

**Interagency Monitoring of Protected Visual
Environments (IMPROVE)**

Semiannual Quality Assurance Report

January 1, 2018 through December 31, 2018

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UCDAVIS

AIR QUALITY RESEARCH CENTER

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1. Introduction

The University of California, Davis (UCD) Air Quality Research Center (AQRC) reviews quality assurance (QA) activities semiannually in this report series as a contract deliverable for the Interagency Monitoring of Protected Visual Environments (IMPROVE) program (contract #P15PC00384). The primary objectives of the series are to:

1. Provide the National Park Service (NPS) with graphics illustrating some of the comparisons used to evaluate the quality and consistency of measurements within the network.
2. Highlight observations that may give early indications of emerging trends, whether in atmospheric composition or measurement quality.
3. Serve as a record and tool for ongoing UCD QA efforts.

The graphics shown in this report are a small subset of the many QA evaluations that UCD performs on a routine basis. More finished analyses such as those available in data advisories are outside the scope of this report, which provides a snapshot of the network's internal consistency and recent trends.

Each network site has a sampler for collection of particulate matter on polytetrafluoroethylene (PTFE), nylon, and quartz filters. The IMPROVE sampler has four sampling modules:

- Module-1A: Collection of fine particles with aerodynamic diameter less than 2.5 μm ($\text{PM}_{2.5}$) on polytetrafluoroethylene (PTFE) filters for gravimetric, energy dispersive X-ray fluorescence (EDXRF), and optical absorption by hybrid integrating plate/sphere (HIPS) analysis at UCD.
- Module-2B: Collection of $\text{PM}_{2.5}$ on nylon filters for ion chromatography (IC) analysis at Research Triangle Institute (RTI) International.
- Module-3C: Collection of $\text{PM}_{2.5}$ on quartz filters for thermal optical analysis (TOA) at Desert Research Institute (DRI).
- Module-4D: Collection of particles with aerodynamic diameter less than 10 μm (PM_{10}) on PTFE filters for gravimetric analysis at UCD.

Additional information and detail regarding analytical and validation procedures can be found in the standard operation procedure (SOP) documents and Quality Assurance Project Plan (QAPP) available at the Colorado State University (CSU) Cooperative Institute for Research in the Atmosphere (CIRA) IMPROVE site at <http://vista.cira.colostate.edu/Improve/particulate-monitoring-network/> and <http://vista.cira.colostate.edu/Improve/quality-assurance/>.

Unless otherwise noted, data evaluated in this report cover sampling dates from January 1, 2018 through December 31, 2018.

2. Summary of Laboratory and Data Quality Issues

2.1 RTI Ion Chromatography Laboratory

Ion analysis is performed by RTI according to a separate contract with NPS. See the RTI 2018 QA Report at <http://vista.cira.colostate.edu/improve/wp-content/uploads/2019/08/2018-RTI-QA-Report.pdf>.

2.2 DRI Thermal Optical Analysis Laboratory

Carbon analysis is performed by DRI according to a separate contract with NPS.

2.3 UCD X-Ray Fluorescence Laboratory

2.3.1 Application Change

The EDXRF analysis conditions, including the secondary targets and integration times (collectively referred to as the *application*), were changed in December 2018 during the annual EDXRF instrument calibrations. The changes were made to lower the detection limits and the measurement variability in some elements as well as to reduce the overall bias between instruments. This change impacts reported data beginning with samples collected October 2018.

See UCD data advisory for further detail, <http://vista.cira.colostate.edu/Improve/data-advisories/> (posted 6/2019).

2.4 UCD Gravimetric Laboratory

2.4.1 MTL Automated Weighing System

Beginning with samples and field blanks collected October 2018 UCD transitioned from manual weighing using Mettler-Toledo XP6 micro balances to the Measurement Technology Laboratories (MTL) AH500E climate-controlled automated weighing system.

See Section 4.2.2 for further details.

2.4.2 MTL PTFE Filters

Beginning with samples and field blanks collected mid-October 2018, UCD transitioned to using PTFE filters from MTL. As discussed in Section 4.2.2, a step change is observed corresponding with the filter manufacturer transition, with field blank filters gaining mass between pre- and post-weight measurements.

See Section 4.2.2 for further details.

2.5 UCD Optical Absorption

2.5.1 Updated HIPS Sphere and Laser

As mentioned in the previous IMPROVE Semiannual Quality Assurance Reports (October 12, 2018 and April 30, 2019) and documented in a UCD data advisory (<http://vista.cira.colostate.edu/Improve/data-advisories/>, posted 4/2019), in April 2018 the HIPS integrating sphere was changed from the legacy 2-inch Spectraflex-coated sphere described in White et al. (2016) to a newer 4-inch Spectralon sphere from the same manufacturer, and the laser was replaced. A calibration was performed following the April 2018 instrument upgrades; samples were analyzed under this calibration beginning with those collected January 2017.

2.5.2 Updated HIPS Detector

As mentioned in the previous IMPROVE Semiannual Quality Assurance Report (April 30, 2019) and documented in a UCD data advisory (<http://vista.cira.colostate.edu/Improve/data-advisories/>, posted 4/2019), in November 2018 new detectors were installed and the instrument was subsequently recalibrated; samples collected beginning March 2018 were analyzed under this calibration. Early investigation suggests that these changes in November 2018 (impacting samples collected March 2018 onward) may have introduced a 5% increase in reported values; this is being further explored through a multiyear reanalysis project.

2.6 Data Quality

2.6.1 Completeness

Sites are evaluated per the Regional Haze Rule (RHR) completeness criteria, where a site fails to meet the criteria if it has,

1. Less than 50% completeness (more than 15 lost samples) per calendar quarter;
2. More than 10 consecutive lost samples;
3. Less than 75% completeness (more than 30 lost samples) per calendar year.

During 2018 there were 11 sites that failed the RHR completeness criteria, as summarized in Table 2-1. Completeness is reported on a quarterly basis to NPS in the Field Status Report prepared by UCD.

Table 2-1: Summary of sites that failed the RHR completeness criteria during 2018.

Site Name	Completeness by Quarter (%)				Consecutive Terminal Samples	Annual Completeness (%)
	1 st Q	2 nd Q	3 rd Q	4 th Q		
Agua Tibia, CA (AGTI1)	77	50	35	48	18	52
Baengnyeongdo Island, KR (BYIS1)	73	0	68	81	39	56
Egbert, Ontario (EBGE1)	97	43	100	94	13	84
Fresno, CA (FRES1)	93	90	87	55	14	81
Gates of the Mountains, MT (GAMO1)	33	0	39	84	59	39
Grand Canyon, AZ (GRCA2)	0	27	87	94	52	52
Hawaii Volcanoes, HI (HAVO1)	47	83	94	90	14	79
Hoover, CA (HOOV1)	60	100	100	84	11	86
Ike's Backbone, AZ (IKBA1)	93	67	77	71	16	77
Sawtooth, ID (SAWT1)	83	93	39	61	11	69
Wheeler Peak, NM (WHPE1)	93	60	0	81	46	58

2.6.2 Data Processing

2.6.2.1 Universal Calibration Constants for Flow Rate

Historically, the IMPROVE program has used site- and module-specific calibration constants to calculate flow rate, which were updated during UCD site maintenance visits and as-needed by site operators between UCD visits. With the implementation of the UCD designed and built new controllers (see Section 6.3), upgraded electronics allow for reliable and consistent pressure transducer measurements and application of universal flow rate calibration constants. Beginning with 2018 data – for sites where new controllers are installed – universal constants are used for flow rate calculations, where the constants are determined as described in a UCD data advisory (<http://vista.cira.colostate.edu/Improve/data-advisories/>, posted 9/2019). Flow constants are not expected to change with each site maintenance visit, but will be checked during maintenance to ensure that equipment is operating within specifications.

2.6.2.2 Method Detection Limits (MDLs)

As discussed in Section 4.2.2, the method detection limit (MDL) calculation has been harmonized across the filter types. Beginning with samples collected January 2018, the MDLs for ions and carbon species are calculated as 95th percentile minus median of the field blank loadings, using 50 field blanks collected in and closest to the sampling month for each filter type. The MDL calculation for elements continues to be calculated as 95th percentile minus median of field blank loadings, using 35 field blanks (see *UCD IMPROVE SOP #351: Data Processing and Validation*).

2.6.2.3 XRF Processing by Filter Lot

Beginning with samples collected October 1, 2018, uncertainty and MDL calculations for EDXRF were made filter lot specific. Historically, EDXRF uncertainty and MDL depended on field blank statistics for the full collection of field blanks within the same sampling month. Now, field blank statistics are segregated by filter lot to accommodate differences in EDXRF sensitivity between filter lots, especially lots from different manufacturers.

3. Laboratory Quality Control Summaries

3.1 RTI Ion Chromatography Laboratory

Ion analysis is performed by RTI according to a separate contract with NPS. See the RTI 2018 QA Report at <http://vista.cira.colostate.edu/improve/wp-content/uploads/2019/08/2018-RTI-QA-Report.pdf>.

3.2 DRI Thermal Optical Analysis Laboratory

Carbon analysis is performed by DRI according to a separate contract with NPS.

3.3 UCD X-Ray Fluorescence Laboratory

The UCD XRF Laboratory received and analyzed PTFE filter samples collected January 1, 2018 through December 31, 2018. UCD performed analysis for 24 elements using Malvern Panalytical model E5 energy dispersive x-ray fluorescence (EDXRF) instruments. These analyses were

performed during an analysis period from March 22, 2018 through August 1, 2019 on three instruments, XRF-1, XRF-2, and XRF-3. Details of the sample analysis are shown in Table 3-1.

Table 3-1: Sampling dates and corresponding EDXRF analysis dates during this reporting period. Analysis dates include reanalysis – as requested during validation – of any samples within the sampling year and month.

Sampling Year	Sampling Month	XRF-1 Analysis Dates	XRF-2 Analysis Dates	XRF-3 Analysis Dates
2018	January	NA	4/2/2018 – 5/17/2018	3/30/2018 – 11/06/2018
2018	February	N/A	4/27/2018 – 9/26/2018	3/22/2018 – 6/27/2018
2018	March	7/2/2018 – 7/14/2018	6/9/2018 – 9/26/2018	3/31/2018 – 7/17/2018
2018	April	7/2/2018 – 7/19/2018	6/26/2018 – 8/17/2018	6/25/2018 – 8/17/2018
2018	May	NA	7/30/2018 – 9/15/2018	8/3/2018 – 9/20/2018
2018	June	NA	8/23/2018 – 10/18/2018	8/22/2018 – 1/24/2019
2018	July	NA	9/25/2018 – 4/22/2019	9/26/2018 – 11/27/2018
2018	August	11/21/2018 – 12/19/2018	10/28/2018 – 12/19/2018	10/31/2018 – 12/19/2018
2018	September	12/17/2018 – 3/5/2019	11/21/2018 – 3/5/2019	12/05/2018 – 2/10/2019
2018	October	2/10/2019 – 3/20/2019	1/16/2019 – 3/19/2019	12/24/2018 – 2/11/2019
2018	November	2/10/2019 – 4/16/2019	2/18/2019 – 5/4/2019	3/26/2019 – 8/1/2019
2018	December	3/15/2019 – 4/17/2019	3/26/2019 – 5/4/2019	3/26/2019 – 8/1/2019
2018	All Months	7/2/2018 – 4/17/2019	4/2/2018 – 5/4/2019	3/30/2018 – 8/1/2019

3.3.1 Quality Control System

The quality control system is designed to provide confidence in the reported elemental concentrations of PM_{2.5} aerosol samples collected on PTFE filters. There are a variety of factors that could affect the accuracy of the instrument calibrations or contribute to contamination of the sampled filters. The goal is to provide confidence that the instruments are in control and provide alerts when they are not. The quality control procedures are described in *UCD IMPROVE TI 301D* and are summarized in Table 3-2.

Table 3-2: UCD EDXRF routine QC activities, criteria, and corrective actions.

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 adjust the energy channels
PTFE Blank	Daily	≤ acceptance limits with exceedance of two elements at least in two consecutive days	<ul style="list-style-type: none"> • Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UCD-made ME-RMs	Daily	±10% of reference mass loadings with exceedance of any element not to occur in more than two consecutive days for the elements Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	<ul style="list-style-type: none"> • Check sample for damage/contamination • Further cross-instrumental testing • Replace sample if necessary
UCD-made ME-RMs	Weekly	±10% of reference mass loadings with exceedance of any element not to occur in more than two consecutive days for the elements Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	
Re-analysis set	Monthly	z-score ≤ 1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	
SRM 2783	Monthly	Absolute bias ≤ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	

QC procedures are used to monitor instrument performance in four general categories: daily operation, weekly operation, monthly comparisons, and calibration checks. Daily operation is monitored by running a laboratory blank and a UCD produced multi-element reference material (ME-RM). The mass loadings on the blank and ME-RM are monitored to be within acceptable limits. Weekly QC checks are performed by analyzing another UCD produced ME-RM which is analyzed on all EDXRF instruments once per week while samples are being analyzed; the mass loadings are monitored to be within the acceptance limits. On a monthly basis, a set of re-analysis samples, with a range of elemental mass loadings similar to the range of loadings from samples, are reanalyzed. A z-score test statistic is calculated from these results and plotted monthly to monitor the instrumental response and as an inter-comparison between the instruments. The NIST SRM 2783 air particulate filter standard is also analyzed monthly on all instruments. The QC checks provide feedback on the performance of each instrument for both short- (daily QC checks) and long-term (weekly and monthly QC checks) duration.

Monitoring of the QC checks is done using a number of web-based tools developed in-house at UCD for this purpose. These tools access the QC results directly from the UCD database in near-real-time (EDXRF results transmit to the database within about five minutes) and display the results as plots with acceptance limits to allow immediate observation of any quality issues or QC check failures.

3.3.2 Laboratory QC Summary

QC tests conducted over the course of this reporting period showed good overall control of the instruments and process. All QC checks passed or were investigated and promptly corrected with

no impact to data quality. The following is a summary of QC findings for select elements and corrective actions taken to ensure accuracy of reported data.

Zinc (Zn) is occasionally observed as a contaminant which comes from the overhead sample changer in the EDXRF systems. During this analysis period, one Zn contamination event was observed on XRF-3 on one QC sample; this was the only case where evidence of Zn contamination was observed. No IMPROVE samples were analyzed between the occurrence of high Zn reading and resolution of the issue. Details are described in Section 3.3.4.

During this analysis period, three sulfur (S) contamination events occurred, two on XRF-2 and one on XRF-3. The S contamination was the result of vacuum pump oil which had migrated into the sample chamber of the EDXRF instruments. Samples were not contaminated, however elevated S readings were observed. The chambers were cleaned which resolved the occurrence of high S readings, and routine preventative maintenance was performed. No further S contamination was observed after the maintenance. Details are described in Section 3.3.4.1.

Calcium (Ca) failed blank acceptance on XRF-1 in July 2018 and lead (Pb) failed acceptance for the daily ME-RM on XRF-2 in April 2019. These events were limited to these single QC samples; no other QC samples analyzed showed unacceptable levels of Ca or Pb. After cleaning of the QC samples the values returned to normal, acceptable levels. Due to the singular nature of the events, it was determined that there was no impact to the reported IMPROVE sample results. Details are described in Section 3.3.4.1.

The aluminum (Al) z-score for the monthly reanalysis QC check failed for XRF-2 in November 2018 and January 2019. This was partially attributed to the difficulty of quantifying Al using EDXRF and partly to a bias between the instruments for Al. Because no shift in the aluminum values of either the daily ME-RM or the weekly ME-RM occurred for XRF-2, these two failures were determined to be noise in the z-score value. To avoid this issue in the future, and to replace an aging set of filters that had acquired some Zn contamination, a new set of reanalysis samples was implemented in February 2019. These failures did not impact the reported IMPROVE sample results. Details are described in Section 3.3.6.

In addition to the QC results above, the conditions under which the elements are analyzed by EDXRF (e.g. secondary targets and integration times) were changed during the annual instrument calibrations in December 2018. These changes were made to help reduce variability, detection limits, and bias in some elements (see Section 3.3.3 for further details). However, these changes caused the NIST SRM aluminum (Al) error to fail for XRF-2. In order to improve the Al signal to be in better alignment with the other instruments at typical sample concentrations, the error relative to the SRM increased. This was determined to not impact the IMPROVE sample results as the Al values for the weekly ME-RM and reanalysis samples showed good agreement with the other EDXRF instruments. Details are described in Section 3.3.6.

3.3.3 Instrument Calibrations

EDXRF instrument calibrations are performed annually at UCD; however, additional calibrations may be performed as necessary such as following maintenance or QC failures. Table 3-3 summarizes instrument calibrations for this reporting period.

Table 3-3: Summary of calibrations performed on each EDXRF instrument during this reporting period.

EDXRF Instrument	Calibration Date	Reason for Calibration	Range of Sample Dates Analyzed
XRF-2	1/5/2018	Annual calibration	1/2/2018 – 1/14/2018
XRF-3	1/5/2018	Annual calibration	1/2/2018 – 9/17/2018
XRF-1	1/19/2018	Annual calibration	3/3/2018 – 9/23/2018
XRF-2	4/19/2018	Replaced x-ray tube	1/2/2018 – 9/23/2018
XRF-1	12/19/2018	Annual calibration	9/5/2018 – 12/25/2018
XRF-2	12/20/2018	Annual calibration	7/16/2018 – 12/31/2018
XRF-3	12/20/2018	Annual calibration	6/1/2018 – 10/29/2018
XRF-3	2/18/2019	Replaced detector and x-ray tube	11/10/2018 – 12/16/2018
XRF-3	4/15/2019	Replaced x-ray tube	11/22/2018 – 12/31/2018

The annual calibration in December 2018 also included an updated analytical protocol. In order to improve detection of lead (Pb) and other elements, the analytical protocol for EDXRF analysis was slightly modified by changing the secondary X-ray targets and irradiation times (see Table 3-4). The effects on data quality are expected to be small, detectable only after a sufficient record has been acquired with the new protocol. The EDXRF instruments were recalibrated with the modified protocol, and all IMPROVE samples beginning with samples collected October 2018 were reported with the new calibration and new analytical protocol.

See UCD data advisory for further detail, <http://vista.cira.colostate.edu/Improve/data-advisories/> (posted 6/2019).

Table 4: EDXRF protocols for samples collected before and after implementation of the new analytical protocol.

Sample Element	Secondary Target	Exposure (sec), Old	Exposure (sec), New
Na – K	CaF ₂	600	600
Ca – Cr	Fe	400	400
Mn – Zn	Ge	300	400
As	KBr	300	---
Se – Br	SrF ₂	300	---
As – Br	SrF ₂	---	400
Rb – Sr, Pb	Mo	300	400
Zr	Al ₂ O ₃	200	200

3.3.4 Daily QC Review

At least once daily a PTFE laboratory blank and a UCD produced ME-RM are analyzed. The daily blank results are compared to acceptance limits, which are calculated as three times the standard deviation plus the mean of a set of PTFE laboratory blanks. If the mass loading exceeds the limit for more than two consecutive days, the blank is cleaned and/or 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 the blank QC filter. Sample analysis results are reviewed during data validation (see *UCD IMPROVE SOP #351: Data Processing and Validation*). When contamination is suspected, filters are reanalyzed and the reanalysis result is reported if contamination was present in the original analysis.

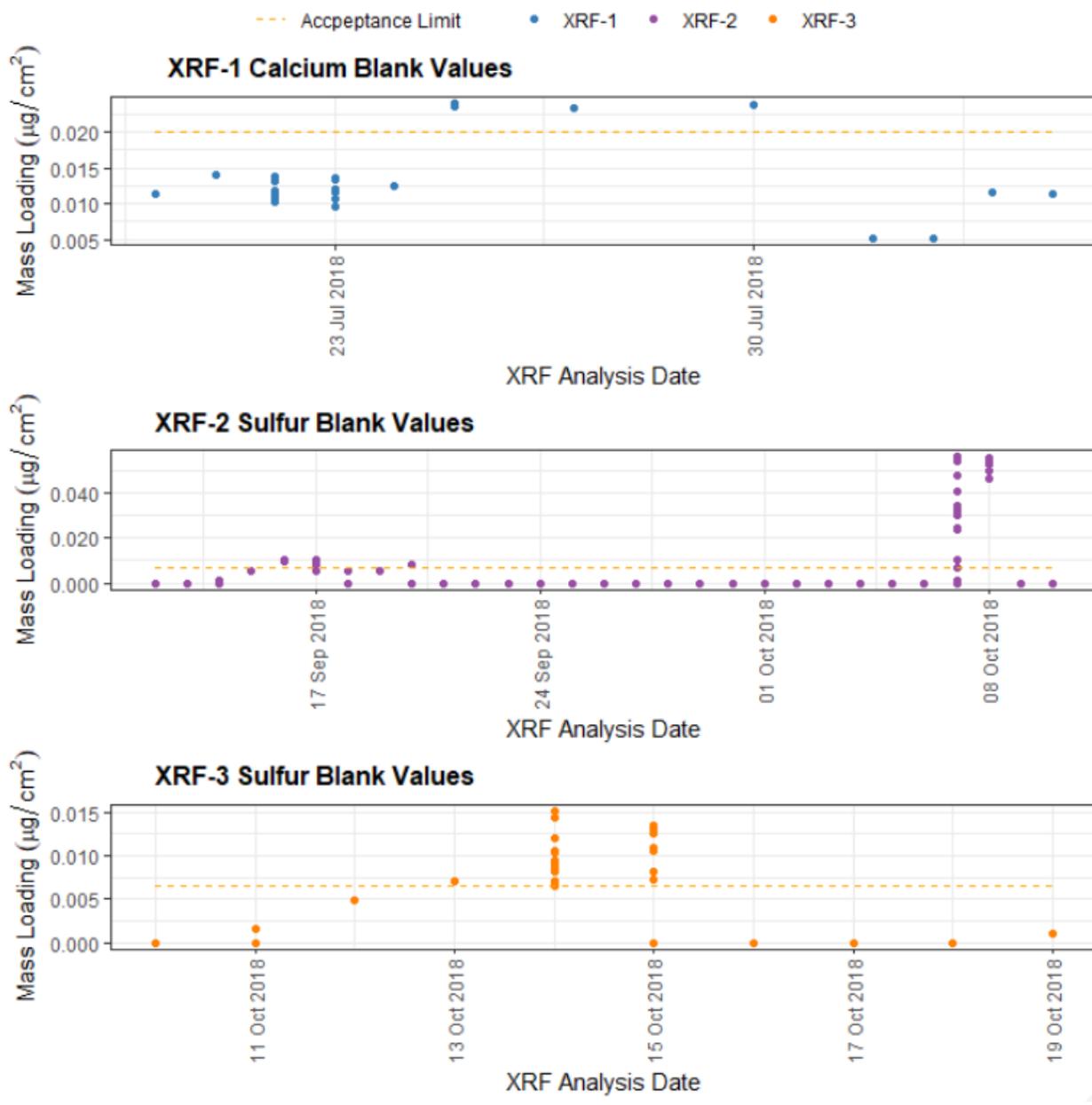
3.3.4.1 Daily Blank QC

Daily QC blank results during this analysis period showed only a few failures. These failures were investigated and corrective actions were taken. Sulfur (S) contamination was discovered on XRF-2 during the weekend of September 16-17, 2018 (see Section 3.3.2). The S mass loading was found to exceed the acceptance limit during repeated measures of the QC blank. On weekends, after all the loaded samples have been analyzed, the daily QC samples, blank, and ME-RM are analyzed repeatedly until Monday morning when the instrument is loaded with new samples. As shown in Figure 3-1, the S QC blank results were within acceptance limits after the IMPROVE samples completed analysis and then increased during repeated analyses of the blank. On Monday, following the weekend exceedances, the blank was removed, cleaned, and then reanalyzed. The blank analysis result for S returned within the acceptance limits and analysis of IMPROVE samples resumed.

Additional S contamination was observed on XRF-2 and XRF-3 in October 2018 (Figure 3-1). It was determined that vacuum pump oil had migrated into the EDXRF analysis chamber and was the source of contamination (see Section 3.3.2). The chambers were cleaned which resolved the occurrence of high S readings, and routine preventative maintenance was performed. No IMPROVE samples were analyzed during the sulfur contamination event on XRF-2. On XRF-3, two IMPROVE samples were analyzed prior to discovery of the S contamination and were subsequently reanalyzed after the condition was corrected. The reanalysis results did not show evidence of sulfur contamination and the original results were reported. Repeated analysis of the blank may have contributed to observation of contamination from the blank analysis results.

Three calcium (Ca) mass loadings from XRF-1 during July 25-30, 2018 exceeded the acceptance limits (Figure 3-1). After cleaning, the blank Ca mass loadings returned to within the acceptance limits and analysis of IMPROVE samples resumed. The Ca contamination was limited to the daily QC blank and did not impact the IMPROVE samples analyzed during this period.

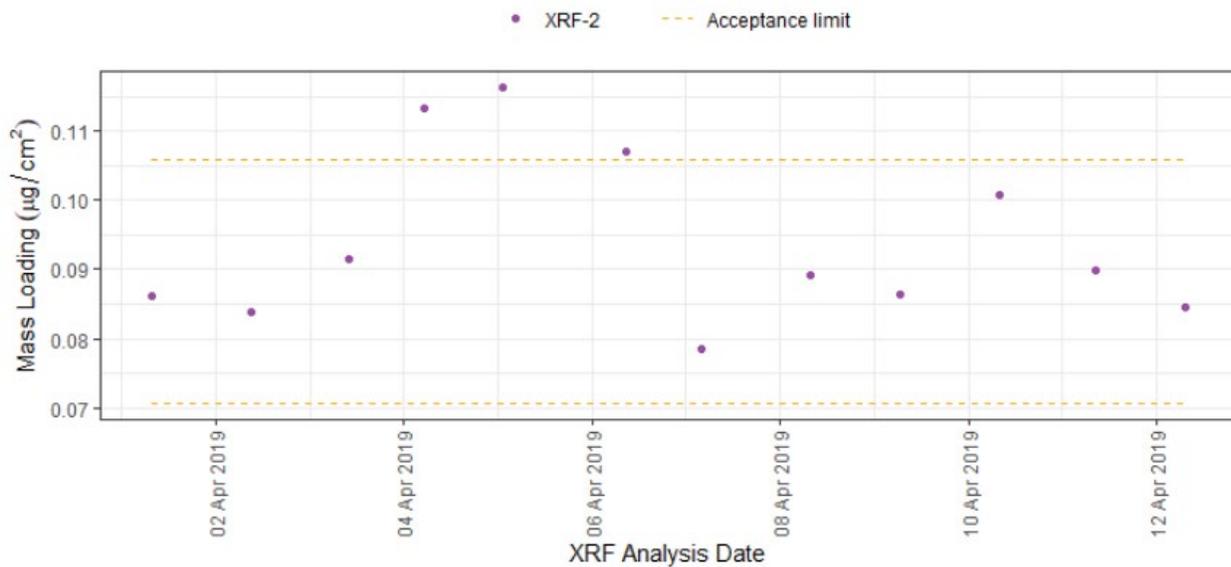
Figure 3-1: Daily blank QC results showing failures for calcium (XRF-1) and sulfur (XRF-2 and XRF-3).



3.3.4.2 Daily ME-RM QC

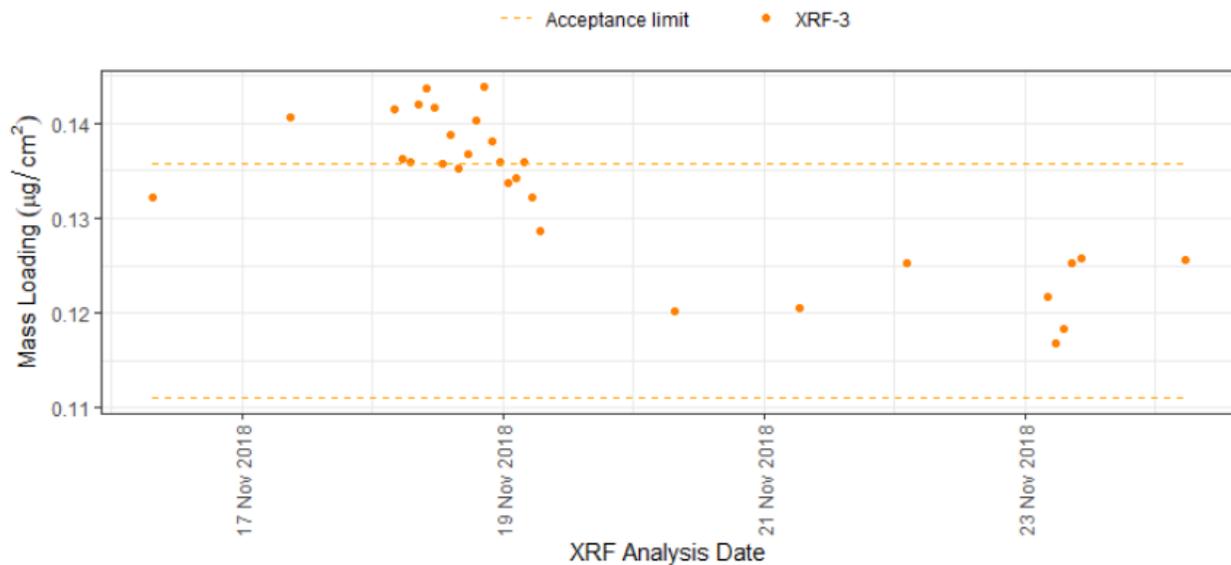
Daily QC ME-RM results during this analysis period showed only a few failures. XRF-2 exceeded the limit for lead (Pb) and XRF-3 exceeded the limit for zinc (Zn). The XRF-2 Pb exceedance occurred during April 4-6, 2019 (Figure 3-2). The daily blank did not show evidence of Pb contamination; the ME-RM result returned to acceptable levels without any intervention and IMPROVE sample results are not expected to be impacted.

Figure 3-2: XRF-2 lead (Pb) results on the daily ME-RM showing the failure in April 2019.



The XRF-3 Zn exceedance occurred during repeated measures over the weekend of November 17-18, 2018 (Figure 3-3). The QC blank results during this time did not show any Zn contamination. The daily ME-RM was cleaned and reanalyzed and the results returned to acceptable levels. Likely a singular contamination of the QC ME-RM, the ME-RM result returned to acceptable levels without any intervention and IMPROVE sample results are not expected to be impacted.

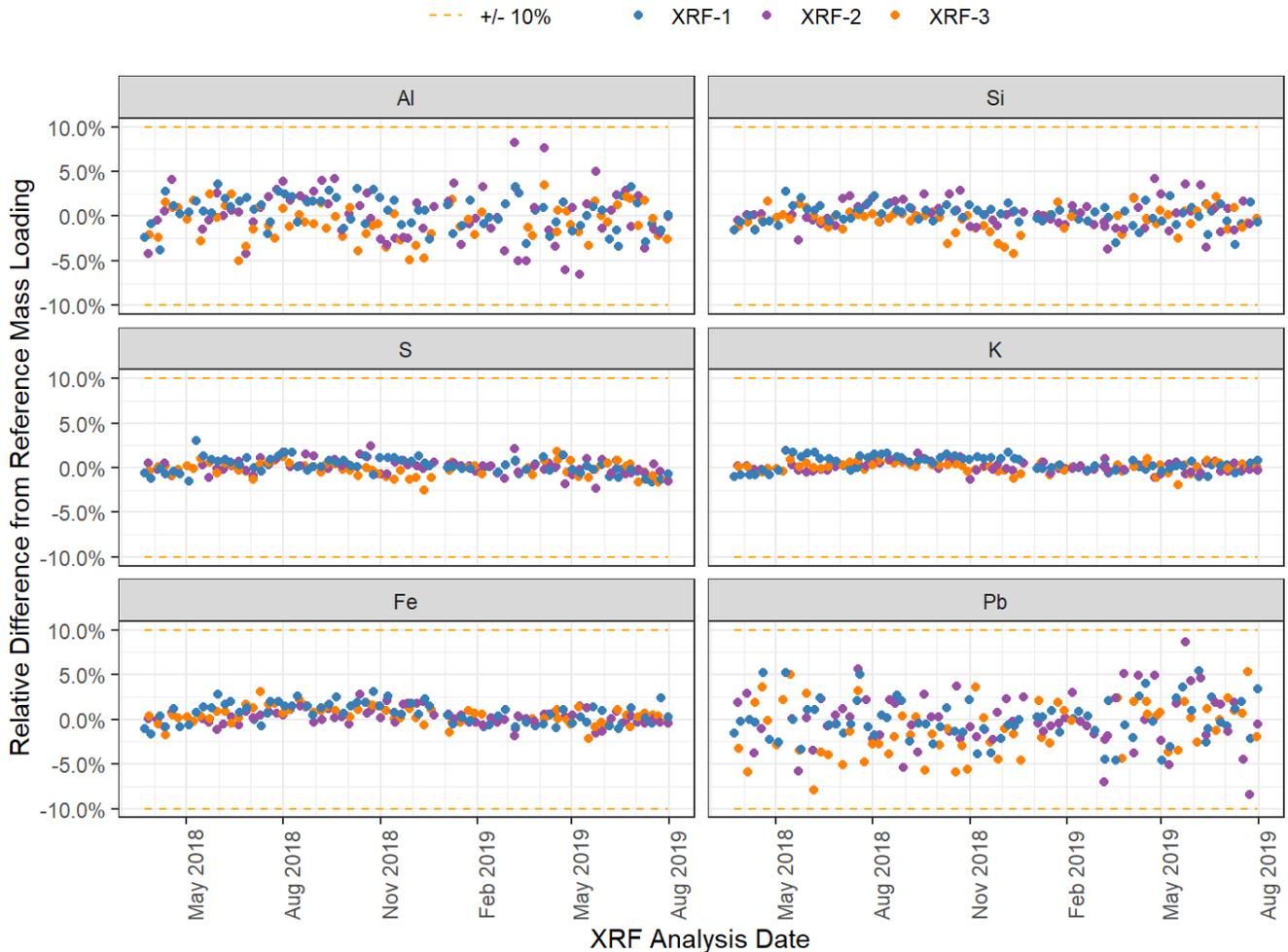
Figure 3-3: XRF-3 zinc (Zn) results on the daily ME-RM showing the failure in November 2018.



3.3.5 Weekly QC Review

The weekly ME-RM is a single QC sample that is measured on each of the EDXRF instruments once per week. It serves as a QC measure to track long-term trends and can be used to compare inter-instrumental responses for investigation of QC issues. During this analysis period there were no QC failures for the weekly ME-RM. Shown in Figure 3-4 are weekly ME-RM results for a few representative elements.

Figure 3-4: EDXRF weekly ME-RM control charts showing a few representative elements.



3.3.5 Monthly QC Review

Monthly QC is performed using a reanalysis set. The reanalysis set was historically a set of ambient aerosol sampled filters which were chosen to represent a typical range of mass loadings for the IMPROVE network samples. In recent years the ambient sampled filters have been replaced by UCD produced ME-RM samples to better control the range of mass loadings for more elements and to allow the opportunity to create multiple ME-RM filters at every mass loading so that backup sets are available if a filter becomes damaged or contaminated. During this analysis period a reanalysis set of ambient sampled filters (15) was used, as well as a newer set of ME-RM filters (16) used beginning February 2019.

The monthly reanalysis monitors both the long-term instrument performance and the agreement between instruments. In order to compare multiple filters with different mass loadings, the reanalysis results are first converted to z-scores. For a given month, the z-score for the i^{th} element and j^{th} filter is

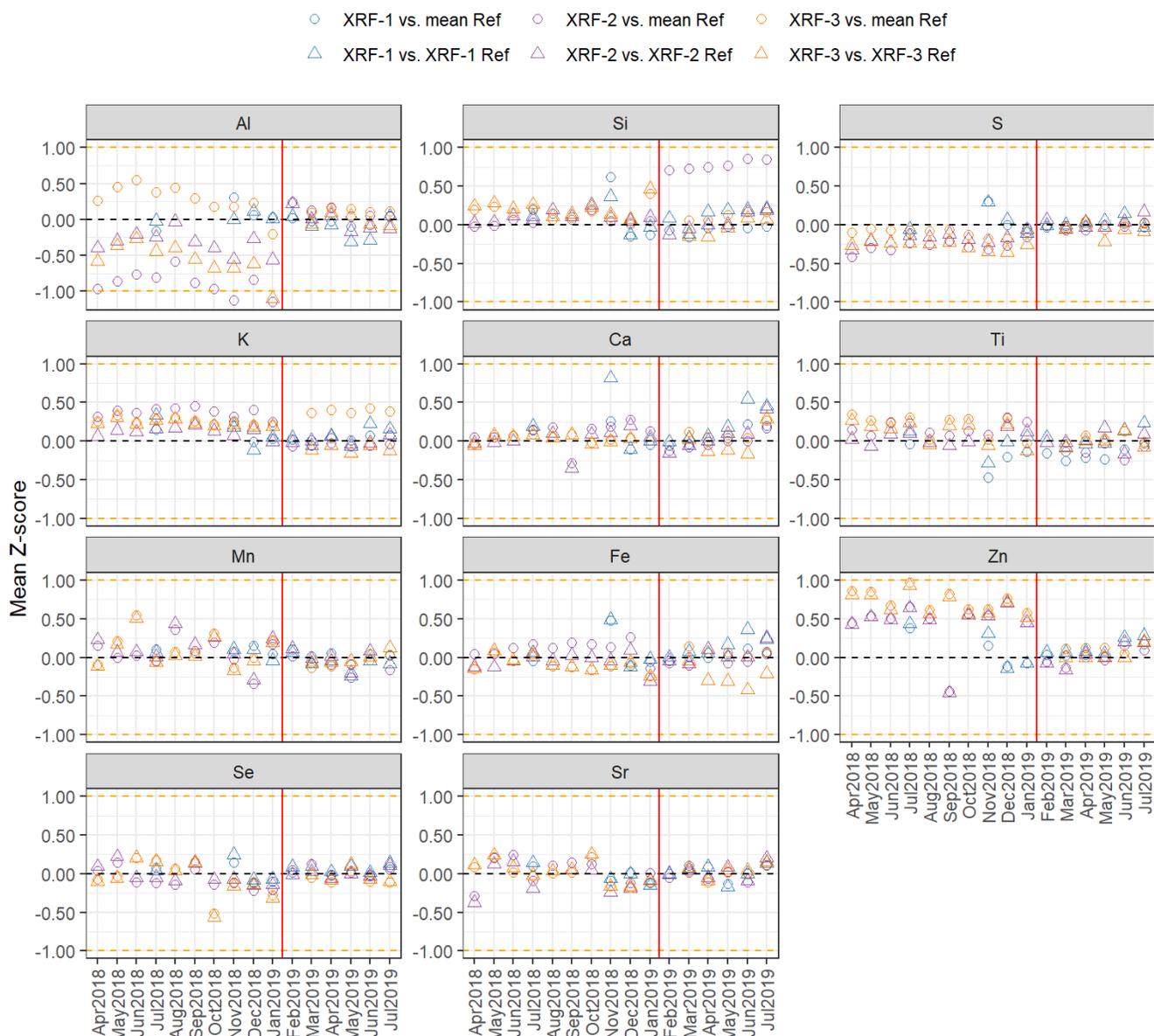
$$z_{ij} = \frac{x_{ij} - \widehat{x}_{ij}}{\sqrt{U(x_{ij})^2 + U(\widehat{x}_{ij})^2}} \quad (\text{Eq. 3-1})$$

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

$$\text{Bias}_i = \frac{1}{N} \sum_j z_{ij} \quad \text{and} \quad \text{RMS}_i = \sqrt{\frac{1}{N} \sum_j z_{ij}^2} \quad (\text{Eq. 3-2})$$

Every month, two different reference values are used to calculate z-scores (Figure 3-5): (1) the average response from the instrument for which the z-score is being calculated, used to evaluate long-term instrument reproducibility, and (2) the average response from all instruments, used to evaluate inter-instrument comparability.

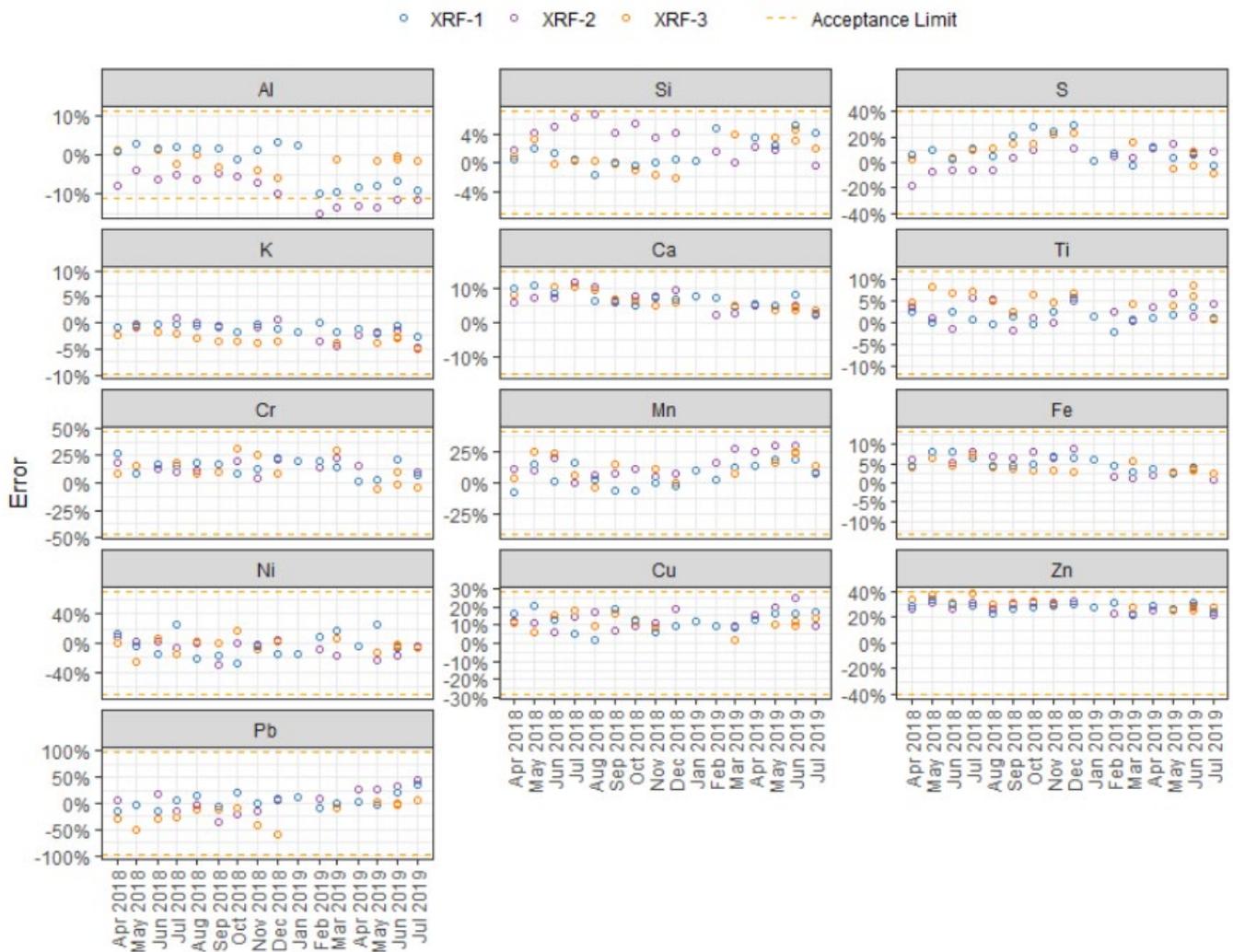
Figure 3-5: Monthly reanalysis control charts. The vertical red line indicates the change in reanalysis sample sets from ambient sampled filters to UCD ME-RM filters.



All reanalysis results were within a z-score value of ± 1 , except for aluminum (Al) which had z-score exceedances for XRF-2 and XRF-3. As mentioned in Section 3.3.2, Al is a difficult element to quantify by EDXRF. The exceedances for XRF-2 in November 2018 and January 2019, and for XRF-3 in January 2019, were not major instrument response shifts. Both daily and weekly ME-RM results were acceptable and showed no shifts in Al response; thus, it was determined that the Al exceedances had no impact on the IMPROVE sample results. The updated calibration and analytical protocol performed in December 2018 (see Section 3.3.2 and Section 3.3.3) reduced the inter-instrumental bias, as seen beginning with the new reanalysis filter set in February 2019.

In addition to the monthly reanalysis set, a NIST SRM 2783 air particulate standard is analyzed monthly. This analysis is used to assess the accuracy of the EDXRF instrument calibrations and to monitor the calibration for changes. The errors between the certified or reference loadings on the SRM and the mass loadings measured by EDXRF are plotted in Figure 3-6. The only exceedances during this analysis period were for Al on XRF-2. The exceedances begin following the updated calibration and analytical protocol performed in December 2018. While the updates were successful at reducing the inter-instrumental bias (Figure 3-5), it resulted in increased error between the NIST SRM 2783 Al reference loading and the measured Al mass loading for XRF-2. However, the Al z-scores are consistent from February through July 2019, indicating the calibration has not changed. Considering the acceptable performance of Al in the daily and weekly ME-RM QC tests, it was decided that the larger error for Al was acceptable given the reduced inter-instrumental bias in Al for mass loadings within the range of the IMPROVE network.

Figure 3-6: Monthly NIST SRM 2783 control charts.



3.4 UCD Gravimetric Laboratory

Future reports will include a quality control summary for the UCD Gravimetric Laboratory.

3.5 UCD Optical Absorption

Future reports will include a quality control summary for the UCD Optical Absorption Laboratory.

4. Quality Assurance and Data Validation

4.1 Concentration-Level QC Checks

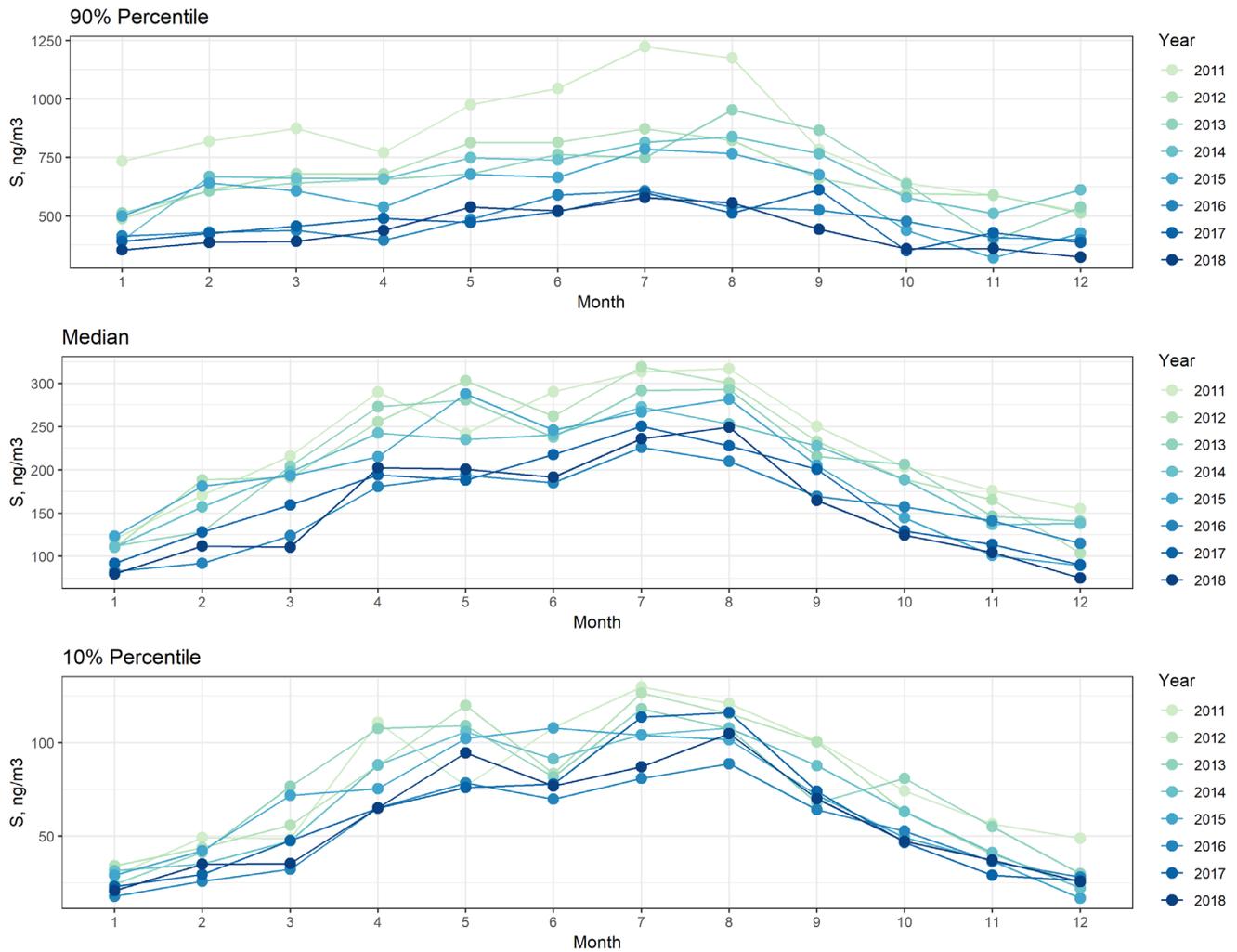
4.1.1 Comparison Across Years

Time series plots of network-scale statistics can reveal possible effects associated with changes in procedures, instrumentation, or sampling media in the analytical laboratories at DRI, RTI, and UCD. Interpretation of these plots is complicated by real atmospheric trends whose presence IMPROVE is intended to detect; these arise from intentional or adventitious changes in emissions, as well as inter-annual fluctuations in synoptic weather patterns.

Figures 4-1 through 4-9 show 90th percentile, median (50th percentile), and 10th percentile concentrations of select species, with seven years of historical network data (2011-2017) providing context for the current year under review (2018).

Similar to 2016 and 2017, sulfur concentrations during 2018 generally continue to be low and relatively stable (Figure 4-1).

Figure 4-1: Multi-year time series of network-wide sulfur (S) concentrations, 2011 through 2018.



Concentrations of vanadium (Figure 4-2) and nickel (Figure 4-3) during 2018 continue to be low similar to observations from 2015, 2016, and 2017. This is likely a continuation of lower concentrations observed corresponding with regulations on international shipping emissions implemented in January 2015 (Spada et al, 2018).

Figure 4-2: Multi-year time series of network-wide vanadium (V) concentrations, 2011 through 2018.

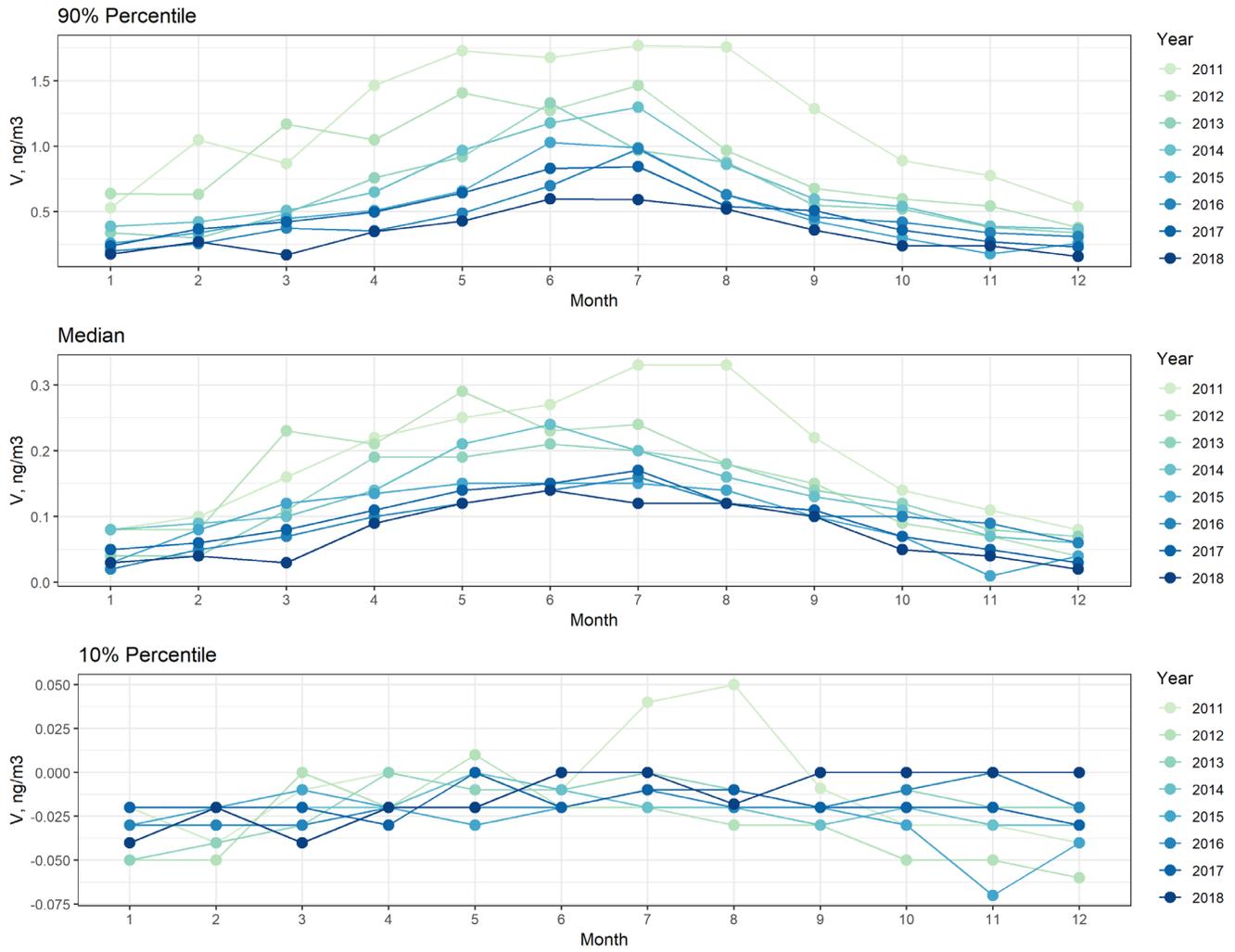
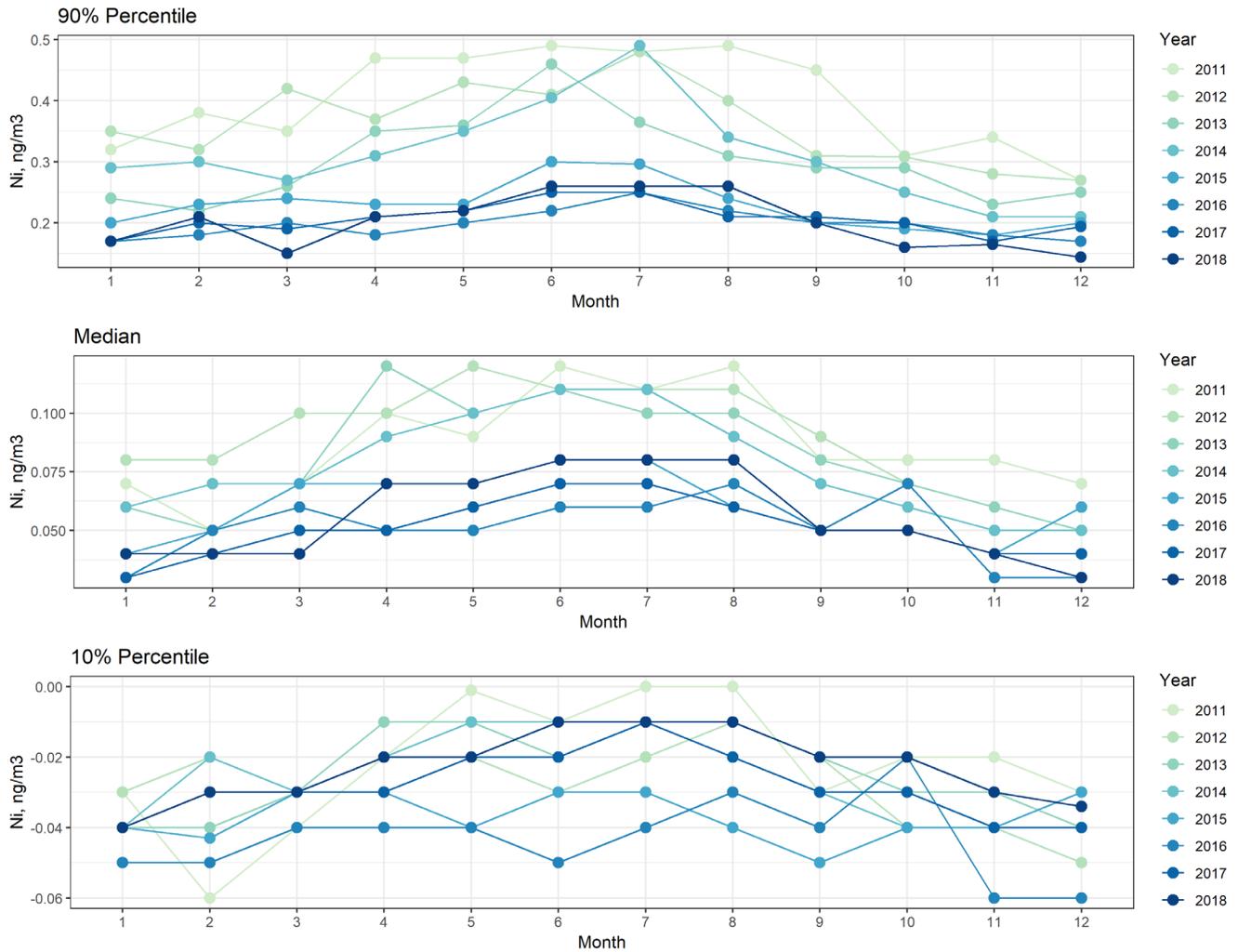


Figure 4-3: Multi-year time series of network-wide nickel (Ni) concentrations, 2011 through 2018.



Wildfires in the northwest U.S. and British Columbia during August 2018 impacted samples collected at many sites. At numerous sites with persistent smoke exposure, organic carbon (OCR, organic carbon by reflectance) was elevated above 30,000 ng/m³ for multiple sampling days, thus impacting aggregate network concentrations at the 50th and 90th percentiles (Figure 4-4). Elemental carbon (ECR, elemental carbon by reflectance; Figure 4-5) and potassium (K; Figure 4-6) are also sharply elevated during August 2018 corresponding with the widespread wildfire smoke. Network-wide 50th and 90th percentiles concentrations for OCR, ECR, and K during August 2018 are the highest observed during the time period being considered (2011 through 2018), including the previously highest concentrations of OCR and ECR observed during the 2017 wildfire season.

Figure 4-4: Multi-year time series of network-wide organic carbon by reflectance (OCR) mass concentrations, 2011 through 2018.

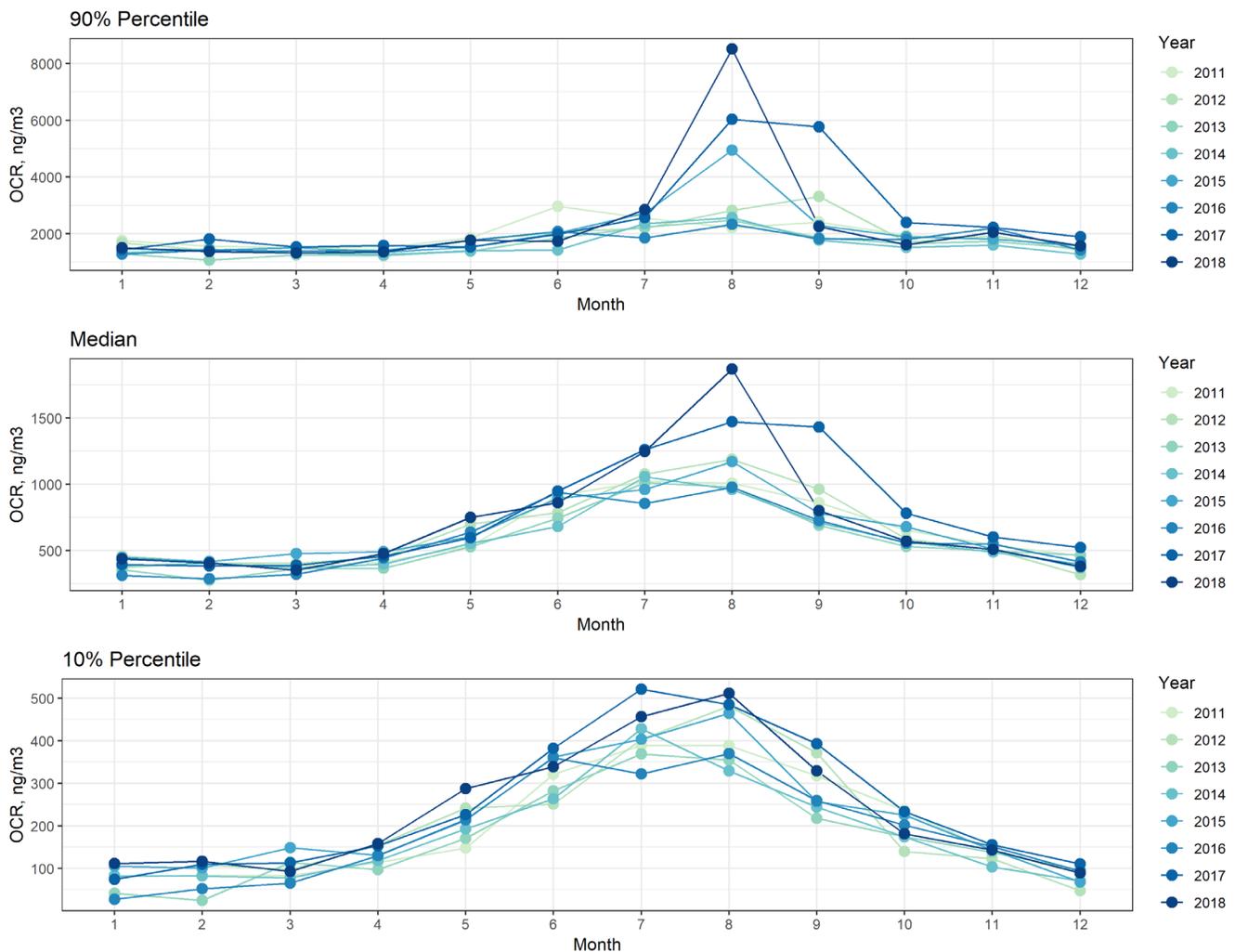


Figure 4-5: Multi-year time series of network-wide elemental carbon by reflectance (ECR) mass concentrations, 2011 through 2018.

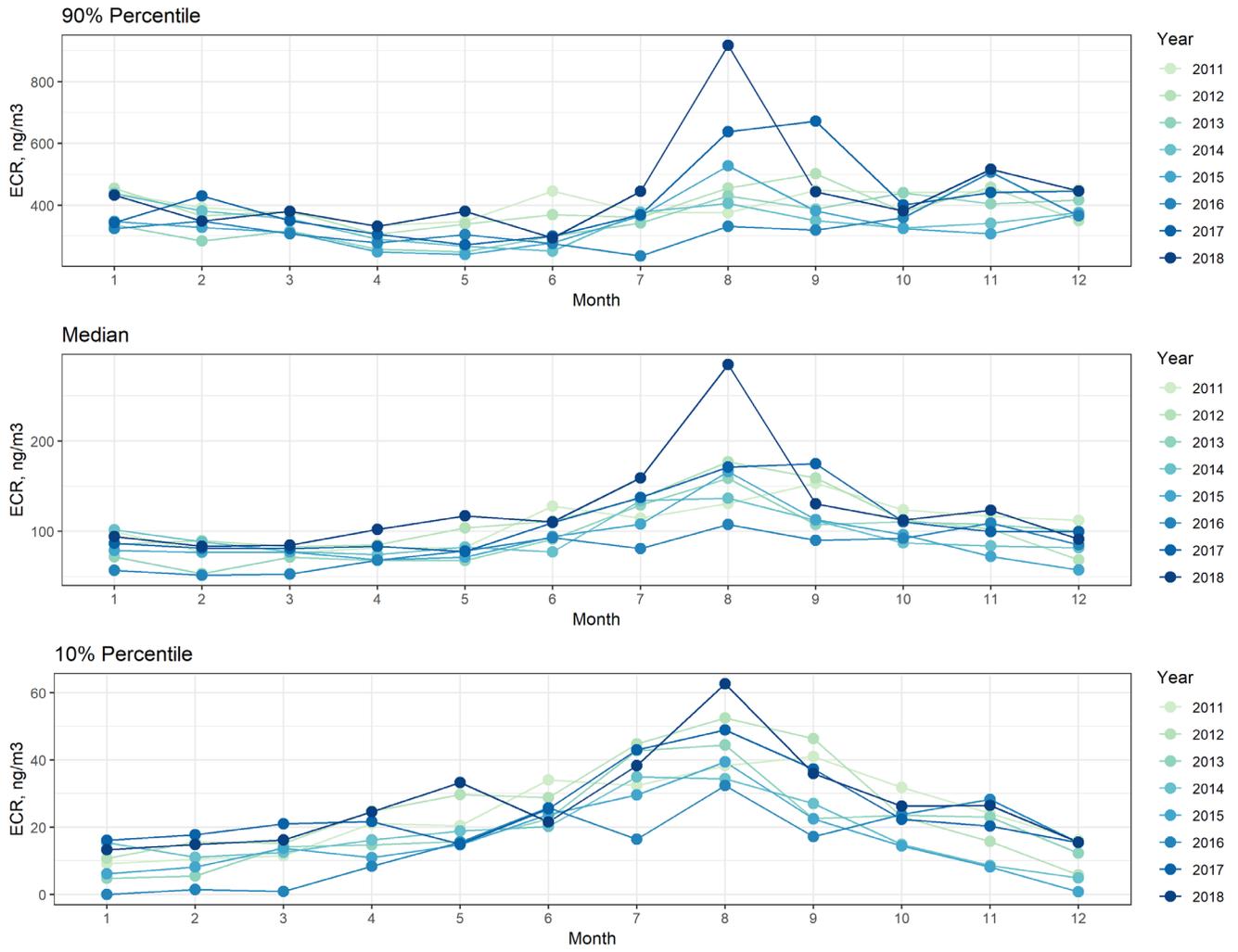
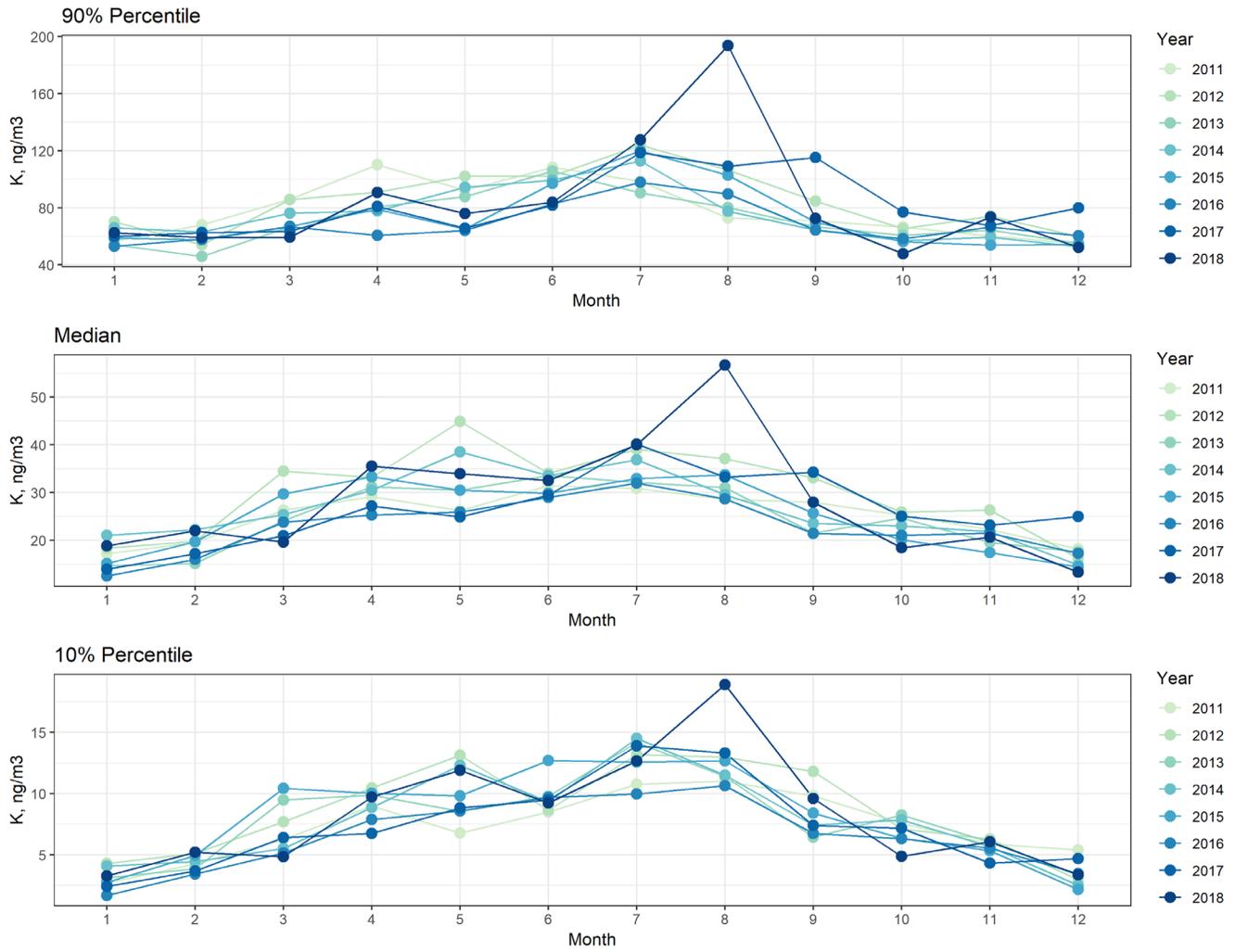
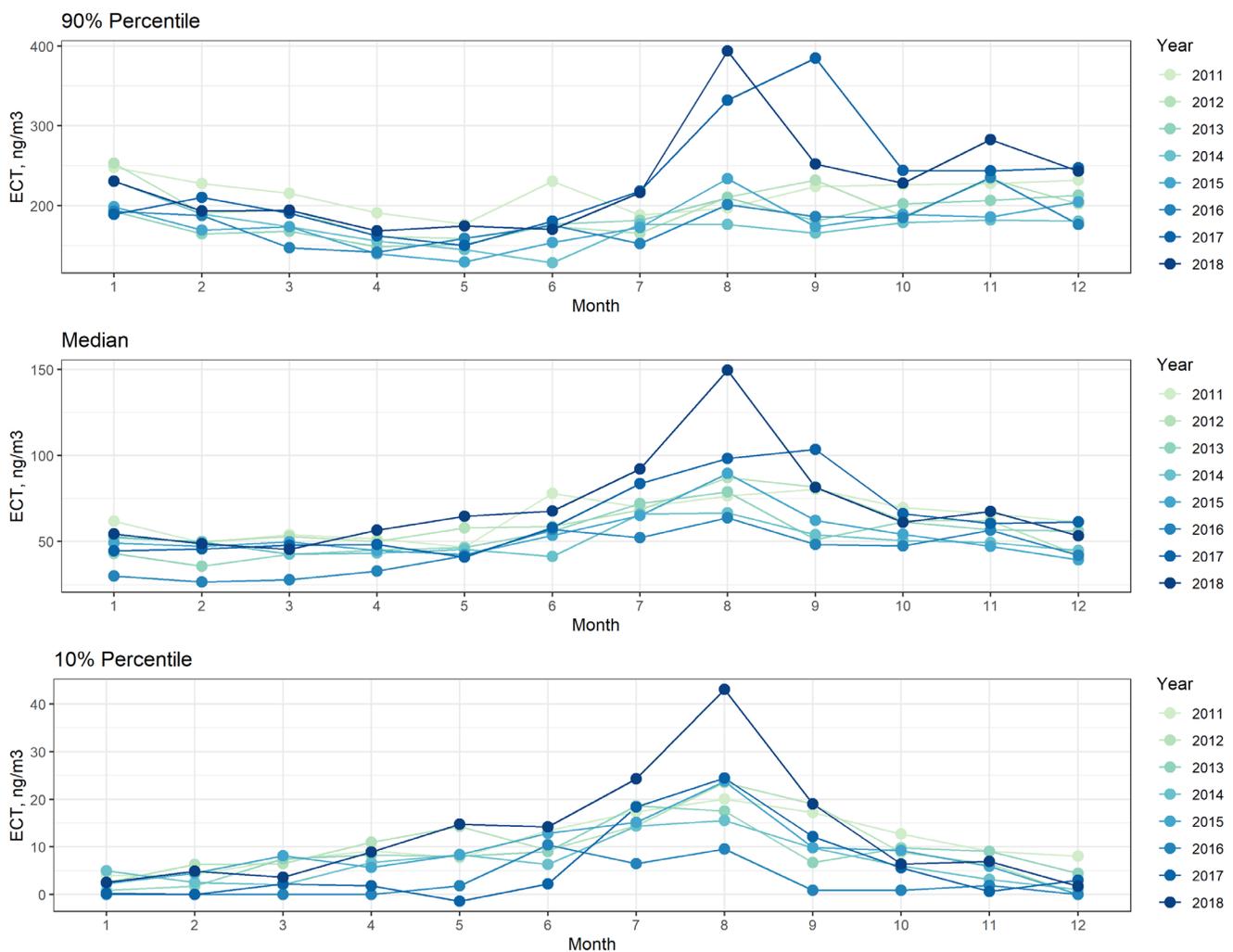


Figure 4-6: Multi-year time series of network-wide potassium (K) mass concentrations, 2011 through 2018.



The elemental carbon by transmittance (ECT; Figure 4-7) is also sharply elevated during August 2018 – with the 10th, 50th, and 90th percentile concentrations the highest observed during the time period being considered (2011 through 2018) – but is less than half the concentration reported for ECR (Figure 4-5) at the 90th percentile. This is likely caused by limitations in the determination of the OC/EC split point, associated with heavily loaded filters with high EC concentrations. Heavily loaded, dark filters can absorb most of the laser light at the start of the analysis, causing the transmittance and/or reflectance laser signals to be at the lower detection limit (near zero). Further darkening of the filter, due to the pyrolysis of organic carbon under the inert atmosphere, is not detectable; thus the pyrolyzed carbon values are zero for these samples. This is an instrument limitation, and the outcome is dependent on the laboratory protocol for thermogram processing.

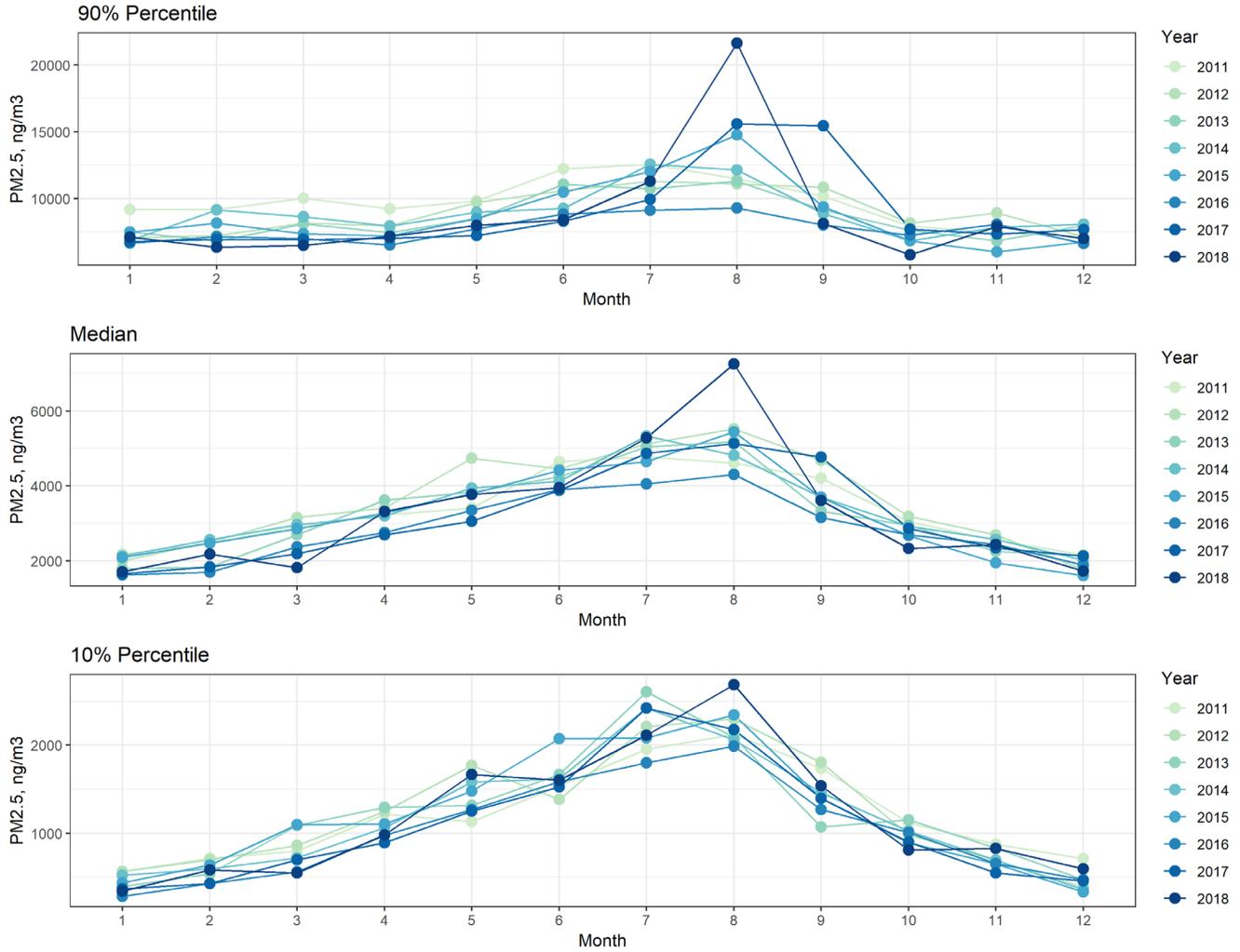
Figure 4-7: Multi-year time series of network-wide elemental carbon by transmittance (ECT) mass concentrations, 2011 through 2018.



As mentioned in the previous IMPROVE Semiannual Quality Assurance Report (April 30, 2019), median PM_{2.5} concentrations were modestly elevated (relative to the previous two years) in April and May 2018, corresponding with elevated concentrations of soil elements (Al, Si, Ca,

Fe, and Ti). However, the dominant PM_{2.5} event during 2018 corresponds with the August wildfire activity, with PM_{2.5} sharply elevated at the 10th, 50th, and 90th percentiles (Figure 4-8).

Figure 4-8: Multi-year time series of network-wide PM_{2.5} mass concentrations, 2011 through 2018.



Unexpectedly, network zinc (Zn; Figure 4-9) and manganese (Mn; Figure 4-10) concentrations were also elevated during August 2018. Wildfire smoke was widespread throughout much of the northwest U.S. during August 2018, and elevated Zn and Mn concentrations are observed corresponding with smoke plumes visible by MODIS satellite imagery (Figure 4-11).

Figure 4-9: Multi-year time series of network-wide zinc (Zn) mass concentrations, 2011 through 2018.

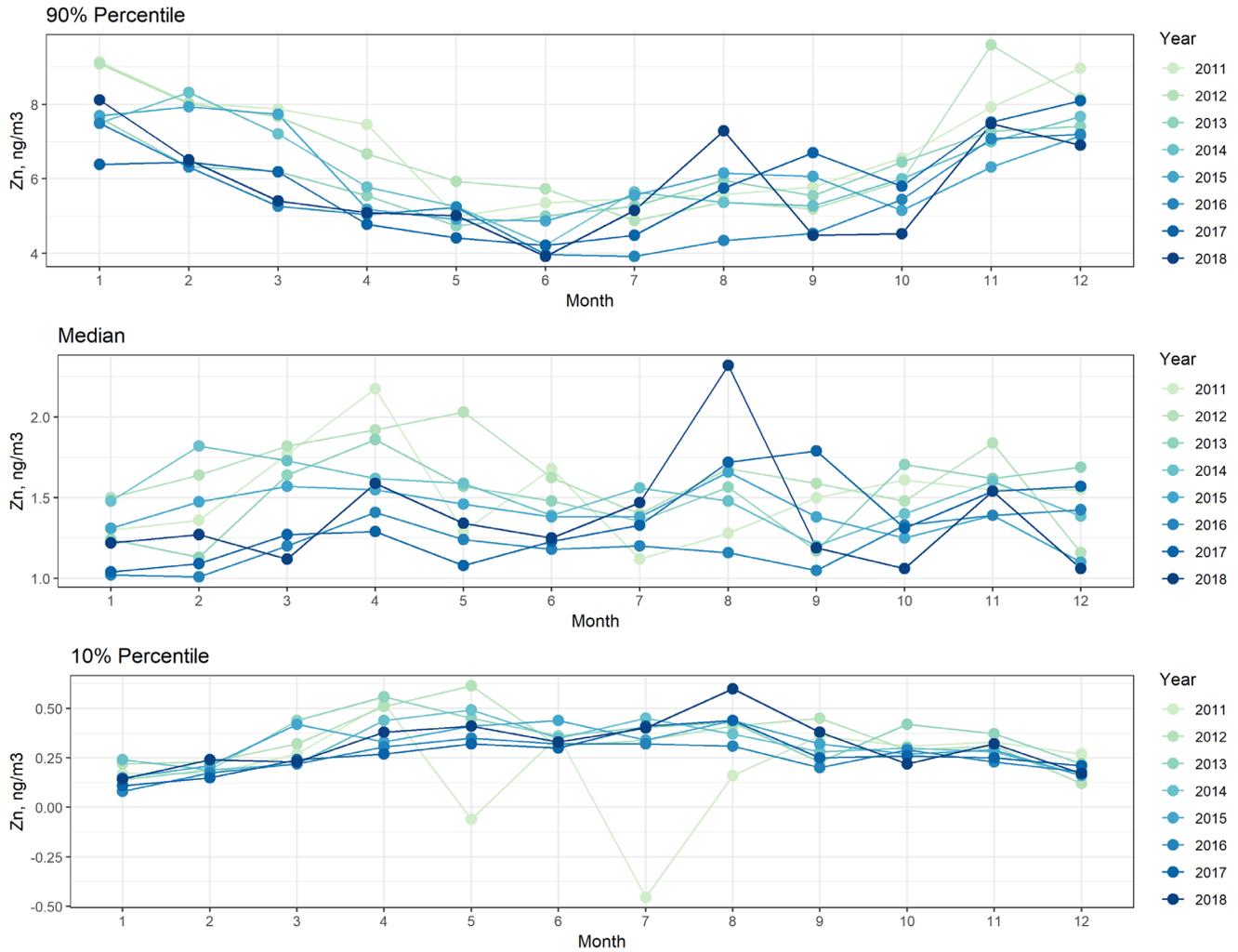


Figure 4-10: Multi-year time series of network-wide manganese (Mn) mass concentrations, 2011 through 2018.

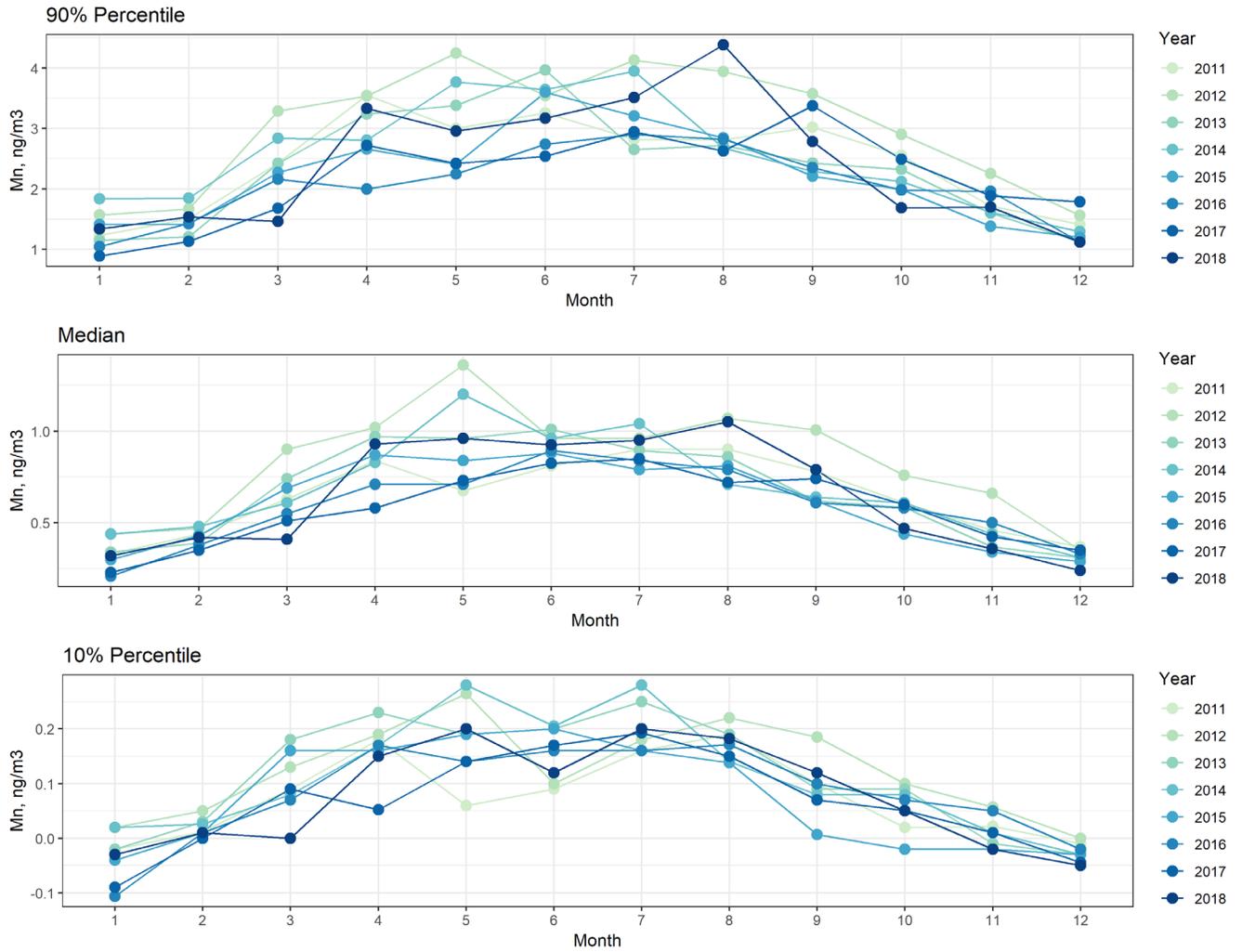
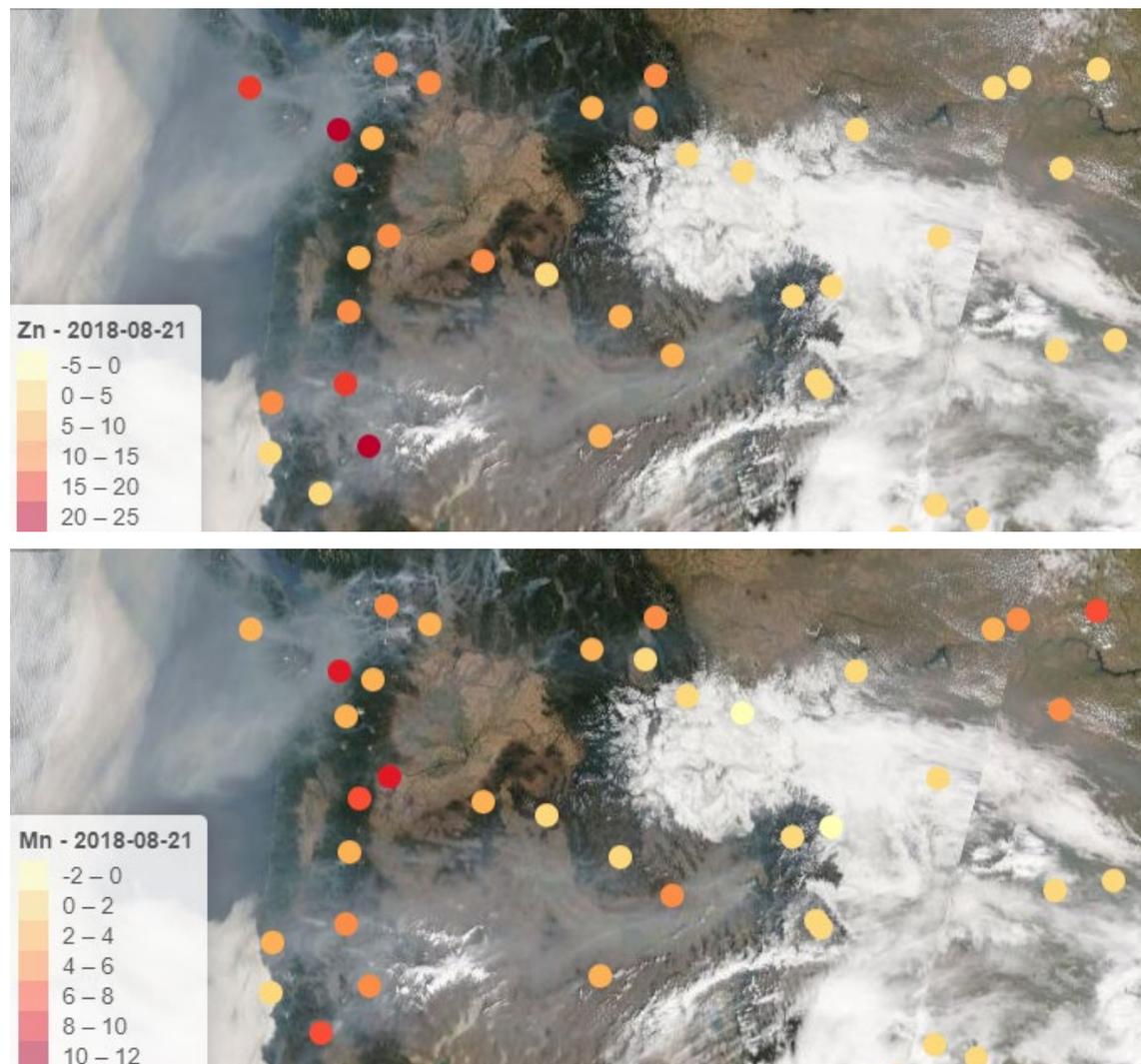


Figure 4-11: Zinc (Zn; top) and manganese (Mn; bottom) measured from samples collected at IMPROVE sites in the northwest U.S. on August 21, 2018. Concentrations in ng/m^3 are indicated per the color bar and are laid over a satellite imagery layer (MODIS Terra visible imagery from NASA GIBS).



4.1.2 Comparisons Between Modules

The following graphs compare two independent measures of aerosol properties that are expected to correlate. Graphs presented in this section explore variations in the correlations, which can result from real atmospheric and anthropogenic events or analytical and sampling issues.

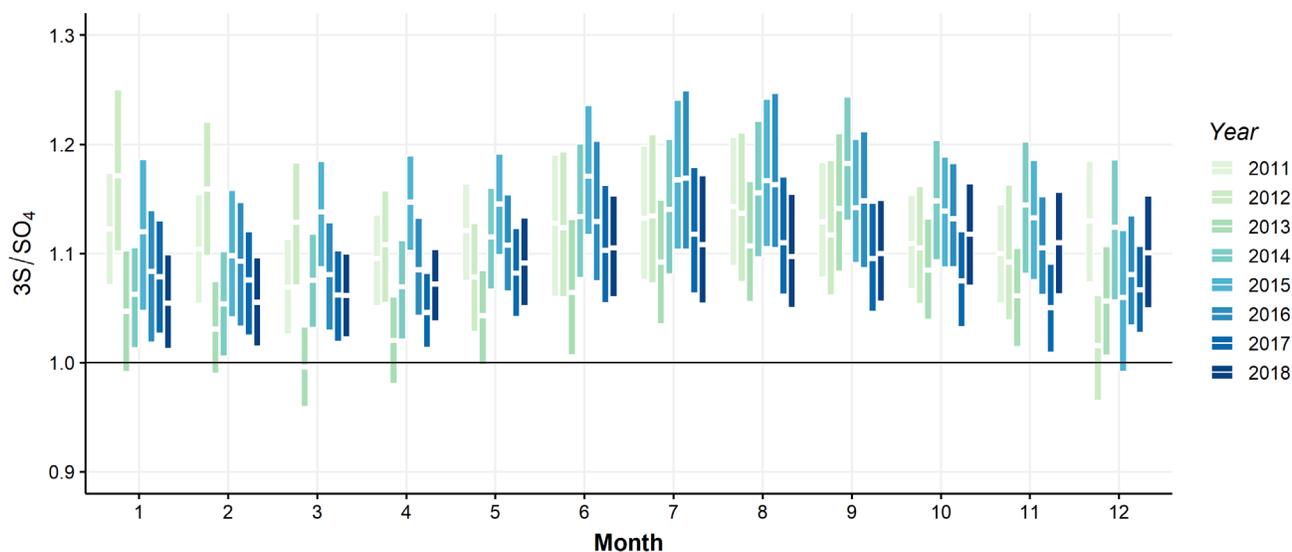
4.1.2.1 Sulfur versus Sulfate

PTFE filters collected from the 1A-Module are analyzed for elemental sulfur using EDXRF, and nylon filters collected from the 2B-Module 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); 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 4-12),

suggesting the presence of some sulfur in a non-water soluble form of sulfate or in a chemical compound other than sulfate.

During 2018 monthly network $(3\times S)/SO_4$ median ratios fell within the range of those previously reported (2011 through 2017), except for the $(3\times S)/SO_4$ median ratio for August which was lower than those previously observed.

Figure 4-12: Multi-year time series of network-wide $(3\times S)/SO_4$ ratios, 2011 through 2018. Bars show 25th to 75th percentile range, middle line indicates median.



4.1.2.2 $PM_{2.5}$ versus Reconstructed Mass (RCM)

PTFE filters from the 1A-Module are analyzed gravimetrically (i.e., weighed before and after sample collection) to determine $PM_{2.5}$ mass. Gravimetric data are compared to reconstructed mass (RCM), where the RCM composite variable is estimated from chemical speciation measurements. The formulas used to estimate the mass contributions from various chemical species are discussed in *UCD IMPROVE SOP #351: Data Processing and Validation*. In the simple case where valid measurements are available for all needed variables, reconstructed mass is the following sum:

$$\begin{aligned} \text{RCM} = & (4.125 \times S) + (1.29 \times \text{NO}_3^-) + (1.8 \times \text{OCR}) + (\text{ECR}) + \\ & (2.2 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} + 2.42 \times \text{Fe} + 1.94 \times \text{Ti}) + (1.8 \times \text{chloride}) \end{aligned}$$

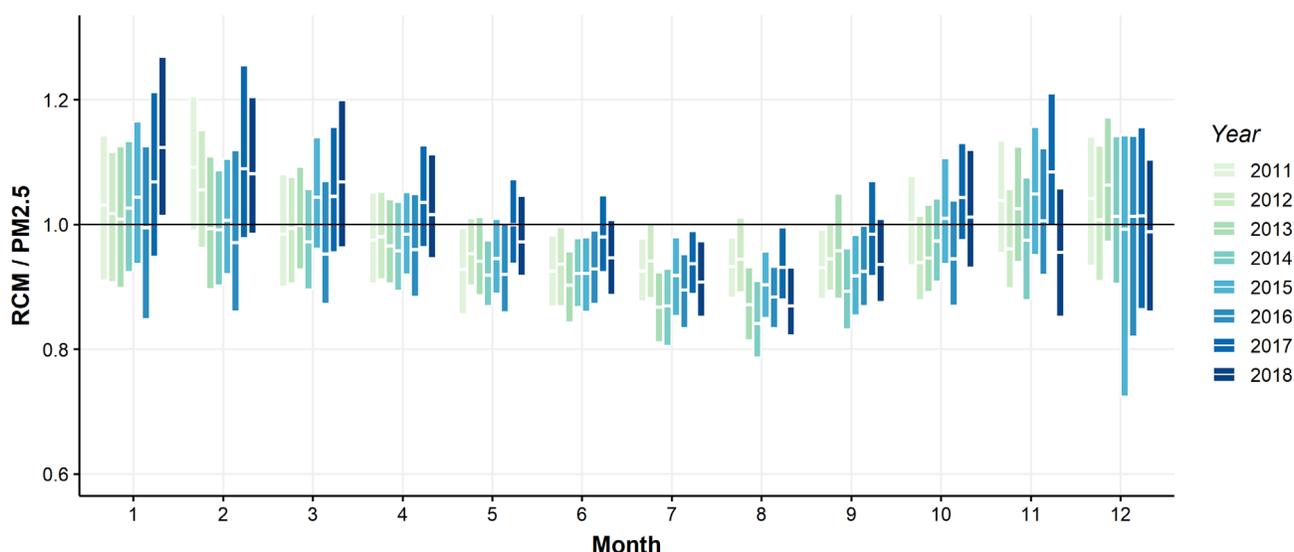
The parenthesized components represent the mass contributions from, in order, ammonium sulfate, ammonium nitrate, organic compounds, elemental carbon, soil, and sea salt.

If the RCM completely captures and accurately estimates the different mass components, the RCM/ $PM_{2.5}$ ratio is expected to be near one. In practice, the RCM/ $PM_{2.5}$ ratio exhibits some seasonal variability (Figure 4-13). The lowest ratios appear during the summer months when hygroscopic sulfates are most abundant, potentially contributing retained water to gravimetric $PM_{2.5}$ and when organic carbon is most oxidized, potentially resulting in an organic carbon mass multiplier larger than the 1.8 value used in the RCM equation. Unbound water is not accounted

for by any of the RCM terms. Conversely, the highest ratios appear during the winter months when peak levels of ammonium nitrate are captured on the retentive nylon filter. Some of this thermally unstable RCM may volatilize from the inert PTFE filter before it can be weighed to determine PM_{2.5}.

The RCM/PM_{2.5} ratios during January and March 2018 are higher than those reported during the previous seven years, whereas RCM/PM_{2.5} ratios for November and December are lower than previous years. As suggested in preceding reports, variation in the RCM/PM_{2.5} ratios could indicate changing organic carbon character. Additionally, water retained on the filter and a weighing environment with unstable relative humidity could be contributing factors.

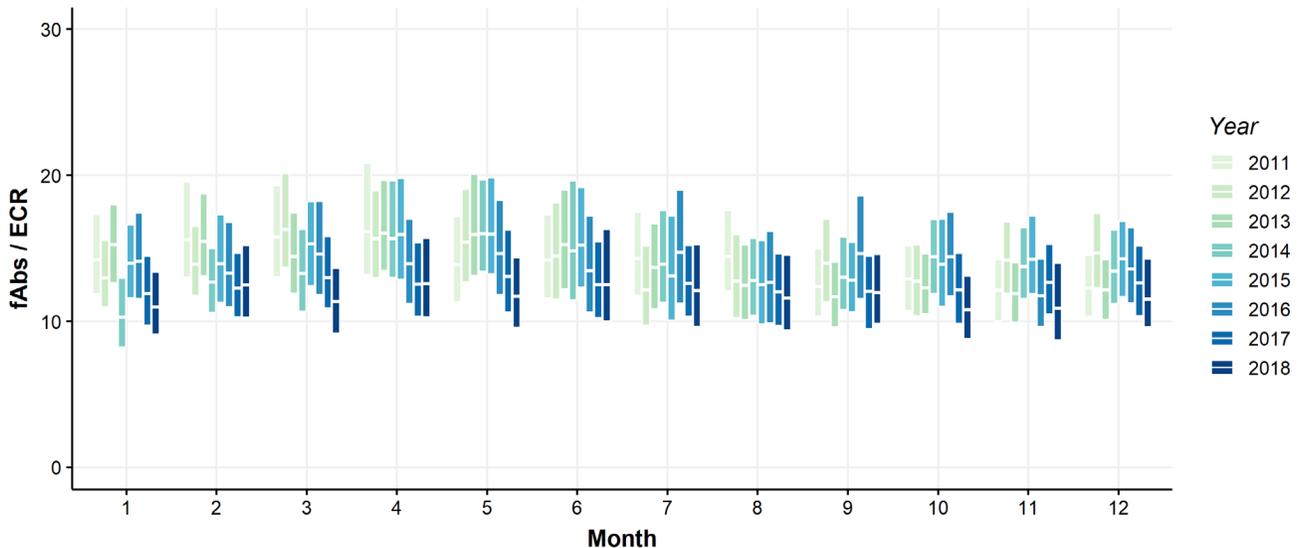
Figure 4-13: Multi-year time series of network-wide RCMN/PM_{2.5} ratios, 2011 through 2018. Bars show 25th to 75th percentile range, middle line indicates median.



4.1.2.3 Optical Absorption versus Elemental Carbon

The hybrid integrating plate/sphere (HIPS) instrument measures optical absorption, allowing for calculation of absorption coefficients (fAbs, where units are Mm⁻¹) from 1A-Module PTFE filters. Absorption coefficients are expected to correlate with elemental carbon from 3C-Module quartz filters (ECR, where units are µg/m³) measured by thermal optical analysis (TOA). The fAbs/ECR ratios during 2018 are generally low relative to the previous seven years, with six (March, May, August, October, November, and December) of the twelve months having median values lower than previously observed (Figure 4-14). The low fAbs/ECR ratios may be driven by high ECR values (Figure 4-5).

Figure 4-14: Multi-year time series of network-wide fAbs/ECR ratios, where fAbs is in Mm^{-1} and elemental carbon by reflectance (ECR) is in $\mu\text{g}/\text{m}^3$, 2011 through 2018. Bars show 25th to 75th percentile range, middle line indicates median.



4.1.3 Comparisons Between Collocated Samples

Select IMPROVE network sites are equipped with collocated sampler modules (Table 4-1), where simultaneous samples are collected 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 IMPROVE collocated sites is calculated as shown in Equation 4-1 and used to evaluate collocated precision (Figure 4-15, elements; Figure 4-16, mass; Figure 4-17, ions; Figure 4-18, carbon; Figure 4-19, optical absorption).

$$\text{Scaled Relative Difference (SRD)} = \frac{(\text{collocated} - \text{routine}) / \sqrt{2}}{(\text{collocated} + \text{routine}) / 2} \quad (\text{Eq. 4-1})$$

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. This convergence is not observed for species that are rarely measured above the MDL.

Table 4-1: Summary of 2018 IMPROVE collocated sites.

Module-A PTFE / PM_{2.5}	Module-B Nylon	Module-C Quartz	Module-D PTFE / PM₁₀
Phoenix, AZ (PHOE)	Phoenix, AZ (PHOE)	Phoenix, AZ (PHOE)	Phoenix, AZ (PHOE)
Yosemite, CA (YOSE)	Mammoth Cave, KY (MACA)	Hercules Glades, MO (HEGL)	Swanquarter, NC (SWAN)
Mesa Verde, CO (MEVE)	Frostburg Reservoir, MD (FRRE)	Medicine Lake, MT (MELA)	Wind Cave, SD (WICA)
St. Marks, FL (SAMA)	San Gabriel, CA (SAGA)	Everglades, FL (EVER)	
Proctor Maple Research Facility, VT (PMRF)			

Figure 4-15: Scaled relative difference for element measurements at sites with collocated modules across the IMPROVE network (2018). Dotted vertical lines indicate method detection limits.

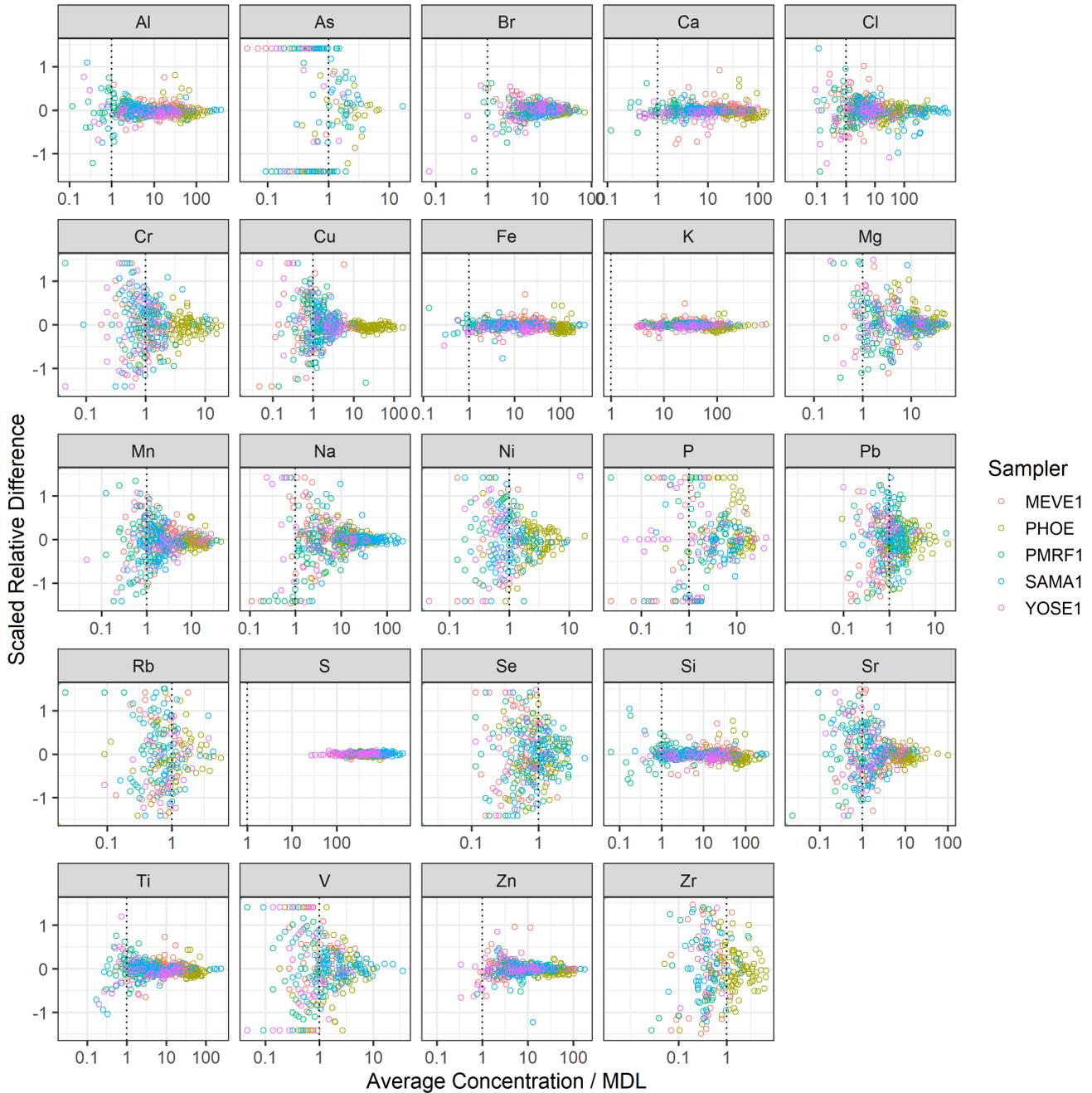


Figure 4-16: Scaled relative difference for PM₁₀ and PM_{2.5} at sites with collocated modules across the IMPROVE network (2018). Dotted vertical lines indicate method detection limits.

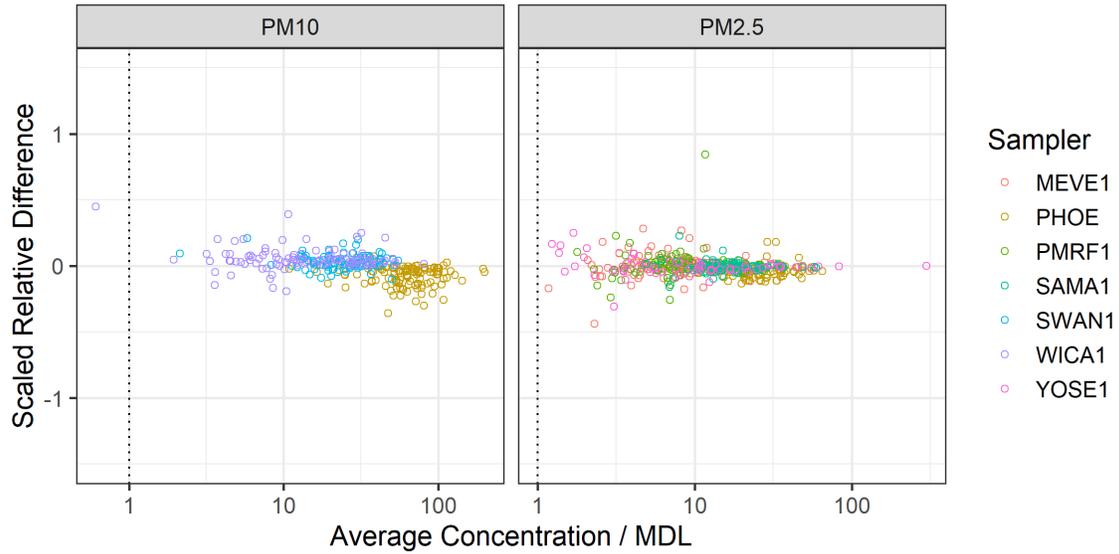


Figure 4-17: Scaled relative difference for ions measurements at sites with collocated modules across the IMPROVE network (2018). Dotted vertical lines indicate method detection limits.

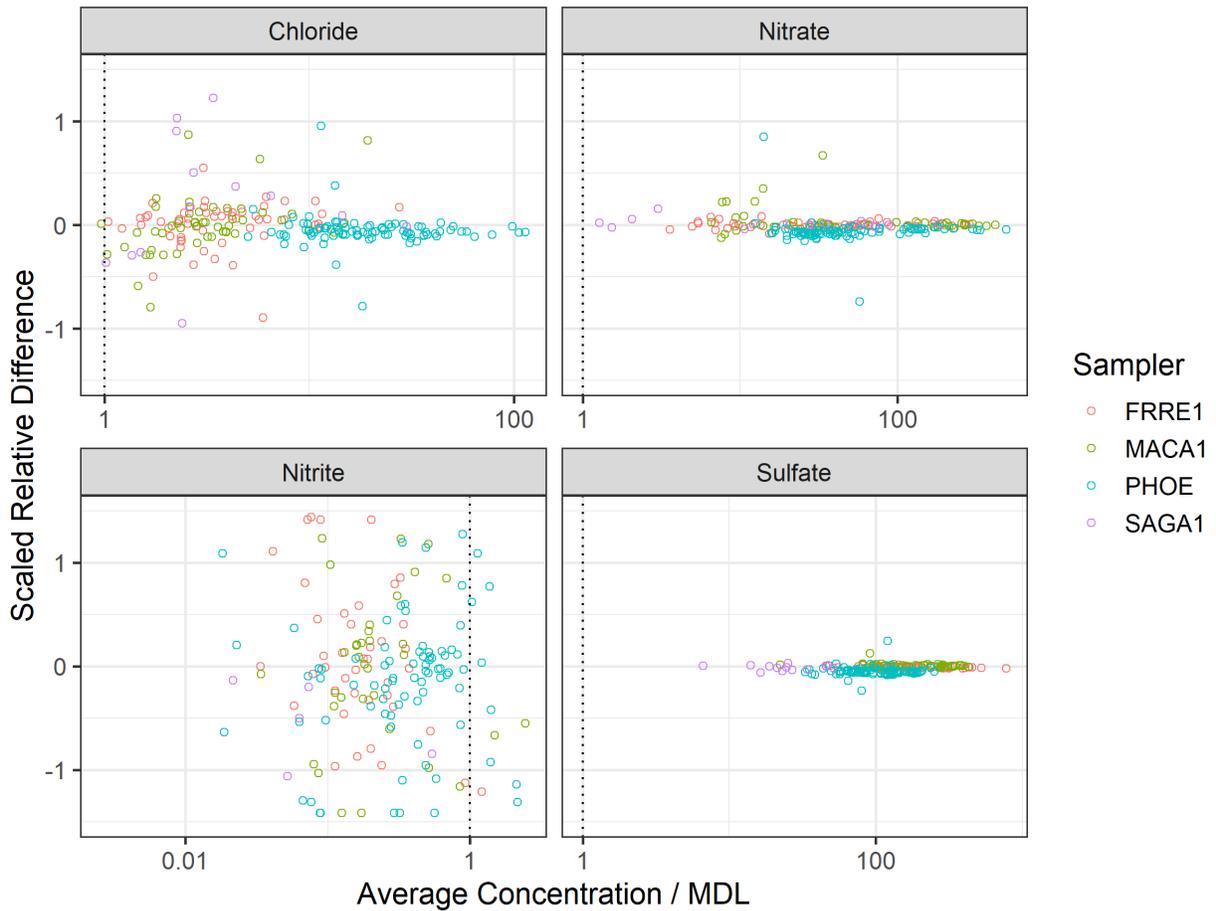


Figure 4-18: Scaled relative difference for carbon measurements at sites with collocated modules across the IMPROVE network (2018). Elemental carbon by reflectance (ECR) fractions are indicated as (1) through (3), organic carbon by reflectance (OCR) fractions are indicated as (1) through (4), R indicates measurement by reflectance, and T indicates measurement by transmittance. Dotted vertical lines indicate method detection limits.

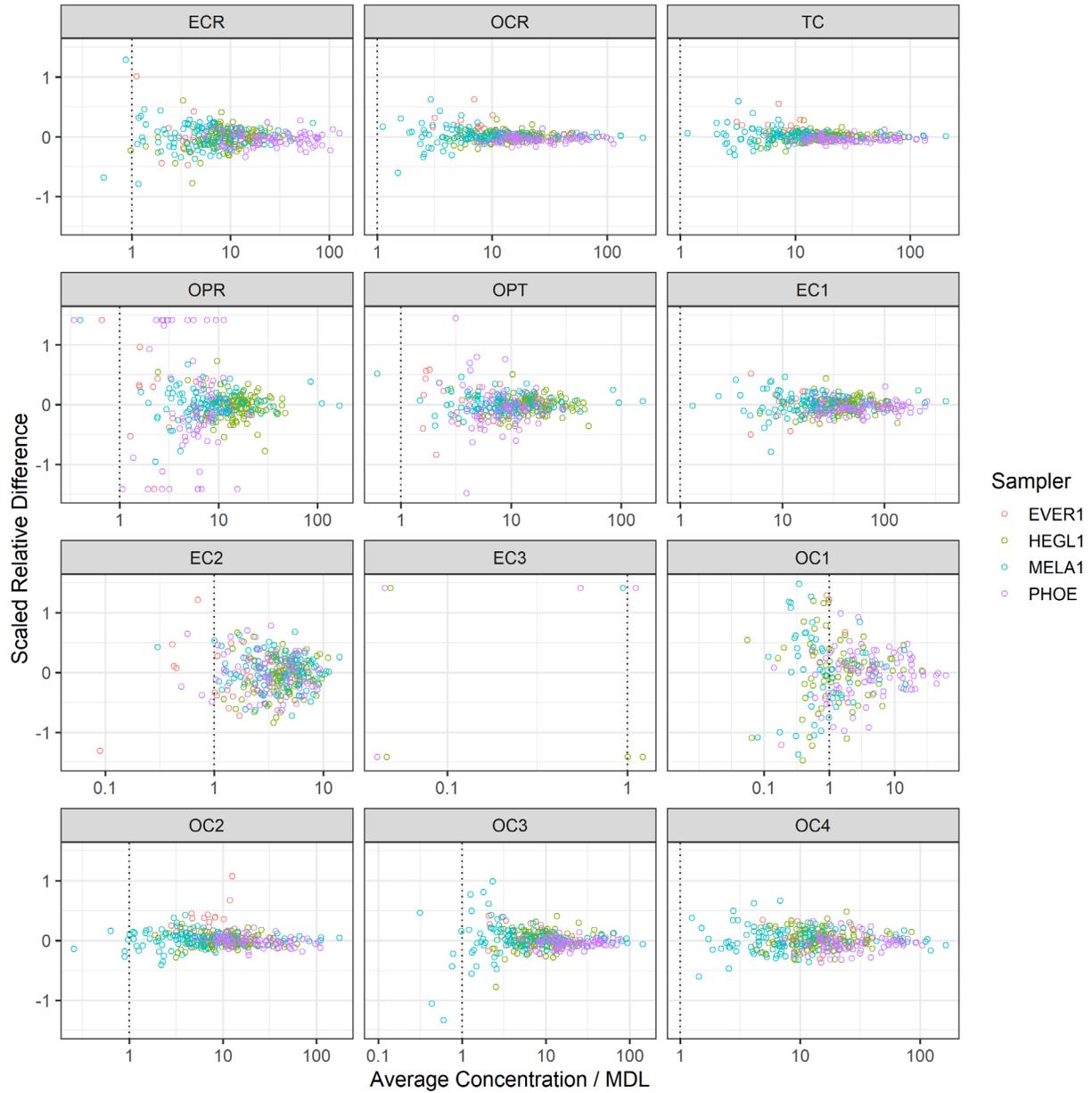
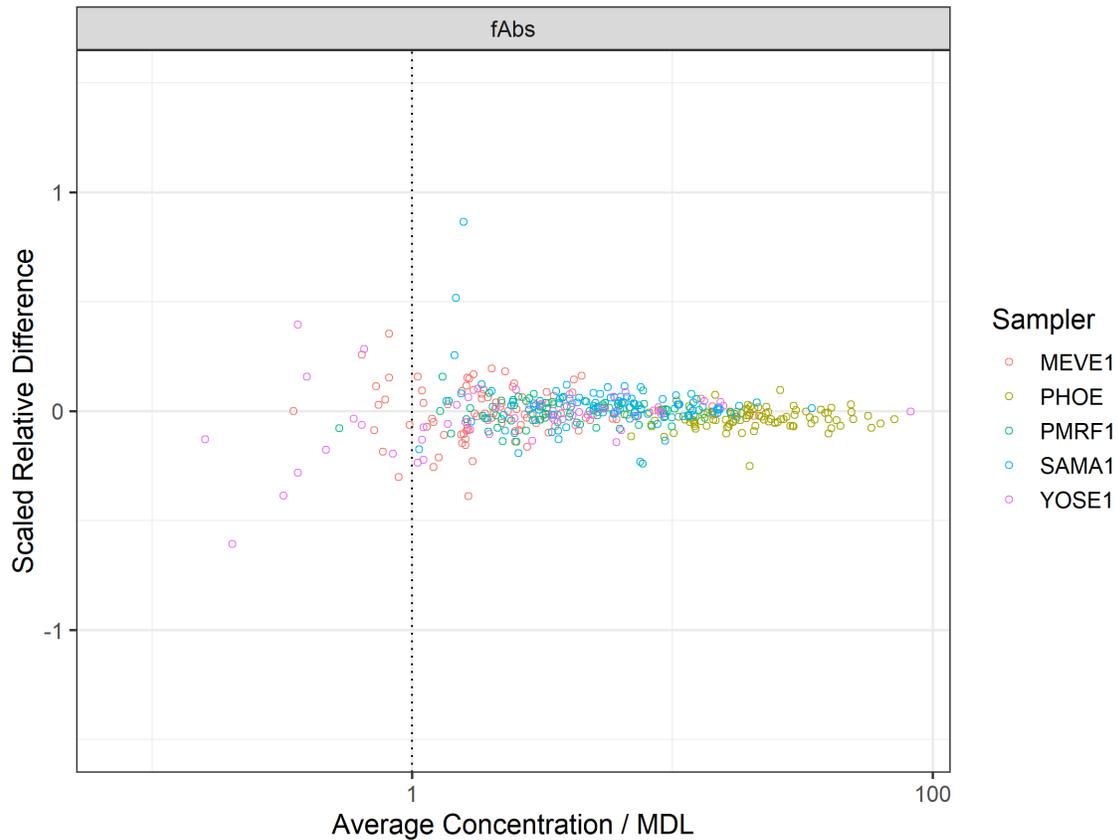


Figure 4-19: Scaled relative difference for optical absorption measurements at sites with collocated modules across the IMPROVE network (2018). Dotted vertical line indicates method detection limit.



Collocated precision is reported with IMPROVE data delivered to the FED and AQS databases as fractional uncertainty. Fractional uncertainty (f , Equation 4-2) is calculated from the scaled relative differences (Equation 4-1) between the sample pairs collected at IMPROVE collocated sites, using a subset of observations with concentrations at least three times the MDL. To limit uncertainty in determination of the necessary percentiles, calculations are performed with a minimum of 60 collocated pairs collected over the most recent two year period. The calculation of fractional uncertainty is documented in *UCD IMPROVE SOP #351: Data Processing and Validation*, and summarized in Equation 4-1 and Equation 4-2.

$$\text{Fractional Uncertainty } (f) = \frac{(\text{84th percentile of SRD}) - (\text{16th percentile of SRD})}{2} \quad (\text{Eq. 4-2})$$

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. Fractional uncertainty for the 2018 IMPROVE data is calculated using data from collocated samples collected 2016-2017 (Table 4-2).

Table 4-2: Fractional uncertainty calculated from collocated samples collected 2013-2016 (reported for 2017 IMPROVE data) and 2016-2017 (reported for 2018 IMPROVE data).

Species	Fractional Uncertainty, 2013-2016	Fractional Uncertainty, 2016-2017
Chloride	0.08	0.08
Nitrite	0.25	0.25
Nitrate	0.04	0.04
Sulfate	0.02	0.02
Organic Carbon (OCR)	0.09	0.08
Elemental Carbon (ECR)	0.14	0.14
Total Carbon	0.08	0.07
Organic Carbon (OC1)	0.26	0.23
Organic Carbon (OC2)	0.13	0.11
Organic Carbon (OC3)	0.13	0.13
Organic Carbon (OC4)	0.13	0.13
Organic Pyrolyzed (OPR)	0.16	0.20
Elemental Carbon (EC1)	0.10	0.11
Elemental Carbon (EC2)	0.18	0.19
Elemental Carbon (EC3)	0.25	0.25
Na	0.14	0.14
Mg	0.15	0.15
Al	0.08	0.08
Si	0.07	0.06
P	0.23	0.27
S	0.02	0.02
Cl	0.17	0.14
K	0.04	0.03
Ca	0.06	0.06
Ti	0.09	0.09
V	0.16	0.17
Cr	0.17	0.15
Mn	0.13	0.14
Fe	0.06	0.05
Ni	0.20	0.13
Cu	0.09	0.13
Zn	0.07	0.08
As	0.25	0.25
Se	0.25	0.25
Br	0.11	0.10
Rb	0.25	0.25
Sr	0.13	0.13
Zr	0.25	0.25
Pb	0.16	0.14
PM _{2.5}	0.03	0.04
PM ₁₀	0.07	0.07
fAbs	0.06	0.06

4.2 Analytical QC Checks

4.2.1 Replicate versus Routine

Analytical precision is evaluated by comparing data from repeat analyses, where two analyses are performed on the same sample using either the same instrument or different instruments. 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 4.1.3) also includes the uncertainties associated with sample preparation, field handling, and sample collection. Analytical precision is used internally as a QC tool.

Comparison between repeat analyses are presented as scaled relative difference (SRD; Equation 4-1), as shown in Figure 4-20 (ions) and Figure 4-21 (carbon).

Repeat analyses are not performed by EDXRF for the routine IMPROVE 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 EDXRF measurements as described in Section 3.3.5 and *UCD IMPROVE SOP #301: XRF Analysis*.

Figure 4-20: Scaled relative difference for repeat ion analyses, 2018.

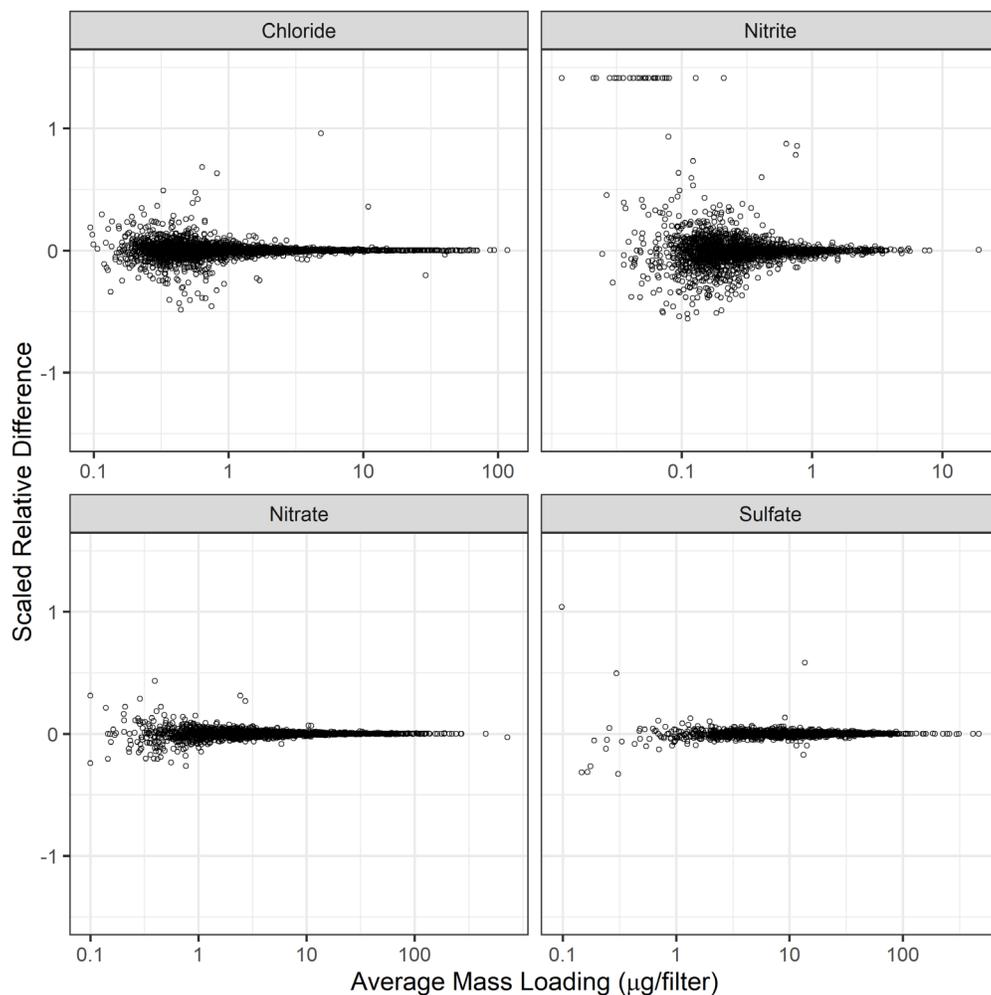
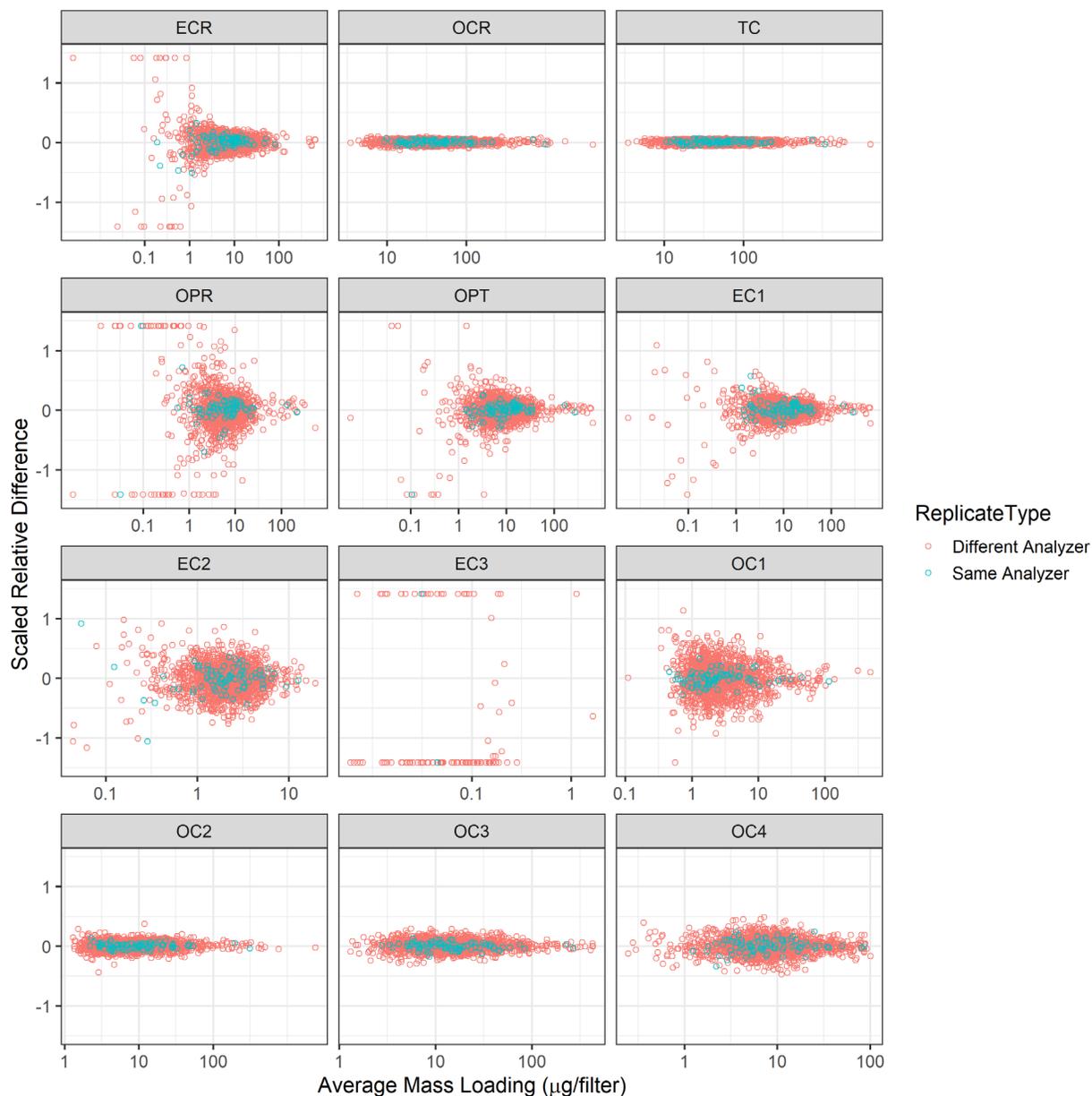


Figure 4-21: Scaled relative difference for repeat carbon analyses, 2018. Analyses performed by the same analyzer are shown in green, and those by different analyzers are shown in red. Elemental carbon by reflectance (ECR) fractions are indicated as (1) through (3), organic carbon by reflectance (OCR) fractions are indicated as (1) through (4), R indicates measurement by reflectance, and T indicates measurement by transmittance.



4.2.2 Blanks

Field blanks are collected at sampling sites across the network by exposing filters to the same conditions and handling as a sample, but without pulling air through the filter. They are analyzed in the laboratory using the same procedures as a sample. An integral part of the QC process, field blank analysis results are used to artifact correct the sampled filters as part of the concentration calculation. Artifacts can result from initial contamination in the filter material, contamination during handling and analysis, and adsorption of gases during sampling and handling.

Nylon filters are received from the manufacturer in lots that typically last one year. Acceptance criteria are established to evaluate background concentrations for each new lot of filters, however, there can be substantial variability in ion species across different lots (Figure 4-22 through Figure 4-25). Transition to new lots occurs over a period of weeks; thus the shift in field blank concentrations gradually manifest over time rather than abruptly.

As noted in previous reports, a known contamination issue occurred at the RTI laboratory during summer 2017, and evidence of the event are seen in both the chloride (Figure 4-22) and sulfate (Figure 4-24) field blank time series. An earlier contamination issue in 2011 from lack of refrigeration is also observed in the chloride field blank time series (Figure 4-22). This issue was resolved with implementation of sample refrigeration beginning early 2011, and corresponds with a decrease in intermittent high chloride field blank concentrations. See UCD data advisory for further detail, <http://vista.cira.colostate.edu/Improve/data-advisories/> (posted 3/2019).

Figure 4-22: Time series of chloride measured on nylon filter field blanks, January 1, 2011 through December 31, 2018. Red vertical lines indicate manufacturer lot transition.

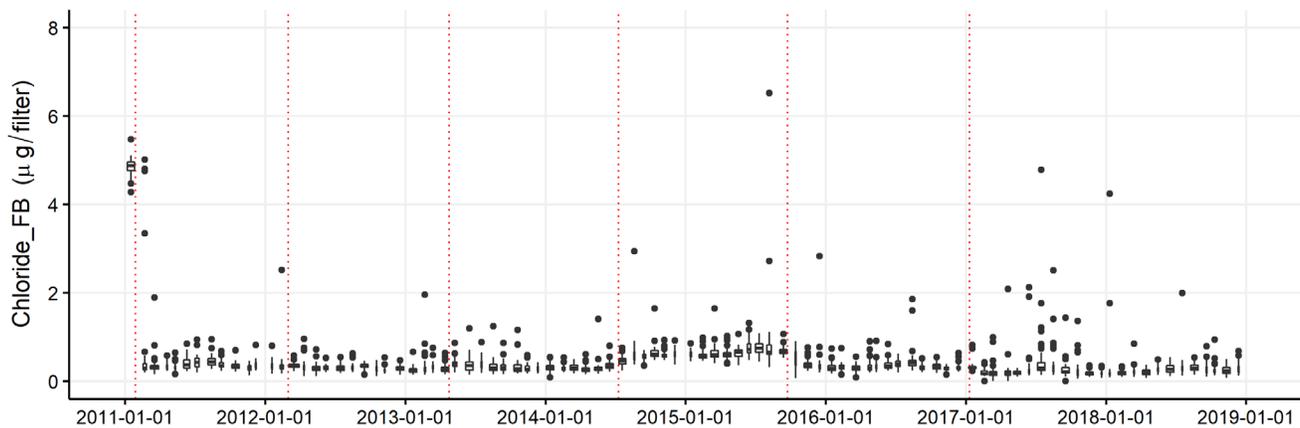


Figure 4-23: Time series of nitrate on nylon filter field blanks, January 1, 2011 through December 31, 2018. Red vertical lines indicate manufacturer lot transition.

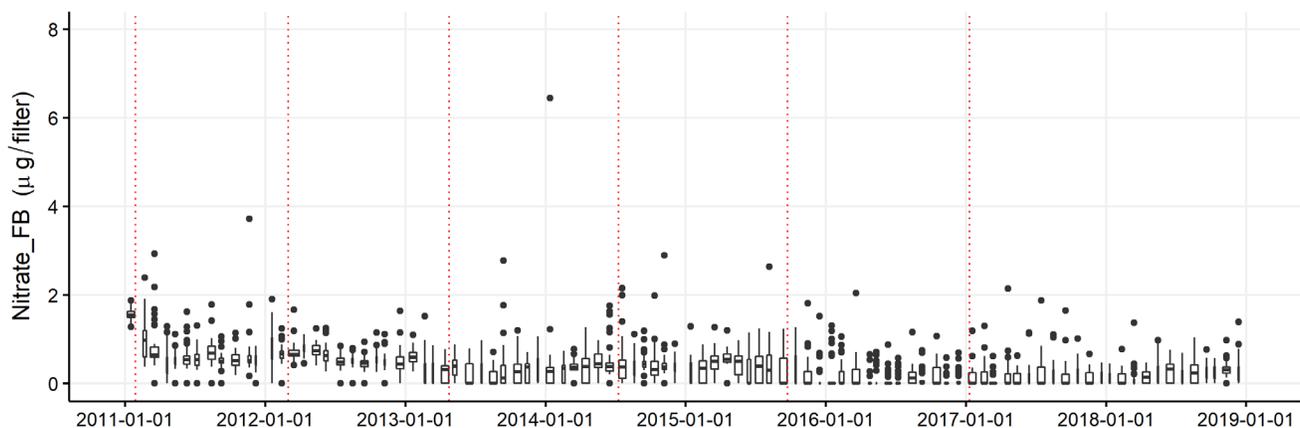


Figure 4-24: Time series of sulfate on nylon filter field blanks, January 1, 2011 through December 31, 2018. Red vertical lines indicate manufacturer lot transition.

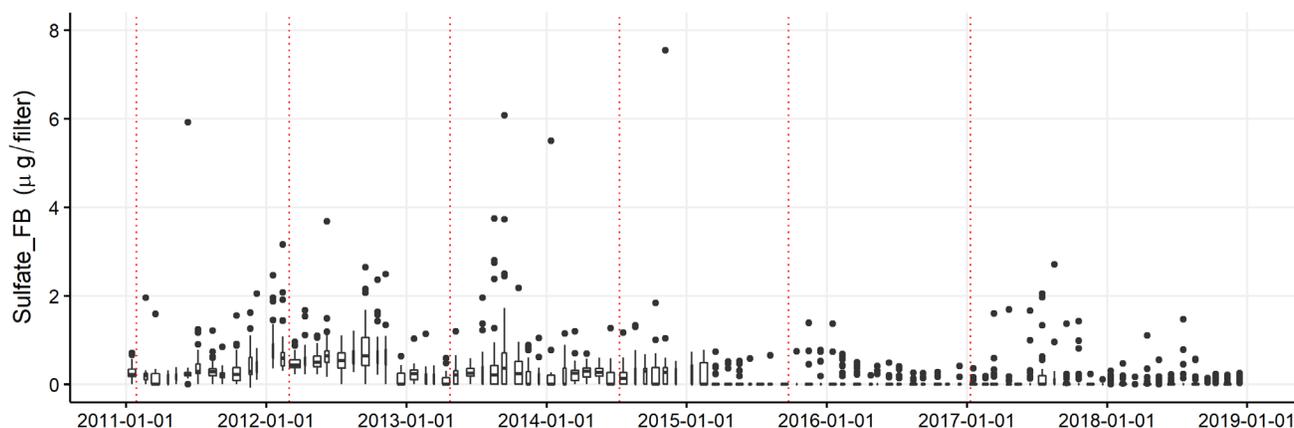
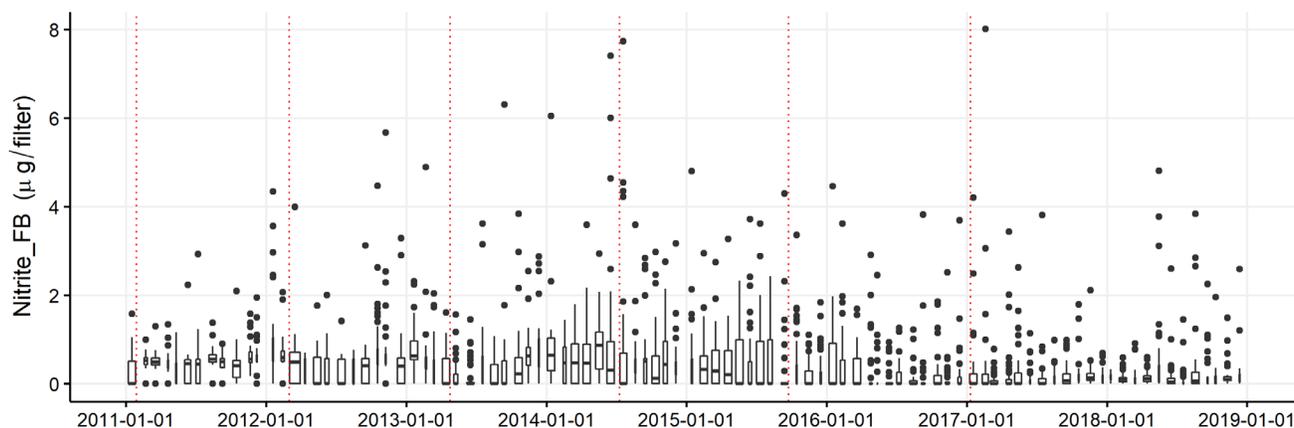


Figure 4-25: Time series of nitrite on nylon filter field blanks, January 1, 2011 through December 31, 2018. Red vertical lines indicate manufacturer lot transition.



Quartz filters are pre-fired by DRI. Quartz filter field blanks typically have low concentrations of elemental carbon by reflectance (ECR; Figure 4-26). In occasional cases the median field blank ECR concentration is greater than zero and an artifact correction is applied; this has been more frequent since mid-2016. Conversely, higher field blank concentrations are observed for organic carbon by reflectance (OCR), with the highest values during summer months often over 5 $\mu\text{g}/\text{filter}$ (Figures 4-27).

Figure 4-26: Time series of elemental carbon by reflectance (ECR) on quartz filter field blanks, January 1, 2011 through December 31, 2018.

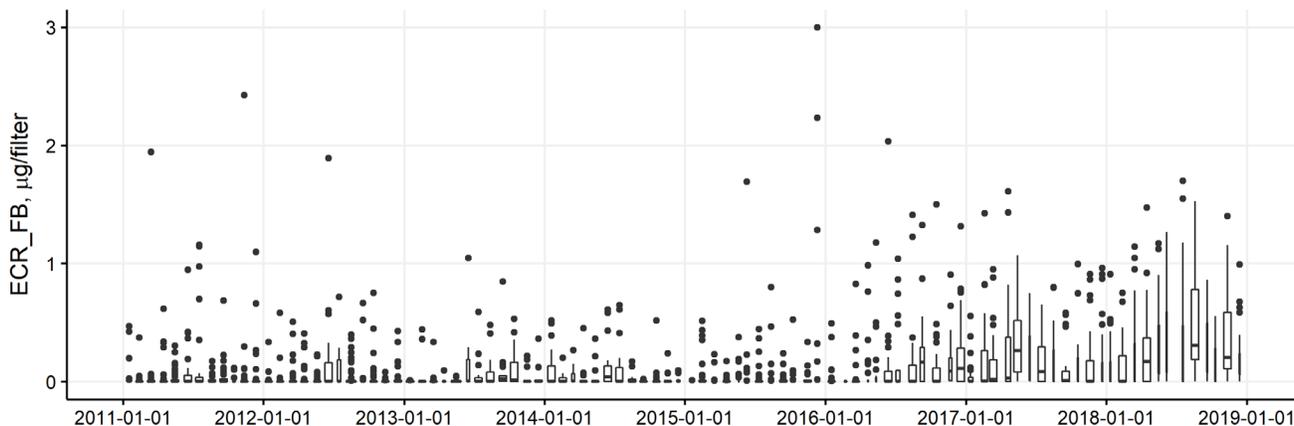
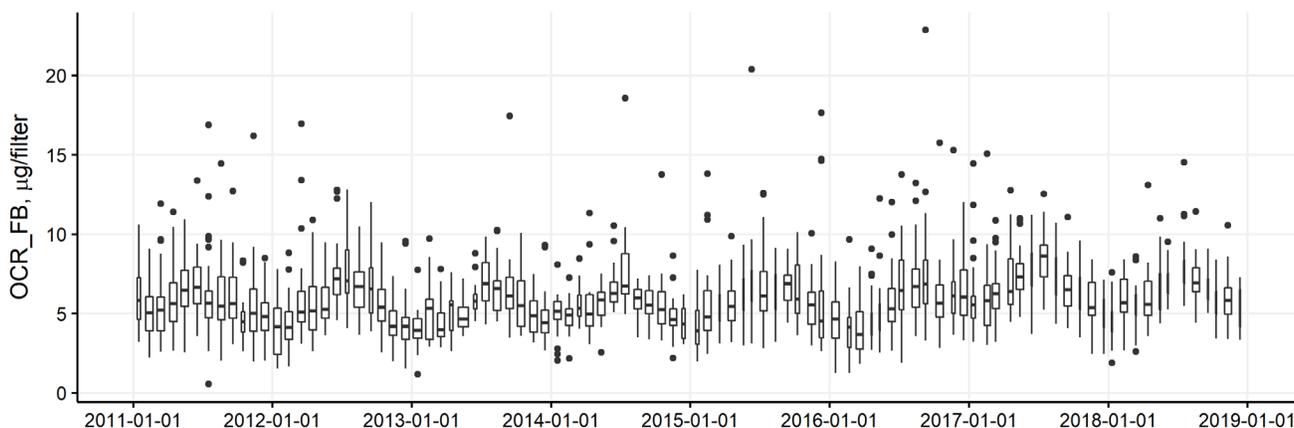


Figure 4-27: Time series of organic carbon by reflectance (OCR) on quartz filter field blanks, January 1, 2011 through December 31, 2019.



PTFE filter field blanks from the A-module (fine particles, $PM_{2.5}$; Figure 4-28) and D-module (coarse particles, PM_{10} ; Figure 4-29) are gravimetrically analyzed to monitor contamination levels and balance stability. Beginning with samples and field blanks collected October 2018 gravimetric analysis at UCD transitioned from manual weighing using Mettler-Toledo XP6 micro balances to the MTL AH500E climate-controlled automated weighing system. Additionally, at the same time, UCD transitioned to using MTL PTFE filters instead of Pall Corporation PTFE filters. As seen in Figure 4-28 and Figure 4-29, there is a step increase in $PM_{2.5}$ and PM_{10} measured from field blanks corresponding with the transition, indicating that the filters gain mass between pre- and post-weight measurements. UCD is investigating this issue; it is unclear what part of the filters is gaining mass – either the filter ring or the PTFE film – and if the gain is from water or potentially volatile organic carbon.

Figure 4-28: Time series of PM_{2.5} on PTFE filter field blanks, January 1, 2011 through December 31, 2018. Red vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Blue vertical line indicates manufacturer transition to Measurement Technology Laboratories (MTL) as manufacturer.

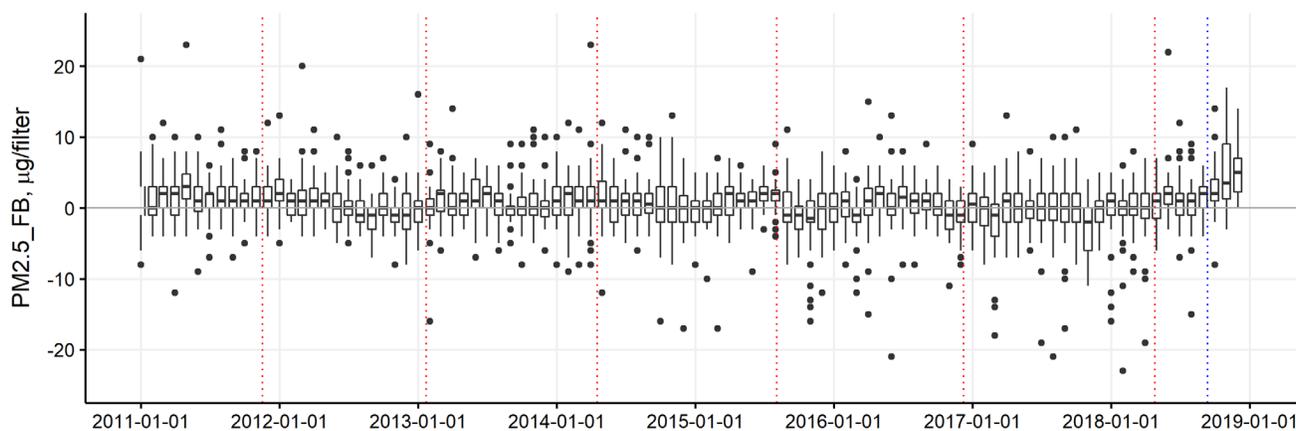
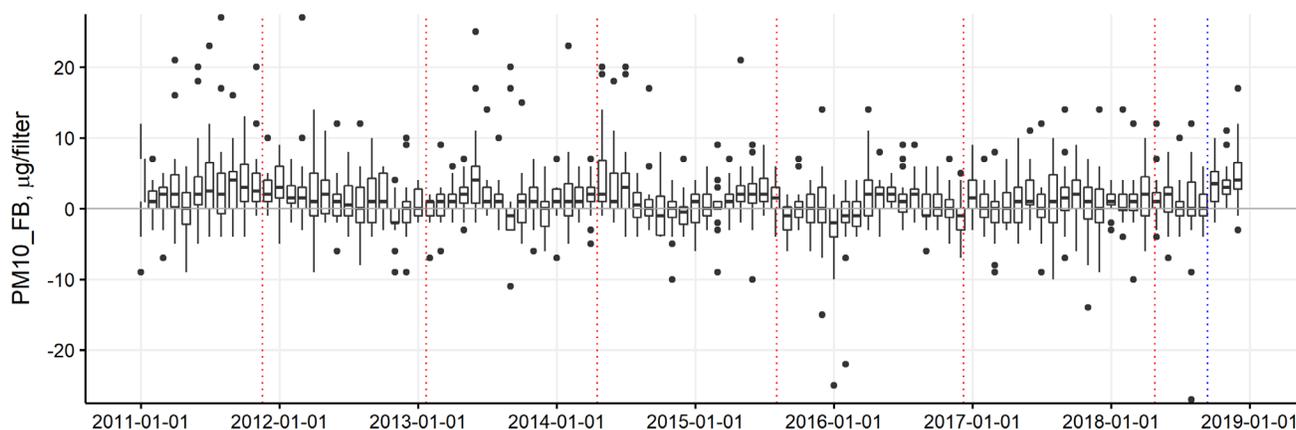


Figure 4-29: Time series of PM₁₀ on PTFE filter field blanks, January 1, 2011 through December 31, 2018. Red vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Blue vertical line indicates manufacturer transition to Measurement Technology Laboratories (MTL) as manufacturer.



Field blanks are used for calculation of method detection limits (MDLs) reported for each species. Prior to 2018, MDLs for ions and carbon species were calculated as $2 \times$ the standard deviation of the field blank loadings, using a minimum of three field blanks collected in the sampling month for each filter type. Beginning with samples collected January 2018, UCD harmonized the MDL calculation for ions and carbon species to be 95th percentile minus median of the field blank loadings, using 50 field blanks collected in and closest to the sampling month for each filter type. The MDL calculation for elements was not changed and is calculated as 95th percentile minus median of field blank loadings, using 35 field blanks (see *UCD IMPROVE SOP #351: Data Processing and Validation*). It is anticipated that this calculation change for ions and carbon species will stabilize the MDLs, making them less susceptible to influence from field blank outliers. Table 4-3 summarizes the MDLs, listing average MDLs calculated for 2017 data for comparison with average MDLs calculated for data from 2018.

Table 4-3: Average method detection limits (MDLs) and percentage of reported data above the MDLs calculated for 2017 and 2018 data.

Species	2017		2018 (January – June)	
	Average MDL (ng/m ³)	% Above MDL	Average MDL (ng/m ³)	% Above MDL
Chloride	15.25	55	4.25	87
Nitrite	30.13	7	18.92	11
Nitrate	15.39	98	10.79	99
Sulfate	13.84	100	3.88	100
Organic Carbon (OCR)	110.22	94	76.02	96
Elemental Carbon (ECR)	15.63	93	22.78	88
Total Carbon	117.81	95	82.71	97
Organic Carbon (OC1)	36.96	24	27.19	29
Organic Carbon (OC2)	35.88	83	20.02	91
Organic Carbon (OC3)	59.81	89	37.47	92
Organic Carbon (OC4)	31.37	94	16.41	97
Organic Pyrolyzed (OPR)	10.77	94	15.05	93
Elemental Carbon (EC1)	10.04	98	10.19	98
Elemental Carbon (EC2)	12.31	94	16.07	84
Elemental Carbon (EC3)	9.23	0	4.58	0
Na	4.44	79	4.33	84
Mg	2.61	79	2.70	83
Al	4.05	91	3.73	92
Si	7.31	90	6.25	93
P	0.22	34	0.22	31
S	0.42	100	0.38	100
Cl	0.41	84	0.44	86
K	1.16	99	1.08	99
Ca	2.63	93	2.61	94
Ti	0.40	82	0.34	87
V	0.12	41	0.11	35
Cr	0.11	33	0.11	40
Mn	0.33	66	0.33	68
Fe	2.56	92	1.98	95
Ni	0.11	25	0.11	26
Cu	0.22	54	0.22	53
Zn	0.23	90	0.22	92
As	0.22	18	0.22	16
Se	0.22	27	0.22	27
Br	0.14	96	0.15	96
Rb	0.24	15	0.23	18
Sr	0.23	47	0.22	57
Zr	1.32	7	1.30	6
Pb	0.65	34	0.65	34
PM _{2.5}	306.26	97	306.86	97
PM ₁₀	416.49	98	418.19	98
fAbs	0.35	85	0.35	82

5. Data Management and Reporting

5.1 Documentation

Current standard operations procedures (SOPs) are available at:

<http://vista.cira.colostate.edu/Improve/>

<https://aqrc.ucdavis.edu/improve-documentation>

Table 5-1: Summary of upcoming project documentation deliverables.

Deliverable	Upcoming Delivery Date
SOPs and TI documents	June 15, 2020
Quarterly Site Status Report	November 15, 2019 (2019 Q3) February 15, 2020 (2019 Q4)
Annual Quality Assurance Report* (January through December 2019 data)	September 30, 2020

* Per direction from NPS, after delivery of this report the Quality Assurance Report will be delivered annually (rather than semiannually) in advance of the IMPROVE Steering Committee Meeting.

5.2 Data Deliveries

Summarized in Table 5-2 are dates that data were delivered to FED and AQS databases for samples collected January 1, 2018 through December 31, 2018.

Data is redelivered annually following completion of a full year of data validation. The redelivery captures updates and changes to processing to improve data consistency and quality. The 2018 data (January 2018 through December 2018) was redelivered to NPS – including a summary of changes made – on October 9, 2019, and subsequently made available on the FED and AQS databases.

Table 5-2: Summary of data deliveries, January 1, 2018 through December 31, 2018.

Data (Month Samples Collected)	FED/AQS Delivery Date
January 2018	November 16, 2018
February 2018	November 16, 2018
March 2018	December 21, 2018
April 2018	December 21, 2018
May 2018	March 8, 2019
June 2018	March 8, 2019
July 2018	April 30, 2019
August 2018	April 30, 2019
September 2018	July 11, 2019
October 2018	July 11, 2019
November 2018	August 8, 2019
December 2018	September 20, 2019

6. Site Maintenance Summary

6.1 Summary of Repair Items Sent

UCD maintains and repairs samplers at each IMPROVE site. The UCD Field Group works closely with site operators to address maintenance and repair issues to ensure continuous operation and sample collection at the sites. UCD maintains an inventory of sampler components for shipment to the sites on short notice. Table 6-1 summarizes the equipment shipped to sites for sampler repairs, January 1, 2019 through June 30, 2019.

Table 6-1: Summary of major repair items shipped to IMPROVE sites: 1/1/2019 through 6/30/2019.

Item	Quantity	Sites
Pump	77	GRSM1 (x2), ORPI1, SAMA1, FRES1 (x3), WHPE1, CANY1 (x2), SAWT1 (x4), BRIG1, DENA1, DINO1 (x3), PRIS1 (x2), DETR1, TOOL1 (x4), UPBU1, CABA1, LASU2 (x3), STIL1, ACAD1, BOWA1, RAFA1 (x3), ZICA1, BOAP1, GRSA1 (x3), SEQU1, MELA1, HECA1 (x3), GICL1, SACR1 (x3), MEVE1, NOAB1, BRIS1, MOOS1 (x2), SENE1, VIIS1, SAWE1 (x2), JARB1, STIL1 (x2), REDW1, WHIT1, CAPI1, CABI1, SWAN1, OKEF1, BOND1, BAND1, TALL1, THBA1, LOND1 (x2), PINN1 (x2)
Electronic boxes	30	HOOV1, SHRO1, SHMI1, CHAS1, GRSM1 (x2), VILA1 (x2), QUCI1, SYCA2, OLYM1, GRR11, PHOE5, LAVO1, SAPE1, CACR1 (x2), ATLA1, CABI1, LASU2 (x2), NOAB1 (x5), MOOS1, OKEF1 (x2), WHIT1,
Controller	20	GRBA1, WIMO1, SAGA1, THRO1, RAFA1, GRSM1, MEVE1, GRBA1, STAR1, BOLA1, SHRO1, STIL1, FRES1 (x2), PHOE5, JARI1, NOAB1, JOSH1, BRIS1, YELL1
Networking Device	18	THRO1, OWVL1, MOOS1, FRES1, ISLE1, WIMO1, GICL1, WHPA1, YELL2, BIBE1, MAKA2, CRLA1, PRIS1, FCPC1, BOLA1, CORI1, GAMO1, SENE1
Controller Card	10	HOOV1, GAMO1, CRLA1, STIL1, NOAB1, NOCA1, UPBU1, TOOL1 (x2), PRIS1
Relay Box	6	BRIG1, TOOL1, GRSM1, SNPA1, SHEN1, FLTO1
Module Cable	2	FLTO1, GRSM1
Temp Probe	1	RAFA1
Module	1	OWVL1
Motor Assembly	1	PASA1
Other	3	MOMO1, MELA1, GUMO1

6.2 Field Audits

CSU CIRA performs field audits at IMPROVE sites to measure and evaluate sampler flow and site conditions. Results are reported to the UCD Field Group, and issues are addressed during site visits and through coordination with site operators. Table 6-2 summarizes the field audits that CSU CIRA performed January 1, 2019 through June 30, 2019.

Table 6-2: CSU CIRA field audits 1/1/2019 through 16/30/2019.

2019 Site Audits (January through June)					
January	February	March	April	May	June
		LASU2	CHIR1	PHOE1	SAGU1
		VILA1	DOME1	NOGA1	SAWE1
			FRES1	LASU2	WHRI1
			GRCA2	VILA1	
			HOOV1		
			KAIS1		
			MEAD1		
			NOGA1		
			ORPI1		
			OWVL1		
			PINN1		
			SAGU1		
			SAGA1		
			RAFA1		
			SAWE1		
			SEQU1		
			MEVE1		
			SHMI1		

6.3 Summary of Site Visits

The UCD Field Group visits IMPROVE network sites biennially to provide routine maintenance and cleaning. Sites are occasionally visited more frequently to address emergency issues. Table 6-3 summarizes the visits that UCD performed January 1, 2019 through June 30, 2019.

UCD has developed and is currently deploying new sampler controllers. Between July 1, 2018 and December 30, 2018, UCD installed 46 new controllers (Table 6-3). As of June 30, 2019 there were a total of 123 new controllers installed across the network. Prior to new controller installation, availability of internet access is evaluated at each site and, in cases where it is not available, a hot spot device is installed. Sites with new controllers are monitored in real time by UCD technicians, allowing faster follow up and recovery in cases where samples are lost or equipment has failed. Installation of new controllers is expected to be completed during 2019.

Table 6-3: UCD field visits to IMPROVE sites, 1/1/2019 through 6/30/2019.

Site Name	Date Visited	Repair Notes	Improvements Requested
SWAN1	2/8/2019	Installed new controller.	
ROMA1	2/10/2019	Installed new controller.	
OKEF1	2/11/2019	Installed new controller.	
SAMA1	2/12/2019	Installed new controller.	
CHAS1	2/13/2019	Installed new controller.	
EVER1	2/15/2019	Installed new controller.	
ORPI1	3/30/2019	Installed new controller.	
SAGU1	3/28/2019	Installed new controller.	
SAWE1	3/27/2019	Installed new controller.	

NOGA1	3/29/2019	Installed new controller.	
CHIR1	3/26/2019	Installed new controller.	
TONT1	3/25/2019	Installed new controller.	
IKBA1	3/24/2019	Installed new controller.	
GICL1	4/20/2019	Installed new controller. Installed satellite internet service.	
GUM01	4/23/2019	Installed new controller. Relocated pumps inside sampling enclosure.	
BIBE1	4/22/2019	Installed new controller.	
SACR1	4/25/2019	Installed new controller. Fixed electrical breaker box.	
WHIT1	4/27/2019	Installed new controller.	
BOAP1	4/26/2019	Installed new controller. Fixed electrical breaker box.	
CAVE1	4/24/2019	Installed new controller.	
PHOE1	4/18/2019	Installed new controller.	
PHOE5	4/18/2019	Installed new controller.	
BIRM1	5/16/2019	Installed new controller.	
GRSM1	5/10/2019	Installed new controller. Installed Purple Air sensor.	
LIGO1	5/11/2019	Installed new controller.	
COHU1	5/13/2019	Installed new controller.	
ATLA1	5/17/2019	Installed new controller. Upgraded site to four module sampler.	
SIPS1	5/14/2019	Installed new controller.	New shed planned for late 2019.
MACA1	5/7/2019	Installed new controller.	
SHRO1	5/12/2019	Installed new controller.	
MING1	5/8/2019	Installed new controller.	
DETR1	6/25/2019	Installed new controller.	
EGBE1	6/26/2019	Installed new controller.	Sampler platform needs work; scheduled for Oct 2019.
PITT1	6/24/2019	Installed new controller. Upgraded site to four module sampler.	
FRRE1	6/21/2019	Installed new controller.	
JARI1	6/19/2019	Installed new controller.	
SHEN1	6/18/2019	Installed new controller.	
QUCH1	6/22/2019	Installed new controller. Fixed roof leak.	
DOSO1	6/20/2019	Installed new controller.	
MEVE1	6/18/2019	Installed new controller.	
WEMI1	6/17/2019	Installed new controller.	Sampler platform needs to be rebuilt.
SHMI1	6/16/2019	Installed new controller.	
SAPE1	6/12/2019	Installed new controller.	
BAND1	6/13/2019	Installed new controller.	
GRSA1	6/15/2019	Installed new controller.	
WHPE1	6/14/2019	Installed new controller.	

7. References

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