion Analysis Laboratory

2.1.1 Analysis Delays

Deliveries of analysis data from DRI to UC Davis were delayed, contributing to noncompliance with 120 days requirement for delivery of data to AQS following receipt of filters by analytical laboratories. See Section 5.1.

2.2 UC Davis X-Ray Fluorescence Laboratory

2.2.1 Vanadium

During a portion of this reporting period XRF analyses of vanadium were overestimated by about 30%. Results from an inter-laboratory comparison, confirmed by further comparison with ICP-MS analysis, revealed that vanadium calibrations based on commercial standards for samples collected from January 2017 through October 2017 resulted in erroneously high measurements. XRF calibrations performed in January 2018 utilized newly purchased, re-certified, and UCD-produced vanadium standards thus eliminating the overestimation beginning with samples collected November 2017.

For further detail and corrective actions see Section 3.2.1.1.

2.2.2 Zinc

For analyses performed during this reporting period, periodic zinc contamination was observed on the daily QC laboratory blank and daily QC multi-elemental reference sample on the EDXRF instruments, XRF-1 and XRF-4. The cause of these random contamination events was determined to be related to the instrument design, specifically operation of the sample changer. Samples analyzed during this period were checked for unusually high zinc mass loadings compared to site specific and network wide historical values. Ten samples in 2017 with unusual Zn mass loadings were reanalyzed and for cases where the original result had contamination the reanalysis results were reported.

For further detail see Sections 3.2.1.3 and Section 4.2.2.1.

2.2.3 Calcium

During this reporting period, both XRF-1 and XRF-4 showed gradual increase in calcium mass loadings of their QC samples. The calcium buildup is likely caused by atmospheric deposition or instrument wear on these filters, which are analyzed daily and remain in the instruments' sample changers indefinitely. This gradual buildup of calcium is not expected on actual samples which are loaded and analyzed once. However, samples are monitored for unusually high calcium values and reanalyzed as necessary.

For further detail see Section 3.2.1.2 and Section 4.2.2.1.

2.2.4 Trace Element MDLs

Quantification of trace elements is an ongoing challenge using EDXRF. In some cases, for example in the case of lead (Pb), the MDL increased corresponding with the November 2015 contract transition, due in part to analytical method changes. UC Davis is exploring ways to

optimize the XRF application, including the potential for utilizing alternative secondary targets, in an effort to improve MDLs for trace elements.

2.3 DRI Thermal/Optical Analysis Laboratory

2.3.1 Analysis Delays

Deliveries of analysis data from DRI to UC Davis were delayed, contributing to noncompliance with 120 days requirement for delivery of data to AQS following receipt of filters by analytical laboratories. See Section 5.1.

2.3.2 QC Criteria Failures

In some cases, DRI analyzed samples while instruments were operating outside of the defined QC criteria. There were instances of impacted data for samples collected during 2017.

Per direction from the EPA, these data were redelivered to AQS with QX (Does Not Meet QC Criteria) qualifier flag applied.

For further detail see Section 3.2.3.1 and Section 4.3.2.

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). 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. Quartz filters flagged with the QX qualifier, as detailed in Section 2.3.2, were not invalidated and are included in the count of valid samples.

Table 3.1-1: Network sample completeness by filter type, January 2017 through December 2017. 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 # collected samples)	% Valid (relative to # of scheduled samples)
PTFE	13,329	13,336	12,844	492	96.3	96.4
Nylon	13,329	13,336	12,828	508	96.2	96.2
Quartz	13,329	13,320	12,398	922	93.1	93.0

Across the network there were nine sites with sample completeness less than 75% for at least one filter type (Table 3.1-2). Seven of the nine cases had low completeness resulting from invalid quartz filters.

Table 3.1-2: Network sites with less than 75% sample completeness (relative to the number of collected samples) for at least one filter type, January 2017 through December 2017. 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
12-011-0034-5 (Region 4)	Broward County, FL (NCore/STN)	65.6	58.2	54.9	BA (79%) Other (21%)	BA (63%) AN (16%) Other (21%)	BA (64%) AN (27%) Other (9%)
37-067-0022-5 (Region 4)	Winston-Salem, NC	95.1	95.1	57.3	AL (67%) AV (33%)	AL (67%) AV (33%)	AN (58%) AH (23%) Other (19%)
72-021-0010-5 (Region 2)	Bayamon, Puerto Rico (NCore/STN)	87.9	86.8	59.3	BI (36%) AF (27%) Other (37%)	BI (33%) AF (25%) Other (42%)	AH (59%) AN (11%) Other (30%)
44-007-1010-5 (Region 1)	East Providence, RI (NCore/STN)	96.7	97.5	64.2	AB (25%) AG (25%) AH (25%) AJ (25%)	AB (33%) AG (33%) AH (33%)	AN (39%) AH (36%) Other (25%)
45-079-0007-5 (Region 4)	Parklane, SC (NCore/STN)	95.9	95.9	67.2	AF (60%) AH (20%) AO (20%)	AF (60%) AH (20%) AO (20%)	AN (55%) AH (25%) Other (20%)
39-153-0023-5 (Region 5)	Akron, OH	67.9	77.4	88.9	AN (29%) BA (18%) BJ (18%) Other (35%)	BA (25%) BJ (25%) Other (50%)	BJ (50%) Other (50%)
53-077-0009-5 (Region 10)	Yakima, WA	100	100	70.5	---	---	AH (67%) AN (33%)
30-093-0005-5 (Region 8)	Butte, MT	95.1	98.4	72.1	AQ (67%) BJ (33%)	BJ (100%)	AN (59%) AH (24%) Other (17%)
08-031-0026-5 (Region 8)	La Casa, CO (NCore/STN)	73.8	75.4	88.5	AV (84%) Other (16%)	AV (90%) AQ (7%) AP (3%)	AN (57%) AV (21%) Other (22%)

Samples can be invalidated for a variety of reasons as detailed in the *UCD CSN TI 801C: CSN Data Validation* 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 to SASS and URG samples from January 2017 through December 2017. Codes are ordered by frequency of occurrence.

Null Code	SASS PTFE	SASS Nylon	URG Quartz	Null Code Description
AP	1	1	0	Vandalism
TS	1	1	0	Holding time or transport temperature is out of specs
AZ	1	1	1	QC Audit
BE	1	1	1	Building/site repair
DA	0	0	1	Aberrant data (corrupt files, aberrant chromatography, spikes, shifts)
AK	0	0	2	Filter leak
AM	1	1	4	Miscellaneous void
BB	6	6	5	Unable to reach site
SA	5	5	5	Storm approaching
AL	5	5	7	Voided by operator
AR	8	6	7	Lab error
AC	9	9	8	Construction/repairs in area
AI	2	2	8	Insufficient data (cannot calculate)
AQ	14	15	8	Collection error
AJ	12	6	10	Filter damage
BI	10	10	11	Lost or damaged in transit
AO	12	12	12	Bad weather
SV	6	7	16	Sample volume out of limits
AG	9	9	21	Sample time out of limits
AB	33	33	35	Technician unavailable
BJ	44	39	39	Operator error
BA	44	43	53	Maintenance/routine repairs
AV	97	97	65	Power failure
AF*	71	72	119	Scheduled but not collected
AH	40	53	221	Sample flow rate or CV out of limits
AN	112	126	341	Machine malfunction

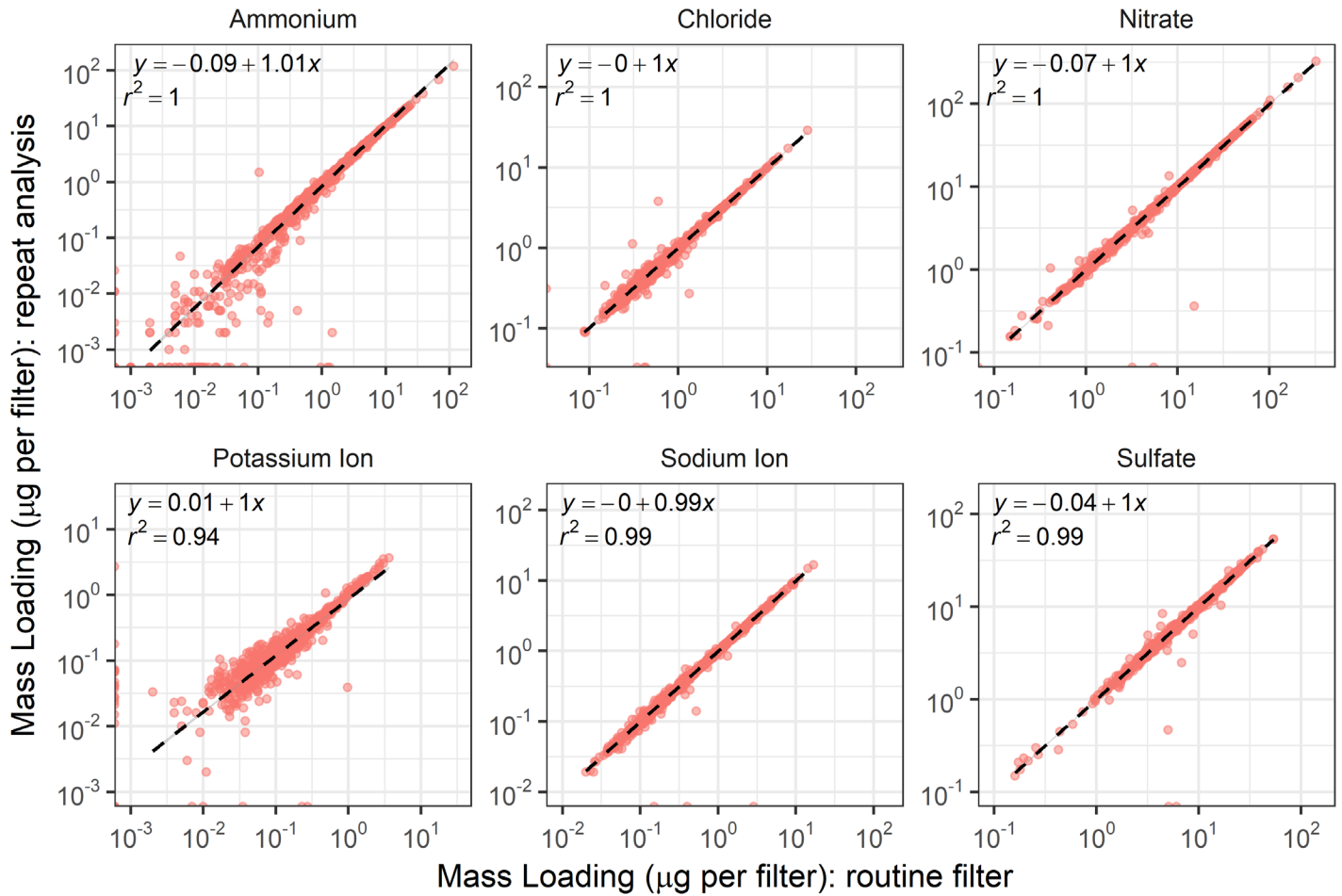
* Filters that receive this flag were intended for sampling and shipped to the site, but were not sampled.

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 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.

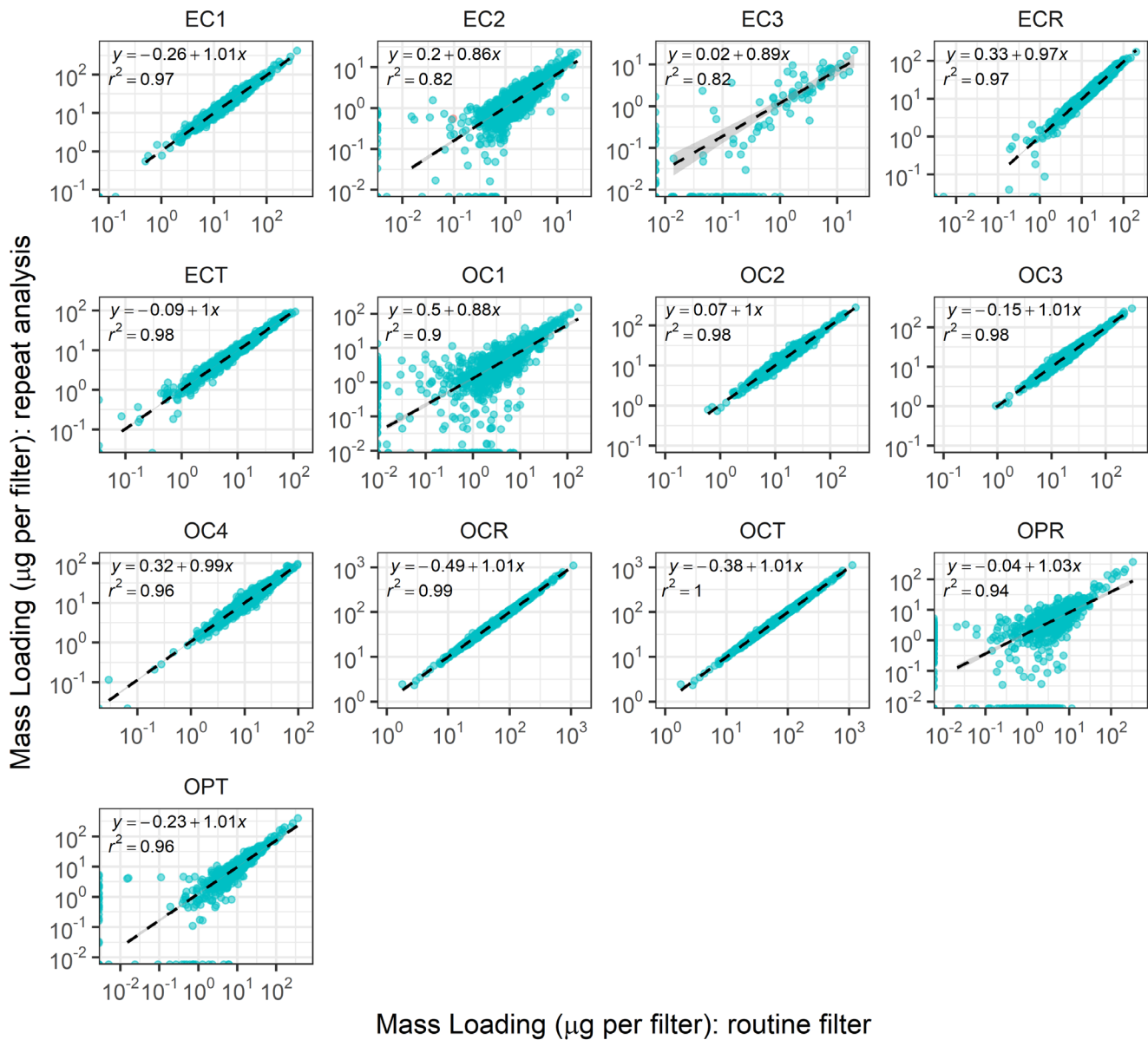
Comparisons of ion mass loadings from repeat analyses (replicates and/or duplicates) on nylon filters analyzed by IC show generally good agreement (Figure 3.1-1).

Figure 3.1-1: Ion repeat analysis (replicates and/or duplicates) results; data from samples collected during 2017.



Comparison of carbon mass loadings from repeat analyses (replicates and/or duplicates) on quartz filters analyzed by TOA generally show agreement (Figure 3.1-2).

Figure 3.1-2: Carbon repeat analysis (replicates and/or duplicates) results; data from samples collected during 2017. 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).



Repeat analyses (replicates and/or duplicates) are not performed by XRF for the routine CSN samples. Rather, reanalysis is performed on the same set of filters on a monthly basis to assess both the short- and long-term stability of the XRF measurements as described in *UCD CSN SOP #302: XRF Analysis*. See Section 4.2.2.4.

3.1.3 Blanks

Field blanks are an integral part of the QC 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)

There is some variability in field blank mass loadings by species and month, as shown in Figure 3.1-3 through 3.1-8 for ions measured from nylon filters, and Figure 3.1-9 and 3.1-10 for organic carbon and elemental carbon, respectively, measured from quartz filters. The 10th percentile of network sample concentrations is indicated in Figure 3.1-3 through Figure 3.1-10 to facilitate understanding of field blank concentrations in context of network sample concentrations; 90% of network sample concentrations 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 to accommodate occasional outliers.

Figure 3.1-3: Time series of ammonium measured on nylon filter field blanks (FB), for field blanks collected January 2016 through December 2017. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; blue, 2017) 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 which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers. The black horizontal dashes indicate the 10th percentile of network samples.

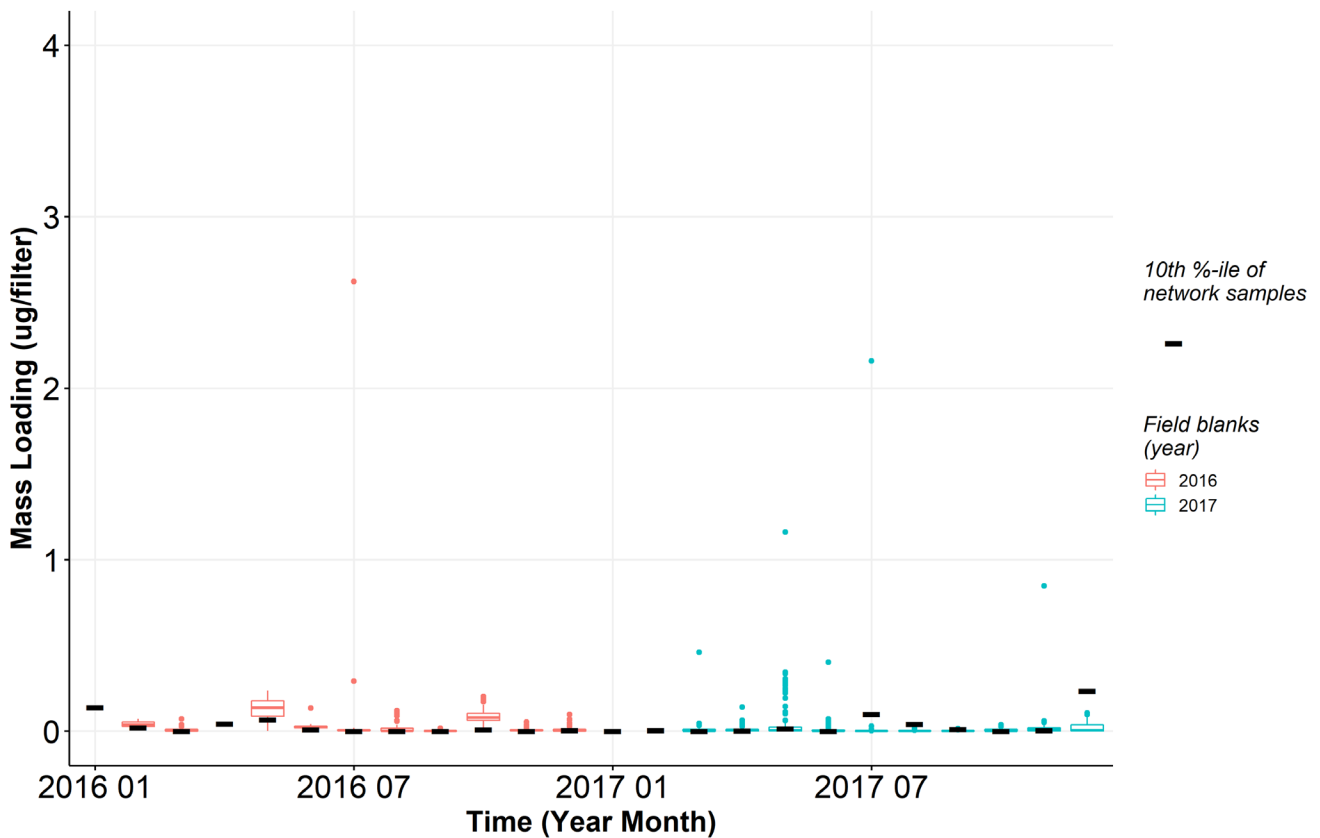


Figure 3.1-4: Time series of chloride measured on nylon filter field blanks (FB) for field blanks collected January 2016 through December 2017. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; blue, 2017) horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers. The black horizontal dashes indicate the 10th percentile of network samples.

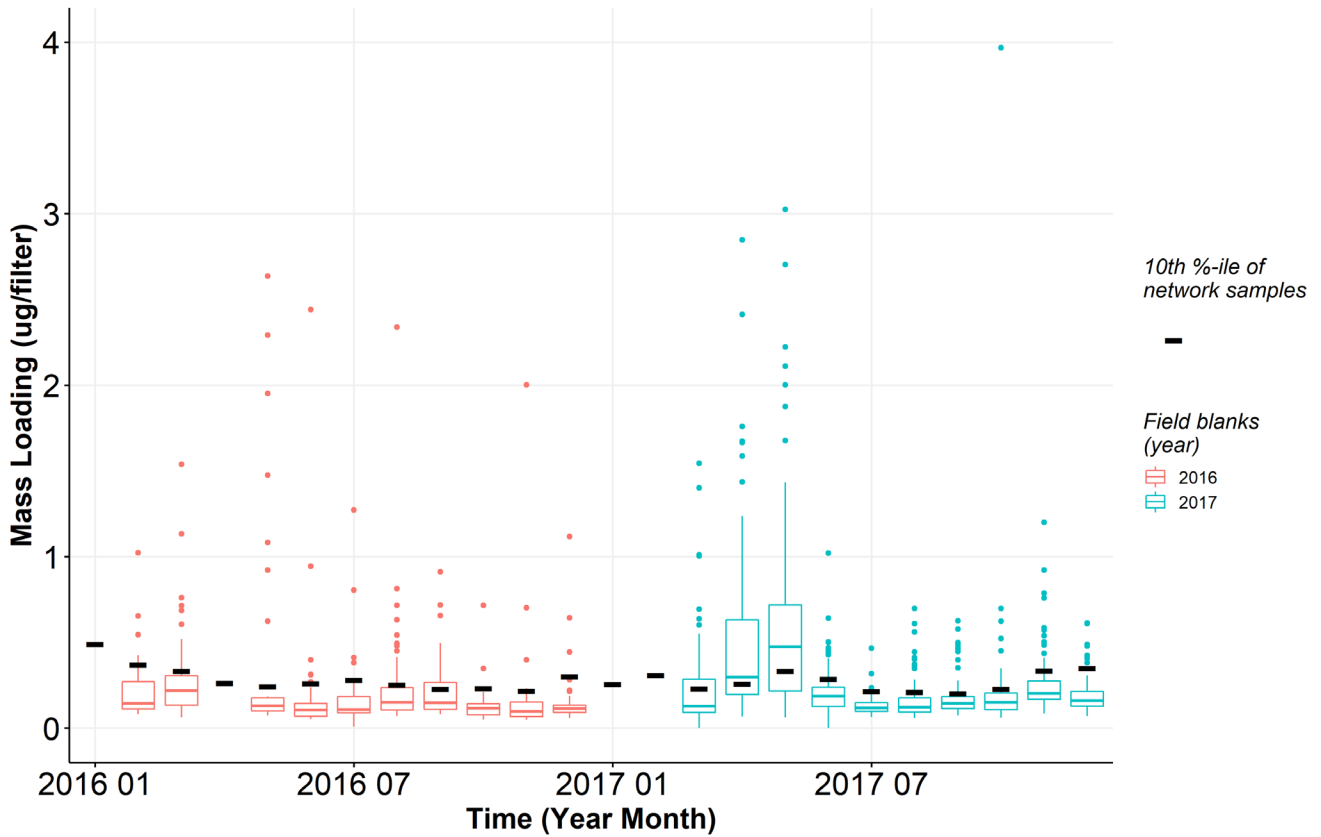


Figure 3.1-5: Time series of nitrate measured on nylon filter field blanks (FB), for field blanks collected January 2016 through December 2017. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; blue, 2017) horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers. The black horizontal dashes indicate the 10th percentile of network samples.

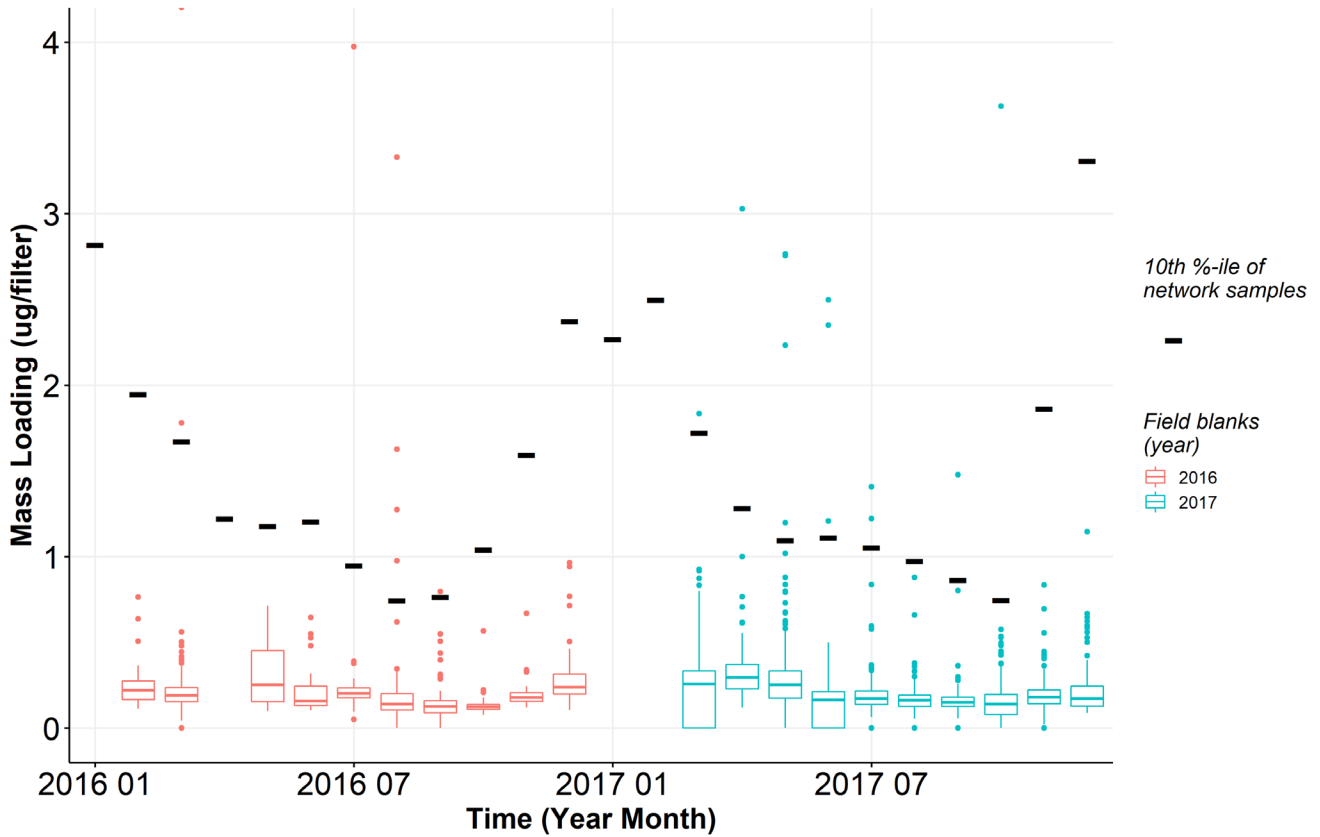


Figure 3.1-6: Time series of potassium ion measured on nylon filter field blanks (FB), for field blanks collected January 2016 through December 2017. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; blue, 2017) horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers. The black horizontal dashes indicate the 10th percentile of network samples.

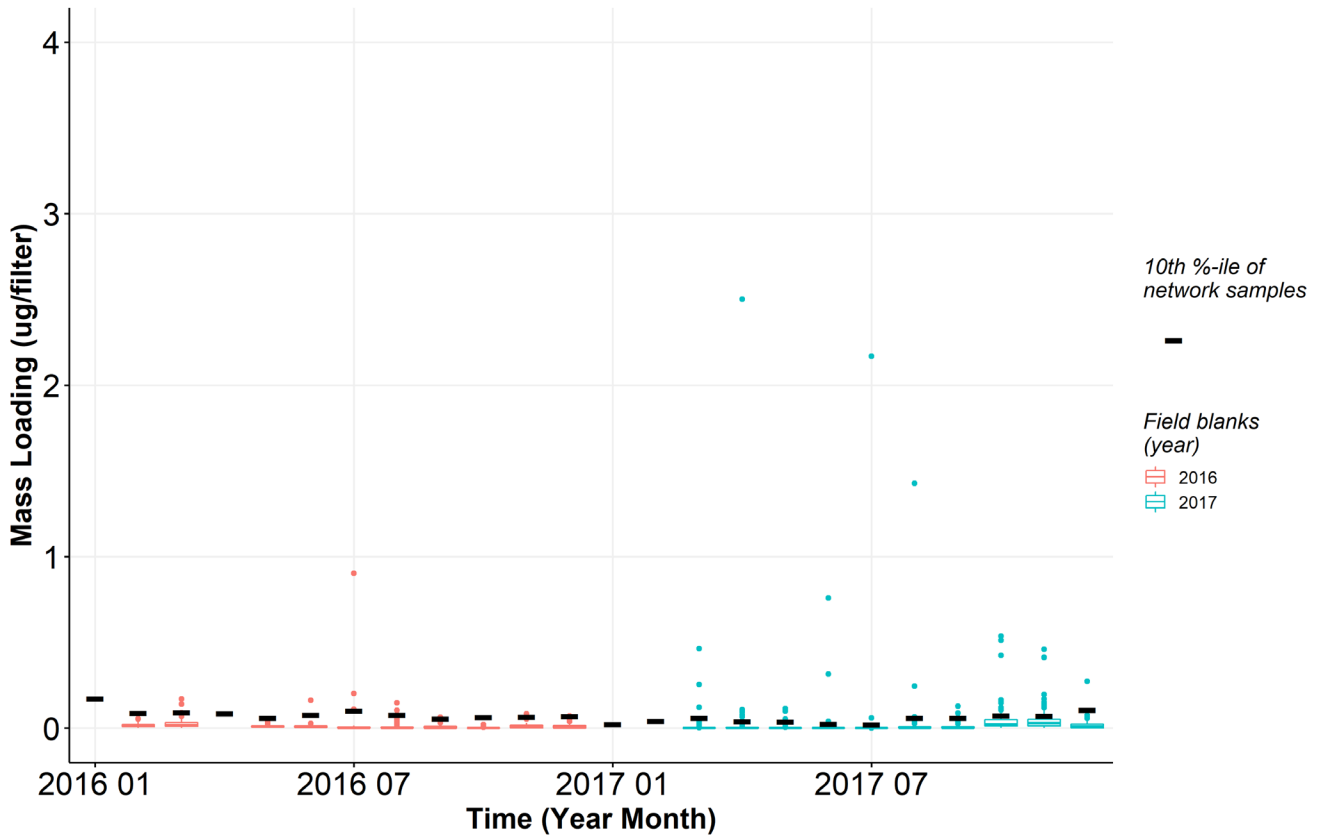


Figure 3.1-7: Time series of sodium ion measured on nylon filter field blanks (FB), for field blanks collected January 2016 through December 2017. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; blue, 2017) horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers. The black horizontal dashes indicate the 10th percentile of network samples.

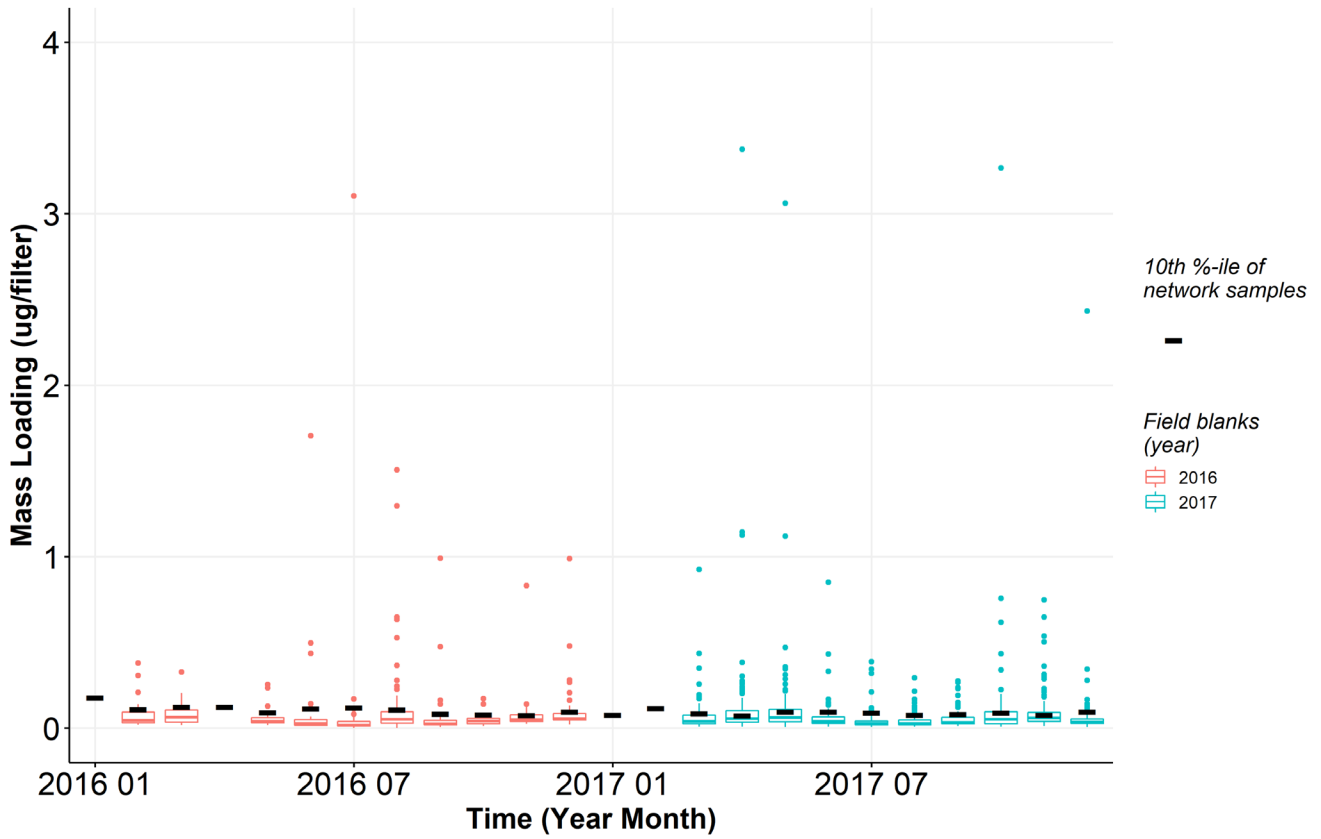


Figure 3.1-8: Time series of sulfate measured on nylon filter field blanks (FB), for field blanks collected January 2016 through December 2017. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; blue, 2017) horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers. The black horizontal dashes indicate the 10th percentile of network samples.

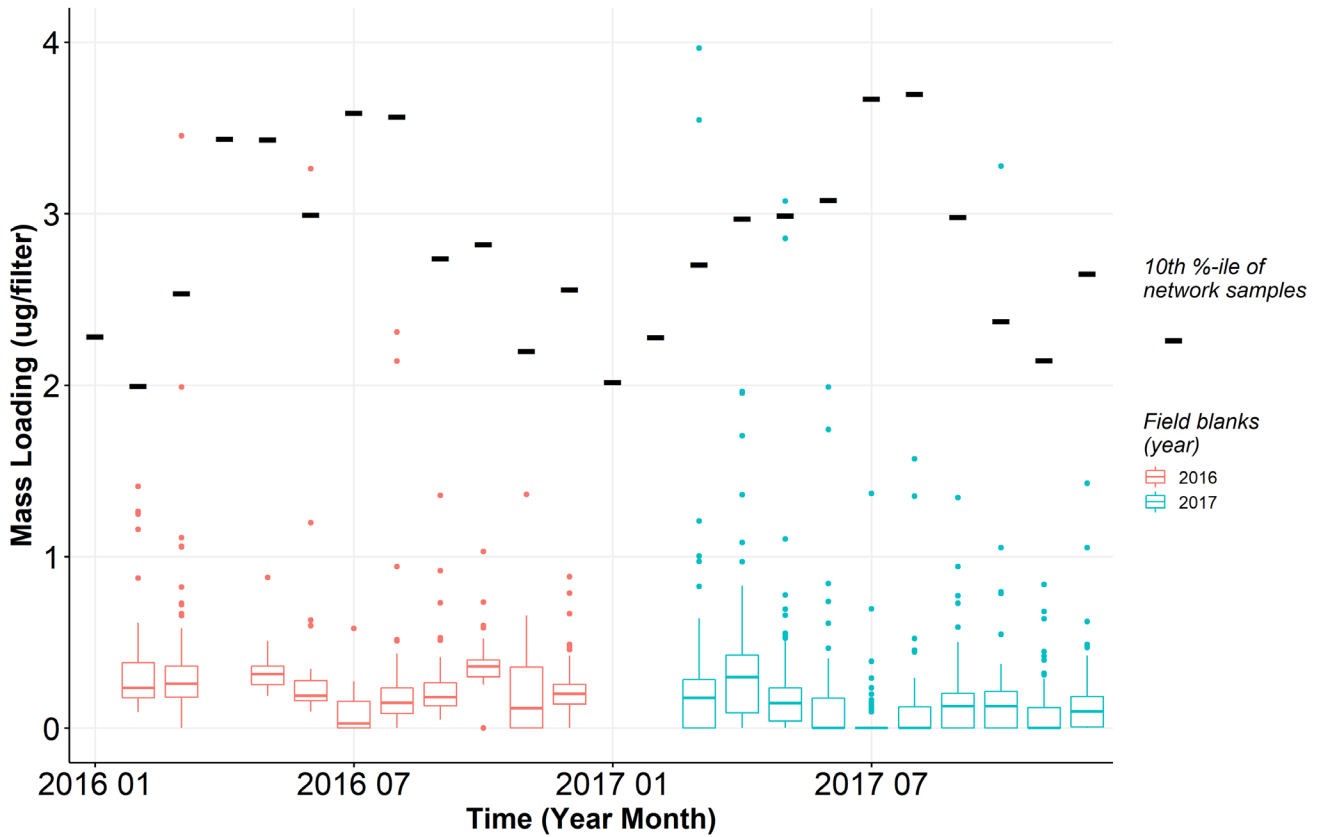


Figure 3.1-9: Time series of organic carbon by reflectance (OCR) measured on quartz filter field blanks (FB), for field blanks collected January 2016 through December 2017. Gaps in time series are present when no quartz filter field blanks were collected. The colored (red, 2016; blue, 2017) horizontal 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 which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers. The black horizontal dashes indicate the 10th percentile of network samples.

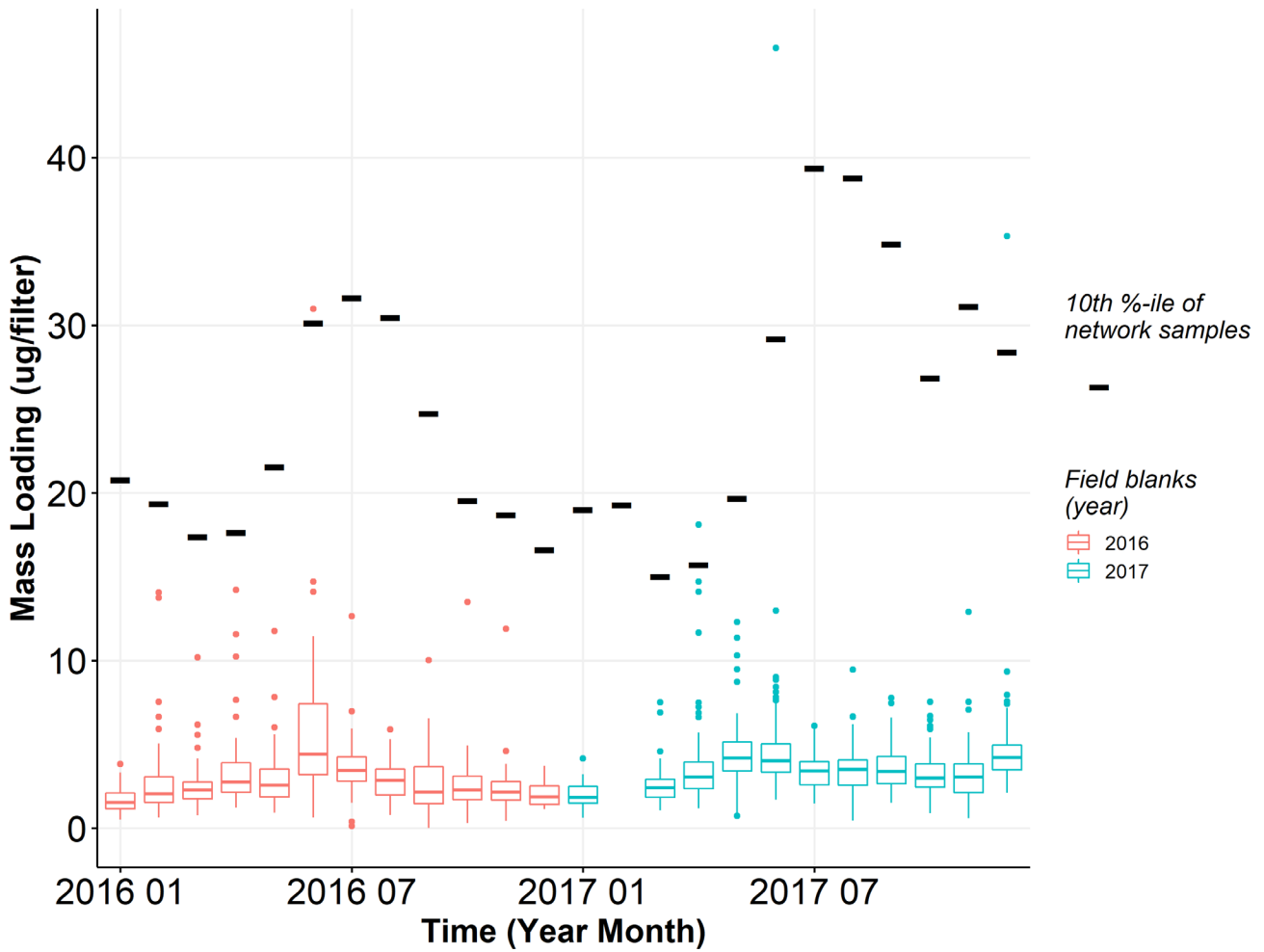
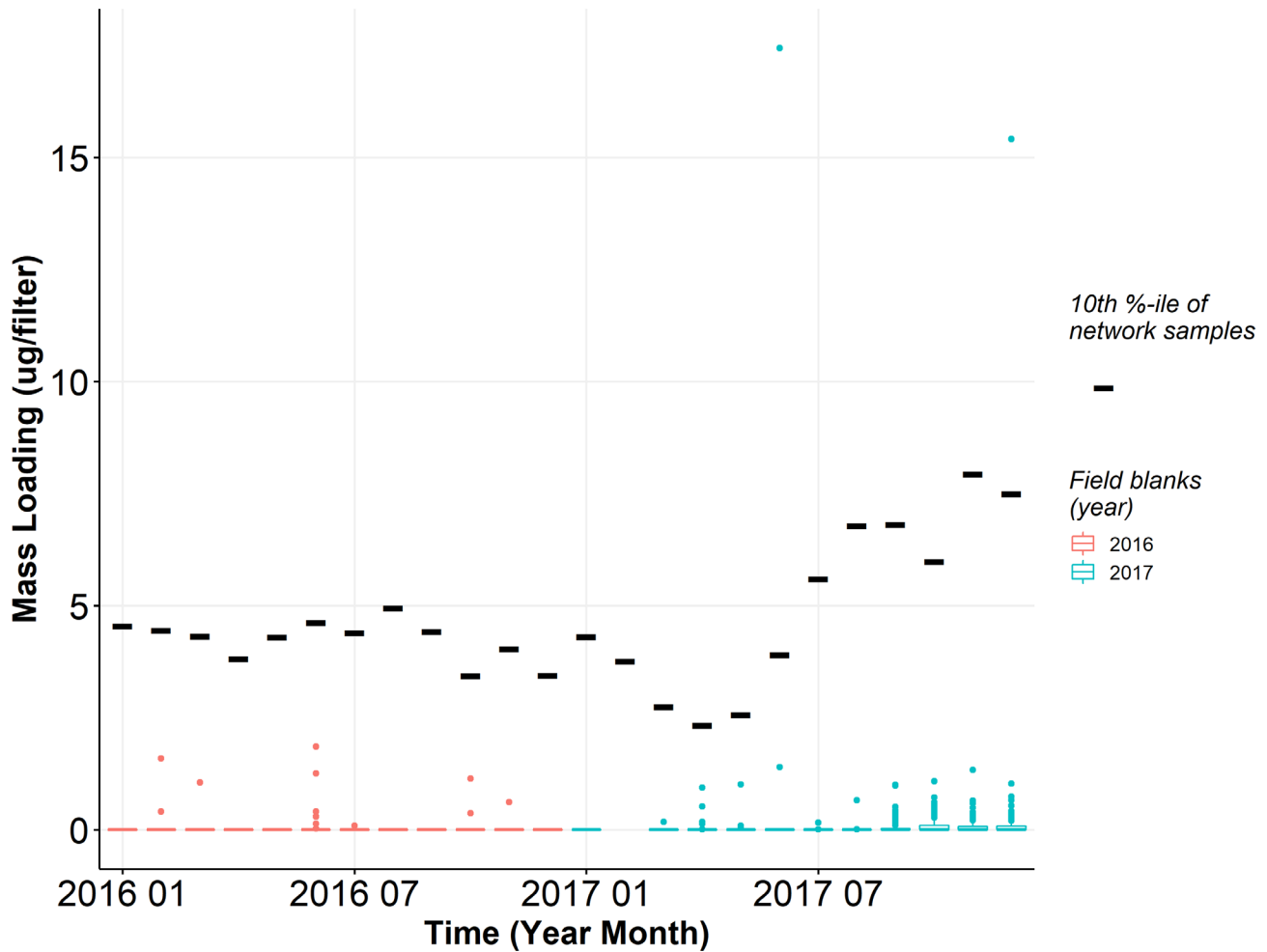


Figure 3.1-10: Time series of elemental carbon by reflectance (ECR) measured on quartz filter field blanks (FB), for field blanks collected January 2016 through December 2017. Gaps in time series are present when no quartz filter field blanks were collected. The colored (red, 2016; blue, 2017) horizontal 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 which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers. The black horizontal dashes indicate the 10th percentile of network samples.



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.

3.1.3.2 *Method Detection Limits*

Network wide method detection limits (MDLs) are updated monthly and delivered to AQS for each species. A sufficient number of field and/or laboratory blanks must be available in order to calculate MDLs representative of the network. For samples collected November 2015 through January 2017, MDLs were calculated at follows:

- Elements: Calculated for each species as 3× standard deviation of lab blanks. Recalculated for each new lot of PTFE filters.
- Ions and carbon: Calculated monthly for each species as 3× standard deviation of field blanks, using 50 nylon (for ions) or quartz (for carbon) field blanks collected in and closest to the sampling month.

The method used for calculating MDLs has evolved as availability of field blanks has increased. Beginning in March 2017, field blank collection increased to one field blank for each filter type per site per month, allowing for a more robust MDL calculation method. For data from samples collected February 2017 onward, 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. For most cases, the MDLs calculated using this method are higher than analytical MDLs calculated by the laboratories using laboratory blanks, which are assigned as the MDL floor values. Field blanks capture artifacts from both field and laboratory processes, with expectations 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. However, when the MDL determined from field blanks is lower than the analytical MDL, the analytical MDL floor value is assigned.

The average MDLs calculated using the updated method during this reporting period are compared to the average MDLs calculated using the old method from the previous reporting period (Table 3.1-4). MDLs calculated using the old and updated methods are similar for most species; cases with differences >50% between the methods are highlighted in Table 3.1.4. The updated MDL calculation results in MDL values that are more stable over time.

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 November 2015 through December 2016 (previous reporting period) and February 2017 through December 2017 (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 >50% between the old (November 2015 – December 2016) and updated (February 2017 – December 2017) MDL calculation methods.

Species	November 2015 – December 2016		February 2017 – December 2017	
	Average MDL, µg/m ³	% Above MDL	Average MDL, µg/m ³	% Above MDL
Ag	0.019	1.4	0.017	2.7
Al	0.038	32.4	0.038	30.1
As	0.003	7.2	0.003	6.2
Ba	0.086	1.9	0.081	1.5
Br	0.005	17.7	0.005	15.8
Ca	0.027	65.1	0.034	56.8
Cd	0.024	0.7	0.016	2.9
Ce	0.116	0.9	0.096	1.3
Cl	0.005	42.9	0.007	31.9
Co	0.003	1.5	0.003	0.9
Cr	0.004	14.4	0.004	20.1
Cs	0.078	0.5	0.056	2.5
Cu	0.009	18.9	0.011	10.9

Species	November 2015 – December 2016		February 2017 – December 2017	
	Average MDL, µg/m ³	% Above MDL	Average MDL, µg/m ³	% Above MDL
Fe	0.023	85.1	0.027	79.8
In	0.031	0.2	0.037	0.0
K	0.016	95.8	0.012	98.4
Mg	0.055	9.0	0.042	12.5
Mn	0.007	7.2	0.006	8.3
Na	0.070	27.3	0.088	20.9
Ni	0.002	11.1	0.002	14.7
P	0.002	9.9	0.002	8.0
Pb	0.015	4.7	0.012	7.4
Rb	0.008	1.1	0.009	0.3
S	0.009	99.4	0.005	99.5
Sb	0.047	1.1	0.040	2.3
Se	0.006	1.3	0.005	1.6
Si	0.015	90.3	0.020	83.7
Sn	0.046	0.9	0.050	0.5
Sr	0.007	2.7	0.007	2.2
Ti	0.003	45.8	0.003	41.4
V	0.002	5.5	0.002	7.9
Zn	0.004	78.0	0.003	78.9
Zr	0.037	0.9	0.036	1.0
Ammonium	0.015	80.7	0.006	81.6
Chloride*	---	---	0.047	60.1
Nitrate	0.095	89.7	0.036	98.5
Potassium Ion	0.008	90.5	0.047	29.5
Sodium Ion	0.043	53.2	0.016	66.6
Sulfate	0.144	96.1	0.047	99.4
Elemental Carbon (EC1)	0.011	99.5	0.007	99.5
Elemental Carbon (EC2)	0.010	95.7	0.009	95.5
Elemental Carbon (EC3)	0.002	3.6	0.002	3.6
Elemental Carbon (ECR)	0.017	99.1	0.013	99.4
Elemental Carbon (ECT)	0.014	98.6	0.012	98.9
Organic Carbon (OC1)	0.024	60.6	0.019	76.8
Organic Carbon (OC2)	0.050	98.9	0.036	99.5
Organic Carbon (OC3)	0.151	94.8	0.053	98.7
Organic Carbon (OC4)	0.031	99.3	0.012	99.7
Organic Carbon (OCR)	0.213	98.9	0.081	99.6
Organic Carbon (OCT)	0.216	99.0	0.083	99.6
Organic Pyrolyzed (OPR)	0.010	79.2	0.008	72.4
Organic Pyrolyzed (OPT)	0.013	95.8	0.010	93.9

* Chloride results were not reported until February 2017.

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 2017.

3.2.1 Elemental Analysis

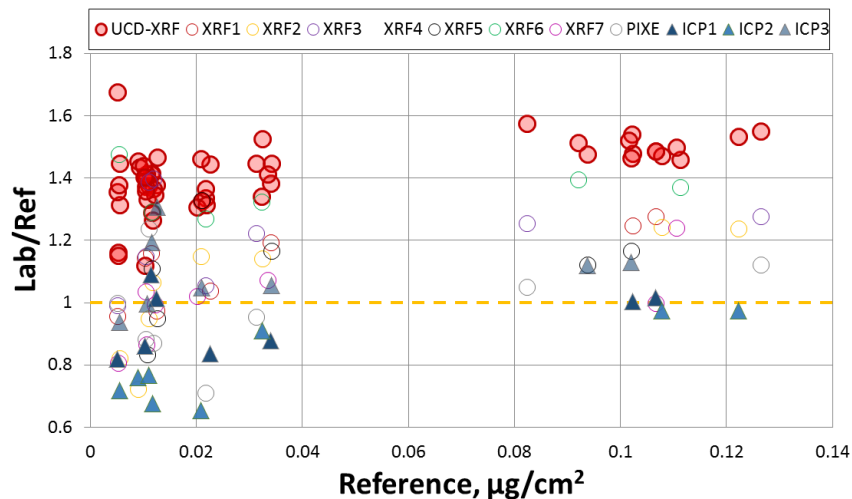
3.2.1.1 Vanadium

As discussed in Section 2.2.1, during a portion of this reporting period (samples collected from January 2017 through October 2017) XRF analyses of vanadium (V) were overestimated by about 30%. This issue and resulting corrective actions are detailed here.

Reported elemental concentrations rest on linear calibrations of the Panalytical Epsilon 5 instruments since their implementation for EDXRF analysis at UC Davis. The calibration factors are derived from observed instrumental responses to a variety of certified standards and reference materials of known composition. UC Davis certifies and calibrates with some standards created in their own laboratory, aerosolizing known materials and collecting them on PTFE filters using IMPROVE (Interagency Monitoring of PROtected Visual Environments) samplers and/or Met One samplers utilized for CSN. The resulting deposits better mimic actual ambient samples than the vacuum-deposited thin-film membranes traditionally obtained from commercial vendors. Such in-house standards are certified for 18 of the elements reported for CSN, including Na, Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Se, Sr, and Pb. However, XRF calibrations for vanadium were based solely on two commercial standards for analysis of samples collected through October 2017.

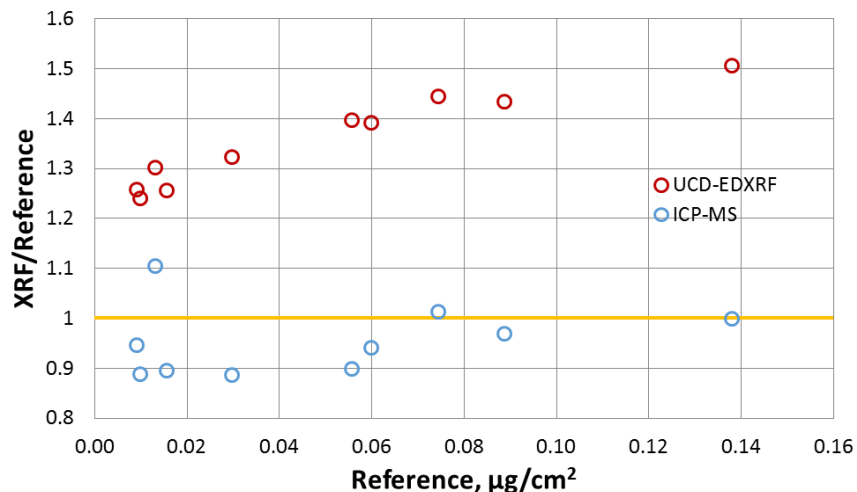
During inter-laboratory comparison studies of novel multi-element reference materials (ME-RM) under development, it was discovered that UC Davis XRF results for vanadium were higher than expected by about 30-50%, while results from other laboratories (including analyses by XRF, PIXE, and ICP-MS) were within 20% of expected values (Figure 3.2-1).

Figure 3.2-1: Inter-laboratory comparison of multi-element reference materials for vanadium, where the UC Davis results are shown as filled red circles and results from other laboratories are shown as circles and triangles.



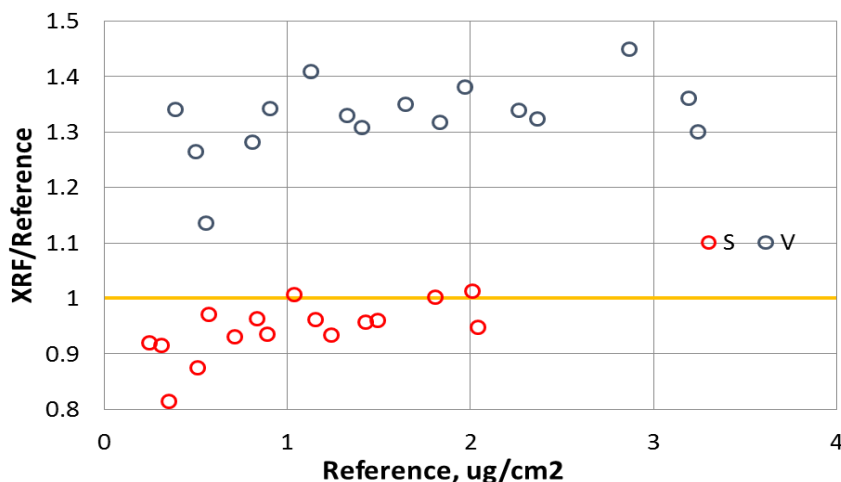
Overestimation by UC Davis XRF analysis was confirmed by further comparisons with ICP-MS analysis by a collaborating laboratory (Figure 3.2-2).

Figure 3.2-2: Comparison of multi-element reference materials for vanadium at UC Davis using EDXRF and a collaborating laboratory using ICP-MS.



UC Davis' ability to design and generate custom reference materials provided further confirmation with single-compound (vanadyl sulfate) standards of known hydration, whose loadings could be gravimetrically certified (Figure 3.2-3).

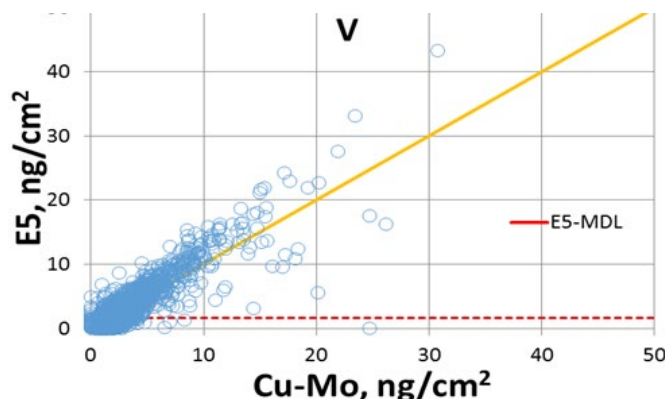
Figure 3.2-3: UC Davis XRF results for single vanadyl sulfate standards that conform to expectations for sulfur (red circle) but are high for vanadium (blue circle).



Inter-laboratory comparison studies of UC Davis ME-RMs, together with UC Davis' custom single-compound standards, converged to indicate that the existing calibration of the UC Davis Panalytical Epsilon-5 instruments for vanadium was about 30% high. Continuity of the historical vanadium record was already tested, when the newer Epsilon 5 (E5) instruments were used to reanalyze the 15-year archive of samples collected from 1995 to 2009 at Great Smoky Mountains NP (GRSM) as part of the IMPROVE program. These had previously been analyzed and reported from the UC Davis-built copper- and molybdenum-anode XRF systems, which had been calibrated using a different set of standards. The new measurements

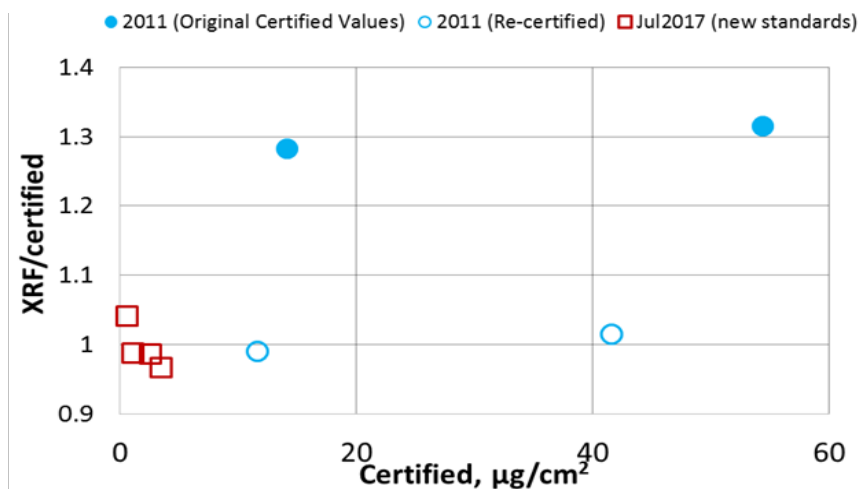
were about 30% higher than those previously reported (Figure 3.2-4).

Figure 3.2-4: Reanalyses by Panalytical Epsilon 5 (E5) of 1995 – 2009 samples from Great Smoky Mountains National Park (GRSM, IMPROVE) previously analyzed versus earlier Cu-Mo XRF system.



As a final step, UC Davis returned the certified calibration standards from 2011 to the manufacturer for recalibration. UC Davis also purchased an additional set of standards. Recalibrated standards' values for vanadium mass loadings are about 30% lower compared to previously certified values and in agreement with newly purchased standards and standards generated at UC Davis (Figure 3.2-5). Annual calibration records show the Panalytical analyzers' raw response to the two original standards was consistent throughout 2011 – 2017, indicating that the recertified values can be applied retroactively. Impacted data were not flagged or retroactively updated. Further detail is available in the UC Davis data advisory: <https://aqrc.ucdavis.edu/csn-documentation>.

Figure 3.2-5: Reported versus quoted vanadium mass loadings for commercial thin-film standards. The reported XRF values are based on a calibration to the loadings certified in 2017 for the two standards originally purchased in 2011.



3.2.1.2 Calcium

As discussed in Section 2.2.3 and Section 4.2.2.1, laboratory QC filters that are exposed to the environment for prolonged periods for repeat analysis show a general increase in calcium mass loadings. These increases are not observed if the QC filter is cleaned with air or replaced with a new filter. The contamination appears to occur mostly on filters that are analyzed multiple times

and therefore should not impact routine samples or field blanks. Even so, CSN samples and field blank filters were monitored during QA checks for calcium contamination. Six filters identified as having potential contamination were reanalyzed and reanalysis results were reported accordingly.

3.2.1.3 Zinc

As discussed in Section 2.2.2 and Section 4.2.2.1, the design of the sample changer arm on the EDXRF instruments results in sporadic cases of zinc contamination. Ten filters identified as having potential contamination were reanalyzed and reanalysis results were reported accordingly.

3.2.2 Ion Analysis

3.2.2.1 Chloride

As discussed in the UC Davis Chemical Speciation Network 2016 Annual Report (<https://aqrc.ucdavis.edu/csn-documentation>), a chloride contamination issue was discovered in the network beginning in November 2015; the contamination was traced to cleaning wipes used in the filter handling laboratory. Following resolution of the issue, chloride data were reported to AQS beginning with data from samples collected during February 2017.

See Section 4.1 for further details.

3.2.3 Carbon Analysis

3.2.3.1 QC Criteria Failures

As discussed in Section 2.3.2, in some instances DRI analyzed samples while instruments were operating outside of the defined QC criteria. For these cases, an internal QC flag was applied.

Per direction from the EPA, these data were redelivered to AQS with QX (Does Not Meet QC Criteria) qualifier flag applied.

For further detail see Section 2.3.2 and Section 4.3.2.

3.2.3.2 Carbon Data Reprocessing

All reportable CSN carbon analyses were performed by DRI, a subcontractor to UC Davis on the CSN contract. After examination of data from the IMPROVE and CSN programs, DRI determined the Model 2015 (used for analyses from January 1, 2016 onward) carbon signal integrations threshold differed from that of the Model 2001 (used for analysis prior to January 1, 2016). DRI reprocessed CSN carbon data from January 1, 2016 through September 13, 2017, and analysis of the differences between the original and reprocessed data was prepared by UC Davis. The EPA determined that reprocessed carbon results would not be delivered to AQS because the impact on the data was minor. UC Davis prepared a data advisory: <https://aqrc.ucdavis.edu/csn-documentation>.

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: CSN Data Validation* 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 or on a case-by-case basis. The use and application of flags evolves as problems are identified and remedied, and also in response to process improvements that are implemented to improve the quality and consistency of data for the end user.

4. Laboratory Quality Control Summaries

4.1 DRI Ion Analysis Laboratory

The DRI Ion Analysis Laboratory, as a subcontractor to UC Davis, received and analyzed nylon filters from batches 22 through 38 for samples collected January 1, 2017 through December 31, 2017. Analysis of these samples was performed April 11, 2017 through June 13, 2018. DRI performed analyses of both anions (chloride [Cl⁻], nitrate [NO₃⁻], and sulfate [SO₄²⁻]) and cations (sodium [Na⁺], ammonium [NH₄⁺], and potassium [K⁺]) on these nylon filter samples using three DIONEX ICS-5000+ Systems (Chow and Watson, 2017) and reported the results of those analyses to UC Davis. Chloride was reported to AQS beginning with data from samples collected during February 2017; reasoning for not delivering chloride prior to February 2017 is discussed in the UC Davis Chemical Speciation Network 2016 Annual Report (<https://aqrc.ucdavis.edu/csn-documentation>).

4.1.1 Summary of QC Checks and Statistics

Samples received at the DRI Ion Analysis Laboratory were logged in following the chain-of-custody procedure specified in *DRI CSN SOP #2-117*. Samples were analyzed using DIONEX ICS-5000+ or ICS-6000 Systems following *DRI CSN SOP #2-228* for anions and *DRI CSN SOP #2-229* for cations. QC measures for the DRI ion analysis are summarized in Table 4.1-1. The table indicates the frequency and standards required for the specified checks, along with the acceptance criteria and corrective actions.

During daily startup, an eight-point calibration is performed over the range from 0.02 to 3 µg/mL (e.g., 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, and 3.0 µg/mL) before analysis starts. Then two deionized-distilled water (DDW) samples and a method blank are analyzed, followed by two types of QC control standards: (1) 1–2.5 µg/mL QC standards diluted from NIST certified Dionex standard solutions; and (2) DRI-made control standards (e.g., 1.00 µg/mL Cl⁻, 1.00 µg/mL NO₃⁻, 1.00 µg/mL SO₄²⁻ for anions and 0.39 µg/mL NH₄⁺ and 1.03 µg/mL Na⁺ for cations). During routine analysis, after every 10 samples, one duplicate, one DDW, and a selected QC check standard (same as calibration solution concentrations; diluted from certified Environmental Research Associates (ERA) stock solutions) at various concentrations (0.1–3 µg/mL) are analyzed.

Table 4.1-1: QC measures for ion (anion and cation) analysis by ion chromatography.

Requirement	Frequency	Calibration Standard	Acceptance Criteria	Corrective Action
Multipoint Calibration	Daily or every batch of ~100, whichever comes first	NIST certified ERA	± 10% of certified value	Identify and correct problem before analyzing samples; and recalibrate
Minimum Detection Limit (MDL) ^a	Initially, then annually or after major instrument maintenance	Nylon filter lab blanks (7 or more)	Within ± 10% of previous instrument limit	Troubleshoot instrument and check filter lots
DDW	Four initially to establish background, followed by one every 10 samples	DDW with resistance ≥ 18 MΩ	Within 3 standard deviations of MDLs ^a	Verify instrument response to DDW without extraction
Method blank ^b	One for every 40 samples	DDW with resistance ≥ 18 MΩ	Within 3 standard deviations of MDLs ^a	Check instrument response for DDW with extraction
QC Control Standards	Daily or every run	DRI-made or Dionex NIST-certified multi-component standard solution	± 10% of listed value	Rerun the QC standard and reanalyze samples between this standard and previous QC standard
QC Check Standards	Every 10 samples	NIST-certified multi-component standard solution from ERA	± 10% of listed value	Reanalyze samples between this standard and previous check standard
Duplicates ^c	10% of samples	N/A	± 10% when value > 10x MDL ^a	Reanalysis of duplicate sample
Laboratory Validation	Every sample	N/A	See note ^d	Reanalysis of problem sample or flagging per SOP

^a MDL indicated here is an internal laboratory QA indicator, distinct from the MDL reported to AQS.

^b 15 mL DDW solution that follows the same extraction procedure as the sample extraction.

^c Duplicate indicates analysis results obtained from two different aliquots of the same filter sample extract analyzed on the same instrument.

^d Per Section 5.1 in *DRI SOP #2-228* and *DRI SOP #2-229*. Non-quantitative criteria such as baseline position and noise, identification of peaks, shape of peak and integration with respect to baseline.

4.1.2 Summary of QC Results

Table 4.1-1 outlines corrective actions for failed QC checks. For failed method blanks, instrument malfunction was ruled out first. Next, the blank was reanalyzed to rule out contamination during the extraction process and within the IC system. For the cases of failed method blanks in Table 4.1-2, reanalysis of the blanks resulted in concentrations below QC threshold and sample data were not affected. When the Dionex and DRI-made QC control standards (Tables 4.1-3 and 4.1-4) that were run after multipoint calibration and before sample analysis failed to pass the acceptance criteria, the multipoint calibration, the QC control standard, and any samples that were analyzed were rerun to ensure that the QC standards passed acceptance criteria. Failed ERA QC check standards that were analyzed every 10th sample (Table 4.1-5) resulted in reanalysis of all samples between the failed standard and the nearest previous passing QC standard. Reported sample data all passed acceptance criteria for the QC check standards. Duplicate analyses (Table 4.1-6) that exceeded acceptance criteria were reanalyzed and compared to the original analysis. If the second duplicate met acceptable tolerance, the first duplicate data point was considered spurious and was replaced. If the second duplicate analysis

did not meet tolerance standards, all ten samples in the set were reanalyzed. Sample data are not affected by reanalyzing duplicates.

4.1.2.1 Method Blanks

Table 4.1-2 lists the number of method blanks analyzed during the report period and their concentration statistics. Both median and average concentrations are near or below the MDLs (MDL indicated here is an internal laboratory QA indicator, distinct from the MDL reported to AQS).

Table 4.1-2: Method blank counts and concentrations for all reported ions.

Ions	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺
Count	386	386	386	386	386	386
Median (µg/mL)	0.000	0.000	0.000	0.000	0.000	0.000
Average (µg/mL)	0.001	0.003	0.001	0.001	0.000	0.000
St. Dev. (µg/mL)	0.003	0.006	0.004	0.002	0.001	0.001
Min (µg/mL)	0.000	0.000	0.000	0.000	0.000	0.000
Max (µg/mL)	0.036	0.039	0.034	0.032	0.005	0.015
# Exceed 3×MDL^a	0	10	1	0	1	0

^a MDL indicated here is an internal laboratory QA indicator, distinct from the MDL reported to AQS.

4.1.2.2 QC Control Standards

Table 4.1-3 and Table 4.1-4 list the analysis statistics for Dionex and DRI-made ion QC control standards, respectively. The control charts of these analyses are shown in Figure 4.1-1a and Figure 4.1-1b. The average difference between the measured and nominal concentrations are within the ±10% limit (Table 4.1-1), although a few individual checks failed the 10% acceptance criteria (see Figure 4.1-1b). Corrective actions for failed analyses are shown in Table 4.1-1. Table 4.1-5 summarizes analysis statistics for the ERA QC check standards at different concentration levels. Some individual standards failed QC criteria, but were reanalyzed following the procedure outlined in Table 4.1-1. All reported CSN sample ion concentrations passed the QC control and check standard verification.

Table 4.1-3: Statistics for Dionex ion QC control standards.

Ions	Nominal (µg/mL)	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	# Fail	Ave % Recovery	% St. Dev.
Cl ⁻	1.000	130	1.017	1.011	0.929	1.075	0	101.1%	3.2%
NO ₃ ⁻	1.000	130	0.922	0.932	0.900	1.033	0	93.2%	3.2%
SO ₄ ²⁻	1.000	130	1.067	1.064	0.984	1.099	0	106.4%	2.2%
Na ⁺	1.000	129	0.997	1.002	0.937	1.096	0	100.2%	2.9%
NH ₄ ⁺	1.250	129	1.289	1.292	1.222	1.369	0	103.3%	2.9%
K ⁺	2.500	129	2.606	2.609	2.384	2.749	0	104.38%	5.6%

Table 4.1-4: Statistics for DRI-made ion QC control standards.

Ions	Nominal (µg/mL)	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	# Fail	Ave % Recovery	% St. Dev.
Cl ⁻	1.000	130	0.986	0.992	0.897	1.078	4	99.2%	4.3%
NO ₃ ⁻	1.000	130	0.921	0.932	0.860	1.099	6	93.2%	4.0%
SO ₄ ²⁻	1.000	130	0.998	1.010	0.904	1.137	3	101.0%	6.0%
Na ⁺	1.030	133	1.030	1.029	0.930	1.190	1	99.9%	4.2%
NH ₄ ⁺	0.390	133	0.331	0.390	0.331	0.444	10	99.9%	2.4%
K ⁺	0.000	133	0.001	0.001	0.000	0.011	0	NA	0.2%

^aNA=Not applicable

Table 4.1-5: Statistics for ERA QC control standards.

Ion	Nominal (µg/mL)	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	Ave% Recovery	% St. Dev.
Cl⁻	0.2	64	0.187	0.189	0.179	0.213	94.5%	0.9%
	0.5	387	0.480	0.482	0.415	0.541	96.3%	2.0%
	1	375	0.979	0.984	0.844	1.097	98.4%	3.9%
	2	339	2.015	2.028	1.669	2.327	101.4%	7.6%
	3	294	3.072	3.096	2.922	3.483	103.2%	10.0%
NO₃⁻	0.2	64	0.187	0.189	0.177	0.208	94.7%	0.8%
	0.5	387	0.472	0.477	0.414	0.546	95.4%	2.1%
	1	375	0.962	0.971	0.864	1.155	97.1%	4.0%
	2	339	2.001	2.020	1.623	2.359	101.0%	7.9%
	3	294	3.080	3.098	2.889	3.495	103.3%	10.4%
SO₄²⁻	0.2	64	0.193	0.195	0.180	0.220	97.3%	1.1%
	0.5	387	0.484	0.485	0.425	0.550	96.9%	2.2%
	1	375	0.975	0.977	0.879	1.158	97.7%	3.7%
	2	339	2.003	2.016	1.651	2.356	100.8%	7.5%
	3	294	3.052	3.075	2.771	3.471	102.5%	11.0%
Na⁺	0.2	62	0.187	0.188	0.170	0.201	94.0%	0.7%
	0.5	401	0.503	0.499	0.426	0.562	99.9%	2.1%
	1	373	1.004	1.001	0.907	1.082	100.1%	2.9%
	2	330	1.982	1.987	1.715	2.161	99.3%	5.9%
	3	312	3.017	3.017	2.727	3.358	100.6%	8.4%
NH₄⁺	0.2	62	0.195	0.193	0.169	0.218	96.7%	0.9%
	0.5	401	0.472	0.476	0.407	0.580	95.1%	1.9%
	1	373	0.983	0.982	0.877	1.124	98.2%	3.2%
	2	330	2.001	2.002	1.780	3.297	100.1%	4.7%
	3	312	3.023	3.024	2.738	3.297	100.8%	7.8%
K⁺	0.2	62	0.193	0.192	0.162	0.211	95.9%	1.1%
	0.5	401	0.500	0.497	0.420	0.576	99.4%	3.1%
	1	373	0.962	0.976	0.842	1.163	97.6%	5.2%
	2	330	2.185	2.533	1.737	3.550	126.7%	53.6%
	3	312	3.058	3.076	2.770	3.550	102.5%	11.3%

Figure 4.1-1a: Control charts for Dionex ion QC control standards. The limits are $\pm 10\%$ of the nominal concentrations (red dashed lines).

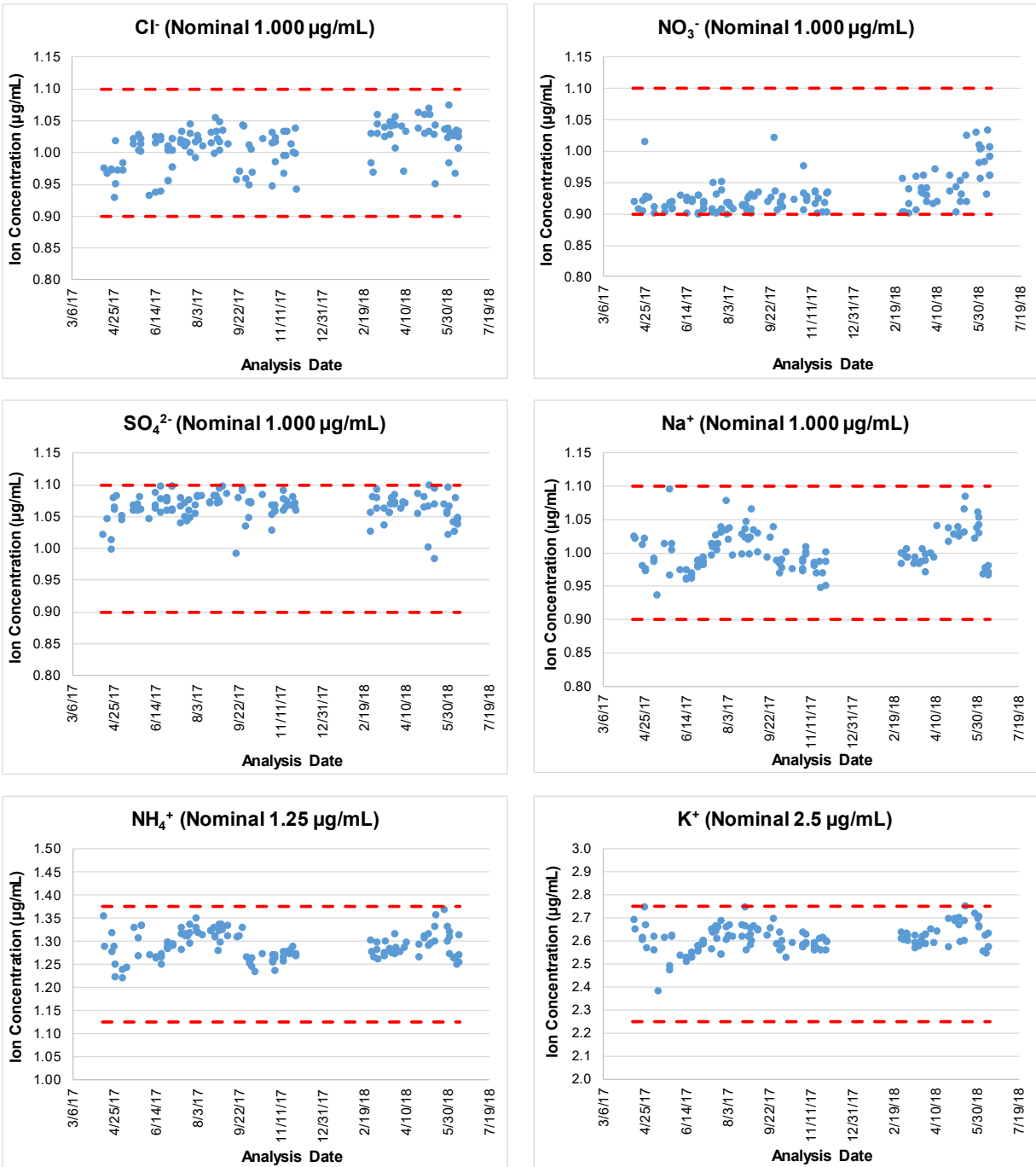
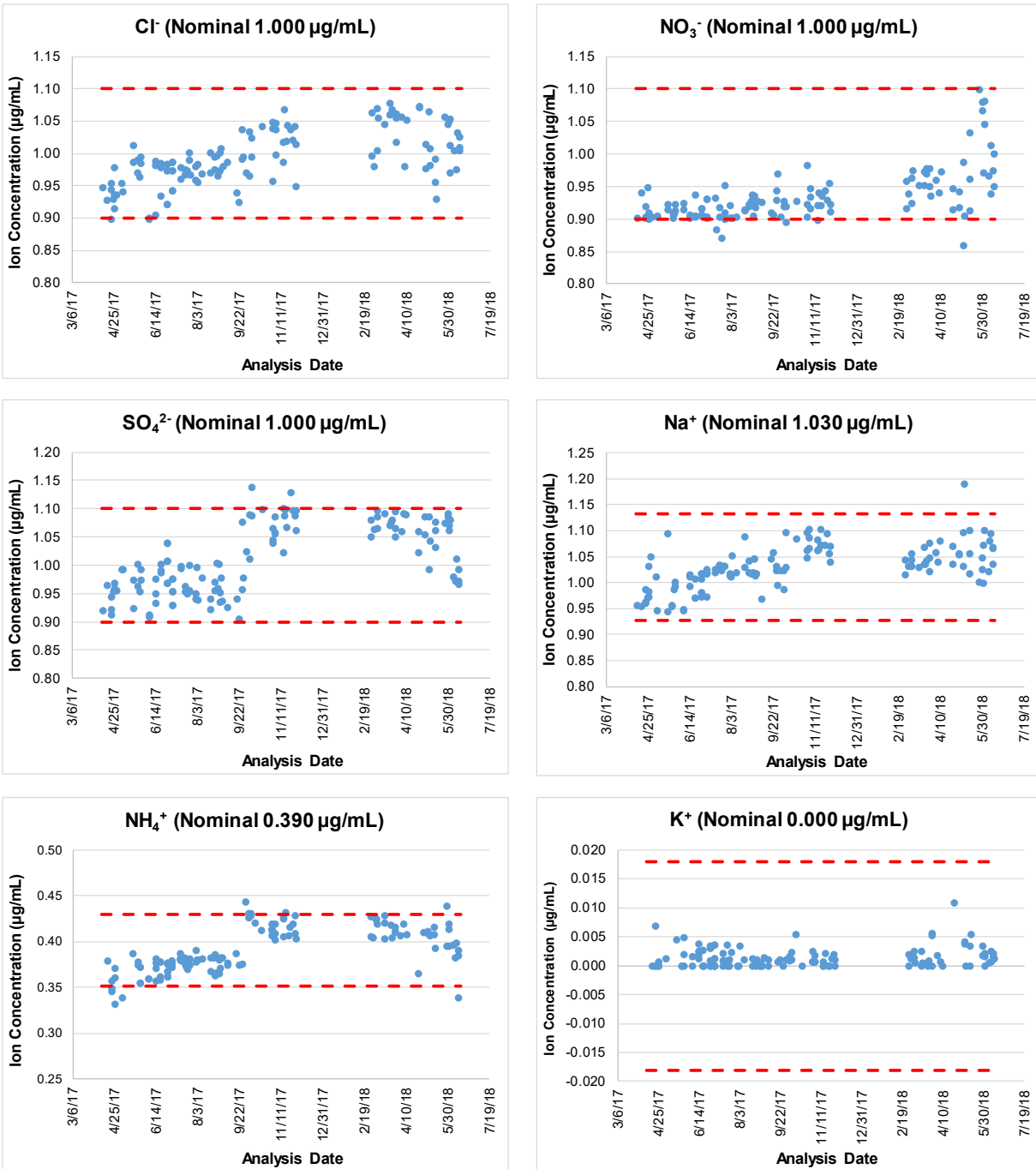


Figure 4.1-1b: Statistics for DRI-made ion QC control standards. The limits are $\pm 10\%$ of the nominal concentrations (red dashed lines), except for K^+ which is $3 \times MDL^a$ (red dashed lines).



^a MDL indicated here is an internal laboratory QA indicator, distinct from the MDL reported to AQS.

4.1.2.3 Duplicate Analyses

Table 4.1-6 gives the criteria and summary statistics for duplicate analysis results. Duplicate analysis results are obtained from two different aliquots of the same filter sample extract run on the same instrument. The criteria used for each ion were that 1) if the average concentration was less than 10 times the lower quantifiable limit (LQL), the absolute value of the average difference should be less than ten times the LQL, and 2) if the average concentration was greater than or equal to ten times the LQL, then the relative percent difference (RPD) should be less than 10%. LQLs are given in Tables 4.1-7a and b. The LQLs are used as internal QA indicators, distinct from the MDLs reported to AQS.

Table 4.1-6: Ion duplicate analysis criteria and statistics.

Range	Criteria	Statistic	Na ⁺	NH ₄ ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Units
Ion ≤ 10× LQL	< LQL	Count	1346	770	1409	1426	907	600	
		No. Fail	0	13	0	0	0	0	
		% Fail	0	1.7	0	0	0	0	%
		Mean	0.005	0.016	0.010	0.013	0.029	0.044	µg/filter difference
		St. Dev.	0.009	0.024	0.013	0.020	0.038	0.056	µg/filter difference
		Max	0.134	0.149	0.099	0.194	0.275	0.377	µg/filter difference
		Min	0.000	0.000	0.000	0.000	0.000	0.000	µg/filter difference
		Median	0.003	0.006	0.006	0.006	0.016	0.021	µg/filter difference
Ion > 10× LQL	RPD ^a <10%	Count	114	690	51	34	553	860	
		No. Fail	0	8	0	0	0	0	
		% Fail	0	1.2	0	0	0	0	%
		Mean	1.0%	1.8%	2.3%	0.6%	0.7%	0.9%	RPD
		St. Dev.	1.3%	2.1%	2.5%	0.8%	0.8%	1.0%	RPD
		Max	5.9%	14.3%	9.7%	3.7%	6.8%	7.9%	RPD
		Min	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%	RPD
		Median	0.5%	1.0%	1.3%	0.4%	0.4%	0.5%	RPD

^aRPD= 100 × absolute value [original sample – duplicate sample] / [(original sample + duplicate sample) / 2]

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 audits of the DRI Ion Analysis laboratory during 2017.

4.1.4.2 Performance Evaluations

The EPA provided five nylon samples for anion and cation analysis as part of the EPA Office of Air Quality Planning and Standards (OAQPS) interlaboratory performance evaluation. This

evaluation was carried out during the timeframe when DRI also analyzed CSN samples collected during 2017. Reported z-scores were all below 2, indicating satisfactory interlaboratory comparison results.

4.1.4.3 Training

All new laboratory staff receive training in performing tasks in the SOPs for 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 Field Blanks

Over the sampling period (January 1, 2017 through December 31, 2017) there were 1,368 valid nylon filter field blanks. Table 4.1-7a and Table 4.1-7b summarize the field blank statistics. The lower quantifiable limits (LQLs) are defined as three times the standard deviation of field blanks and are used as internal laboratory QA indicators, distinct from the MDLs reported to AQS.

Table 4.1-7a: Nylon filter field blank statistics in µg/mL.

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)	LQL (µg/mL)
Cl ⁻	1349	0.011	0.020	0.000	1.625	0.061	0.184
NO ₃ ⁻	1349	0.012	0.020	0.000	2.975	0.090	0.269
SO ₄ ²⁻	1349	0.005	0.018	0.000	1.119	0.081	0.243
Na ⁺	1349	0.003	0.007	0.000	1.331	0.049	0.146
NH ₄ ⁺	1349	0.000	0.001	0.000	0.683	0.019	0.058
K ⁺	1349	0.000	0.002	0.000	0.363	0.012	0.036

Table 4.1-7b: Nylon filter field blank statistics in µg/filter (extraction volume 15 mL).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)	LQL (µg/filter)
Cl ⁻	1349	0.169	0.305	0.000	24.378	0.921	2.764
NO ₃ ⁻	1349	0.181	0.293	0.000	44.625	1.347	4.041
SO ₄ ²⁻	1349	0.070	0.275	0.000	16.779	1.215	3.646
Na ⁺	1349	0.042	0.109	0.007	19.969	0.730	2.189
NH ₄ ⁺	1349	0.000	0.022	0.000	10.243	0.288	0.863
K ⁺	1349	0.000	0.024	0.000	5.450	0.182	0.545

4.2 UC Davis X-Ray Fluorescence (XRF) Laboratory

The UC Davis XRF Laboratory received and analyzed PTFE filters from batches 1 through 38, which includes samples collected January through December 2017. UC Davis performed analysis for 33 elements using energy dispersive X-ray fluorescence (EDXRF) instruments. These analyses were performed during an analysis period from April 6, 2017 to September 6, 2018. Two EDXRF instruments, XRF-1 and XRF-4, performed all analyses during this period; see Table 4.2-1 for details.

Table 4.2-1: Sampling dates and corresponding EDXRF analysis dates covered in this report. Analysis dates include reanalysis – as requested during QA Level 1 validation – of any samples within the sampling year and month.

Sampling Year	Sampling Month	XRF-1 Analysis Dates	XRF-4 Analysis Dates
2017	January	04/06/2017 – 05/01/2017	04/06/2017 – 05/01/2017
2017	February	05/01/2017 – 05/21/2017	05/01/2017 – 09/22/2017
2017	March	05/21/2017 – 06/18/2017	05/21/2017 – 06/17/2017
2017	April	06/23/2017 – 07/24/2017	06/10/2017 – 10/17/2017
2017	May	07/24/2017 – 08/21/2017	07/23/2017 – 08/25/2017
2017	June	08/21/2017 – 09/21/2017	08/22/2017 – 09/19/2017
2017	July	09/21/2017 – 01/03/2018	09/19/2017 – 10/20/2017
2017	August	10/19/2017 – 02/08/2018	10/19/2017 – 02/16/2018
2017	September	11/15/2017 – 02/08/2018	11/20/2017 – 04/02/2018
2017	October	12/12/2017 – 04/27/2018	12/16/2017 – 01/24/2018
2017	November	01/27/2018 – 02/27/2018	01/26/2018 – 02/25/2018
2017	December	02/24/2018 – 09/06/2018	02/26/2018 – 03/25/2018
2017	All Months	04/06/2017 – 09/06/2018	04/06/2017 – 04/02/2018

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: Frequency and types of checks performed and associated criteria and corrective actions for analysis by EDXRF.

Analysis	Frequency	Criterion	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	<ul style="list-style-type: none"> XRF software automatically adjusts the energy channels
PTFE Blank	Daily	≤ acceptance limits with exceedance of a single element allowed for a maximum of 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 sample	Daily	±10% of reference mass loadings for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	<ul style="list-style-type: none"> Check sample for damage/contamination Further cross-instrumental testing Replace sample if necessary
Micromatter Al&Si sample	Weekly	±10% of reference mass loadings	
UC Davis Multi-element sample	Weekly	±10% of reference mass loadings for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	
Reanalysis samples	Monthly	z-score between ±1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	
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 Micromatter Al&Si ME-RM and a UC Davis-made ME-RM are also analyzed weekly to check

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 sporadic failures of the QC criteria, which were investigated promptly and corrected with minimal impact on sample analysis. The following summarizes the QC issues which occurred during the analysis period reported here.

Random occasional zinc contamination was observed on QC filters for both XRF-1 and XRF-4. This sporadic zinc 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 are not impacted. See Section 2.2.2, Section 3.2.1.3, and Section 4.2.2.1 for further detail.

Both XRF-1 and XRF-4 also exhibited some failures of the acceptance criteria for all QC checks of Ca. Investigation is ongoing, with initial findings suggesting gradual increase in Ca concentrations on QC filters may be caused by environmental deposition during extended residence in the instruments. Samples are only exposed to the environment for a day or two during routine analysis, thus are not susceptible to gradual Ca contamination. However, samples are carefully monitored for atypical and abrupt calcium contamination events and reanalyzed as necessary. The reported data are not impacted. See Section 2.2.3, Section 3.2.1.2, and Section 4.2.2.1 for further detail.

4.2.2.1 Results of Daily QC Checks

Possible contamination and instability issues are monitored by analyzing a PTFE blank daily. The EDXRF results are compared to acceptance limits, which are calculated as three times the standard deviation plus the mean of a set of laboratory PTFE blanks. Figures 4.2-1a and 4.2-1b show the results of daily analyses of laboratory blanks on both instruments. If the mass loading exceeds the limit for more than two consecutive days, the blank is replaced to distinguish between blank contamination and instrument contamination. Some occasional exceedance of the acceptance limits is 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 a blank. Analysis results are reviewed during QA Level 1 validation (*UCD CSN TI 801C*), and elements associated with occasional contamination (Zn and Ca; see Section 4.2.2) 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 10 samples from 2017 were reanalyzed for suspected Zn contamination (six from XRF-1, four from XRF-4). Of those, three were found to have Zn contamination and the reanalysis result was reported (two from XRF-1 and one from XRF-4). Six samples were reanalyzed for suspected Ca contamination (two from XRF-1 and four from XRF-4). Only one sample was found to have Ca contamination and the reanalysis result was reported.

Both XRF-1 and XRF-4 had sporadic elevated measurements of Zn on laboratory blanks throughout the analysis period (as discussed in Section 2.2.2 and Section 3.2.1.3). These elevated levels were not measured over consecutive days thus did not fail the acceptance criteria; however, these occurrences are monitored closely. Zn contamination likely comes from wear on the sample changer; Zn is a common contaminant in elemental analysis systems.

Both XRF-1 and XRF-4 show gradual increases in Ca (as discussed in Section 2.2.3 and Section 3.2.1.2), which is reduced immediately after the blank filter is changed. This indicates contamination of the blank filter likely from atmospheric deposition and/or instrument wear. This situation worsened on XRF-4 for analyses performed during 2018. The cause of Ca increase on QC filters with long, multi-day, residences in the instrument is being investigated.

In June and November 2017 for XRF-1 and XRF-4, respectively, there were slightly elevated signals for Fe, Ni, and Cr for laboratory blanks. These were isolated events due to small stainless steel contamination on the blank filters from instrument wear. The exceedances did not occur on consecutive days thus did not fail the acceptance criteria. Replacing the contaminated blank filters resolved the issue and no samples were affected. The reported data are not impacted.

Lastly, Cl had a few exceedances on both XRF-1 and XRF-4 during the analysis period. For the larger exceedances laboratory blanks were replaced which corrected the exceedance; for others the signal decreased without correction. The cause of the Cl exceedances is unknown; as a volatile element it has a highly variable signal from QC filters.

Figure 4.2-1a: Results of daily analyzed PTFE laboratory blanks during the analysis period for samples collected January through December 2017. Elements Na through Zn shown.

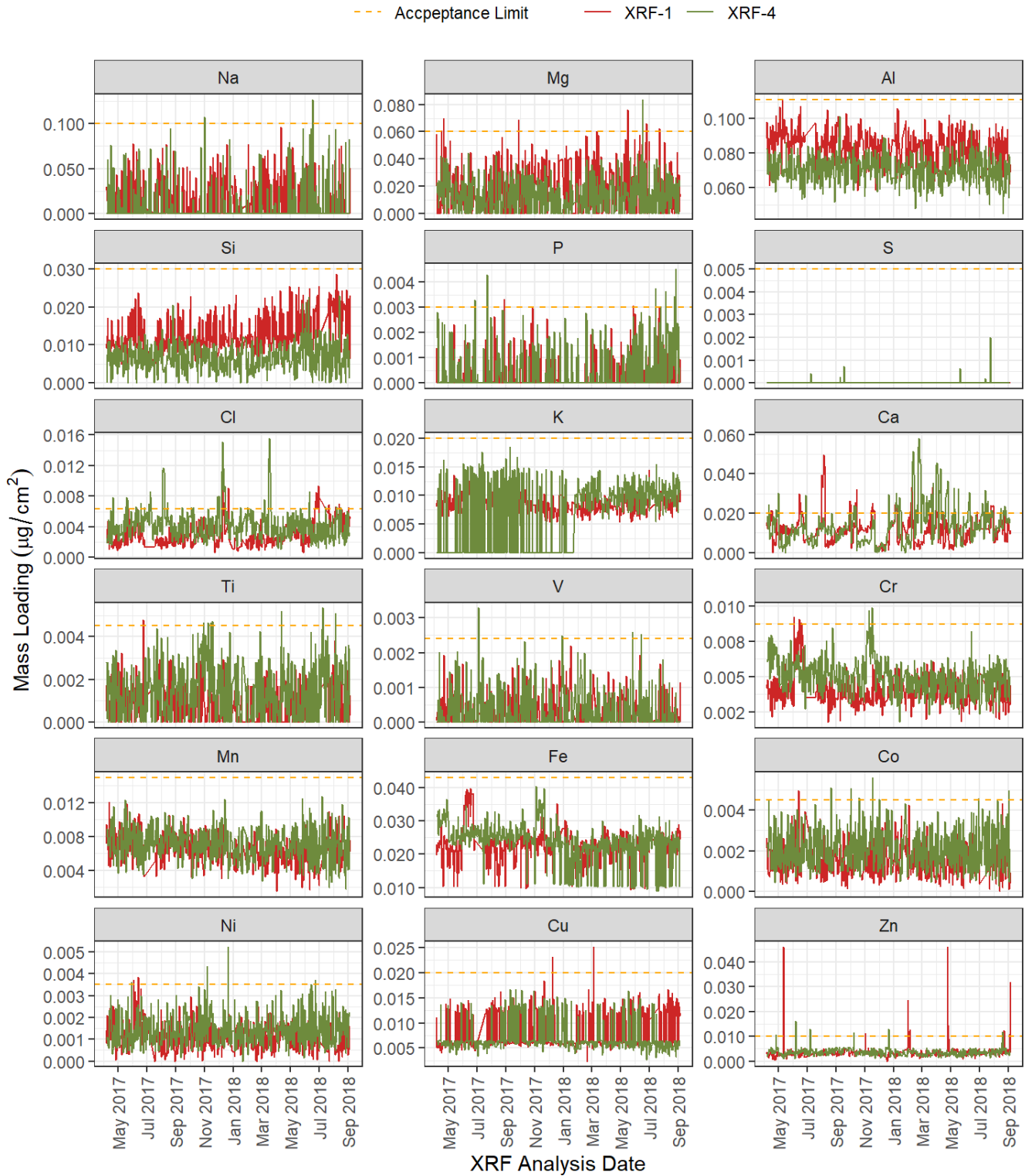
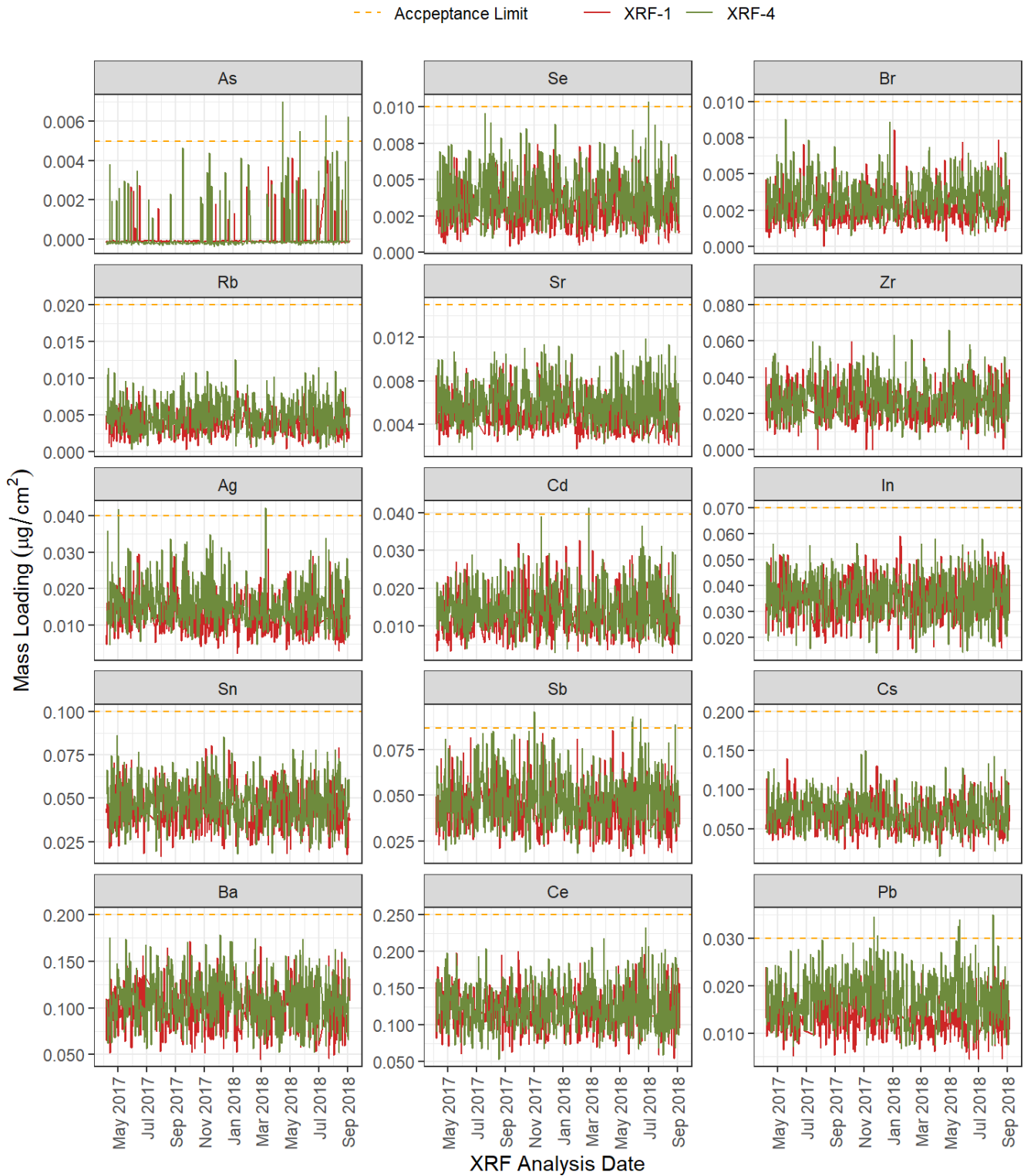


Figure 4.2-1b: Results of daily analyzed PTFE laboratory blanks during the analysis period for samples collected January through December 2017. Elements As through Pb shown.



Daily operational performance of the instruments is monitored by a multi-element reference material (ME-RM). Each instrument had its own daily ME-RM produced by UC Davis. The acceptance limits are set to +/- 10% RSD 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 are replaced (*UCD CSN TI 302D*).

Tables 4.2-3 and 4.2-4 show the results of the UC Davis ME-RMs. A small number of criteria exceedances are expected statistically, but this should be no more than 3% 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. Unacceptable QC results for Ca are expected to be from the same source as discussed for laboratory blank contamination (see Section 2.2.3, Section 3.2.1.3, and Section 4.2.2). The laboratory blanks were replaced when contamination occurred; however, the ME-RM samples were not replaced in response to contamination.

Table 4.2-3: Descriptive statistics of XRF-1 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM from 04/06/2017 to 09/06/2018, N = 537 (see Table 4.2-1 for corresponding sampling dates).

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.646	1.463	1.789	0.0	0	1.9
Si	2.799	2.504	3.061	0.0	0	1.0
S	10.959	9.826	12.010	0.0	0	0.9
K	1.669	1.497	1.829	0.0	0	0.7
Ca	1.941	1.688	2.063	7.1	4.3	2.1
Ti	0.129	0.114	0.139	2.0	0	3.5
Cr	0.701	0.629	0.769	0.0	0	0.9
Mn	0.337	0.304	0.372	0.0	0	2.1
Fe	1.992	1.777	2.171	0.0	0	1.4
Ni	0.117	0.105	0.129	0.0	0	2.3
Cu	0.546	0.488	0.596	0.0	0	1.4
Zn	0.406	0.357	0.436	0.2	0	1.6
Pb	0.644	0.578	0.707	0.0	0	2.4

Limits are +/- 10% of the reference loading (TI 302D).

Table 4.2-4: Descriptive statistics of XRF-4 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM from 04/06/2017 to 04/02/2018, N = 350 (see Table 4.2-1 for corresponding sampling dates).

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.469	1.285	1.571	0.6	0	2.5
Si	2.921	2.597	3.174	0	0	2.0
S	10.673	9.588	11.718	0	0	1.0
K	1.662	1.493	1.825	0	0	1.1
Ca	1.989	1.701	2.079	0.9	0	1.8
Ti	0.133	0.118	0.144	0.6	0	3.2
Cr	0.706	0.633	0.774	0	0	1.2
Mn	0.335	0.300	0.367	0	0	2.3
Fe	1.997	1.784	2.181	0	0	2.6
Ni	0.116	0.103	0.126	0	0	2.6
Cu	0.544	0.488	0.597	0	0	1.5
Zn	0.384	0.338	0.413	0	0	2.5
Pb	0.635	0.573	0.700	0	0	2.5

Limits are +/- 10% of the reference loading (TI 302D).

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) and a ME-RM purchased from Micromatter containing only Al and Si. The UC Davis weekly ME-RM was replaced in September 2017. Weekly results are compared to acceptance limits 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 of this report and can be found in *UCD CSN 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.

Table 4.2-5 and Table 4.2-6 show the EDXRF statistics of the weekly UC Davis ME-RM run until September 2017.

Table 4.2-5: Descriptive statistics of XRF-1 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM from 04/10/2017 to 09/27/2017, N = 20 (see Table 4.2-1 for corresponding sampling dates).

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	0.898	0.803	0.981	0	0	2.6
Si	1.441	1.288	1.574	0	0	1.2
S	5.430	4.835	5.910	0	0	0.9
K	0.790	0.711	0.869	0	0	0.4
Ca	0.863	0.773	0.944	0	0	1.2
Ti	0.059	0.054	0.065	0	0	4.4
Cr	0.318	0.287	0.351	0	0	1.1
Mn	0.154	0.139	0.169	0	0	2.4
Fe	0.895	0.806	0.985	0	0	0.8
Ni	0.052	0.049	0.060	5.0	0	4.2
Cu	0.115	0.105	0.128	0	0	2.4
Zn	0.108	0.095	0.116	0	0	2.1
Pb	0.279	0.249	0.305	0	0	3.7

Limits are +/- 10% of the reference loading (TI 302D).

Table 4.2-6: Descriptive statistics of XRF-4 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM from 04/10/2017 to 09/27/2017, N = 24 (see Table 4.2-1 for corresponding sampling dates).

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	0.786	0.705	0.862	0	0	3.2
Si	1.470	1.323	1.617	0	0	2.0
S	5.307	4.730	5.781	0	0	1.3
K	0.793	0.714	0.873	0	0	0.8
Ca	0.868	0.776	0.948	0	0	1.6
Ti	0.061	0.057	0.070	0	0	4.1
Cr	0.320	0.287	0.351	0	0	1.1
Mn	0.153	0.137	0.168	0	0	3.0
Fe	0.901	0.808	0.988	0	0	0.8
Ni	0.052	0.046	0.056	0	0	3.3
Cu	0.117	0.105	0.128	0	0	2.0
Zn	0.108	0.094	0.115	0	0	2.8
Pb	0.284	0.248	0.303	4.2	0	3.9

Limits are +/- 10% of the reference loading (TI 302D).

Table 4.2-7 and Table 4.2-8 show results of the new weekly UC Davis ME-RM, used beginning September 2017.

Table 4.2-7: Descriptive statistics of XRF-1 results ($\mu\text{g}/\text{cm}^2$) of the new weekly UC Davis ME-RM from 09/29/2017 to 09/05/2018, N = 43 (see Table 4.2-1 for corresponding sampling dates).

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.573	1.400	1.711	0	0	2.0
Si	2.572	2.311	2.825	0	0	1.1
S	9.680	8.686	10.616	0	0	0.9
K	1.470	1.314	1.606	0	0	1.1
Ca	1.594	1.435	1.754	0	0	1.6
Ti	0.120	0.108	0.132	0	0	2.6
Cr	0.603	0.542	0.662	0	0	0.9
Mn	0.290	0.258	0.316	0	0	2.7
Fe	1.675	1.501	1.834	0	0	1.6
Ni	0.100	0.090	0.110	0	0	2.4
Cu	0.285	0.255	0.312	0	0	1.5
Zn	0.226	0.200	0.244	0	0	2.3
Pb	0.539	0.480	0.586	0	0	2.4

Limits are +/- 10% of the reference loading (TI 302D).

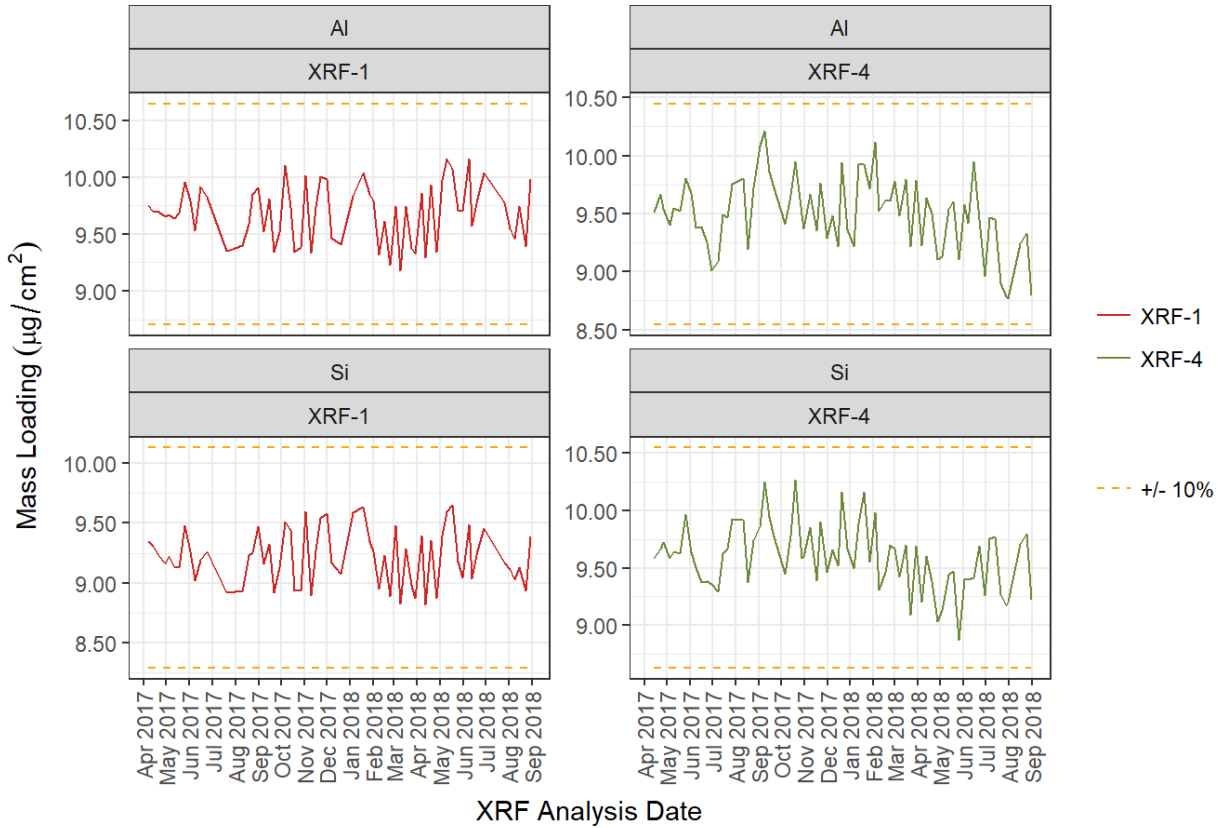
Table 4.2-8: Descriptive statistics of XRF-4 results ($\mu\text{g}/\text{cm}^2$) of the new weekly UC Davis ME-RM from 09/29/2017 to 04/02/2018, N = 51 (see Table 4.2-1 for corresponding sampling dates).

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.405	1.251	1.529	0	0	2.6
Si	2.659	2.386	2.917	0	0	2.6
S	9.663	8.677	10.606	0	0	0.9
K	1.474	1.325	1.619	0	0	0.8
Ca	1.593	1.424	1.740	0	0	0.9
Ti	0.123	0.111	0.135	0	0	3.2
Cr	0.613	0.552	0.675	0	0	1.4
Mn	0.293	0.263	0.322	0	0	2.0
Fe	1.695	1.525	1.864	0	0	3.1
Ni	0.101	0.090	0.110	0	0	2.6
Cu	0.290	0.261	0.319	0	0	1.3
Zn	0.228	0.205	0.250	0	0	1.9
Pb	0.549	0.502	0.614	0	0	2.9

Limits are +/- 10% of the reference loading (TI 302D).

A Micromatter ME-RM containing Al and Si is also run weekly. The results from this sample are plotted in Figure 4.2-2. The acceptance limits are set as +/- 10% of the average of the first five measurement results from each XRF. No issues were observed.

Figure 4.2-2: EDXRF results of the weekly Micromatter ME-RM containing Al and Si. Limits are +/- 10% of the reference loading.



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 both EDXRF instruments. Figures 4.2-3 and 4.2-4 plot the elemental concentrations for both of the weekly UC Davis ME-RM samples used during this analysis. As mentioned in Section 4.2.2.2, the UC Davis weekly ME-RM was replaced in September 2017. The following approach is used to quantify the differences observed in the plots. The scaled relative difference (SRD) between the two instruments is calculated for each element each week as:

$$SRD_i = \frac{(XRF1_i - XRF4_i) / \sqrt{2}}{(XRF1_i + XRF4_i) / 2},$$

where $XRF1_i$ and $XRF4_i$ are the mass loadings of the i^{th} element measured by each instrument.

For each element, i^{th} random error (precision) of each instrument is estimated as the standard deviation of the weekly results SRD_w , $w = 1, \dots, N$:

$$Precision_i = \sqrt{\frac{1}{N} \sum_w (SRD_{i,w} - \overline{SRD}_i)^2}$$

Where \overline{SRD}_i is the mean scaled relative difference for element i over the analysis period.

The bias between instruments is the mean value of the unscaled relative differences,

$$Bias_i = \frac{1}{N} \sum_w \left(\frac{XRF1_i - XRF4_i}{(XRF1_i + XRF4_i) / 2} \right)_w$$

The precision acceptance limit for the i^{th} element is calculated from the variation in the response of each instrument,

$$Precision\ Acceptance\ Limit_i = \sqrt{\sigma_{i,XRF1}^2 + \sigma_{i,XRF4}^2}$$

where σ is the standard deviation in the mass loading measured by the instrument. The bias acceptance limit is calculated as the sum of the error of both instruments to a mean reference mass loading for the i^{th} element of the ME-RM,

$$Bias\ Acceptance\ Limit_i = k * \frac{1}{N} \left(\sum_w \frac{|XRF1_{i,w} - C_{i,ref}|}{C_{i,ref}} + \sum_w \frac{|XRF4_{i,w} - C_{i,ref}|}{C_{i,ref}} \right)$$

where $C_{i,ref}$ is the reference elemental mass loading and k is a coverage factor which is set to a value of two to account for distribution of uncertainties possible in a given measurement. The acceptance limits are based on the mean mass loading for both instruments and provide a historical bias from which to compare the weekly bias of each instrument.

The results from this analysis, for elements greater than ten times the detection limit, averaged over both UC Davis ME-RM samples are presented in Table 4.2-9. The results of the inter-instrument comparison show a larger bias for Na, Mg, and P. These elements are difficult to quantify using the EDXRF method and some differences are expected.

Table 4.2-9: Precision and bias between XRF-1 and XRF-4 from the weekly UC Davis ME-RM calculated from 04/06/2017 to 09/06/2018 (see Table 4.2-1 for corresponding sampling dates). Only elements with mass loadings > 10×MDL are reported. Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Bias %	Bias Acceptance Limit %	Precision %	Precision Acceptance Limit %
Na	-5.0	±17.4	4.4	6.5
Mg	43.7	±79.3	10.7	13.3
Al	12.0	±24.6	2.9	3.9
Si	-2.0	±6.5	2.0	2.7
P	-85.5	±159.5	12.4	16.3
S	1.1	±4.5	1.0	1.5
K	-0.1	±2.7	0.9	1.1
Ca	0.3	±4.5	1.2	1.9
Ti	-2.5	±12.6	3.2	5.1
V	-1.2	±28.8	2.2	11.3
Cr	-0.5	±3.8	1.0	1.7
Mn	-0.1	±8.1	2.3	3.7
Fe	0.7	±5.7	1.4	2.3
Co	0.1	±11.5	3.3	5.2
Ni	0.2	±10.1	3.1	4.5
Cu	-0.9	±6.2	1.9	2.6
Zn	-0.3	±7.3	1.6	3.4
As	-3.3	±8.9	1.9	2.7
Se	-1.3	±7.4	2.2	3.2
Rb	-0.5	±11.1	3.2	5.2
Sr	-0.4	±11.9	3.7	5.0
Pb	-1.1	±10.8	3.2	4.6

Figure 4.2-3: Instrumental comparison using the weekly UC Davis ME-RM. XRF-1: 4/12/2017 to 9/21/2017, N = 19. XRF-4: 4/10/2017 through 9/21/2017, N = 19. (See Table 4.2-1 for corresponding sampling dates.)

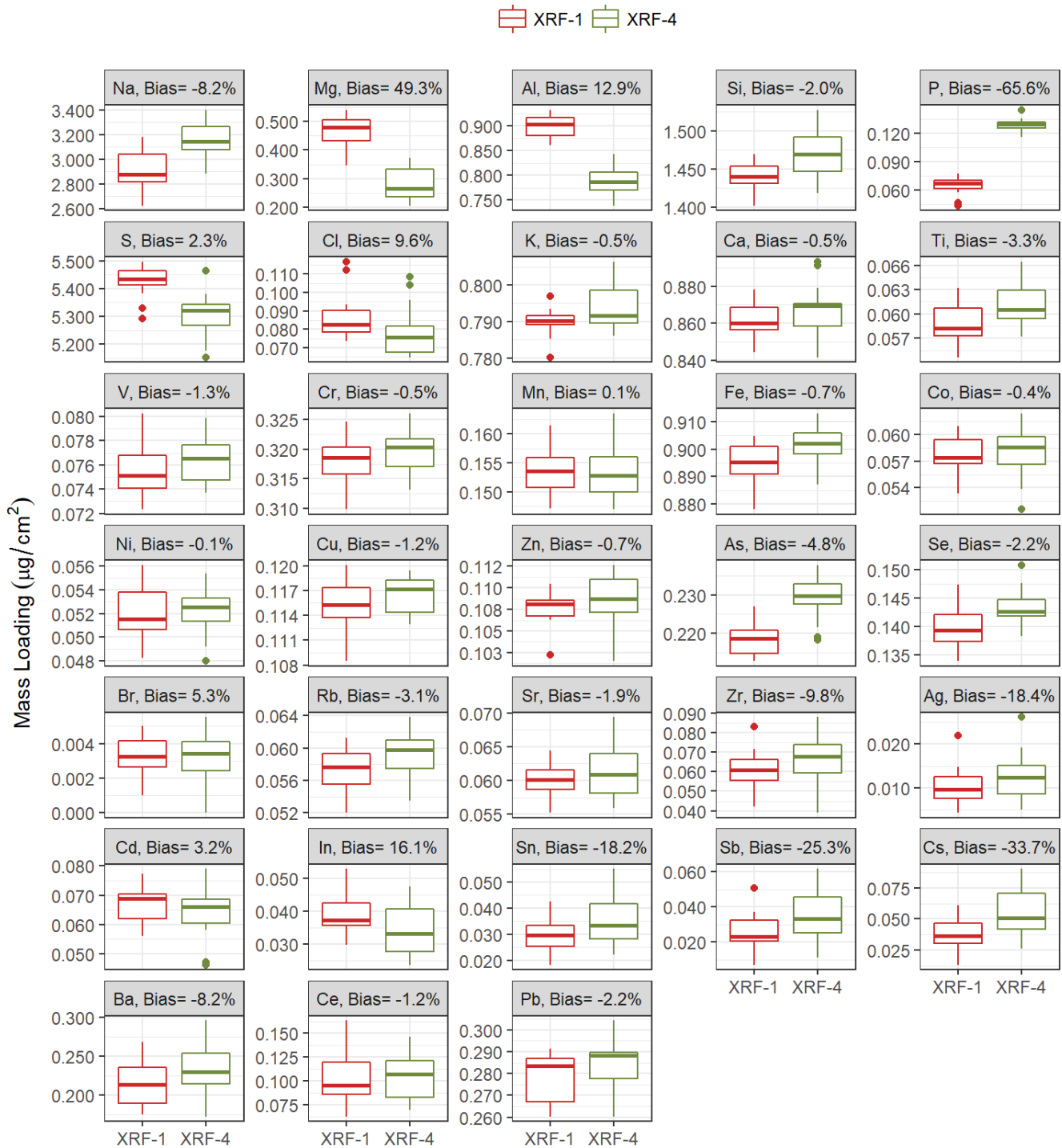
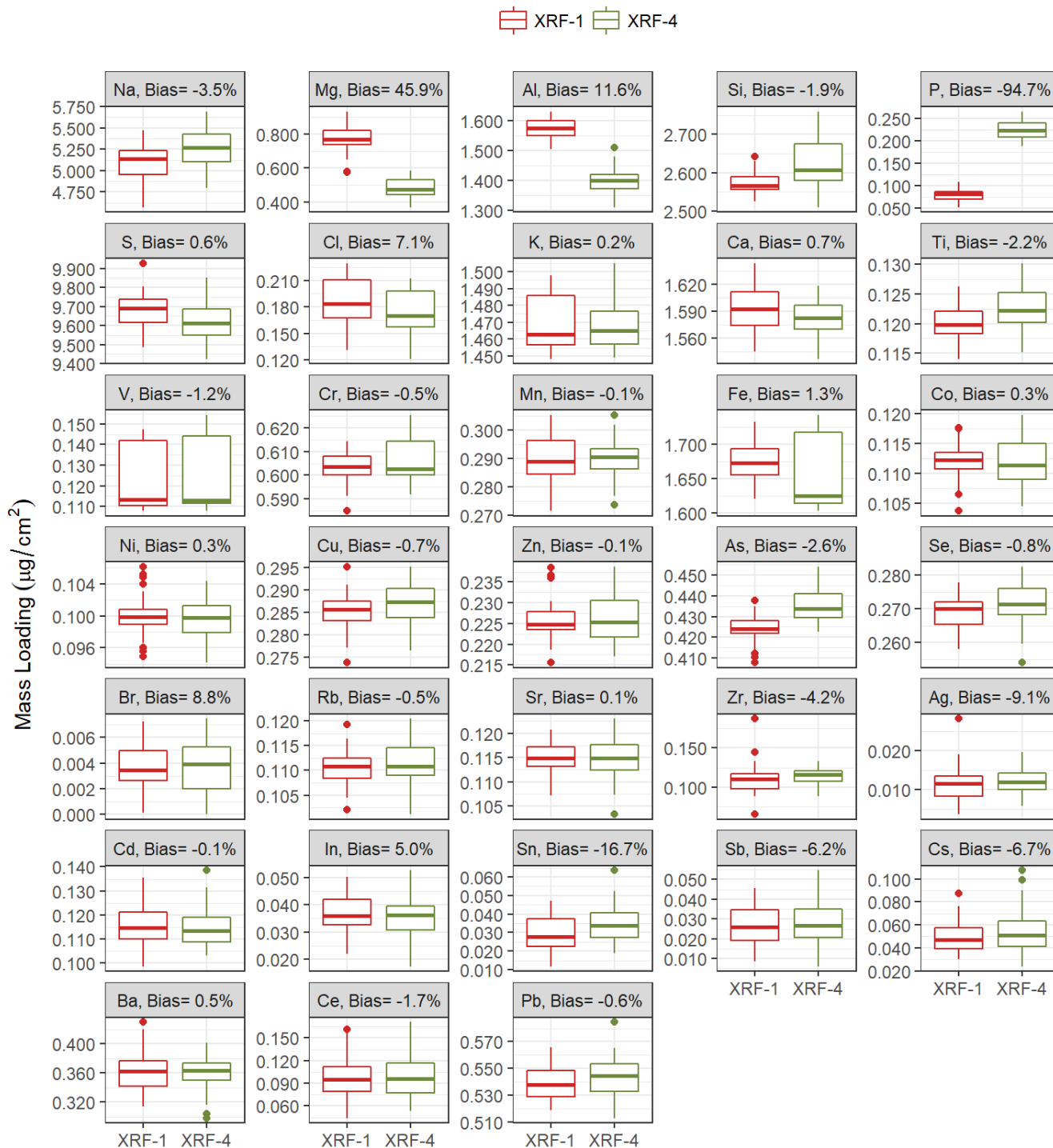


Figure 4.2-4: Instrumental comparison using the new weekly UC Davis ME-RM. XRF-1: 10/2/2017 to 8/28/2018, N = 41. XRF-4: 10/05/2017 to 8/27/2018, N = 41. (See Table 4.2-1 for corresponding sampling dates.)



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 was changed once during 2018. For analyses performed April 2017 through May 2018, the set

consisted of 16 CSN samples and one UC Davis produced ME-RM. The samples were on MTL 47 mm PTFE filters and covered a range of mass loadings representative of the CSN. The second set of 16 filters, used beginning June 2018, were UC Davis ME-RMs and covered a range of mass loadings simulating the CSN and higher for trace elements. In addition to these filters, a NIST SRM 2783 standard was included in the new set. 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

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

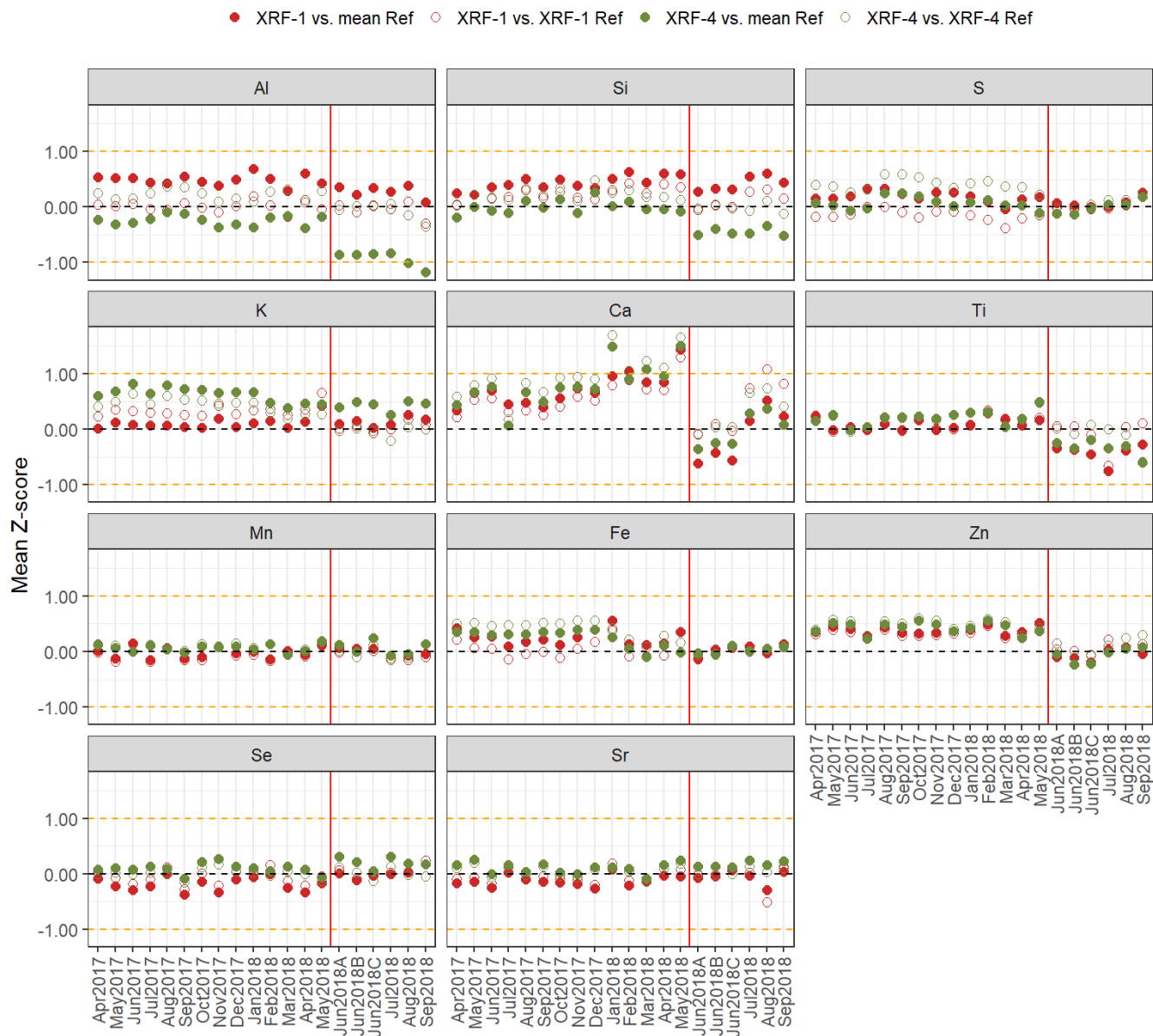
where x_{ij} is that month's result, \hat{x}_{ij} is the reference value for element i in filter j , and $U(x_{ij})$ and $U(\hat{x}_{ij})$ are the uncertainty of that month's result and the reference uncertainty respectively. The instrument-specific reference values for the samples of the reanalysis 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 both 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 well above the MDL (Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se, and Sr). For further detail see *UCD CSN TI 302D*.

Figure 4.2-5 shows the mean z-score plots over the analysis period. Issues observed include increasing mean z-scores for Ca on both instruments and low XRF-4 mean z-scores for Al. The increasing Ca z-scores relate to the previously mentioned Ca contamination on QC filters (see Section 2.2.3, Section 3.2.1.2, Section 4.2.2.1), and are observed for both instruments on both sets of reanalysis filters, occasionally resulting in acceptance criteria exceedances. The XRF-4 low mean z-score for Al is from bias between the XRF-4 and XRF-1 Al values (Table 4.2-9), which drives the XRF-4 mean z-score down with respect to the mean reference. However, the XRF-4 mean z-score with respect to its own reference remains constant with only a slight decrease in September 2018. This indicates that the low z-score values are from an inherent bias in the XRF-4 Al measurement, and are not indicative of instrument change during the analysis period. Changes in the XRF analysis protocol are being investigated to decrease the inter-instrument bias.

Figure 4.2-5: Inter-instrument comparison by z-score of reanalysis sample set. Vertical red line denotes change in re-analysis set. Multiple measures of the new re-analysis set during the month of June 2018 (denoted by A, B, and C) were made for determination of reference values.

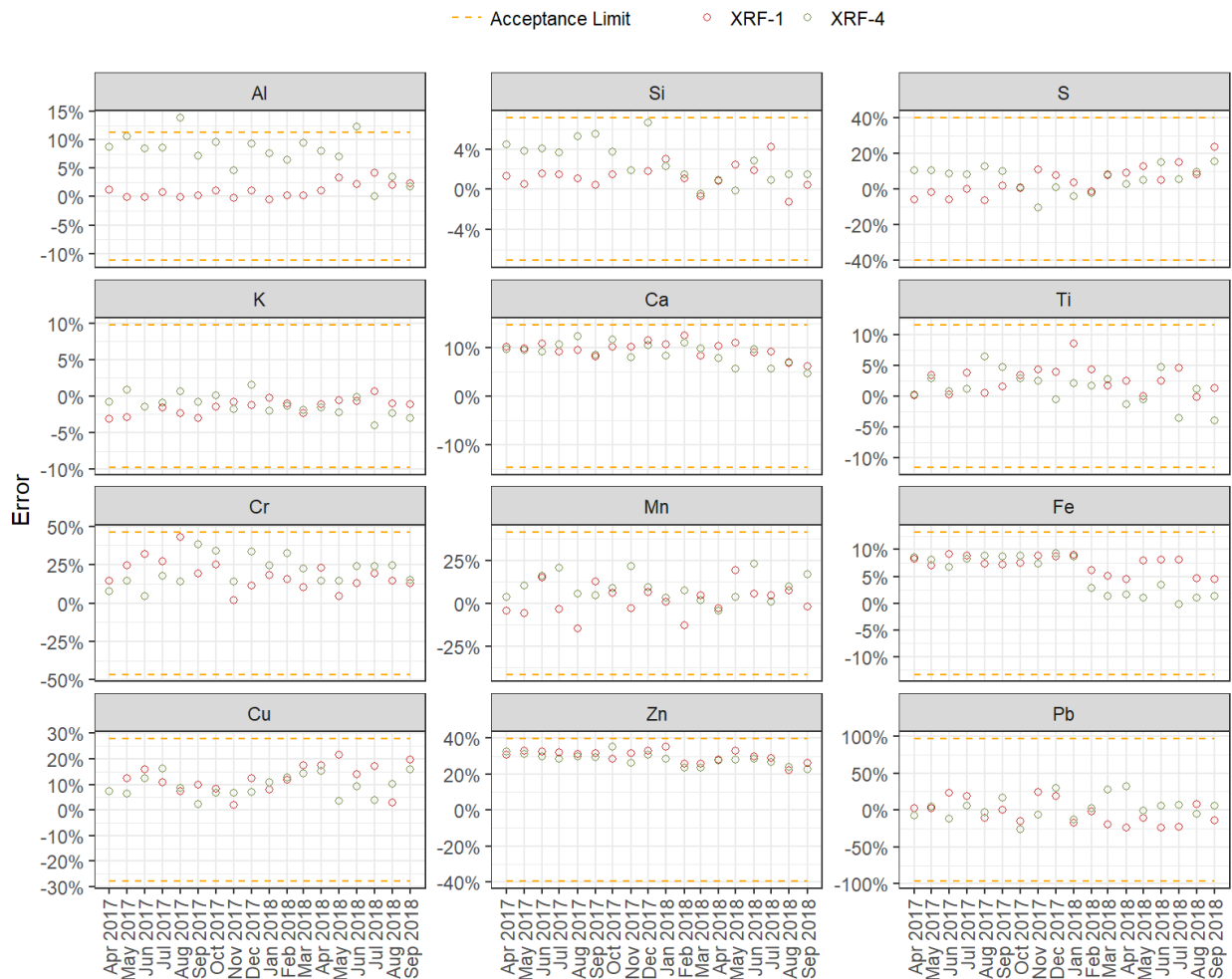


4.2.2.5 Calibration Verification with NIST SRM 2783

The errors of EDXRF instruments from the NIST SRM 2783 certified/reference mass loadings are monitored monthly for selected elements with loadings at least three times higher than the EDXRF 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 limits 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 results for the analysis period are shown in Figure 4.2-6. Both XRF-1 and XRF-4 underwent routine calibrations in January 2017 and January 2018. XRF-4 also underwent calibration in June 2018 due to a replacement of the CaF₂ target in the secondary target wheel. The results from the monthly NIST SRM 2783 analyses indicate that calibrations for both instruments are stable over the one-year calibration period. The overall error for most elements is less than 20%. However, the error in Zn is around 30%. Per Yarkin et al. (2016b), an XRF inter-laboratory comparison reported SRM 2783 Zn error varying from -15% to 30%; the results shown here fit within that range. The only acceptance criteria exceedance was for XRF-4 Al during August 2017 and June 2018 (prior to the new calibration). The error for Al on XRF-4 was near the acceptance limit and had two measures outside of the limits. These two exceedances were within the normal variance of the errors for this instrument (i.e. not outliers) and considering other QC filter results for Al during these time periods, no instrument issues were suspected. After the June 2018 calibration, the XRF-4 Al error was reduced and within the acceptance criteria.

Figure 4.2-6: Error of each XRF instrument from the NIST SRM standard run monthly.



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*

The EPA did not conduct any audits or performance evaluations of the UC Davis XRF laboratory during 2017.

4.2.4.2 *Performance Evaluations*

The UC Davis XRF laboratory actively participates in interlaboratory comparisons.

In 2018 (during the analysis period for samples collected during 2017), UC Davis participated in an interlaboratory comparison with Environment and Climate Change Canada. CuSO₄ and CuO reference materials, generated at UC Davis, were analyzed by XRF, IC, and ICP-MS. Results indicate good agreement between the laboratories with less than 5% absolute difference.

Additionally, the EPA provided five PTFE samples for elemental analysis as part of the EPA Office of Air Quality Planning and Standards (OAQPS) interlaboratory performance evaluation. This evaluation was carried out during the timeframe when UC Davis was also analyzing CSN samples collected during 2017. Reported z-scores were all below 2, indicating satisfactory interlaboratory comparison results.

4.2.4.3 *Training*

Training of all personnel who assist with or operate the XRF 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 (*UCD CSN SOP #302* and *CSN TI 302A-D*), and authorized by the Laboratory Manager can perform XRF analysis on CSN samples.

4.2.4.4 *Accreditations*

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

4.2.5 Summary of Filter Field Blanks

Over the sampling period (January 1, 2017 through December 31, 2017) there were 1,367 valid PTFE filter field blanks. Table 4.2-10 summarizes the field blank statistics.

Table 4.2-10: PTFE filter field blank statistics.

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. ($\mu\text{g}/\text{cm}^2$)
Na	1367	0.000	0.014	-0.002	0.529	0.030
Mg	1367	0.013	0.016	0.000	0.188	0.015
Al	1367	0.081	0.083	0.051	0.431	0.022
Si	1367	0.010	0.016	0.000	0.691	0.041
P	1367	0.000	0.000	0.000	0.012	0.001
S	1367	0.000	0.004	0.000	0.845	0.041
Cl	1367	0.003	0.004	0.000	0.271	0.009
K	1367	0.007	0.007	0.000	0.140	0.011
Ca	1367	0.003	0.010	0.000	0.587	0.033
Ti	1367	0.001	0.001	0.000	0.033	0.002
V	1367	0.000	0.000	0.000	0.003	0.001
Cr	1367	0.005	0.005	0.002	0.104	0.005
Mn	1367	0.007	0.007	0.000	0.036	0.002
Fe	1367	0.024	0.029	0.000	0.461	0.033
Co	1367	0.002	0.002	0.000	0.006	0.001
Ni	1367	0.001	0.002	0.000	0.031	0.002
Cu	1367	0.006	0.007	0.000	0.030	0.003
Zn	1367	0.003	0.003	0.000	0.061	0.003
As	1367	0.000	0.000	0.000	0.006	0.001
Se	1367	0.003	0.003	0.000	0.011	0.001
Br	1367	0.003	0.003	0.000	0.012	0.001
Rb	1367	0.004	0.005	0.001	0.013	0.002
Sr	1367	0.005	0.005	0.002	0.016	0.002
Zr	1367	0.025	0.026	0.000	0.065	0.011
Ag	1367	0.013	0.014	0.004	0.042	0.005
Cd	1367	0.013	0.014	0.003	0.044	0.006
In	1367	0.035	0.036	0.012	0.073	0.008
Sn	1367	0.044	0.045	0.017	0.097	0.012
Sb	1367	0.043	0.044	0.013	0.107	0.013
Cs	1367	0.065	0.067	0.000	0.139	0.020
Ba	1367	0.101	0.103	0.046	0.198	0.025
Ce	1367	0.118	0.121	0.047	0.240	0.029
Pb	1367	0.014	0.015	0.004	0.030	0.005

4.3 DRI Carbon Laboratory

The DRI Carbon Analysis Laboratory, as a subcontractor to UC Davis, received and analyzed quartz filters from batches 22 through 38 for samples collected January 1, 2017 through December 31, 2017. Analysis of these samples was performed May 8, 2017 through April 26, 2018. All analyses were performed using the DRI Model 2015 multi-wavelength carbon analyzer with the IMPROVE_A method and analysis results were reported to UC Davis. Twelve DRI Model 2015 Thermal/Optical Carbon Analyzers (designated as units # 21, 31, 34-38, 40-43, and 47) were used for these CSN IMPROVE_A analyses.

4.3.1 Summary of QC Checks and Statistics

Samples received at the DRI Carbon Laboratory follow the chain-of-custody procedure specified in *DRI CSN SOP #2-231*. This SOP is specific for the Chemical Speciation Network. Quality control (QC) measures for the DRI carbon analysis are included in the SOP and summarized in Table 4.3-1. The table specifies the frequency and standards required for the checks, along with the acceptance criteria, and corrective actions for the carbon analyzers. More detail on individual control measures is provided in specific subsections.

Table 4.3-1. DRI carbon analysis QC measures for Model 2015 analyzer.

QA/QC Activity	Calibration Standard and Range	Calibration Frequency	Acceptance Criteria	Corrective Action
System Blank Check	NA ^a	Once per week	<0.2 µg C/cm ² . See Table 4.3-2 and Figure 4.3-1.	Check instrument.
Laboratory Blank Check	NA	Beginning of analysis day	<0.2 µg C/cm ² . See Table 4.3-3 and Figure 4.3-2.	Check instrument and filter punch and rebake
Calibration Peak Area Check	NIST 5% CH ₄ /He gas standard; 20 µg C (6-port valve injection loop, 1000 µl)	Every analysis	Typical counts 15,000-25,000 and 95-105% of average calibration peak area of the day. See Figure 4.3-4.	Void analysis result; check flowrates, leak, and 6-port valve temperature; conduct an auto-calibration; and repeat analysis with second filter punch.
Auto-Calibration Check	NIST 5% CH ₄ /He gas standard; 20 µg C (Carle valve injection loop, 1000 µl)	Alternating beginning or end of each analysis day	Relative standard deviation of the three injection peaks <5% and calibration peak area 90-110% of weekly average. See Table 4.3-4 and Figure 4.3-3.	Verify if major maintenance has occurred. Troubleshoot and correct system before analyzing samples.
Manual Injection Calibration	NIST 5% CH ₄ /He or NIST 5% CO ₂ /He gas standards; 20 µg C (Certified gas-tight syringe, 1000 µl)	Four times a week (Sun., Tue., Thu., and Sat.)	95-105% recovery and calibration peak area 90-110% of weekly average. See Figure 4.3-5a.	Troubleshoot and correct system before analyzing samples.
Sucrose Calibration Check	10µL of 1800 ppm C sucrose standard; 18 µg C	Thrice per week (began March, 2009)	17.1-18.9 µg C/filter. See Figure 4.3-5b.	Troubleshoot and correct system before analyzing samples.
Potassium Hydrogen Phthalate (KHP) Calibration Check	10µL of 1800 ppm C KHP standard; 18 µg C	Twice per week (Tue. and Thu.)	17.1-18.9 µg C/filter. See Figure 4.3-5c.	Troubleshoot and correct system before analyzing samples.
Multiple Point Calibrations	1800 ppm C Potassium hydrogen phthalate (KHP) and sucrose; NIST 5% CH ₄ /He, and NIST 5% CO ₂ /He gas standards; 9-36 µg C for KHP and sucrose; 2-30 µg C for CH ₄ and CO ₂	Every six months or after major instrument repair	All slopes ±5% of average. See Table 4.3-5.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Sample Replicates (on the same or a different analyzer)	NA	Every 10 analyses	±10% when OCR and TCR ≥10 µg C/cm ² ±20% when ECR > 10µg C/cm ² or <±1 µg/cm ² when OCR and TCR <10 µg C/cm ² <±2 µg/cm ² when ECR <10µg C/cm ² See Table 4.3-8 and Figure 4.3-6.	Investigate instrument and sample anomalies and rerun replicate when difference is > ±10%.
Temperature Calibrations	NIST-certified thermocouple	Every six months, or whenever the thermocouple is replaced	Linear relationship between analyzer and NIST thermocouple values with R ² >0.99. See Table 4.3-6.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Oxygen Level in Helium Atmosphere (using GC/MS) ^b	Certified gas-tight syringe; 0-100 ppmv	Every six months, or whenever leak is detected	Less than the certified amount of He cylinder. See Table 4.3-7.	Replace the He cylinder and/or O ₂ scrubber.

^a NA: Not Applicable.

^b Gas chromatography/mass spectrometer (Model 5975, Agilent Technology, Palo Alto, CA, USA).

4.3.2 Summary of QC Results

Detailed results of the carbon QC are presented in the subsections below. All system blanks (Table 4.3-2) or laboratory blanks (Table 4.3-3) that did not meet the acceptance criteria were reanalyzed and if they did not pass the second analysis, instrument maintenance was performed and additional blanks were run before the analyzer was placed on-line. Exceedance in multipoint calibrations (Table 4.3-5) result in verification of individual calibration points, troubleshooting

the instrument, and repeating calibrations. Exceedances in auto-calibrations (Table 4.3-4), internal calibrations (Figure 4.3-4), as well as CO₂ (Figure 4.3-5a), sucrose (Figure 4.3-5b), and KHP (Figure 4.3-5c) calibrations result in reanalysis and/or instrument maintenance. For cases where CSN samples were analyzed after an exceedance, data were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.3.2 and Section 3.2.3.1). As a corrective action, software tools are being developed to generate QC control charts and summaries to ensure QC exceedances are captured and corrected immediately.

4.3.2.1 System and Laboratory Blanks

Table 4.3-2 lists the number of system blanks analyzed during the report period and their concentration statistics. The system blank control chart is shown in Figure 4.3-1. System blanks are used to ensure that the system is not introducing bias in the carbon analysis. Most system blanks were below the limit of 0.2 µgC/cm². When an exceedance is observed, possible contamination is checked, parts are cleaned, the sample oven is baked, and a second system blank is rerun to ensure that it passes the criterion. One system blank did not pass the acceptance criteria and was rerun to pass.

Table 4.3-2: Statistics of system blanks ran on the Model 2015 analyzer between 5/8/2017 and 5/26/2018. 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). Total carbon is shown by reflectance (TCR).

Parameter	Count	Median (µg/cm ²)	Average (µg/cm ²)	Min (µg/cm ²)	Max (µg/cm ²)	St. Dev. (µg/cm ²)	# Exceedance
OC1	465	0.000	0.000	0.000	0.006	0.000	0
OC2	465	0.000	0.002	0.000	0.049	0.006	0
OC3	465	0.000	0.010	0.000	0.117	0.018	0
OC4	465	0.000	0.001	0.000	0.084	0.006	0
OCR	465	0.000	0.014	0.000	0.171	0.026	0
OCT	465	0.001	0.015	0.000	0.228	0.029	1
OPR	465	0.000	0.001	0.000	0.074	0.005	0
OPT	465	0.000	0.002	0.000	0.074	0.008	0
EC1	465	0.000	0.000	0.000	0.016	0.001	0
EC2	465	0.000	0.002	0.000	0.064	0.006	0
EC3	465	0.000	0.000	0.000	0.060	0.003	0
ECR	465	0.000	0.001	0.000	0.062	0.006	0
ECT	465	0.000	0.000	0.000	0.020	0.001	0
TCR	465	0.001	0.015	0.000	0.228	0.029	1

Figure 4.3-1: Control chart of system blank total carbon by reflectance (TCR) concentrations on the DRI Model 2015 carbon analyzers. The red dash lines indicate the limit of $0.2 \mu\text{g C}/\text{cm}^2$.

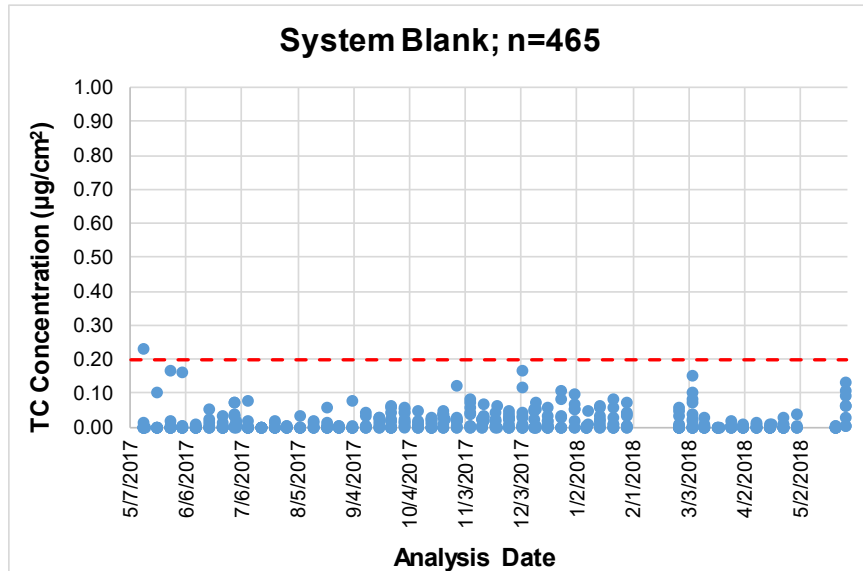
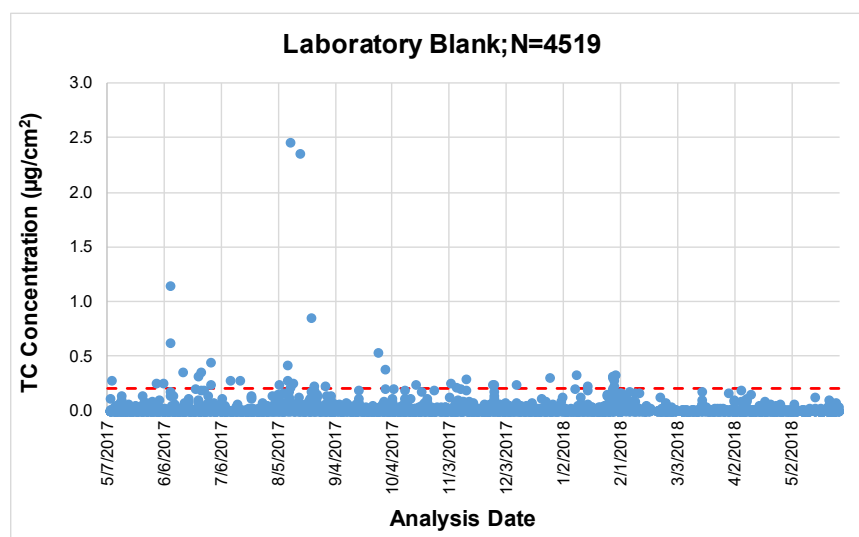


Table 4.3-3 lists the number of laboratory blanks analyzed during the report period and their concentration statistics. The laboratory blank control charts are shown in Figure 4.3-2. Laboratory blank analyses are performed daily to check for system contamination and evaluate laser response. Most laboratory blanks were below the limit of $0.2 \mu\text{gC}/\text{cm}^2$. When an exceedance is observed, the sample oven is baked and a second laboratory blank is run. If the second blank still exceeds the limit, the analyzer is taken offline for cleaning and maintenance. A total of 37 CSN samples were run after failed laboratory blanks; these cases were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.3.2 and Section 3.2.3.1). However, the sucrose analysis that immediately followed the failed laboratory blank indicated acceptable values.

Table 4.3-3: Statistics of laboratory blanks run on the Model 2015 analyzer between 5/8/2017 and 5/26/2018. 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). Total carbon is shown by reflectance (TCR).

Parameter	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
OC1	4519	0.000	0.000	0.000	0.093	0.003	0
OC2	4519	0.000	0.001	0.000	0.688	0.013	1
OC3	4519	0.000	0.005	0.000	0.693	0.022	9
OC4	4519	0.000	0.001	0.000	1.060	0.020	3
OCR	4519	0.000	0.008	0.000	2.058	0.048	34
OCT	4519	0.000	0.010	0.000	2.450	0.062	39
OPR	4519	0.000	0.001	0.000	0.238	0.007	1
OPT	4519	0.000	0.003	0.000	1.339	0.028	3
EC1	4519	0.000	0.001	0.000	1.090	0.017	2
EC2	4519	0.000	0.003	0.000	0.884	0.018	3
EC3	4519	0.000	0.000	0.000	0.105	0.002	0
ECR	4519	0.000	0.003	0.000	1.339	0.028	5
ECT	4519	0.000	0.001	0.000	0.290	0.008	3
TCR	4519	0.000	0.011	0.000	2.450	0.065	41

Figure 4.3-2: Control chart of daily laboratory blank total carbon by reflectance (TCR) concentrations ran on the DRI Model 2015 carbon analyzers. The red dash lines indicate the limit of $0.2 \mu\text{gC}/\text{cm}^2$.



4.3.2.2 *Auto-Calibration and Internal Calibration Peak Area Check*

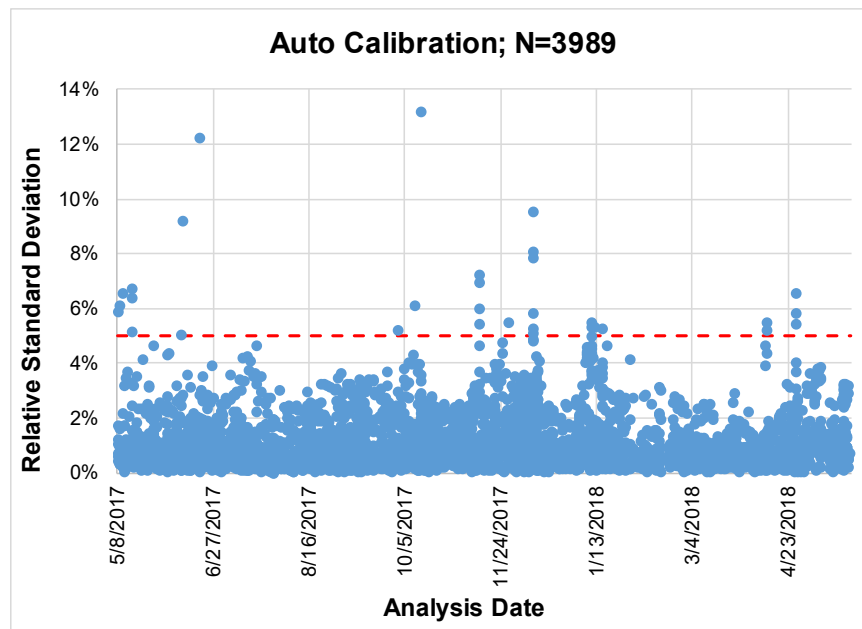
Once per day each analyzer runs an auto-calibration protocol. Using the Carle valve, an aliquot of methane standard is injected once in a He-only atmosphere (organic carbon stage), once in a He/O₂ atmosphere (elemental carbon stage), and finally as the normal internal calibration peak. The three peaks should have similar peak areas if the catalysts are in good condition. The

similarity of the three peaks are measured by the relative standard deviation (RSD), which is the standard deviation divided by the average of the three peak areas. The acceptance limit is RSD <5% and $\pm 10\%$ from weekly average. Table 4.3-4 summarizes the RSD of the three methane injection peaks during the analysis period and the control chart is shown in Figure 4.3-3. There were 32 exceedances and most of them occurred when the analyzer was under maintenance and no samples were run. When an exceedance is observed, the analyzer is checked and the auto-calibration is rerun. The calibration peak areas of previous runs are examined and/or manual injections are done to ensure the analyzer is working properly. A total of 106 CSN samples were analyzed during auto-calibration peak area exceedances; these cases were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.3.2 and Section 3.2.3.1).

Table 4.3-4: Statistics of the relative standard deviation (RSD) of the three methane injection peaks from auto-calibration checks.

Statistic	Auto-Calibration
Count	3989
Median	0.8%
Average	1.1%
Min	0.0%
Max	13.2%
Standard deviation	1.0%
Exceedance	32

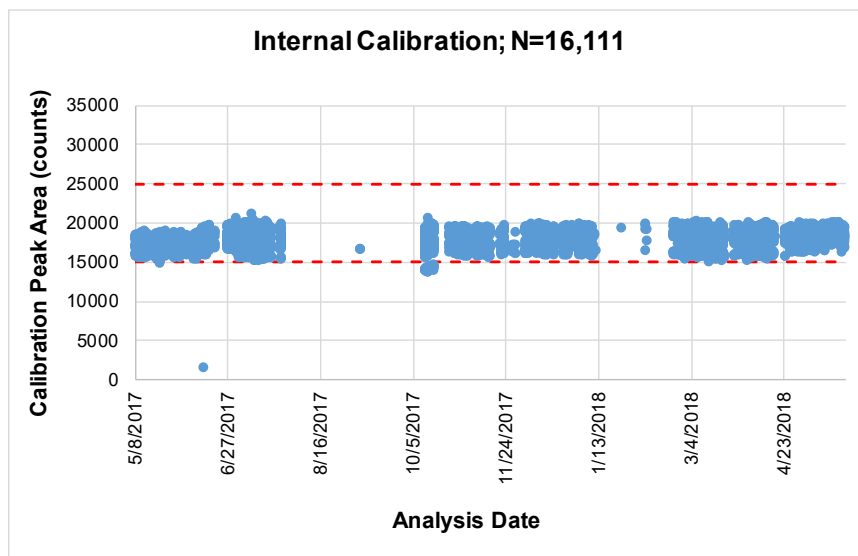
Figure 4.3-3: Control chart of the relative standard deviation of the three methane injection peaks from daily auto-calibration ran on the DRI Model 2015 carbon analyzers. The red dash lines indicate the limit of 5% RSD.



At the end of each run, a fixed amount of methane is injected via a Carle valve as an internal calibration standard. The internal calibration peak area is examined for each sample. Significant changes in calibration peak area counts are monitored and instruments are checked for

performance against daily calibrations. Typical ranges for the internal calibration peaks fall between 15,000 and 25,000 counts for Model 2015. In addition to peak area ranges, the peak areas are also compared to the daily averages. Sudden changes or atypical counts result in instrument maintenance. Metadata concerning QC measures and instrument maintenance are reported to UC Davis quarterly. Figure 4.3-4 shows the daily internal calibration peak area during the reporting period for all analyzers. For the Model 2015, 16,030/16,111 (99.5%) passed both peak area and daily average criteria. A total of 96 original analyses and two replicate analyses exceeded internal calibration QC limits; these cases were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.3.2 and Section 3.2.3.1). However, other QC analyses (e.g., replicates, auto-calibration, and internal calibration peak area check) within the time period indicate acceptable values. One sample, quartz filter F052584, did not meet QC criteria for the calibration peak; the filter was subsequently invalidated by UCD with the AS (Poor QA Results) null code and updated in AQS.

Figure 4.3-4: Control chart of the internal calibration peak area for the DRI Model 2015 carbon analyzers. The red dash lines indicate the typical internal calibration peak area between 15,000 and 25,000 for Model 2015. Sample F052584 (collected 2/24/2017, analyzed 6/14/2017) did not meet QC criteria and was invalidated.



4.3.2.3 *Multipoint Calibration and Manual Injection Check*

Multipoint carbon calibrations are performed semi-annually or whenever major repairs or changes are made to the instruments. The calibration uses four different sources of carbon: methane (CH₄), carbon dioxide (CO₂), sucrose (C₁₂H₂₂O₁₁), and potassium hydrogen phthalate (KHP), each with four injections with different carbon content (except that 15 μL sucrose and KHP are injected twice) resulting in a total of 18 calibration points in the set. The calibration result is plotted as μg carbon in the calibration standard versus total carbon peak area normalized by the internal calibration peak area. A regression slope is obtained by fitting the calibration points with a linear line forced through the origin. The slope relates the measured normalized peak area to carbon content. It represents the response of the entire analyzer to generic carbon compounds, including the efficiency of the oxidation oven and sensitivity of the NDIR. If the ratio of carbon over normalized peak area for individual calibration point differs from the regression slope by more than 10%, the calibration point is treated as an outlier and redone. Daily calibration injections and replicate analysis also verify acceptable slopes. Table 4.3-5

provides summary statistics for full multipoint calibrations by analyzer for the period during which the project samples were analyzed. The QC criterion requires the slope to be within $\pm 5\%$ of average by each analyzer (Table 4.3-1), where the slope is obtained after individual calibration outlier points are removed and redone. There were five cases where samples were run with carbon calibration slopes outside of the QC criteria (all on Analyzer #47); these data were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.3.2 and Section 3.2.3.1).

Table 4.3-5: Multipoint calibration statistics (CSN sample dates 1/1/2017-12/31/17). Units for the slope are μg carbon per ratio of standard injection peak count/calibration gas peak count. For analyzers 31, 37, 38, 40, 41, and 43, more than 6 months passed between calibrations. As noted in Sections 2.3.2 and 3.2.3.1, a calibration calendar has been established by DRI to avoid recurrence of this issue.

Carbon Analyzer	Calibration Date	Slope	r^2	Difference from Analyzer Average	# of Samples Flagged	Comment
21	6/2/2017	19.963	0.998	3%	0	
	9/22/2017	18.841	0.994	-3%	0	
	11/30/2017	19.658	0.995	1%	0	
	5/30/2018	19.348	0.998	-1%	0	
31	6/12/2017	19.703	0.997	0%	0	
	8/16/2017	19.565	0.993	0%	0	
	2/21/2018	19.598	0.998	0%	0	
32	10/24/2017	18.319	0.996	5%	0	
	11/20/2017	17.191	0.996	-2%	0	
	1/9/2018	17.256	0.991	-1%	0	
	6/13/2018	16.664	0.996	-5%	0	
	6/29/2018	17.870	0.998	2%	0	
34	5/5/2017	19.238	0.999	0%	0	
	9/12/2017	18.591	0.999	-3%	0	
	11/14/2017	19.561	0.996	2%	0	
	11/27/2017	18.326	0.996	-5%	0	
	12/5/2017	19.668	0.998	2%	0	
	3/13/2018	19.464	0.995	1%	0	a
	3/15/2018	19.486	0.995	2%	0	
35	6/8/2017	19.343	0.996	1%	0	
	10/9/2017	18.62	0.995	-3%	0	
	12/5/2017	19.421	0.999	1%	0	
	1/26/2018	19.808	0.995	3%	0	
	4/9/2018	18.636	0.994	-3%	0	
36	4/3/2017	19.37	0.992	2%	0	a
	4/28/2017	19.307	0.997	2%	0	
	6/23/2017	19.065	0.997	0%	0	
	11/3/2017	18.698	0.995	-2%	0	
	11/8/2017	19.153	0.996	1%	0	

Carbon Analyzer	Calibration Date	Slope	r ²	Difference from Analyzer Average	# of Samples Flagged	Comment
	1/4/2018	19.274	0.991	1%	0	
	5/9/2018	19.175	0.996	1%	0	a
	5/14/2018	18.389	0.991	-3%	0	a
	5/16/2018	18.888	0.998	-1%	0	a
	5/24/2018	18.742	0.993	-1%	0	a
	5/30/2018	18.853	0.995	-1%	0	
37	5/3/2017	18.814	0.994	-1%	0	
	12/18/2017	19.035	0.993	0%	0	b
	1/5/2018	18.830	0.996	-1%	0	
	6/1/2018	19.180	0.998	1%	0	
38	5/10/2017	18.478	0.995	-2%	0	
	7/2/2017	18.804	0.992	0%	0	
	8/17/2017	18.912	0.996	0%	0	a
	8/18/2017	19.074	0.997	1%	0	
	11/6/2017	18.858	0.997	0%	0	
	6/21/2018	18.973	0.991	1%	0	b
	6/26/2018	18.964	0.996	1%	0	
40	6/21/2017	19.350	0.993	0%	0	
	8/3/2017	19.178	0.993	-1%	0	
	2/13/2018	19.391	0.993	0%	0	
41	7/5/2017	19.254	0.995	0%	0	
	8/17/2017	19.480	0.994	1%	0	
	2/26/2018	18.982	0.996	-1%	0	
42	9/28/2017	19.443	0.997	1%	0	
	1/19/2018	18.897	0.992	-2%	0	
	4/2/2018	19.399	0.998	1%	0	
	5/17/2018	19.090	0.997	-1%	0	
43	5/19/2017	18.580	0.995	0%	0	
	9/8/2017	19.125	0.995	3%	0	
	6/5/2018	18.022	0.971	-3%	0	c
47	7/15/2017	17.520	0.991	-6%	5	
	8/1/2017	19.013	0.998	2%	0	
	9/11/2017	18.604	0.995	0%	0	
	1/26/2018	18.709	0.996	1%	0	
	4/18/2018	18.876	0.997	2%	0	

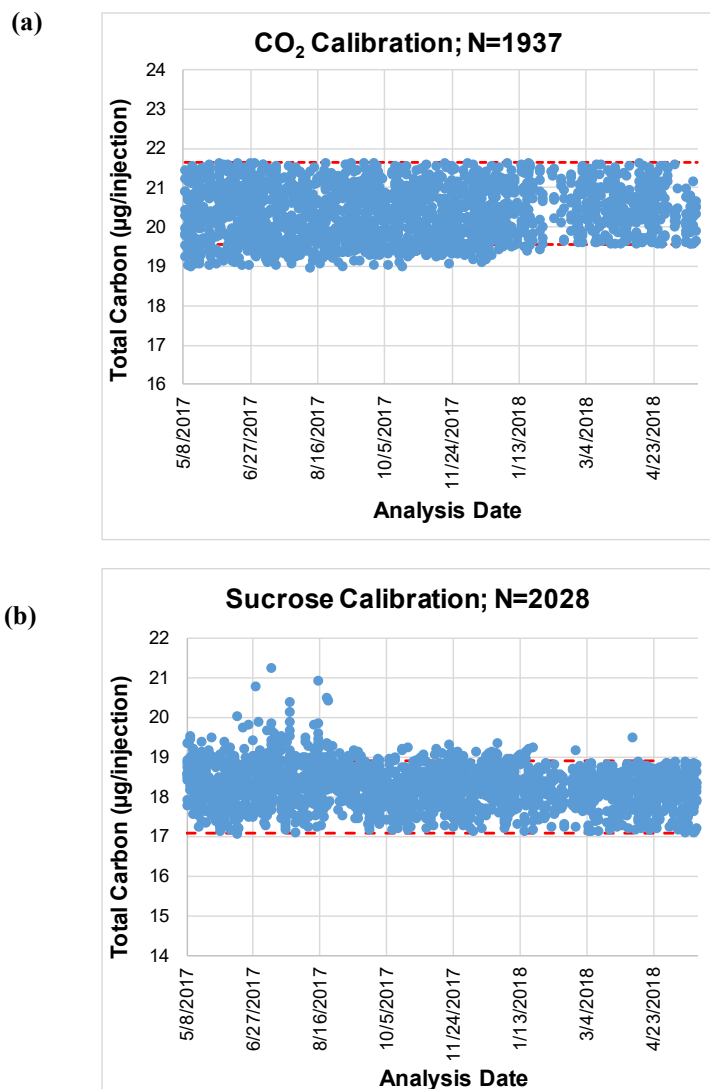
^a Carbon calibration repeated

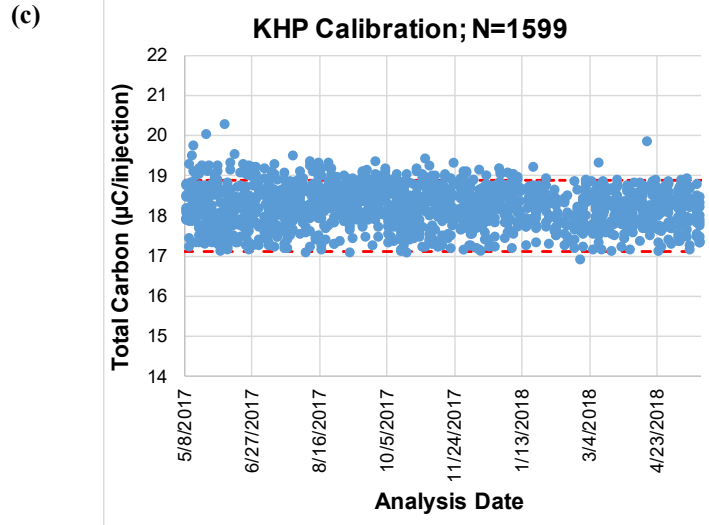
^b Calibration overdue, new QA calendar system implemented to prevent delay

^c Instrument offline from February 2018 to June 2018

CO₂ calibrations are performed on each analyzer four times per week, sucrose calibration checks are done on each analyzer three times per week, and KHP calibrations are done twice per week. Calibration control charts for the Model 2015 analyzers are shown in Figures 4.3-5a through 4.3-5c. For the period during analysis of 2017 CSN samples, 266 out of 1,937 CO₂ calibrations, 190 out of 2,208 sucrose calibration, and 127 out of 1,599 KHP calibrations exceeded the criteria. When an exceedance is observed, the analyzer is checked and the calibration is rerun. No CSN samples were run after any of the CO₂ calibration exceedances. However, there were 30 and 25 CSN samples analyzed after the sucrose and KHP exceedances, respectively; these data were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.3.2 and Section 3.2.3.1). However, for all samples that were run after an exceedance calibration, other QC analyses (e.g., replicates, auto-calibration, and internal calibration peak area checks) within the time period indicate acceptable values.

Figure 4.3-5: Control chart of manual calibration checks for: (a) CO₂, (b) sucrose, and (c) KHP injections. The red dash lines indicate the total carbon limits of 17.1 and 18.9 µgC per injection for sucrose and KHP and 19.57 and 21.63 µgC per injection for CO₂.





4.3.2.4 Temperature Calibrations

Table 4.3-6 provides summary statistics for the multi-point temperature calibrations of each Model 2015 carbon analyzer. The temperature calibrations are performed every six months or after a major instrument repair. Criteria for an acceptable calibration is linear regression coefficient of determination (r^2) >0.99. Separate linear regressions are used for the lower temperatures and higher temperature ranges. These two ranges are separated with a toggle point typically around 200-300 °C, which is set to the temperature at which the two regression lines intercept (see Figure 3-6 in Model 2015 SOP). All calibrations met the acceptable r^2 criteria (r^2 >0.99) during this report period.

Table 4.3-6: Multi-point temperature calibration statistics on the Model 2015 carbon analyzer (CSN sample dates 1/1/2017-12/31/2017). For analyzers 21 and 40, more than 6 months passed between calibrations. As noted in Sections 2.3.2 and 3.2.3.1, a calibration calendar has been established by DRI to avoid recurrence of this issue.

Carbon Analyzer	Calibration Date*	Low T Slope	Low T Intercept	Low T r^2	High T Slope	High T Intercept	High T r^2
21	5/25/2017	1.082	2.647	0.996	1.007	21.494	0.999
	11/22/2017	0.999	9.900	1.000	0.970	15.804	1.000
	5/25/2018	1.038	11.702	0.999	0.989	25.596	0.999
31	8/31/2017	1.003	27.743	1.000	1.024	24.987	0.995
	2/8/2018	1.066	1.937	0.999	1.016	12.757	1.000
	3/29/2018	1.068	2.815	1.000	1.015	18.449	1.000
32	8/28/2017	1.086	10.185	1.000	1.013	29.379	0.996
	Offline	1.129	7.970	0.999	1.022	35.979	0.993
	12/4/17- 7/16/18	1.071	-0.507	0.999	0.982	24.810	0.999
34	8/1/2017	1.110	4.964	1.000	1.015	31.440	0.995
	8/24/2017	1.079	3.448	1.000	1.019	19.294	0.997
	10/26/2017	1.125	0.161	0.999	1.027	26.695	0.995
	3/12/2018	1.055	2.648	0.999	1.018	14.510	0.999

Carbon Analyzer	Calibration Date*	Low T Slope	Low T Intercept	Low T r ²	High T Slope	High T Intercept	High T r ²
	7/16/2018	1.069	2.360	1.000	1.001	20.822	1.000
35	8/28/2017	1.053	2.086	1.000	0.996	15.357	0.999
	10/5/2017	0.989	15.789	1.000	0.999	13.220	0.999
	4/4/2018	1.059	6.988	0.999	0.998	23.598	0.999
	5/16/2018	0.996	12.725	0.999	0.976	16.756	0.999
36	5/23/2017	1.046	8.541	0.998	1.010	15.871	1.000
	6/20/2017	1.057	8.064	1.000	1.010	7.437	0.999
	10/31/2017	1.028	10.745	1.000	0.989	19.705	0.999
	2/26/2018	1.041	7.715	1.000	1.028	1.777	0.998
	4/26/2018	0.841	19.276	0.997	0.877	7.824	1.000
	5/21/2018	0.979	8.527	0.999	1.004	2.841	1.000
	6/5/2018	0.998	14.056	1.000	0.986	19.062	1.000
37	12/7/2017	1.034	21.554	1.000	0.979	35.483	0.997
	2/7/2018	1.052	0.408	1.000	0.988	14.824	1.000
	5/29/2018	1.060	4.289	1.000	0.978	27.330	1.000
38	6/20/2017	1.034	2.173	1.000	1.024	5.939	0.999
	10/31/2017	1.054	-2.295	**	0.996	13.166	**
	2/21/2018	1.076	0.097	1.000	1.024	14.323	1.000
	6/18/2018	1.096	2.330	1.000	1.006	27.547	1.000
40	8/1/2017	1.053	2.086	1.000	0.996	15.357	0.999
	2/5/2018	1.034	1.629	1.000	1.020	5.244	1.000
	5/11/2018	0.994	10.153	0.999	0.982	14.964	1.000
41	8/22/2017	1.033	4.682	1.000	1.027	7.430	1.000
	2/22/2018	1.033	4.682	1.000	1.027	7.430	1.000
	7/23/2018	1.025	9.735	1.000	1.005	16.973	1.000
42	9/26/2017	1.086	3.827	1.000	1.020	21.993	0.997
	12/26/2017	1.112	-1.727	1.000	1.013	24.237	0.996
	2/26/2018	1.022	4.927	0.999	1.026	3.574	1.000
	3/30/2018	1.049	6.483	1.000	1.026	14.628	1.000
	5/15/2018	0.988	10.325	1.000	0.988	9.498	1.000
43	10/30/2017	1.125	0.161	1.000	1.027	26.695	0.995
	2/12/2018	1.146	-4.097	1.000	1.013	24.664	0.996
	5/18/2018	1.050	5.926	1.000	1.005	19.394	1.000
	5/29/2018	1.060	4.289	1.000	0.978	27.330	1.000
47	7/12/2017	1.094	10.587	1.000	1.016	31.998	1.000
	9/20/2017	1.110	14.054	1.000	1.005	41.559	1.000
	1/17/2018	1.062	9.538	1.000	1.013	23.398	1.000
	2/22/2018	1.085	5.700	1.000	1.018	24.721	1.000

* Includes both regular maintenance and semi-annual calibration data

** Calibration point data were deleted from file, therefore r² data not available

4.3.2.5 Oxygen Level Check

Table 4.3-7 provides a summary of the Model 2015 oxygen leak test results that are performed every six months or after major instrument repairs. The results are considered acceptable if the O₂ concentration is < 100 ppm. The O₂ contents were well below 100 ppm, in the range of 8-74 ppm.

Table 4.3-7: Model 2015 oxygen test statistics (CSN sample dates 1/1/2017-12/31/2017).

Carbon Analyzer	O ₂ Statistics (ppm)	Feb 2017		Aug 2017		Feb 2018	
		140 (°C)	580 (°C)	140 (°C)	580 (°C)	140 (°C)	580 (°C)
21	Mean O ₂	28.1	21.3	14.1	10.9	17.9	16.7
	Std Dev	8.9	5.0	0.3	0.1	4.7	4.6
31	Mean O ₂	19.5	18.1	20.0	19.3	19.8	18.3
	Std Dev	5.4	5.1	0.0	0.1	4.6	4.6
32	Mean O ₂	N/A	N/A	18.7	13.9	24.8	26.5
	Std Dev			0.7	0.5	4.7	4.8
34	Mean O ₂	55.3	74.4	12.3	8.7	39.1	50.5
	Std Dev	8.1	10.2	0.1	0.0	5.6	5.6
35	Mean O ₂	28.5	21.4	19.8	19.9	22.6	26.6
	Std Dev	5.3	5.2	0.0	0.4	4.7	4.8
36	Mean O ₂	20.0	21.0	24.3	24.3	20.0	22.7
	Std Dev	5.1	5.5	0.0	0.0	4.7	4.7
37	Mean O ₂	34.8	25.5	21.0	15.7	18.8	16.6
	Std Dev	8.6	5.2	0.7	0.1	4.9	4.6
38	Mean O ₂	22.4	23.5	20.3	18.5	31.2	28.1
	Std Dev	5.1	5.3	1.2	1.3	4.9	4.7
40	Mean O ₂	33.1	24.8	16.7	19.9	24.3	25.3
	Std Dev	7.6	5.3	0.2	0.1	4.7	4.8
41	Mean O ₂	29.0	24.4	14.2	14.5	23.8	20.9
	Std Dev	6.7	5.3	3.0	1.4	4.8	4.7
42	Mean O ₂	21.8	21.0	14.5	14.9	17.5	16.7
	Std Dev	6.9	5.2	0.4	0.0	4.8	4.7
43	Mean O ₂	24.3	19.3	21.7	14.5	26.7	24.8
	Std Dev	5.8	5.14	1.3	0.3	5.0	4.8
47	Mean O ₂	26.1	22.9	19.1	17.0	17.8	16.8
	Std Dev	7.6	5.2	0.5	0.6	4.7	4.8

4.3.2.6 Replicate and Duplicate Analyses

Replicate analysis results are from two or more punches of the same sample filter analyzed on different instruments, while duplicate analysis results are from two punches of the same sample filter analyzed on the same instruments. No valid duplicate analyses are available for this reporting period. A replicate analysis was performed randomly on one sample from every group of 10 samples. Table 4.3-8 gives the criteria and summary statistics for replicate IMPROVE_A carbon analyses during the reporting period January 1, 2017 through December 31, 2017. Control charts for replicate analyses are plotted in Figure 4.3-6.

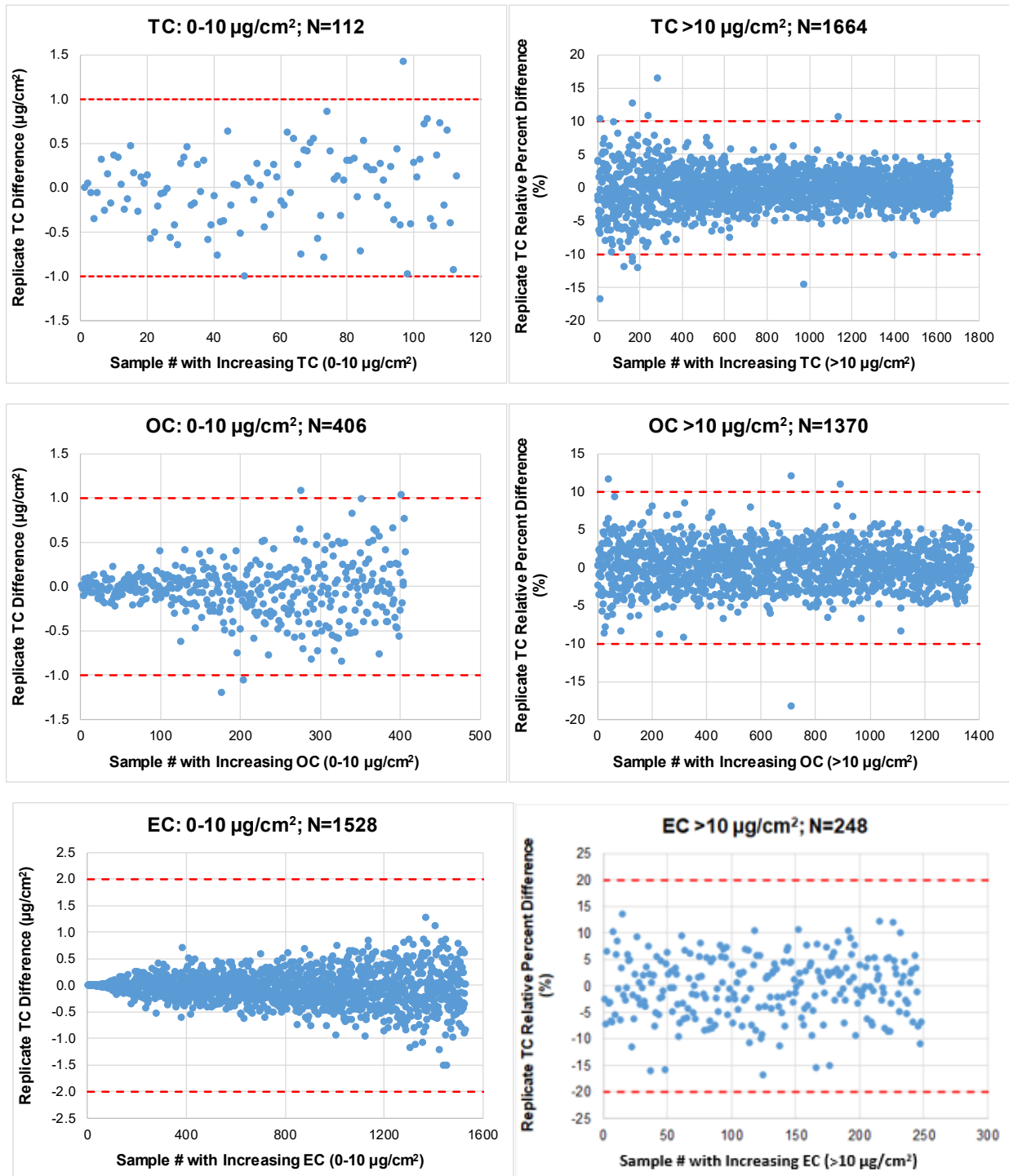
Replicate analysis results for total carbon (TCR), organic carbon (OCR), and elemental carbon (ECR) by reflectance agree well, with only 22/5328 data points (0.41%) for OCR, ECR, and TCR exceeded the criteria. The small size (25 mm) of the filter used in the IMPROVE_A carbon analysis method does not permit more than three punches (each ~0.5 cm²) to be taken from the filter. Samples not meeting replicate criteria (i.e., for TCR, OCR, or ECR < 10 µg C/cm², TCR, OCR < ± 1.0 µg C/cm² and ECR < ± 2.0 µg C/cm²; and for TCR, OCR or ECR ≥ 10 µg C/cm², TCR or OCR < 10% RPD and ECR < 20% RPD) are re-analyzed, typically on a third analyzer. Filter inhomogeneity, which is flagged prior to first analysis, is also examined.

Table 4.3-8: Replicate analysis criteria and statistics (CSN sample dates 1/1/2017-12/31/2017). Total carbon (TCR), organic carbon (OCR), and elemental carbon (ECR) are shown by reflectance.

Range	Criteria	Replicates			
		Statistic	No.	TCR	OCR
TCR, OCR, & ECR < 10 µg C/cm ²	TCR, OCR < ±1.0 µg C/cm ² ECR < ±2.0 µg C/cm ² Units: µg C/cm ²	Count	112	406	1528
		No. Fail	1	5	0
		%Fail	0.90	1.25	0
		Mean	0.34	0.21	0.22
		StdDev	0.25	0.22	0.20
		Max	1.43	1.84	1.49
		Min	0.01	0.00	0.00
		Median	0.30	0.14	0.17
TCR, OCR, & ECR ≥ 10 µg C/cm ²	TCR, OCR %RPD < 10% ECR %RPD < 20% Units: %	Count	1664	1370	248
		No. Fail	12	4	0
		%Fail	0.73	0.29	0
		Mean	2.15	2.23	4.64
		StdDev	1.86	1.71	3.30
		Max	16.64	18.23	16.74
		Min	0.00	0.00	0.07
		Median	1.73	1.94	3.96

Note: RPD = 100 x absolute value [original sample-duplicate sample]/[(original sample+ duplicate sample)/2]

Figure 4.3-6: Replicate (two punches from the same sample filter analyzed on different instruments) analysis results. The limits are $\pm 1.0 \mu\text{g}/\text{cm}^2$ for TCR and OCR $< 10 \mu\text{g}/\text{cm}^2$, $\pm 2.0 \mu\text{g}/\text{cm}^2$ for ECR $< 10 \mu\text{g}/\text{cm}^2$, $\pm 10\%$ relative percent difference for TCR and OCR $\geq 10 \mu\text{g}/\text{cm}^2$, and $\pm 20\%$ relative percent difference for ECR $\geq 10 \mu\text{g}/\text{cm}^2$.



4.3.3 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.

4.3.4 Audits, Performance Evaluations, Training, and Accreditations

4.3.4.1 *System Audits*

The prime contractor (UC Davis) provided 9 quartz audit samples collected during 2017 to DRI for carbon analysis in March 2018. DRI delivered the carbon analysis data on April 18, 2018. The average relative percentage difference between results from the DRI and the reference laboratory (UC Davis) are -2% (negative number meaning DRI lower than reference), -18% and -6% for OC, EC, and TC.

4.3.4.2 *Performance Evaluations*

The EPA provided 5 quartz samples for carbon analysis as part of the EPA Office of Air Quality Planning and Standards (OAQPS) interlaboratory performance evaluation. This evaluation was carried out during the timeframe when DRI also analyzed CSN samples collected during 2017. Reported z-scores were all below 2, indicating satisfactory interlaboratory comparison results.

4.3.4.3 *Training*

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

4.3.4.4 *Accreditations*

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

4.3.5 Summary of Filter Blanks

Over the sampling period (January 1, 2017 through December 31, 2017) there were 1,298 quartz filter field blanks. Table 4.3-9 summarizes the field blank statistics. The lower quantifiable limits (LQLs) are defined as three times the standard deviation of field blanks and are used as internal QA indicators, distinct from the MDLs reported to AQS.

Table 4.3-9: Quartz filter field blank statistics. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), EC, and OC are shown by reflectance (R) and transmittance (T).

Species	Count	Median ($\mu\text{g}/\text{cm}^2$)	Average ($\mu\text{g}/\text{cm}^2$)	Min ($\mu\text{g}/\text{cm}^2$)	Max ($\mu\text{g}/\text{cm}^2$)	St. Dev. ($\mu\text{g}/\text{cm}^2$)	LQL ($\mu\text{g}/\text{cm}^2$)
EC1	1298	0.000	0.011	0.000	5.435	0.192	0.575
EC2	1298	0.000	0.011	0.000	0.779	0.040	0.121
EC3	1298	0.000	0.000	0.000	0.000	0.000	0.000
ECR	1298	0.000	0.017	0.000	4.942	0.186	0.558
ECT	1298	0.000	0.008	0.000	3.812	0.124	0.372
OC1	1298	0.136	0.162	0.000	1.092	0.158	0.473
OC2	1298	0.262	0.283	0.000	2.736	0.155	0.465
OC3	1298	0.504	0.553	0.043	6.172	0.330	0.989
OC4	1298	0.000	0.035	0.000	4.276	0.148	0.444
OCR	1298	0.979	1.038	0.127	13.184	0.614	1.842
OCT	1298	0.982	1.048	0.127	14.314	0.664	1.993
OPR	1298	0.000	0.006	0.000	1.560	0.050	0.149
OPT	1298	0.000	0.015	0.000	3.705	0.115	0.344

5. Data Management and Reporting

5.1 Number of Events Posted to AQS

Summarized in Table 5.1-1 are dates that data were delivered to AQS for samples collected January 1, 2017 through December 31, 2017. Data are expected to be delivered to AQS within 120 days of receipt of filters by the analytical laboratories. Laboratory analysis delays resulted in later deliveries to AQS (see Section 2.1.1 and Section 2.3.1).

Table 5.1-1: Summary of data deliveries to AQS, January 1, 2017 through December 31, 2017.

Data (Month Samples Collected)	Filter Receipt Date	AQS Delivery Date	Days
January 2017	March 15, 2017	October 27, 2017	226
February 2017	April 3, 2017	November 28, 2017	239
March 2017	May 18, 2017	November 28, 2017	194
April 2017	June 29, 2017	January 3, 2018	188
May 2017	July 18, 2017	February 9, 2018	206
June 2017	August 22, 2017	February 9, 2018	171
July 2017	September 8, 2017	March 14, 2018	187
August 2017	October 26, 2017	April 12, 2018	168
September 2017	November 15, 2017	May 23, 2018	189
October 2017	December 14, 2017	June 13, 2018	181
November 2017	January 17, 2018	July 6, 2018	170
December 2017	February 7, 2018	August 2, 2018	176

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 was accepted by the EPA on November 29, 2017. The QAPP is updated annually.

6.2 SOP Revisions

The UC Davis Standard Operating Procedures (SOPs) for Laboratory Analysis and Data Processing/Validation for Chemical Speciation of PM_{2.5} Filter Samples were accepted by the EPA on November 29, 2017. The SOPs are updated annually.

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 and sampling duration 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 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, flags, and comments) are received from the Sample Handling Lab via email and uploaded to the UC Davis CSN database. XRF results are transferred into the database through an automated service. IC and TOR analysis result files are received via email from DRI. Results 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 Lab.
- 3) *UCD CSN TI 801B – Data Processing*: Sample volume and analysis results are combined to calculate concentrations. 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. 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) 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 801D – 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 DRI using thermal analysis with a correction for pyrolysis based on optical monitoring as it is heated. Measurements from 2005 through 2015 were made with DRI Model 2001 analyzers monitoring at the single wavelength 633 nm; starting with January 2016 samples, DRI switched to Model 2015 analyzers monitoring seven wavelengths centered at 635 nm. OCR concentrations at the median and 90th percentile were elevated during August and September, but otherwise trend similarly to previous years. The ECR concentrations are lower at the median and 90th percentile during the first six months of 2017, but trend similarly to previous years during the latter half of 2017.

Figure 6.4-1: Multi-year time series, organic carbon by reflectance (OCR).

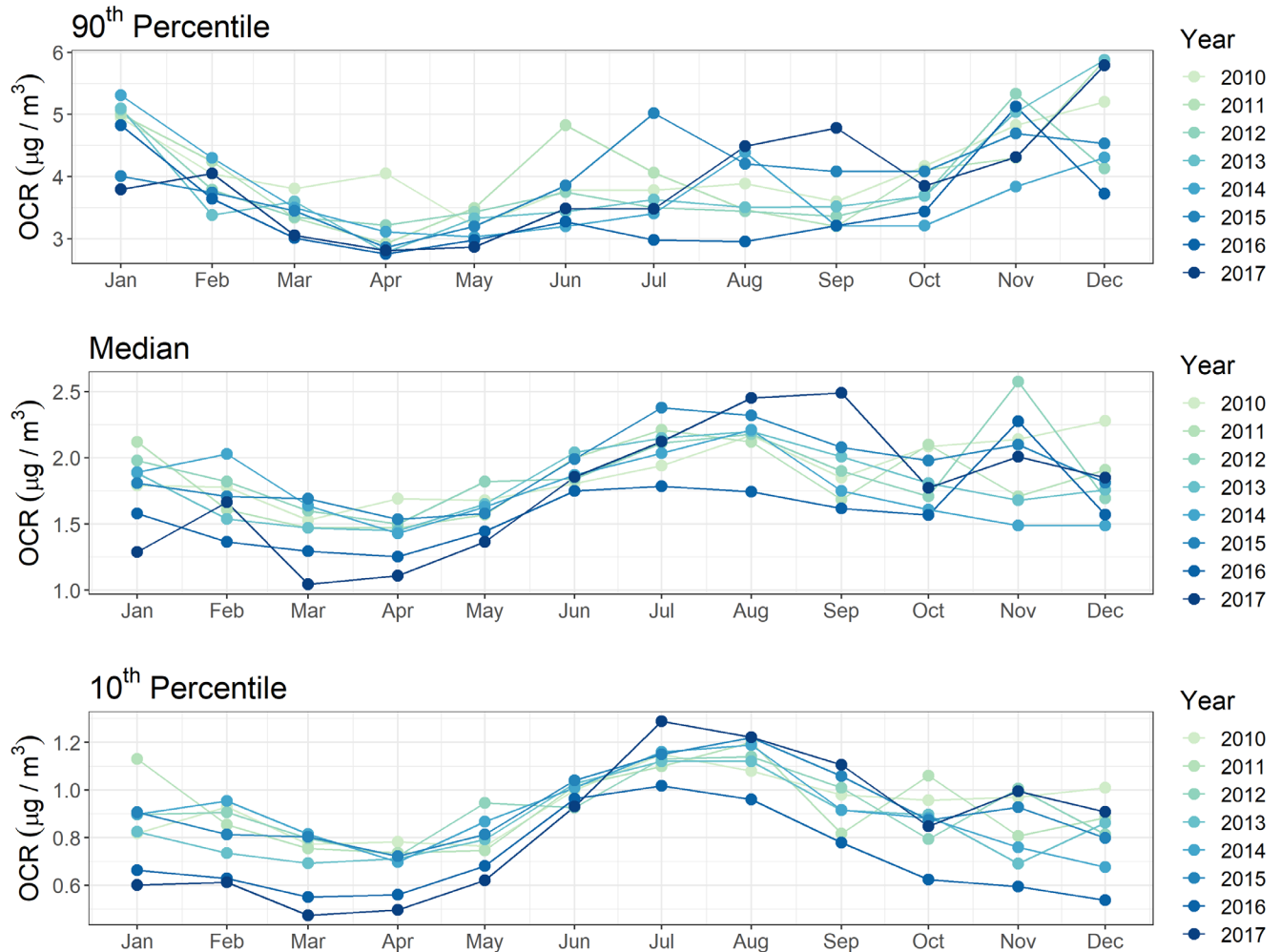
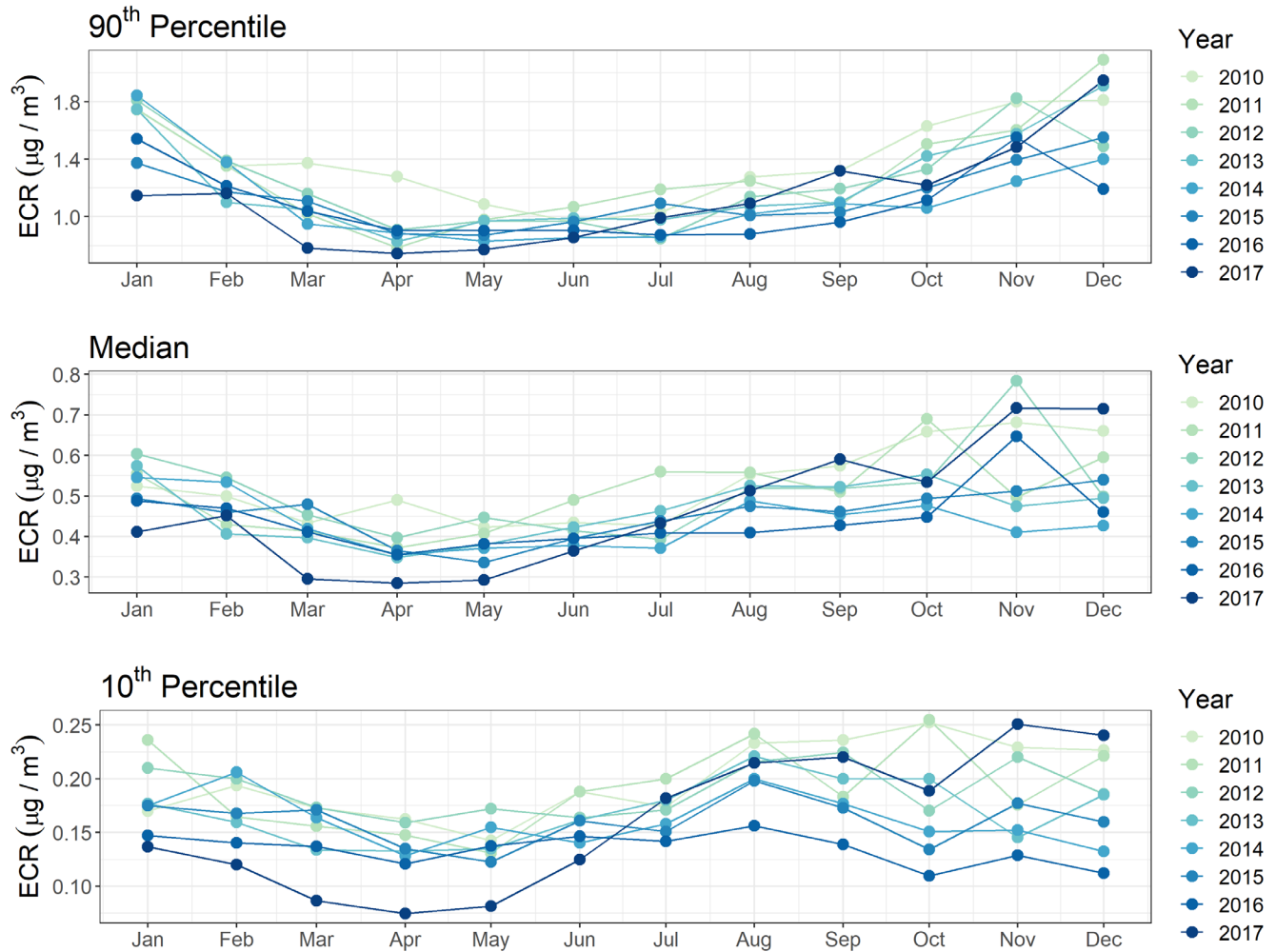
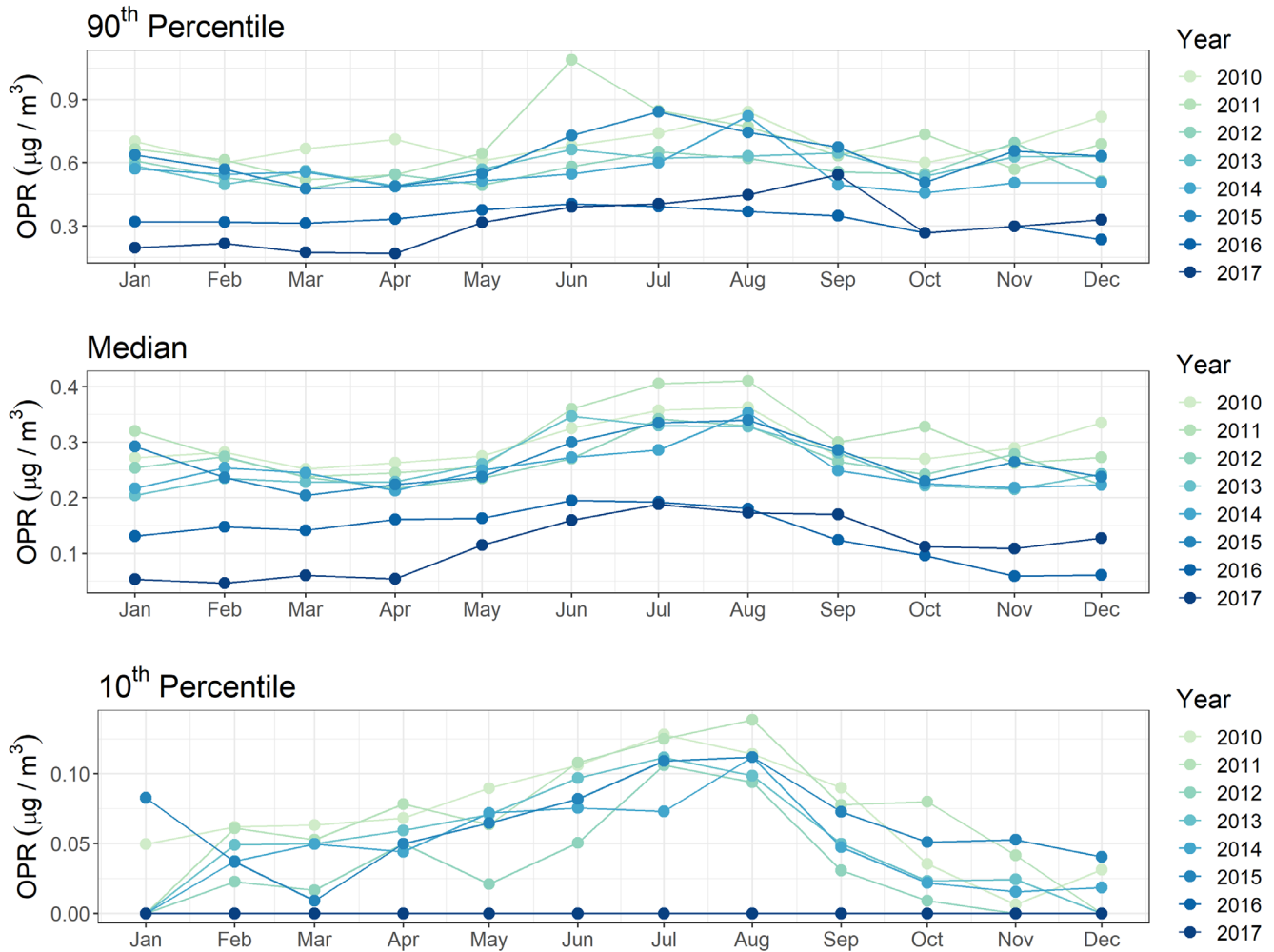


Figure 6.4-2: Multi-year time series of network-wide elemental carbon by reflectance (ECR) concentrations.



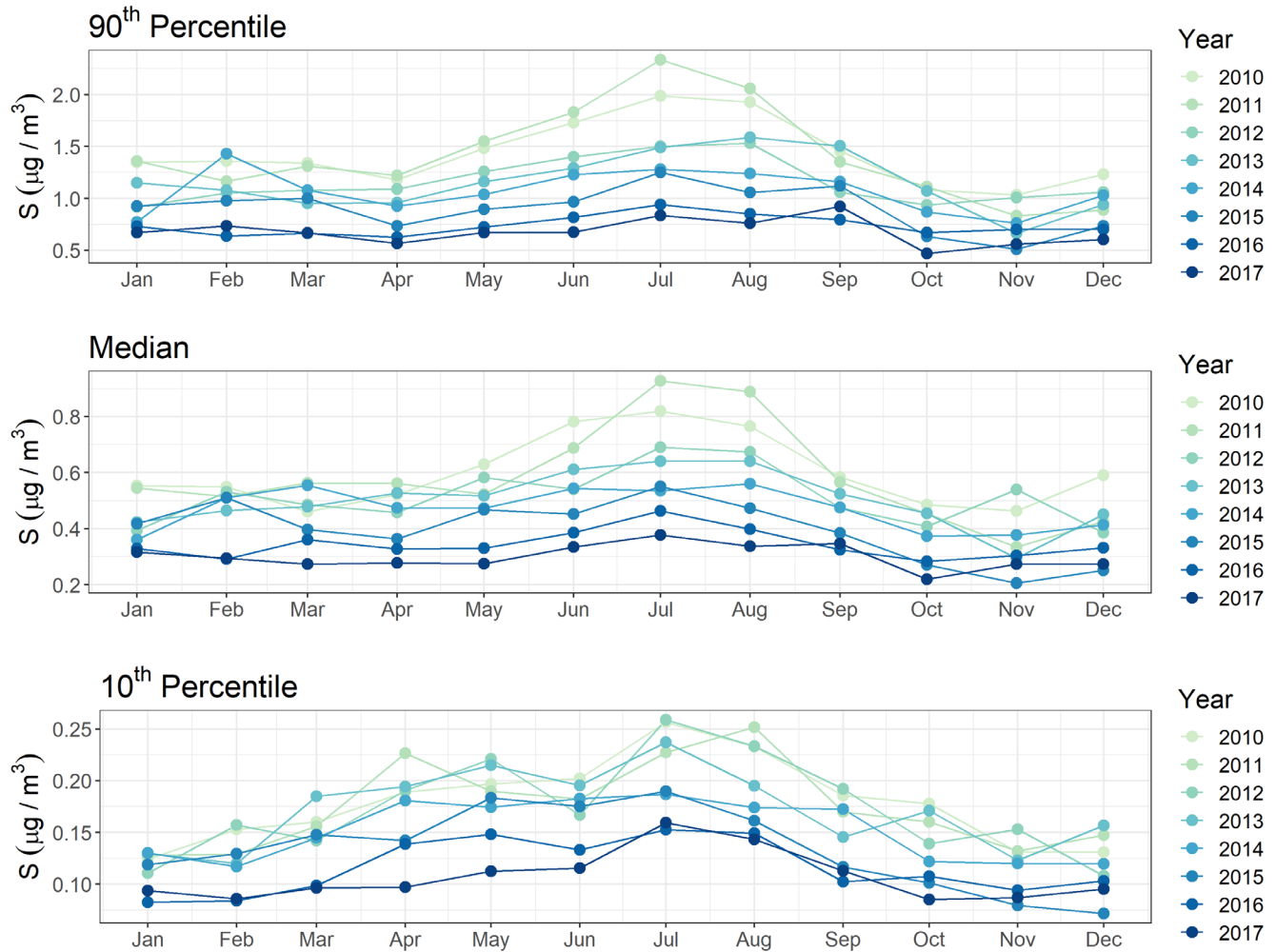
During TOR analysis some of the OC pyrolyzes during the heating phase. The organic pyrolyzed carbon (OPR) is combusted with the EC collected on the filter, and is accounted for by monitoring the laser signal and identifying an OC/EC split point based on return of the last signal to its initial value. To some extent, the split point – and thus the amount of OPR – is operationally defined based on instrument parameter settings. As seen in Figure 6.4-3, corresponding with the change in analyzers from DRI Model 2001 to DRI Model 2015 that occurred on January 1, 2016, the OPR concentrations at the median and 90th percentile decreased.

Figure 6.4-3: Multi-year time series of network-wide organic pyrolyzed carbon by reflectance (OPR) concentrations.



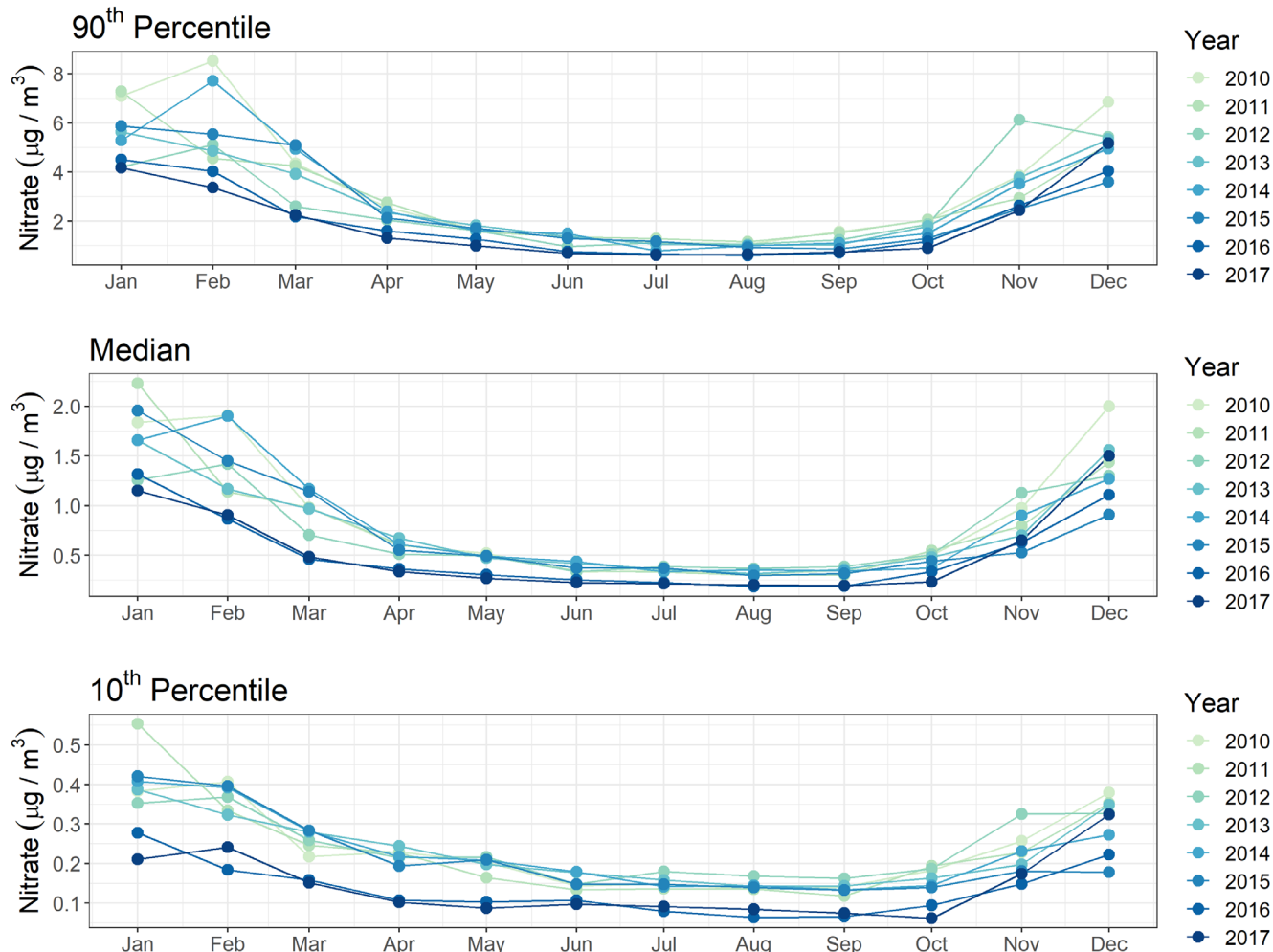
Similar to 2016, the 2017 sulfur concentrations generally continue to be low (Figure 6.4-4) with reduced seasonal variability.

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



The 2016 and 2017 nitrate concentrations show strong seasonality with elevated winter concentrations; however, 2016 and 2017 concentrations are generally lower relative to previous years (Figure 6.4-5).

Figure 6.4-5: Multi-year time series of network-wide nitrate concentrations.



6.4.1.2 Comparisons Between Modules

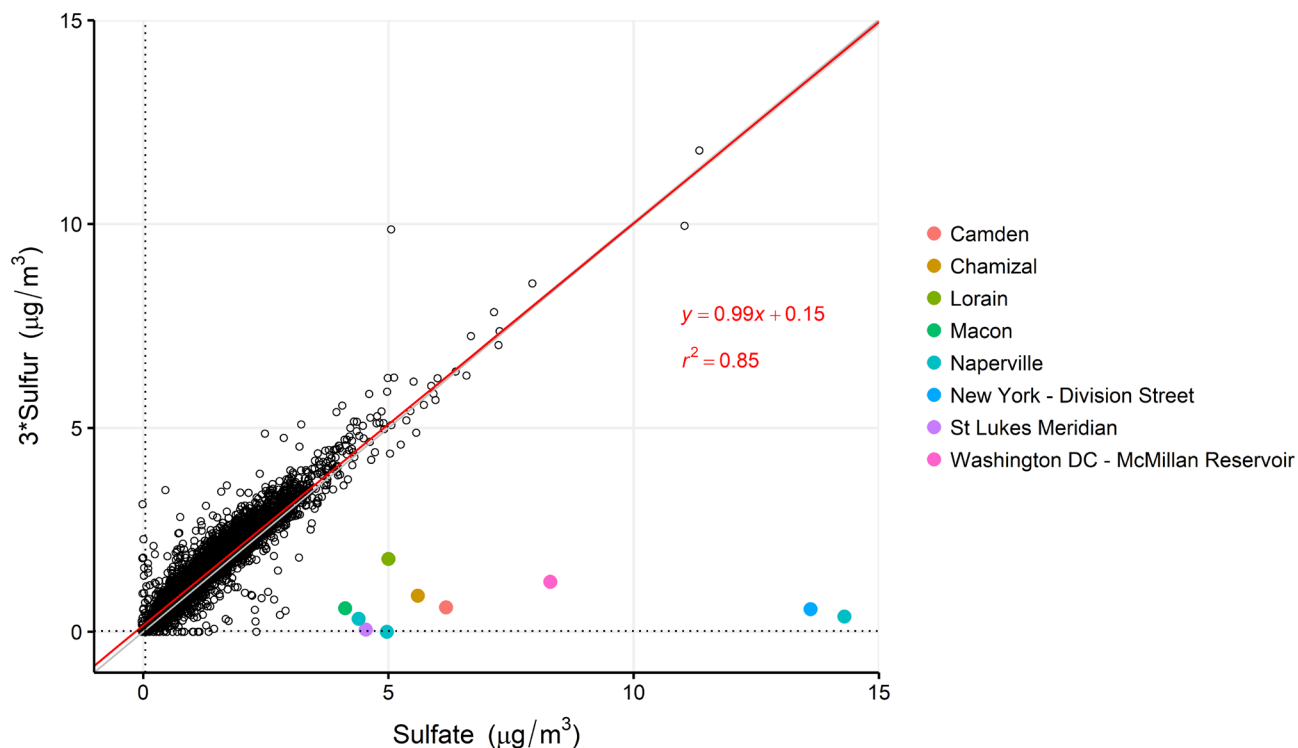
The following graphs compare two independent measures of aerosol properties that are expected to correlate. These graphs highlight cases where the two measurements do not correlate well, which can result from real atmospheric and anthropogenic events or analytical and sampling issues.

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 (Figure 6.4-6), suggesting the presence of some sulfur in a non-water soluble form of

sulfate or in a chemical compound other than sulfate. However, instances are observed where $(3 \times S)/SO_4$ ratios are lower than typically observed (Figure 6.4-3; colored points).

Figure 6.4-6: Scatter plot of $(3 \times S)$ versus SO_4 , January 1, 2017 through December 31, 2017. Number of observations (complete pairs) is 12,753. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression.



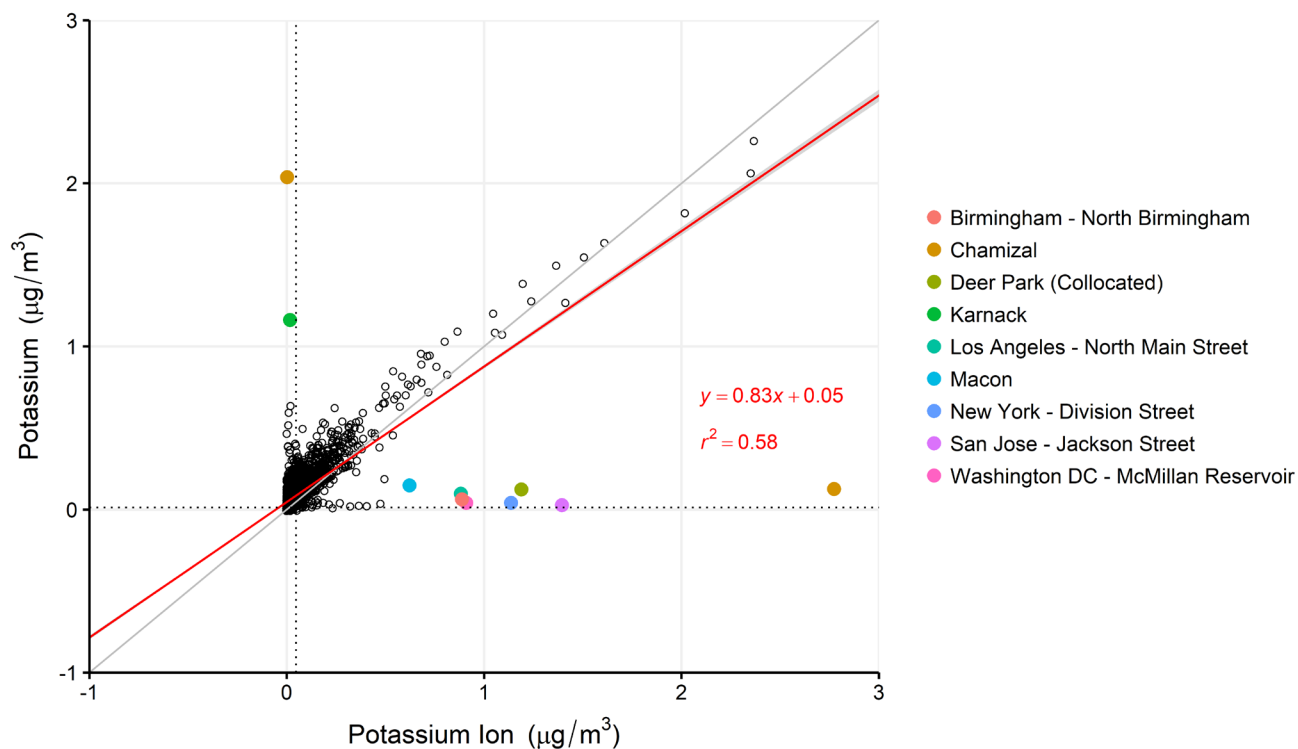
In some cases the S/SO_4 ratio was observed to be unexpectedly elevated during this reporting period, primarily during early November 2017. These cases were noted anecdotally during UCD Level 1 validation, and do not exhibit a clear spatial or temporal pattern. Investigation – and in some cases reanalysis – by the ions (DRI) and elements (UCD) laboratories did not reveal evidence of laboratory error. The ‘5’ qualifier flag (outlier) is automatically applied during UCD Level 1 validation for cases where parameters – including the S/SO_4 ratio – exceed predefined bounds. For the S/SO_4 ratio the bounds are defined as 0.67 to 1.80 (historical bounds carried over from previous contractor; currently being evaluated/updated by UC Davis), and ratios outside this range are flagged. During November 2017, 149 valid sulfur and sulfate pairs received the ‘5’ qualifier flag from a total of 1,059 valid sulfur and sulfate pairs reported for that month. Months preceding and following November 2017 had fewer flagged pairs (October, 14 pairs; December, 5 pairs).

Potassium versus Potassium Ion

PTFE filters are analyzed for elemental potassium using XRF, and nylon filters are analyzed for potassium ion using IC. Similar to the S/SO_4 ratio relationship, the potassium/potassium ion ratio can be used to identify 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. This expectation is generally met, with greater variability at low

concentrations (Figure 6.4-7). A known exception to this expectation is for soil-borne potassium, which is not water soluble; high soil contributions are thus expected to result in ratios greater than one.

Figure 6.4-7: Scatter plot of potassium versus potassium ion, January 1, 2017 through December 31, 2017. Number of observations (complete pairs) is 12,753. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression.



PM_{2.5} versus Reconstructed Mass (RCM)

Gravimetric data are compared to 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 – CSN Data Processing*. In the simple case where valid measurements are available for all needed variables, reconstructed mass is the following sum:

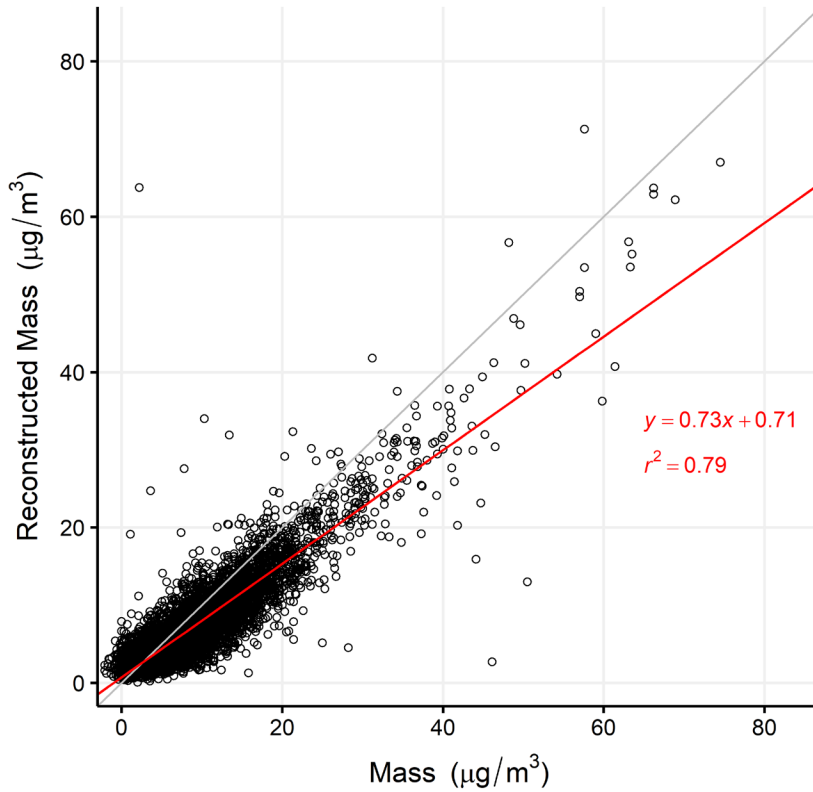
$$\text{RCM} = (4.125 \times \text{S}) + (1.29 \times \text{NO}_3^-) + (1.4 \times \text{OC}) + (\text{EC}) + \\ (2.2 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} + 2.42 \times \text{Fe} + 1.94 \times \text{Ti}) + (1.8 \times \text{chloride})$$

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 6.4-8), but RCM tends to underestimate AirNow Tech mass.

Figure 6.4-8: Scatter plot of RCM versus AirNow Tech PM_{2.5} mass data (Mass), January 1, 2017 through December 31, 2017. Number of observations (complete pairs) is 9,286. Solid gray line indicates 1:1. Solid red line indicates regression.



6.5 Uncertainty Estimates and Collocated Precision Summary Statistics

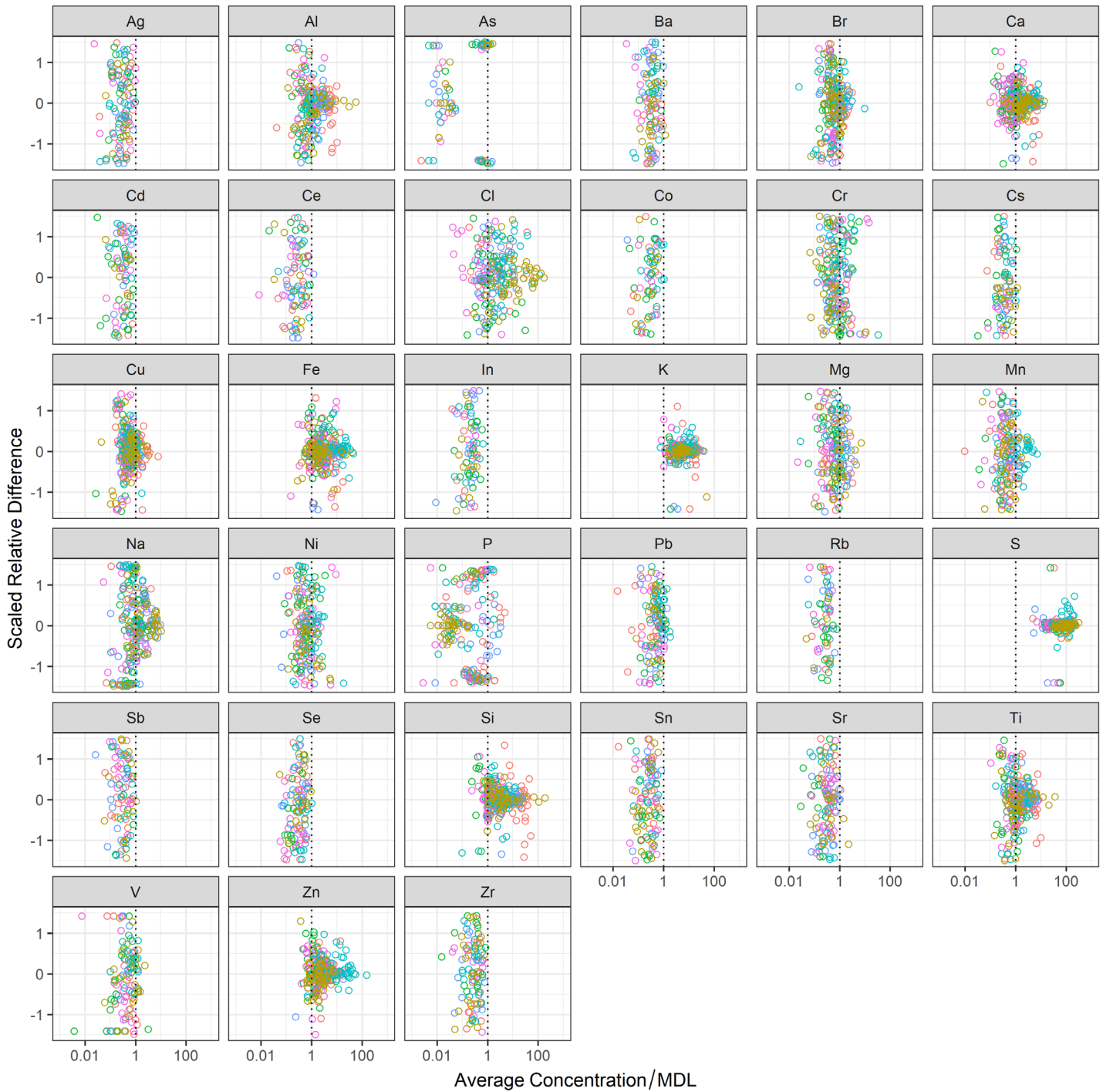
Several network sites are equipped with collocated samplers, where simultaneous samples are collected on independent samplers and analyzed using the same analytical protocols. Differences between the resulting data provide a measure of the total uncertainty associated with filter substrates, sampling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

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

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. They 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. Fe, K, Si, and Zn are examples of elements that are measured at a wide range of concentrations and display this behavior. S is measured well above the MDL and has good collocated measurement agreement throughout the range. This convergence is not observed for many elements and carbon fractions that are rarely measured above the MDL.

Figure 6.5-1: Scaled relative difference for element measurements at sites with collocated samplers across the network (January 1, 2017 through December 31, 2017). Dotted vertical lines indicates 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 difference for ion measurements at sites with collocated samplers across the network (January 1, 2017 through December 31, 2017). Dotted vertical lines indicates MDL.

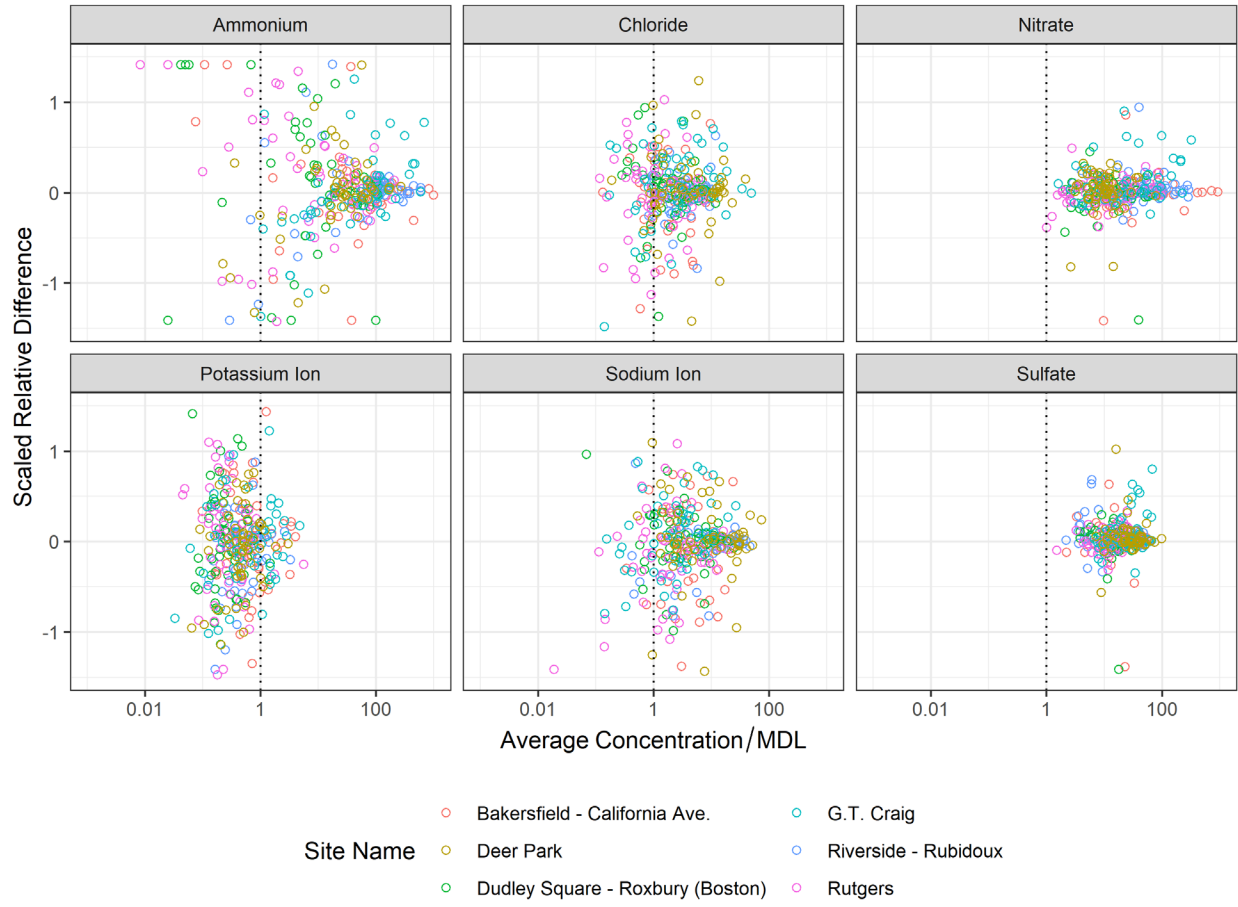
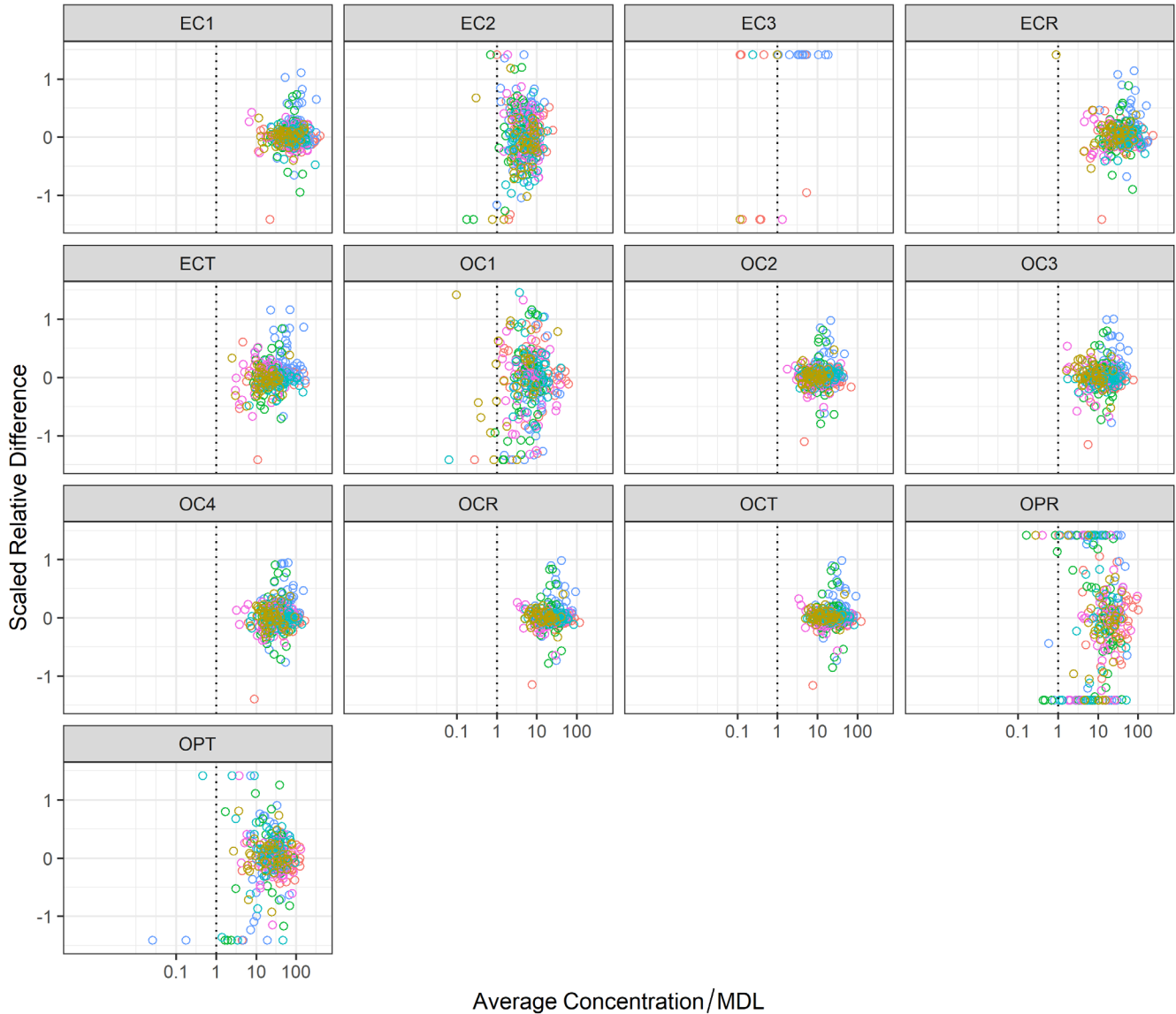


Figure 6.5-3: Scaled relative difference for carbon measurements at sites with collocated samplers across the network (January 1, 2017 through December 31, 2017). Dotted vertical lines indicates MDL. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).



- | | | |
|------|--|--------------------------------------|
| Site | ○ Bakersfield - California Ave. (06-029-0014) | ○ 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) |

There can be substantial variability in collocated agreement between different pairs of collocated sites, even in cases where measurements are well above the MDL. To illustrate, potassium (Figure 6.5-4), sulfate (Figure 6.5-5), and organic carbon by reflectance (Figure 6.5-6) are shown with scaled relative difference plotted separately for each of the collocated site pairs. For the nylon and PTFE filters, G.T. Craig, OH (AQS ID #39-035-0060) site shows cases of poor collocated agreement, even at high concentrations. For the quartz filter, poor agreement is more apparent at the Riverside, CA (AQS ID #06-065-8001) and Dudley Square, MA (AQS ID #25-025-0042) sites.

Figure 6.5-4: Scaled relative difference potassium at sites with collocated samplers across the network (January 1, 2017 through December 31, 2017). Dotted vertical lines indicates MDL.

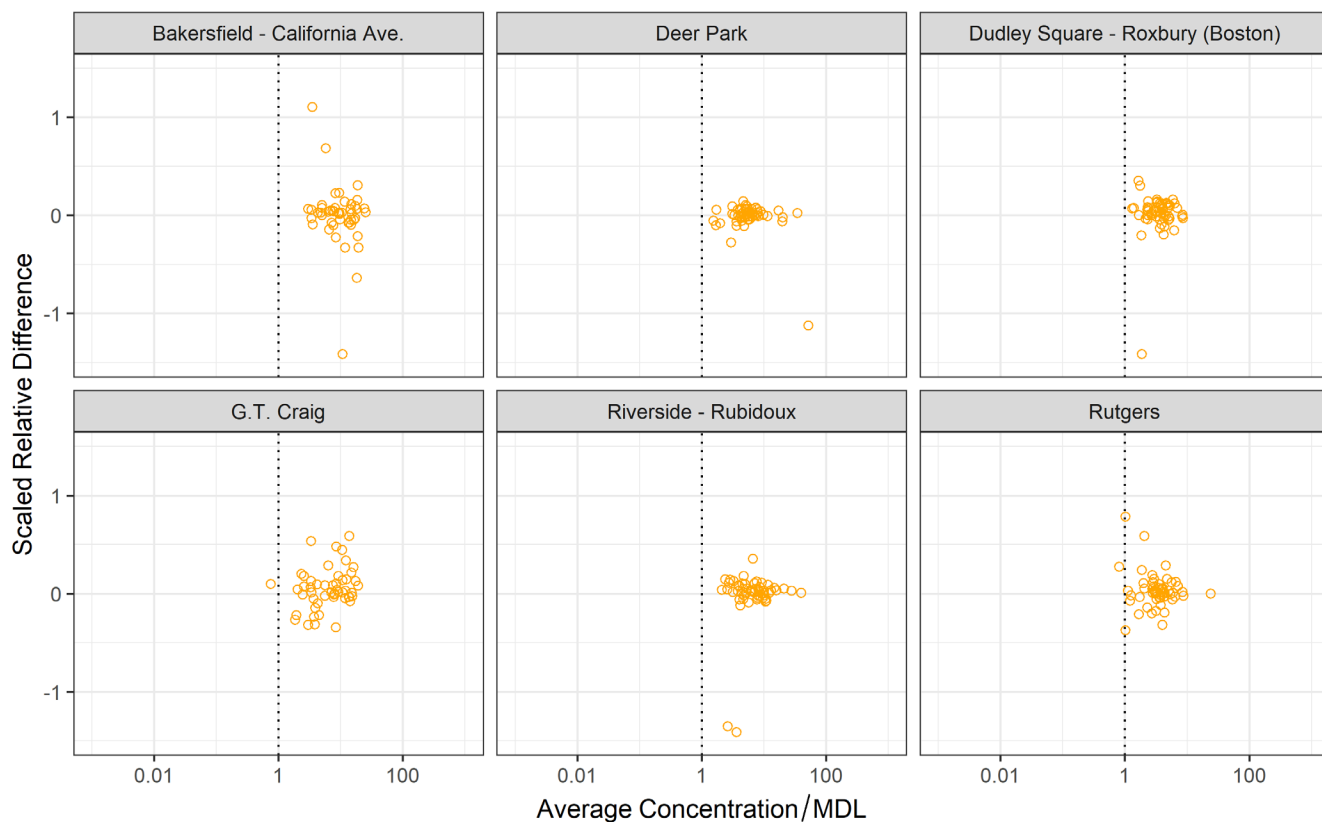


Figure 6.5-5: Scaled relative difference for sulfate at sites with collocated samplers across the network (January 1, 2017 through December 31, 2017). Dotted vertical lines indicates MDL.

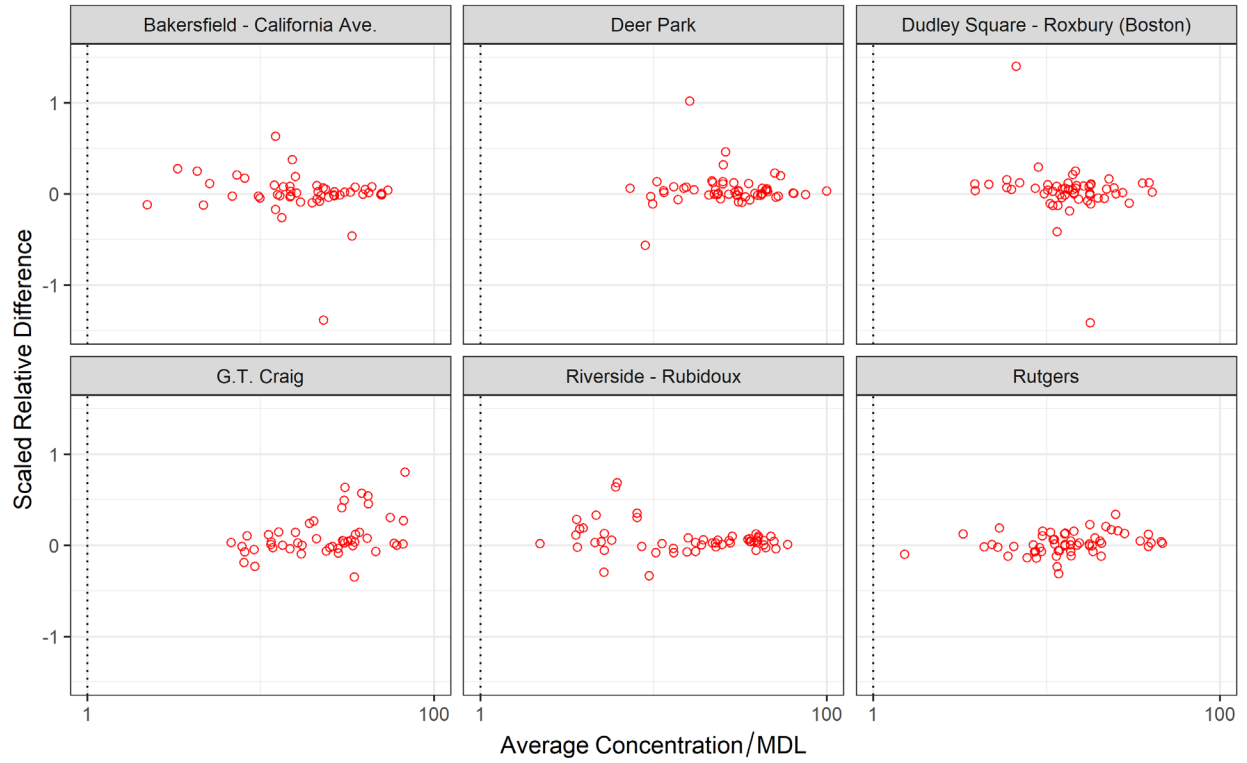
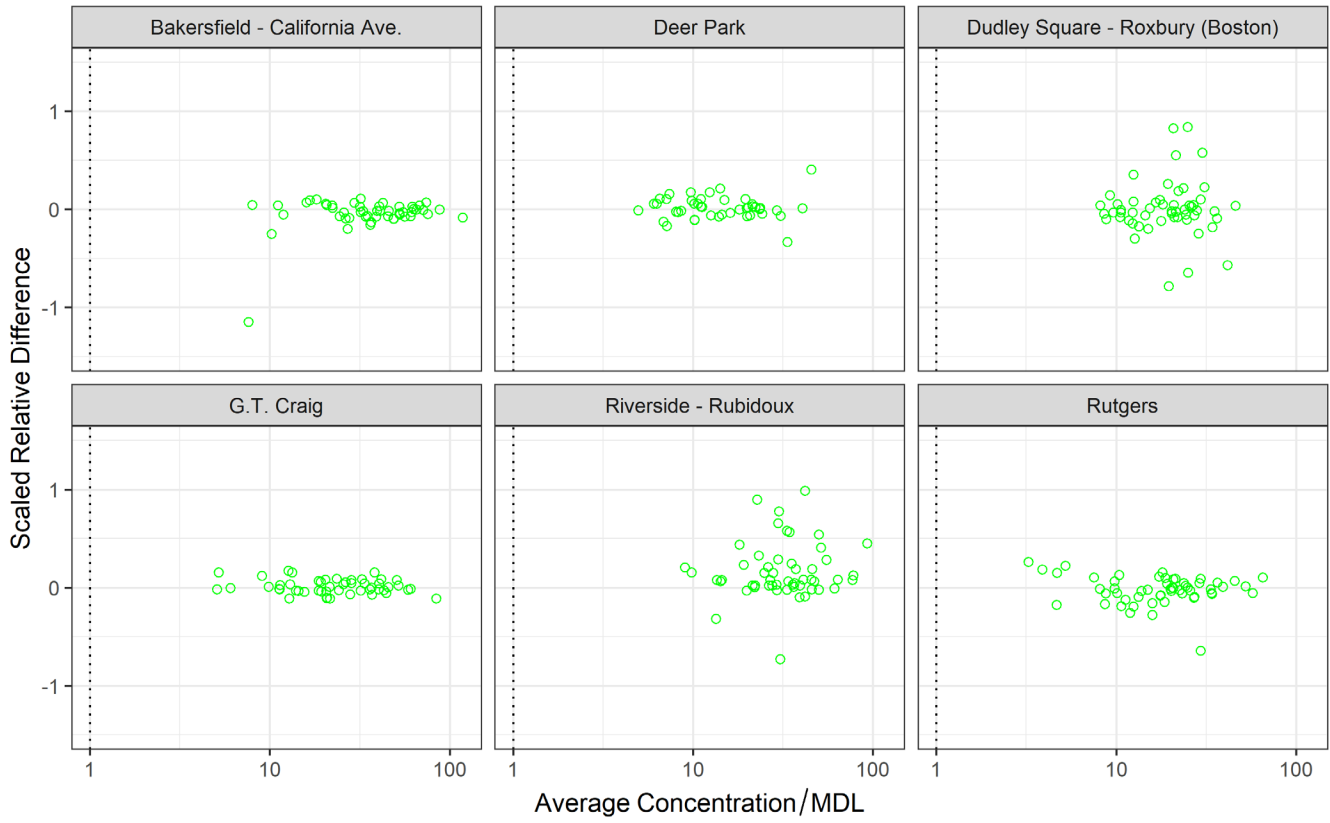


Figure 6.5-6: Scaled relative difference for organic carbon by reflectance (OCR) at sites with collocated samplers across the network (January 1, 2017 through December 31, 2017). Dotted vertical lines indicates MDL.



Collocated precision is reported with CSN data delivered to AQS 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. To limit uncertainty in determination of the necessary percentiles, calculations are performed using multiple years of collocated data (January 1, 2009 through December 31, 2014 for this reporting period) with a minimum of 60 collocated pairs per year. The calculation for fractional uncertainty is documented in *UCD CSN TI 801B*, and summarized in Equation 6.5-1, Equation 6.5-2, and Equation 6.5-3.

$$\text{Collocated Precision (cp)} = \frac{(84\text{th percentile of SRD}) - (16\text{th percentile of SRD})}{2} \quad (\text{Eq. 6.5-2})$$

$$\text{Fractional Uncertainty} = 100 \times \sqrt{\frac{1}{n} \sum_{i=1}^n (cp)_i^2} \quad (\text{Eq. 6.5-3})$$

Tables 6.5-1 (elements), 6.5-2 (ions), and 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 insufficient pairs were available, in which cases a fractional uncertainty of 0.25 is assigned. Historical data (2009-2014) are used to calculate fractional uncertainties for this reporting period because insufficient data were available following the contract transition (November 20, 2015). As more data becomes available, the fractional uncertainty will be updated annually and calculated using collocated data from the previous two years.

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. As shown in Equation 6.5-4 and Equation 6.5-5, CV is calculated from sample pairs collected at CSN collocated sites (Rice and Landis, 2016), using the subset of observations with concentrations at least three times the MDL.

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

$$CV_i = \frac{|RPD_i|}{\sqrt{2}} \quad (\text{Eq. 6.5-5})$$

where X_i and Y_i are the measurements from routine and collocated sites, respectively, for the i^{th} pair of measurements. Tables 6.5-1 (elements), 6.5-2 (ions), and 6.5-3 (carbon) list median CV calculated from collocated samples collected during 2017.

Table 6.5-1: Fractional uncertainty (calculated from collocated samples collected 2009 through 2014) and median coefficient of variation (CV; calculated from samples collected during 2017) for elemental species. Fractional uncertainty and CV values not reported for species with less than 60 collocated pairs with concentrations at least three times the MDL.

Species	Fractional Uncertainty (%) 2009 – 2014	Pairs	Coefficient of Variation (%) 2017	Pairs
Na	16.4	1,270	---	32
Mg	24.5	365	---	4
Al	25.2	1,209	---	37
Si	15.2	3,897	8.0	151
P	17.3	93	---	3
S	6.2	5,530	3.6	320
Cl	34.2	1,740	24.3	79
K	10.6	4,825	4.9	236
Ca	16.8	4,067	7.0	72
Ti	17.4	697	---	51
V	12.8	499	---	0
Cr	38.9	83	---	1
Mn	15.4	623	---	6
Fe	17	5,520	8.5	127
Co	---	10	---	0
Ni	17.8	400	---	0
Cu	26.9	2,313	---	3
Zn	12.3	3,144	8.0	120
As	18.8	155	---	0
Se	---	43	---	0
Br	15	1,610	---	1
Rb	---	0	---	0
Sr	---	58	---	0
Zr	---	3	---	0
Ag	---	1	---	0
Cd	---	0	---	0
In	---	0	---	0
Sn	---	0	---	0
Sb	---	0	---	0
Cs	---	7	---	0
Ba	16.5	123	---	0
Ce	---	21	---	0
Pb	18.5	381	---	0

Table 6.5-2: Fractional uncertainty (calculated from collocated samples collected 2009 through 2014) and median coefficient of variation (CV; calculated from samples collected during 2017) for ions. Fractional uncertainty and CV values not reported for species with less than 60 collocated pairs with concentrations at least three times the MDL.

Species	Fractional Uncertainty (%) 2009 – 2014	Pairs	Coefficient of Variation (%) 2017	Pairs
Ammonium	7.1	5,466	13.7	248
Chloride*	---	---	7.7	129
Nitrate	7.6	5,767	7.2	311
Potassium Ion	12.6	2,072	---	54
Sodium Ion	24.7	3,562	9.0	178
Sulfate	4.9	5,680	5.7	320

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

Table 6.5-3: Fractional uncertainty (calculated from collocated samples collected 2009 through 2014) and median coefficient of variation (CV; calculated from samples collected during 2017) for carbon fractions. Fractional uncertainty and CV values not reported 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	Fractional Uncertainty (%) 2009 – 2014	Pairs	Coefficient of Variation (%) 2017	Pairs
Elemental Carbon (EC1)	12.9	1,948	9.7	312
Elemental Carbon (EC2)	36.8	992	20.9	205
Elemental Carbon (EC3)	---	4	---	0
Elemental Carbon (ECR)	15.5	1955	10.5	311
Elemental Carbon (ECT)	12.8	1,606	9.9	306
Organic Carbon (OC1)	32.9	1,039	22.2	190
Organic Carbon (OC2)	13.6	1,877	7.7	309
Organic Carbon (OC3)	17.8	1,860	9.5	287
Organic Carbon (OC4)	15.7	1,487	12.3	310
Organic Carbon (OCR)	11.6	2,033	6.5	310
Organic Carbon (OCT)	7.3	1,774	6.1	310
Organic Pyrolyzed (OPR)	25.1	919	25.4	162
Organic Pyrolyzed (OPT)	17.3	1,557	15.9	280

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