Interagency Monitoring of Protected Visual Environments (IMPROVE)

Semiannual Quality Assurance Report

January 1, 2019 through June 30, 2020

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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 # 140P2121D0004). 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 ($PM_{2.5}$) 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 $PM_{2.5}$ on nylon filters for ion chromatography (IC) analysis at Research Triangle Institute (RTI) International.
- Module-3C: Collection of $PM_{2.5}$ 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/.

Unless otherwise noted, data evaluated in this report cover sampling dates from January 1, 2019 through June 30, 2020.

2. Summary of Laboratory and Data Quality Issues

2.1 COVID-19 Related Laboratory Shutdown

During this reporting period, the UCD AQRC laboratories were shut down and inaccessible to lab staff beginning March 19, 2020 due to the University entering suspended operations in reaction to the local shelter-in-place orders. Restricted access to the lab was restored in early May 2020 and routine IMPROVE sample analysis was restarted. Due to the limited lab access and the cessation of routine analysis, there were no monthly QC checks performed in the month of April, 2020. All QC checks, including the monthly check, were performed prior to restarting routing sample analysis in late April, 2020. Other than the delay in analysis, this shutdown did not impact the sample results.

2.2 Laboratory Move

During this reporting period, the UCD AQRC Laboratories moved from Crocker Nuclear Lab on the main UC campus, to an off-campus building two miles away in Davis. The new laboratory and office space is located at 1560 Drew Ave., Davis, CA 95618.

2.2.1 XRF Lab Move

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

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

2.2.2 Gravimetric Lab Move

A second, new MTL weighing system including a new ultra-balance was ordered and installed into the new laboratory location to smooth the move transition. The new MTL weighing system was set up in the new laboratory on November 4, 2020; we conducted testing on the new system and put it into routine operation on February 1, 2021. The existing MTL weighing system was moved to the new laboratory on February 23, 2021, and a new ultra-balance was installed in it. Some software modifications were required to accommodate two weighing systems, so the first system was not operational in the new location until March 3, 2021.

With two weighing chambers in use, the same balance is being used to perform the pre- and post-sampling gravimetric measurements. This protocol starts with samplings dates in late February 2021.

2.2.3 Optical Lab Move

The HIPS lab moved to the new laboratory location in March 2021. As part of the move, a new custom-built optical table was constructed at the Drew Ave. lab and the HIPS instrument was installed on this new optical table. Testing and calibration after installation was completed and sample analysis began at the new location in March 2021.

2.3 X-ray Fluorescence Laboratory

2.3.1 High Silicon Background on XRF-2

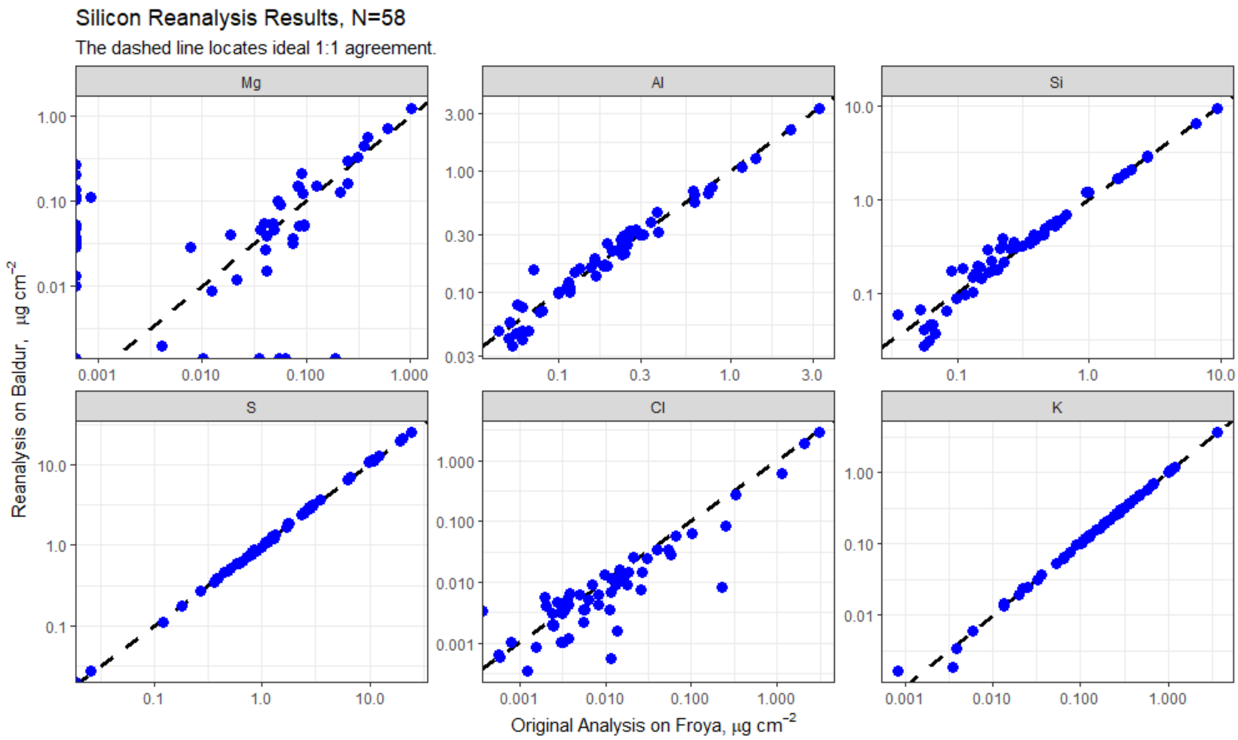
XRF-2 began failing the daily blank QC for silicon on December 12, 2019. Sample analysis was halted and the issue was investigated with the help of the instrument manufacturer. After maintenance and calibration, the silicon background remained high through the remainder of the analysis period. Analysis of IMPROVE samples collected from September 2019 to May 2020 continued until October 19, 2020 despite the QC failure. In October 2020, the instrument was more thoroughly inspected by the manufacturer and it was determined the CaF2 secondary target, which generates the X-rays for analysis of elements from Na through K, was covered in a black dust. The supposition is the dust had come from the bearing of the wheel which holds the secondary targets. The target wheel was cleaned and the CaF2 target was turned over to its clean side which returned the silicon background to an acceptable level.

Continuing to analyze samples after the silicon QC failed is a deviation from UCD SOPs and procedures. The laboratory manager and staff have been fully trained in the QC procedures and analysis will be halted in the future during suspected instrument error. This was demonstrated recently when another instrument had questionable QC results and analysis was immediately halted (this incident did not occur during the analysis period covered by this report). Additionally, software change requests have been issued for the XRF lab web application to ensure conformity with all QC criteria and improve visibility of failure characteristics as a further corrective action.

Data Impact:

The continued analysis of sampled filters after failure of the Si QC Blank acceptance criteria was investigated by reanalyzing 58 IMPROVE samples on a separate XRF instrument (Baldur). Since the primary concern is silicon, only the CaF_2 target was used (sodium to potassium analytes) for the reanalysis. The results are shown in Figure 2-1. The agreement was reasonable and not large enough to warrant reanalyzing all the samples analyzed when the QC was failing.

Figure 2-1: Comparison of XRF reanalysis on a different instrument (Baldur) versus the original analysis results on an instrument that was failing the Silicon QC criterion (Froya). The dashed lines denote perfect 1:1 agreement between the original and reanalysis results.



2.3.2 High Aluminum and Silicon Response on XRF-4

The daily ME-RM QC measurement on XRF-4 showed higher than acceptable measures from 3/12/2020 until 3/21/2020. These results occurred just after a "detector forced heat up" error had occurred on the instrument. The error occurred overnight on 3/10/2020 and automatically stopped analysis. The instrument manufacturer was called the next day and remotely checked the system; they could find nothing wrong with the detector temperature, gave the instrument an all clear for analysis, and diagnosed the issue as a sensor error. QC was run before restarting sample analysis on 3/11/2020 and passed. The first QC exceedance for Al and Si was on 3/12/2020 with QC for these two elements officially failing on 3/16/2020 and continued until 3/21/2020 when all analysis on the instrument was stopped.

During this period only eight IMPROVE samples were analyzed on the instrument on 3/12/2020 when the first QC exceedance occurred. During the rest of the period, the instrument analyzed CSN samples. A random reanalysis of 16 of the CSN samples on another instrument showed less than a 10% difference from the original results on XRF-4 for all elements indicating this issue had no impact on the data. Therefore, it was determined that there was no impact on the IMPROVE sample data and no reanalysis was performed.

Further investigation by the manufacturer finally discovered that their original assessment was incorrect and the detector had slightly warmed up from its liquid nitrogen cooled state. This slight warm up can have an effect on the detector electronics and was the cause for the slightly elevated response to aluminum and silicon. Following the manufacturer's recommendations, the detector was allowed to warm up fully to room temperature and was then cooled back down to liquid nitrogen temperature. This resolved the issues and returned the aluminum and silicon responses to normal.

Data Impact: None.

2.3.3 Detector Issue on XRF-3

On 7/27/2020 QC checks of both the daily and weekly QC ME-RM samples indicated rising concentrations of multiple elements. QC criteria remained within the acceptance limit however, the rise of a few percent in concentration across multiple elements prompted the lab to stop analysis on this instrument. The rising concentrations began with the daily QC check on 7/17/2020; a random selection of 16 samples analyzed between 7/17 and 7/24/2020 were reanalyzed on another instrument and did not show any significant difference in elemental concentrations. After investigation by the manufacturer the detector response was found to be deteriorating and the detector was replaced on 8/20/2020. XRF-3 was recalibrated after the detector replacement and all QC tests passed. IMPROVE sample analysis resumed on XRF-3 on 9/2/2020.

Data Impact: None.

2.3.4 X-ray Intensity Loss on XRF-5

On 9/14/2020 XRF-5 (Baldur) displayed low intensity on the daily ME across multiple elements, with the most pronounced declines in Al and Si. While this did not cause a QC failure (threshold is 3 in a row), it did raise suspicion. The daily ME result on 9/15/2020 looked normal with samples continuing to be analyzed while the issue was investigated. On 9/16/2020 the daily ME showed a 3% drop in S and K compared to historical data. This indicated an ongoing issue and sample analysis paused and the samples analyzed since the last good daily QC check, on the morning of 9/11/2020, were scheduled to be reanalyzed on another instrument. The reanalyzed samples included 20 IMPROVE samples.

Troubleshooting by the manufacturer indicated the X-ray tube and high voltage generator needed to be replaced. After delays with parts, the instrument was recalibrated and passed all QC checks on 11/7/2020. IMPROVE sample analysis resumed on XRF-5 on 11/17/2020.

On 2/4/2021 the same issue occurred again and analysis on XRF-5 was immediately stopped. All samples analyzed since the last good QC results on 2/3/2021 were reanalyzed on another instrument (these were all CSN samples). The issue was determined to be a faulty high voltage generator. Multiple replacements were tried, but all concluded with the same failure which Panalytical traced back to a faulty model upgrade from their supplier. An older model generator was eventually obtained and XRF-5 was repaired, calibrated, passed all QC tests, and started analyzing IMPROVE samples again on 6/16/2021.

Data Impact: None.

2.3.5 X-ray Intensity Loss on XRF-3

On 3/31/2021, the weekly automated detector calibration resulted in new parameters that were significantly different than previous detector calibrations. In addition, the daily QC ME-RM sample showed a slight loss of X-ray intensity on the heavy elements, so all analysis was stopped. Further attempts to run the automated detector calibration did not correct the issue, so the manufacturer was notified. A manufacturer technician came out on 4/7/2021 and determined the detector sleeve had shifted and broken. The sleeve was replaced, but low intensity continued, so the detector was moved closer to the sample. This repair required the instrument to be recalibrated which was done, QC tests passed, and XRF-3 started analyzing samples again on 4/23/2021.

Another intensity drop occurred on 5/20/2021 and sample analysis was stopped on 5/21/2021. All samples analyzed since the last good QC (morning of 5/19/2021) were reanalyzed on another instrument. After prolonged troubleshooting it was determined that a new X-ray tube and high voltage generator were required. Out-of-stock parts delayed the repair which finished on 7/12/2021. Calibration was completed, all QC tests passed, and XRF-3 resumed IMPROVE sample analysis on 7/23/2021.

These calibrations are not listed in Table 3-3 as this issue and both calibrations occurred after XRF-3 analyzed its last sample from this reporting period. This issue is being included here for completeness.

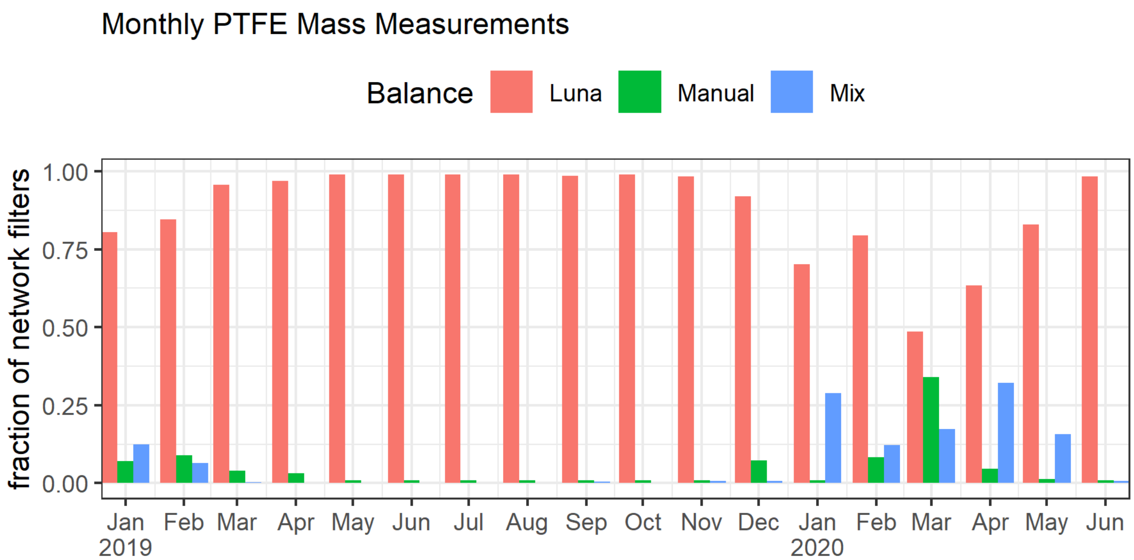
Data Impact: None.

2.4 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. Figure 2-2 shows the fraction of IMPROVE network samples weighing on the MTL automated system (Luna), the manual balance, and a mix of the two (e.g., pre-sampling gravimetric measurement on MTL chamber and post-sampling gravimetric measurement on manual balance).

Figure 2-2: Fraction of IMPROVE network sample weighed on the MTL weighing system (Luna), the manual balance, or a mix of the two (e.g., pre-sampling mass from Luna and post-sampling mass from manual balance).



In addition, beginning with samples and field blanks collected mid-October 2018, UCD transitioned to using PTFE filters made by MTL instead of Pall Corporation. PTFE filter field blanks from the 1A module (fine particles, $PM_{2.5}$; Figure 2-3) and 4D module (coarse particles, PM_{10}; Figure 2-4) are gravimetrically analyzed to monitor contamination levels and balance stability. As seen in Figure 2-3 and Figure 2-4, 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. We have done some experiments, including collecting Pall brand field blanks using the weighing system, and confirmed that the mass gain is connected to the filters themselves, not the weighing chamber. 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. We continue working with both Pall Corporation and MTL to acquire PTFE filters that meet all of our quality specifications.

Figure 2-3: Time series of $PM_{2.5}$ on PTFE filter field blanks, January 1, 2011 through June 30, 2020. Blue vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Red vertical line indicates manufacturer transition to Measurement Technology Laboratories (MTL) as manufacturer.

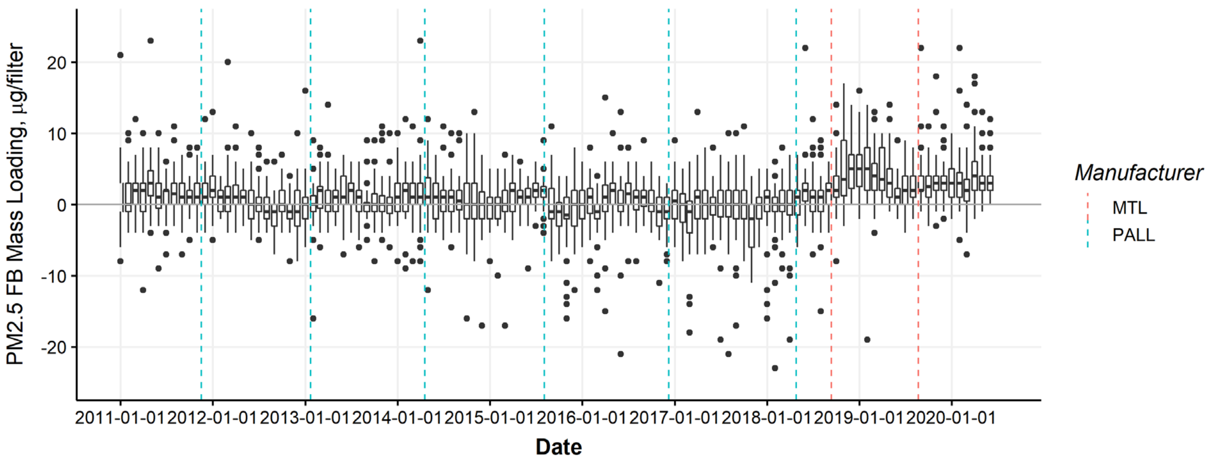
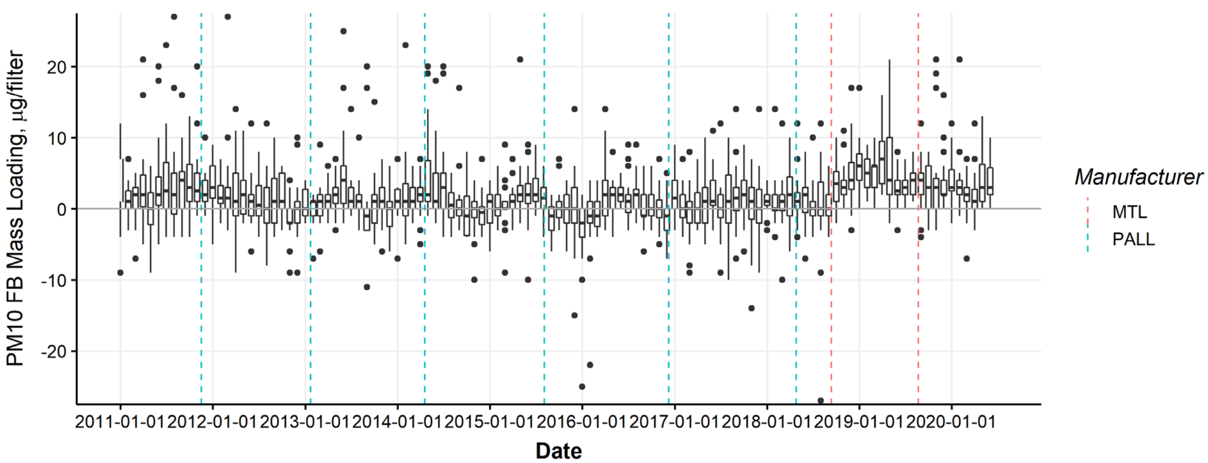


Figure 2-4: Time series of PM_{10} on PTFE filter field blanks, January 1, 2011 through June 30, 2020. Blue vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Red vertical line indicates manufacturer transition to Measurement Technology Laboratories (MTL) as manufacturer.



2.5 Optical Absorption with the Hybrid Integrating Plate and Sphere (HIPS) Instrument

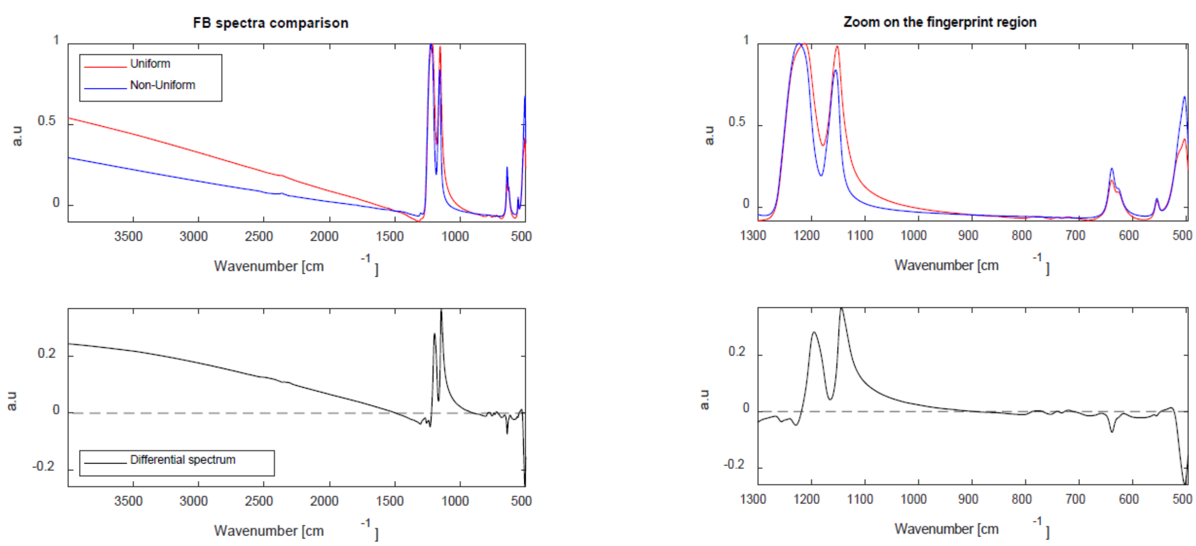
2.5.1 Updated HIPS Control Software

In April 2020 the control software for the HIPS instrument was upgrade from a combination of Excel macros and a data acquisition card to LabVIEW control software that pulls digital data directly off the new detector controller which was installed in November 2018. The new LabVIEW control software provides an intuitive user interface to the instrument and automates more of the measurement process including writing instrument results directly to the AQRC database rather than an Excel worksheet.

2.5.2 PTFE Filter Inconsistencies Affect HIPS Measurements

IMPROVE blank filters collected in October 2019 produced anomalous results in HIPS suggesting a change in PTFE filter material in the middle of manufacturer's lot. These filters have a non-uniform appearance and also appeared shiny under careful visual inspection indicating a change in spectral reflectance. The new filter material required a different calibration, but we could not distinguish between the two types of filters once sample was collected on them. With the exception of blanks, separating uniform and non-uniform filters in the October data could not be achieved using HIPS. FTIR analysis, on the other hand, successfully identified both blanks and sampled filters as either uniform or non-uniform. This change in PTFE material occurred during October 2019 and remained throughout the filter lot. After being presented with this evidence, MTL discovered that their supplier had been providing PTFE that was outside of specifications. In August 2020, MTL produced new filters and corrected the problem. The filter classification derived from the FTIR study enabled each filter to be assigned to the correct HIPS calibration such that no sample data was lost.

Figure 2-5: Spectra of uniform and non-uniform filters (top). The full mid-infrared range (left) and the fingerprint region (right) are shown. The difference between the two spectra are shown in the bottom row, highlighting that the PTFE structure is different in uniform and non-uniform filters.



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 2019 there were 14 sites that failed the RHR completeness criteria, as summarized in Table 2-1. By the end of the second quarter of 2020, there were 21 sites that failed the RHR completeness criteria, as summarized in Table 2-2. Site losses in 2020 were high mainly as a result of COVID-19 related shut downs. 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 2019.

Site Name	Completeness by Quarter (%)				Consecutive Terminal Samples	Annual Completeness (%)
	1st Q	2nd Q	3rd Q	4th Q		
Agua Tibia, CA (AGTI1)	90	87	55	47	6	69
D.L. Bliss State Park (BLIS1)	70	100	35	0	49	51
Bosque del Apache, NM (BOAP1)	50	97	61	90	12	74
Breton National Wildlife Refuge, LA (BRIS1)	87	87	81	0	35	64
Baengnyeongdo Island, KR (BYIS1)	80	33	97	100	13	78
Flathead, MT (FLAT1)	60	60	71	100	7	73
Flat Tops, CO (FLTO1)	57	90	90	97	12	84
Fort Peck, MT (FOPE1)	37	90	81	93	8	75
Gates of the Mountains, MT (GAMO1)	57	93	74	67	5	73
Hells Canyon, OR (HECA1)	77	77	58	83	7	74
Ike's Backbone, AZ (IKBA1)	33	97	81	80	9	73
Mingo, MO (MING1)	60	100	87	90	12	84
Theodore Roosevelt, ND (THRO1)	60	97	100	100	12	89
Virgin Islands (VIIS1)	67	60	84	70	9	70

Table 2-2: Summary of sites that failed the RHR completeness criteria during the first two quarters of 2020.

Site Name	Completeness by Quarter (%)				Consecutive Terminal Samples	Annual Completeness (%)
	1st Q	2nd Q	3rd Q	4th Q		
Breton National Wildlife Refuge, LA (BRIS1)	39	20			21	
Birmingham, AL (BIRM1)	97	13			26	
Brigantine, NJ (BRIG1)	90	0			33	
Fort Peck, MT (FOPE1)	87	47			9	
Gates of the Mountains, MT (GAMO1)	90	23			21	
Ike's Backbone, AZ (IKBA1)	90	7			28	
Lava Beds, CA (LABE1)	77	17			28	
Mingo, MT (MING1)	94	7			28	
Mount Hood, OR (MOHO1)	100	40			18	
Monture, MT (MONT1)	97	13			26	
Moosehorn, ME (MOOS1)	100	50			15	
Mount Zirkel, CO (MOZI1)	77	30			19	
Penobscot, ME (PENO1)	87	60			12	
Puget Sound, WA (PUSO1)	84	0			35	
San Pedro Parks, NM (SAPE1)	84	17			28	
Shining Rock, NC (SHRO1)	74	0			37	
Sipsey, AL (SIPS1)	94	37			14	
Snoqualamie Pass, WA (SNPA1)	84	47			19	
Stilwell, OK (STIL1)	94	37			19	
Tonto, AZ (TONT1)	97	27			21	
White Pass, WA (WHPA1)	68	47			8	

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. Accuracy is checked by bringing a secondary standard flow check device to each site; volumetric flow measurements from the flow check device are compared against the universal flow calculations as shown in Figures 2-6 and 2-7 below. The poor agreement in 2020 at low flow rates was related to a problem with the flow check device that was discovered after a maintenance trip that lasted multiple months. We believe the agreement in 2021 is more reflective of the actual performance but will continue checking these comparisons.

Figure 2-6: Flow rate measured by the $PM_{2.5}$ samplers using universal calibration constants versus flow rate measured by the flow check device at maintenance visits in 2020 (left) and 2021 (right). The lines indicated perfect agreement.

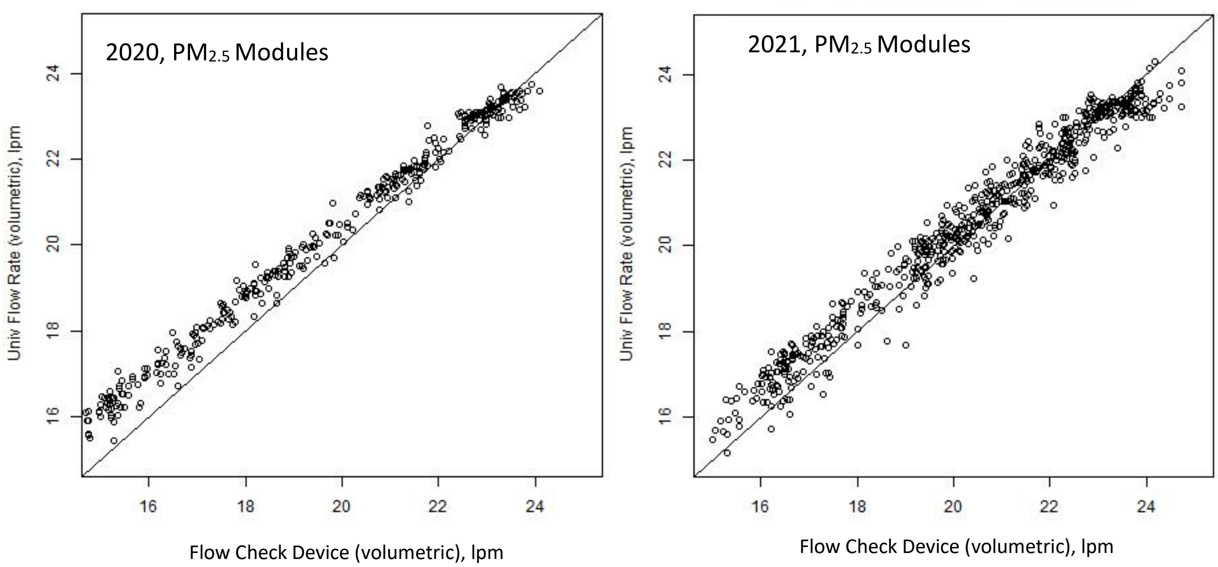
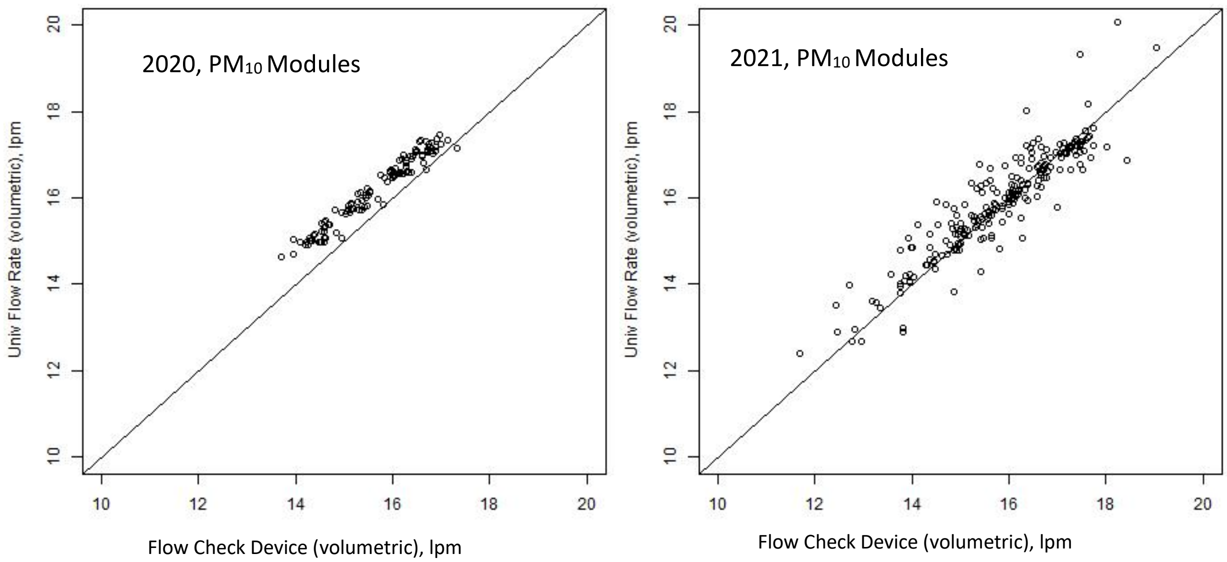


Figure 2-7: Flow rate measured by the PM_{10} samplers using universal calibration constants versus flow rate measured by the flow check device at maintenance visits in 2020 (left) and 2021 (right). The lines indicated perfect agreement.



3. Laboratory Quality Control Summaries

3.1 X-ray Fluorescence Laboratory

The UCD XRF Laboratory received and analyzed PTFE filter samples collected January 1, 2019 through June 30, 2020. 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 April 20, 2019 through June 14, 2021 on five instruments, XRF-1, XRF-2, XRF-3, XRF-4, and XRF-5. Details of the sample analysis are shown in Table 3-1. Sample analysis was paused on March 19, 2020 in response to the COVID-19 pandemic. Analysis resumed April 27, 2020. There is a gap in the QC data during this period as no personnel were onsite to perform XRF analyses. No monthly QC was performed in April 2020 due to limited staffing.

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	XRF-4 Analysis Dates	XRF-5 Analysis Dates
2019	January	2019-05-21 – 2019-06-12	2019-04-20 – 2019-06-11	2019-04-22 – 2020-09-08	2019-05-20 – 2019-07-02	2019-05-20 – 2019-06-12
2019	February	2019-05-21 – 2019-07-04	2019-05-07 – 2019-07-09	2019-05-23 – 2020-09-08	2019-05-21 – 2019-07-09	2019-05-23 – 2019-07-09
2019	March	2019-06-04 – 2019-07-16	2019-06-06 – 2019-09-17	2019-06-06 – 2020-09-08	2019-06-05 – 2019-07-13	2019-06-06 – 2020-02-13
2019	April	2019-07-09 – 2019-08-14	2019-07-09 – 2019-08-17	2019-07-10 – 2020-09-05	2019-07-10 – 2019-08-13	2019-07-09 – 2019-08-14
2019	May	2019-08-05 – 2020-08-03	2019-07-18 – 2019-09-26	2019-07-19 – 2020-09-06	2019-08-06 – 2019-09-13	2019-08-06 – 2019-08-15
2019	June	2019-09-09 – 2020-01-01	2019-08-23 – 2019-11-05	2019-08-28 – 2020-09-06	2019-09-09 – 2019-09-20	2019-09-09 – 2019-09-20
2019	July	2020-08-03 - 2020-08-03	2019-09-30 - 2019-12-06	2019-09-27 - 2020-09-06	2019-09-12 - 2019-10-17	2019-09-09 - 2019-10-17
2019	August	2019-11-12 - 2020-08-04	2019-10-22 - 2019-12-10	2019-10-22 - 2020-09-07	2019-10-13 - 2019-10-17	2019-10-16 - 2019-10-17
2019	September	2019-12-09 - 2020-01-14	2019-12-06 - 2020-06-30	2019-12-06 - 2020-09-05	2019-12-09 - 2020-01-23	2019-12-09 - 2020-01-21
2019	October	2020-04-02 - 2020-07-24	2020-01-09 - 2020-04-28	2020-01-09 - 2020-09-05	2020-01-09 - 2020-02-13	2020-01-09 - 2020-03-12
2019	November	2020-03-09 - 2020-05-08	2020-02-05 - 2020-06-08	2020-02-11 - 2020-09-02	2020-02-12 - 2020-05-05	2020-02-12 - 2020-03-12
2019	December	2020-03-09 - 2020-05-09	2020-03-10 - 2020-06-09	2020-02-28 - 2020-09-03	2020-03-12 - 2020-05-09	2020-03-10 - 2020-05-09
2020	January	2020-05-10 - 2020-08-01	2020-05-12 - 2020-07-10	2020-05-08 - 2020-09-03	NA	NA
2020	February	2020-07-20 - 2020-09-14	2020-06-01 - 2020-08-31	2020-06-08 - 2020-10-20	2020-08-11 - 2020-08-11	2020-08-13 - 2020-08-13
2020	March	2020-07-20 - 2020-09-15	2020-07-22 - 2020-09-10	2020-07-18 - 2020-12-10	2020-08-10 - 2020-09-11	2020-08-09 - 2020-09-10
2020	April	2020-08-04 - 2020-11-13	2020-07-28 - 2021-02-02	2020-09-04 - 2021-02-22	2020-08-11 - 2021-01-19	2020-08-09 - 2020-12-16
2020	May	2020-08-05 - 2020-12-19	2020-09-10 - 2021-02-17	2020-09-04 - 2021-01-21	2020-09-08 - 2021-01-29	2020-09-09 - 2021-01-29
2020	June	2020-11-13 - 2021-06-14	2020-11-09 - 2021-06-13	2020-09-04 - 2021-01-29	2020-11-15 - 2021-02-19	2020-11-07 - 2021-01-29
	All Months	2019-05-21 – 2021-06-14	2019-04-20 – 2021-06-13	2019-04-22 – 2021-02-22	2019-05-20 – 2021-02-19	2019-05-20 – 2021-01-29

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)	• XRF software automatically adjust the energy channels
PTFE Blank	Daily	≤ acceptance limits with exceedance of any elements not to occur in more than two consecutive days	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UCD-made ME-RMs	Daily	± 10 % of reference mass loadings for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb with exceedance of any element not to occur in more than two consecutive days	• Check sample for damage/contamination • Further cross-instrumental testing • Replace sample if necessary
UCD-made ME-RMs	Weekly	± 10 % of reference mass loadings for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb with exceedance of any element not to occur in two consecutive measurements	
Re-analysis set	Monthly	z-score between ± 1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se, and Sr	
SRM 2783	Monthly	Bias within 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 for all but one instrument. All QC checks passed or were investigated and promptly corrected with no impact to data quality with the exception of silicon on XRF-2. Laboratory and QC issues are discussed in detail in section 2.3. The following is a summary of minor QC findings with more details in the following sections.

Aluminum (Al) failed blank acceptance on XRF-3 in January 2020, potassium (K) failed blank acceptance on XRF-3 in November 2019, chlorine (Cl) failed blank acceptance on XRF-4 in August 2020 and iron (Fe) failed blank acceptance on XRF-3 in December 2020 and XRF-4 in June 2019. These events were limited to these single QC samples; no other QC samples analyzed showed unacceptable levels of Al, K, Cl, or Fe. After cleaning 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.

Aluminum and silicon (Si) results for the daily QC ME-RM sample on XRF-4 failed acceptance in March 2020. This was traced back to a detector fault which only affected higher loadings of Al and Si such as on the QC ME-RM. The detector issue was then corrected and Al and Si results returned to acceptable levels. No IMPROVE samples were analyzed during the failure so there was no impact on the data. Details are described in sections 2.3.3 and 3.3.4.2.

Results for a number of elements increased on XRF-3 in July 2020 for the daily QC ME-RM. These increases did not fail QC acceptance, but they were investigated and linked back to an issue with the detector. No other failures were noted for this instrument, with no impact on the data. However, the QC results remained high and worsened. All analysis was stopped on the instrument in July 2020 and an investigation into the cause for the worsening element signals was started. After further testing it became apparent the detector was deteriorating. The detector was replaced in August 2020 and sample analysis resumed in September 2020 after calibration and QC tests. See sections 2.3.5 and 3.3.4.2 for further details.

Aluminum, silicon, sulfur, and potassium on the daily QC ME-RM sample for XRF-5 dropped below acceptable levels in September 2020. Sample analysis was stopped and all samples analyzed since the last good QC results were reanalyzed on another instrument. The issue was determined to be the X-ray tube or high voltage generator and both were replaced. After calibration and QC tests passed, sample analysis resumed in November 2020. The issue reoccurred in early February 2021 causing analysis to stop and all affected samples to be reanalyzed on another instrument. This time the issue was pinpointed to the high voltage generator and it was again replaced after some delay. After calibration and QC tests passed, analysis resumed in June 2021. See sections 2.3.4 and 3.3.4.2 for further details.

There was a drop in elemental concentrations for a number of elements on the daily QC ME-RM for XRF-3 in late March 2021. Analysis was stopped and all samples analyzed since the last passing QC results were reanalyzed on a different instrument. The issue was determined to be a broken detector sleeve which was replaced. After calibration and QC tests were passed, analysis of samples was resumed. Then in late May 2021 the same drop in concentrations occurred. All affected samples were reanalyzed on another instrument. This time the issue was determined to be the X-ray tube or high voltage generator. Both were replaced and after calibration and QC tests passed, sample analysis resumed in July 2021. See sections 2.3.5 and 3.3.4.2 for further details.

Weekly and monthly QC checks had no failures over the analysis period for the 2019 IMPROVE samples other than the high z-score results for silicon on XRF-2. This Si background issue is explained below and in sections 2.3.1 and 3.3.4.1. Also, in the monthly SRM QC test it became apparent that the SRM in use, serial number 1720, had acquired some contamination. Most notably sulfur (S) contamination was noticed on the SRM in November 2019. Also, chromium (Cr) and zinc (Zn) levels had been climbing over time indicating gradual environmental deposition on the filter from its use. The SRM was therefore replaced by serial number 1617 in December 2019 which corrected the high S, Cr, and Zn signals. There was no impact on the sample data. See sections 3.3.5 and 3.3.6 for further details.

In addition to the QC results above, the silicon background on XRF-2 rose above acceptable levels in December 2019. An investigation into the cause was initiated, including inspection and maintenance by the manufacturer and a new calibration. No cause was determined and the calibration failed to correct the issue as the Si background continued to fail QC checks. However, analysis on the instrument was not stopped. Samples continued to be analyzed on the instrument until all analysis was stopped in October 2019. 4993 IMPROVE samples were analyzed on XRF-2 while the Si blank level was failing acceptance. Corrective actions have been taken which include further training of staff on SOPs and QC procedures and updates to the QC software have been initiated to ensure faster detection of QC issues and immediate response to failure conditions. The impact on the data has been assessed and determined to be insignificant. Details are described in sections 2.3.1, 3.3.4.1, and 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-1	2018-12-19	Annual calibration	2019-01-03 – 2019-09-30
XRF-1	2020-01-30	Annual calibration	2019-05-24 – 2020-06-08
XRF-1	2020-11-25	Annual calibration	2020-05-31 – 2020-06-29
XRF-2	2018-12-20	Annual calibration	2019-01-03 – 2019-09-15
XRF-2	2019-12-22	Annual calibration	2019-09-03 – 2020-05-27
XRF-2	2020-11-06	Annual calibration	2020-04-03 – 2020-06-29
XRF-3	2019-04-15	Replaced X-ray tube	2019-01-03 – 2019-09-30
XRF-3	2019-12-27	Annual calibration	2019-03-07 – 2020-03-01
XRF-3	2020-08-31	Replaced detector	2019-01-03 – 2020-06-30
XRF-3	2020-12-22	Annual calibration	2020-04-03 – 2020-06-29
XRF-4	2019-01-01	Annual calibration	2019-01-03 – 2019-09-30
XRF-4	2019-12-20	Annual calibration	2019-09-06 – 2020-06-08
XRF-4	2020-11-25	Annual calibration	2020-04-03 – 2020-06-29
XRF-5	2019-01-01	Annual calibration	2019-01-03 – 2019-09-30
XRF-5	2019-12-20	Annual calibration	2019-03-25 – 2020-05-03
XRF-5	2020-11-06	Replaced X-ray tube	2020-04-03 – 2020-06-29

The annual calibration in December 2018 and January 2019 included an updated analytical protocol. To improve detection of some heavy 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. The EDXRF instruments were recalibrated with the modified protocol, and all IMPROVE samples collected in 2019 and after were analyzed using the new analytical protocol. See UCD data advisory for further detail, http://vista.cira.colostate.edu/Improve/data-advisories/ (posted 6/2019).

Table 3-4: EDXRF analytical protocol change. All samples collected in 2019 and 2020 were analyzed under the new 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_2O_3	200	200

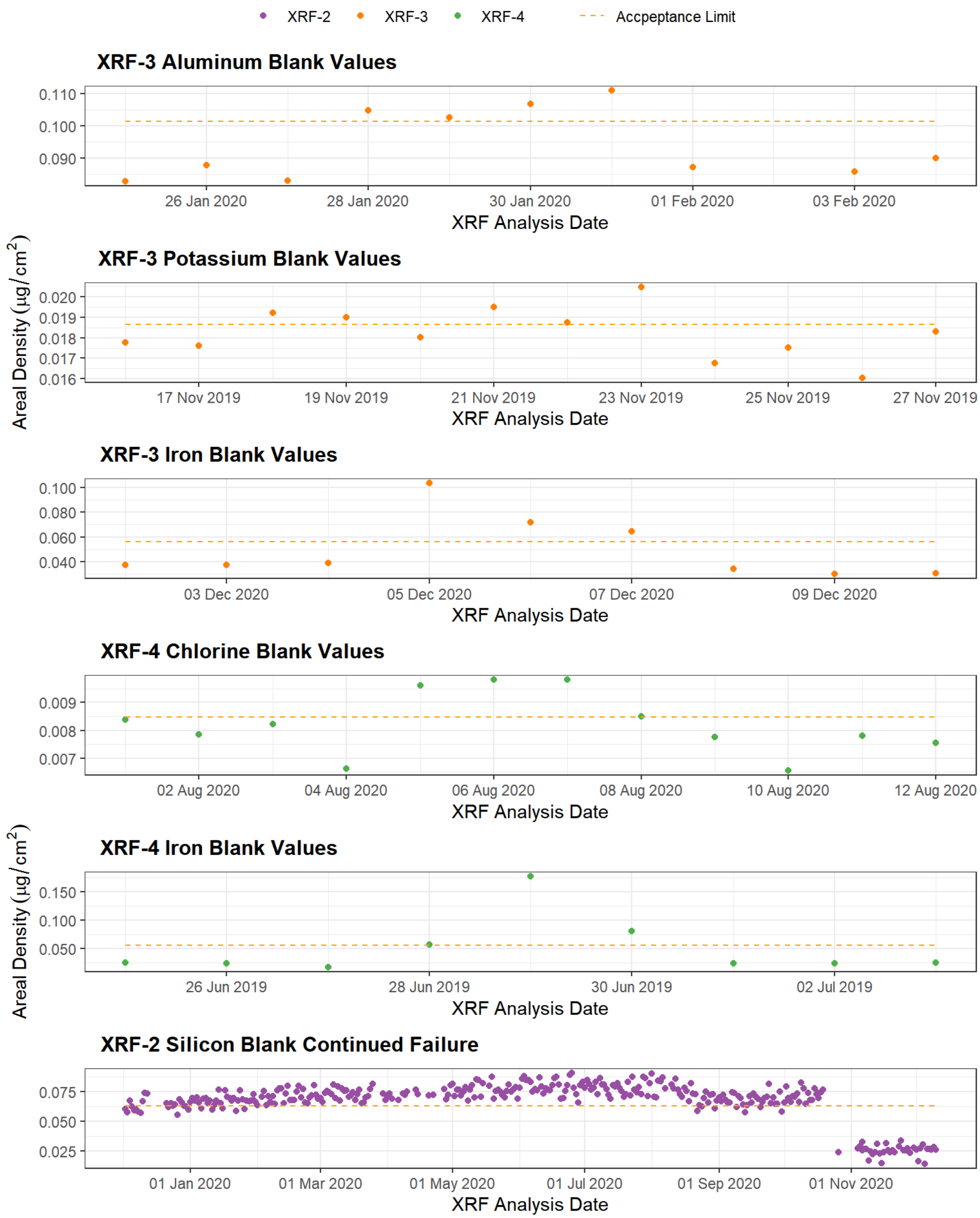
3.3.4 Daily QC Review

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 a few failures. These failures were investigated and corrective actions were taken in all but the silicon issue on XRF-2 which will be discussed below. First, there were five minor QC blank failures which all had the same resolution. The first case included three consecutive days of exceedance for potassium on XRF-3 occurring November 21, 22, and 23, 2019. The second case was three consecutive days of exceedance for iron on XRF-4 occurring June 28, 29, and 30, 2019. The third case was four consecutive days of exceedance for aluminum on XRF-3 occurring January 28-31, 2020. The fourth case was three consecutive exceedances of chlorine on XRF-4 occurring August 5, 6, and 7, 2020. Finally, the fifth case was three consecutive days of exceedance for iron on XRF-3 occurring December 5, 6, and 7, 2020. Figure 3-1 shows the control charts during the time periods associated with these failures. In all cases, the exceedances were corrected by gently blowing the filter off with air or replacing the blank with a new one. This returned the blank results to acceptable levels. The QC failures were caused by contamination on the blank filters and not an instrument issue, therefore, there was no impact on the sample results during these blank exceedances.

The last QC failure was due to silicon exceedance of the acceptance limits on XRF-2. The first failure occurred when silicon exceeded acceptance on December 10, 11, and 12, 2019. After the exceedance on December 12, 2019 all sample analysis was stopped on the instrument. The manufacturer was called to service XRF-2, but did not find any issues. The instrument then underwent routine preventative maintenance by the manufacturer and subsequent calibration. As can be seen in the last plot of Figure 3-1, the silicon blank results continued to exceed the acceptance limits for the remainder of the analysis period. The impact on the data was found to be insignificant, see section 2.3.1 for further details.



3.3.4.2 Daily ME-RM QC

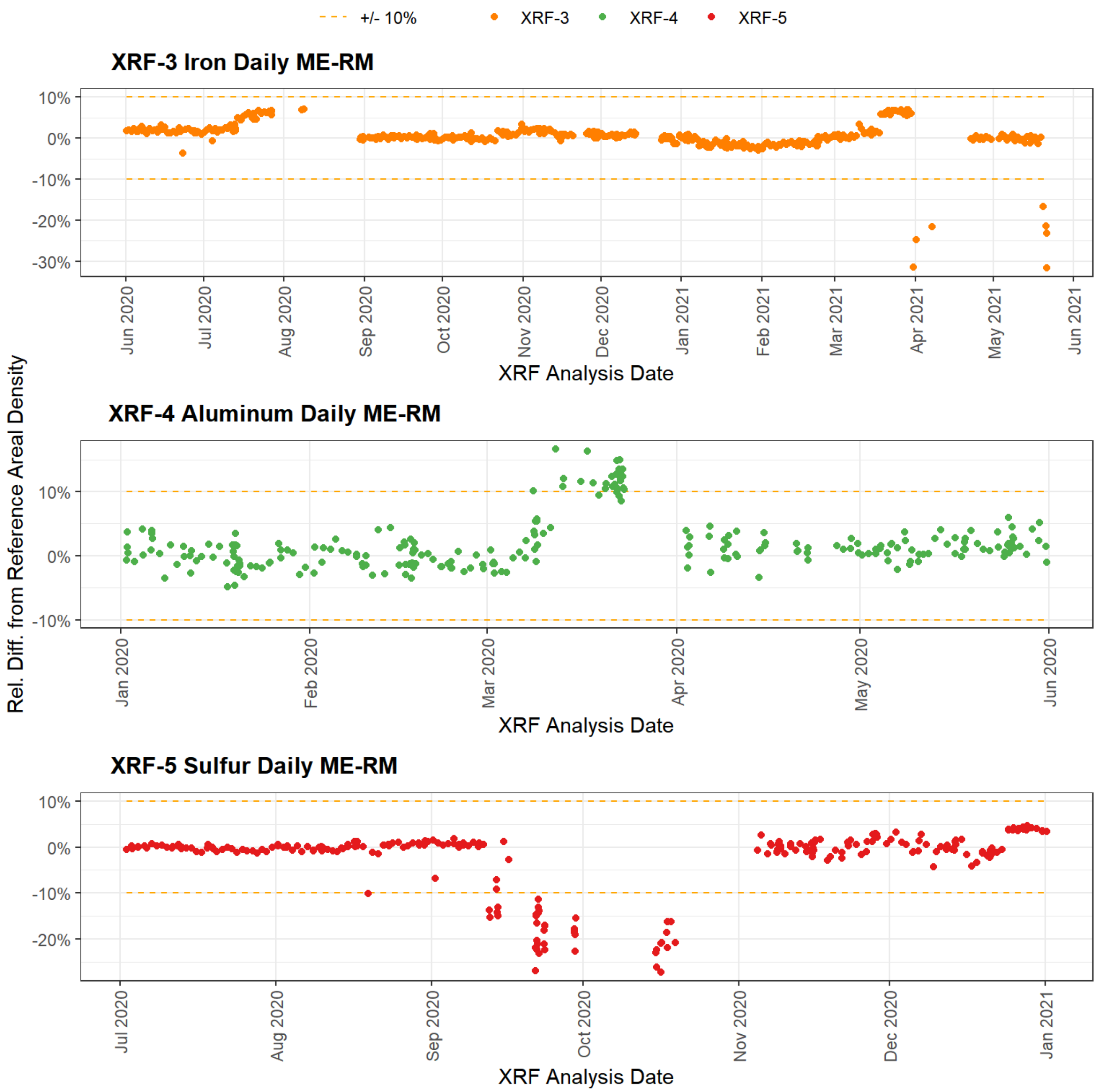
Daily QC ME-RM results during this analysis period showed only a few failures. XRF-4 failed the daily ME-RM QC criteria for Al and Si from March 12 to March 23, 2020. Figure 3-2 includes a portion of the control chart for aluminum on XRF-4 and shows the exceedances. An investigation determined the issue was with the detector, but did not impact the sample results. See section 2.3.2 for more details.

XRF-3 showed increases in multiple elemental values on the daily QC ME-RM results starting July 17, 2020. Many elements were near the upper acceptance limit and continued to show the possibility of failing QC checks. The decision was made to stop analyzing samples on XRF-3 on July 26, 2020 even though there were no other QC failures as these failures seemed imminent. Figure 3-2 includes a portion of the control chart for iron on XRF-3 during this period. The manufacturer was contacted to help investigate the issue and it was determined that the detector was beginning to fail. Sample analysis was stopped before significant failure of the detector and was not started on the instrument until after the detector was replaced in October 2020. There is no impact on the sample data from this issue. See section 2.3.3 for details.

XRF-5 had a drop in intensity which caused failures of multiple elements on the daily QC ME-RM from 9/12/2020 to 9/16/2020 until sample analysis was stopped. All samples analyzed during this failure period were reanalyzed on another instrument. The problem was attributed to a failed X-ray tube and the tube and high voltage generator were replaced and the system was calibrated on 11/7/2020. However, the same issue occurred again on 2/4/2021 and sample analysis was stopped again. All affected samples were reanalyzed on another instrument. This time the issue was attributed to a failed high voltage generator which was later replaced. Figure 3-2 includes a portion of the control chart for sulfur on XRF-5 where both intensity drops can be seen. There was no impact to sample results as all samples were reanalyzed on another instrument. See section 2.3.4 for details.

XRF-3 also had an intensity drop for multiple elements which failed QC acceptance. The failures began March 31, 2021. Initial investigation found a broken detector sleeve which was replaced followed by calibration of the instrument. This held for a short while until the intensity fell off again May 20, 2021. The X-ray tube and high voltage generator were replaced and the system was recalibrated and began analysis again in July 2021. No samples from this reporting period were affected by these failures, they are only being included for completeness. Figure 3-2 includes the two intensity loss events for iron on XRF-3. Details can be found in section 2.3.5.

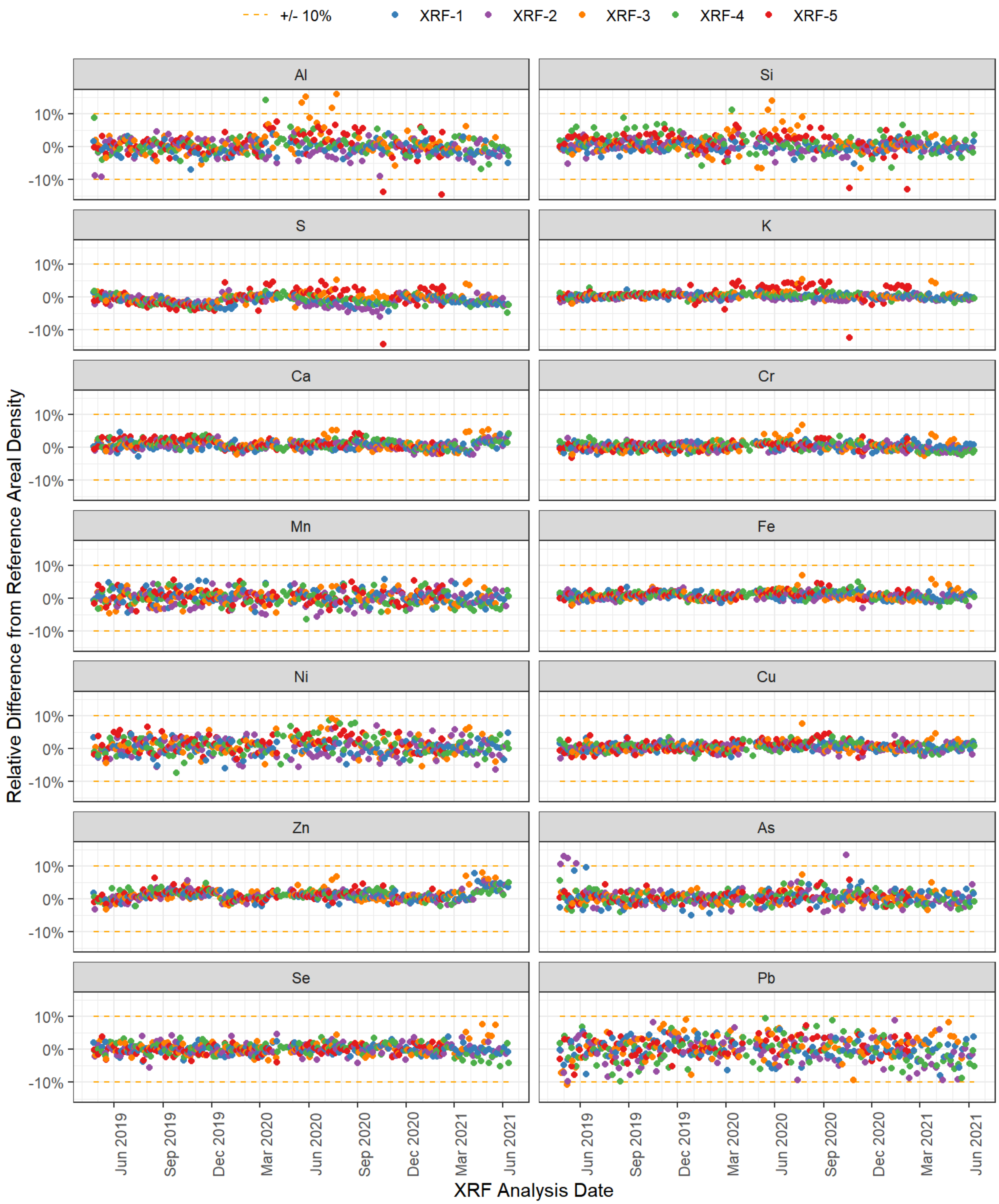
Figure 3-2: EDXRF daily ME-RM control charts showing important QC events.



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 3-3 are weekly ME-RM control charts. There are a few exceedances for Al, Si, K, and As, but these do not fail the QC acceptance criteria.

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



3.3.6 Monthly QC Review

Monthly QC is performed using a reanalysis set. The reanalysis set is comprised of 16 UCD produced ME-RM samples generated to mimic the range of mass loadings of ambient aerosol samples.

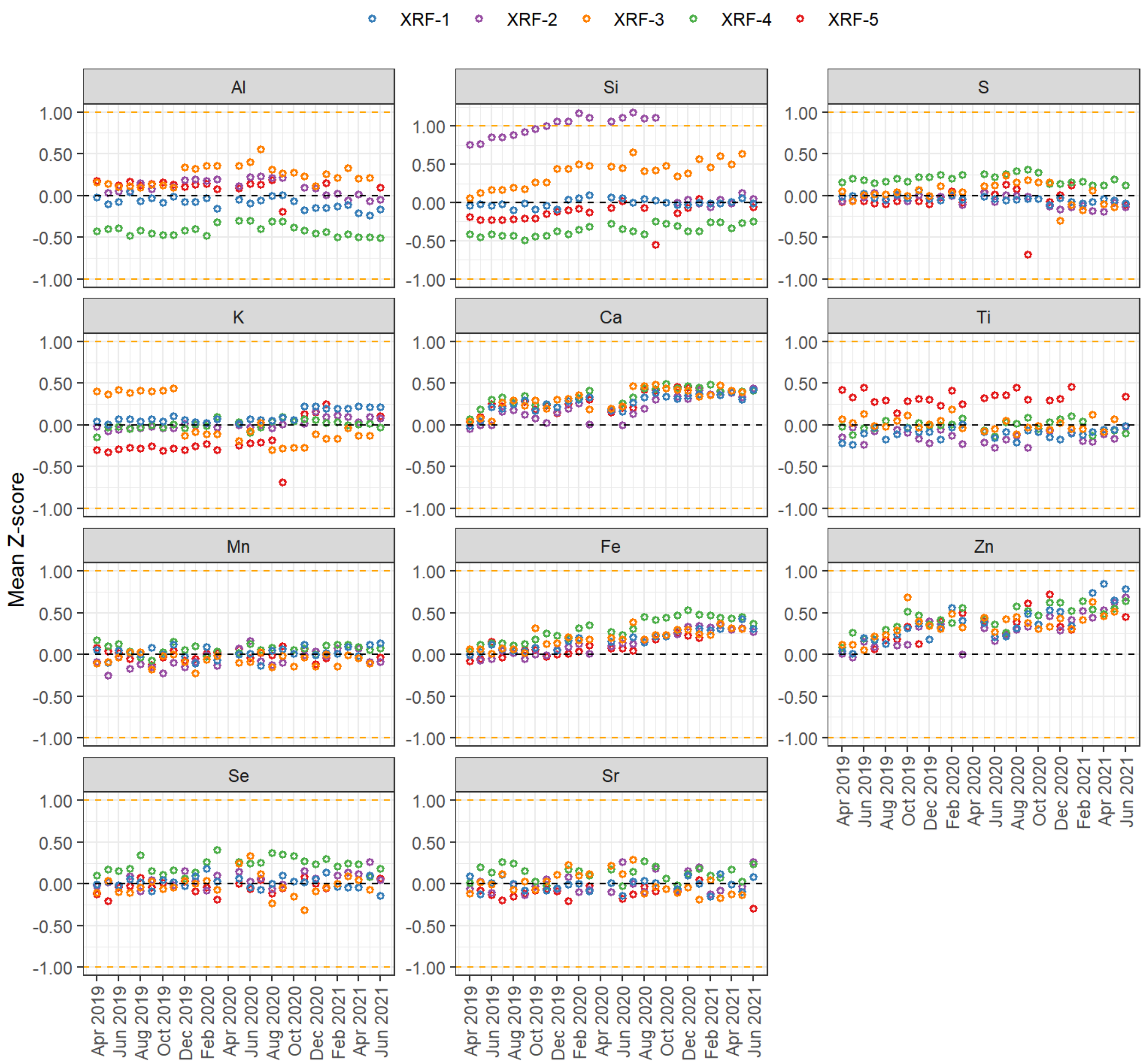
The monthly reanalysis monitors both the long-term instrument performance and the agreement between instruments. In order to compare multiple filters with different mass loadings, the reanalysis results are first converted to z-scores. For a given month, the z-score for the i^{th} element and j^{th}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

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

x_{ij} $\widehat{x_{ij}}$

$U(x_{ij})$ $U(\widehat{x_{ij}})$

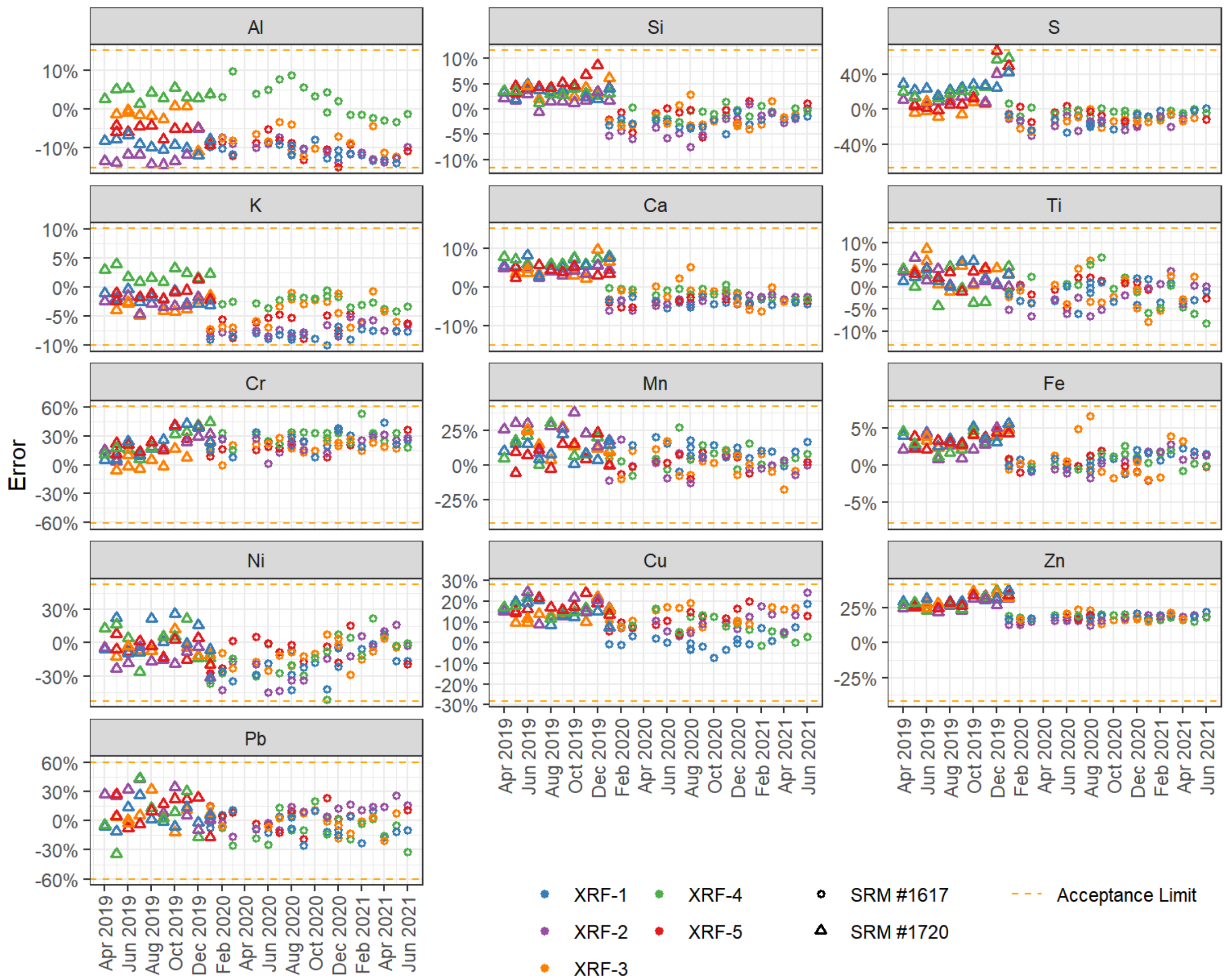
Figure 3-4: Monthly reanalysis control charts.



All reanalysis results were within a z-score value of ±1, except for silicon on XRF-2. As mentioned in sections 2.3.1 and 3.3.4.1, the silicon background on this instrument became elevated during this analysis period. The instrument was allowed to continue analyzing samples, deviating from the SOP. It was determined there was no serious impact on the sample results, see section 2.3.1 for details. The low Al, Si, S, and K results for XRF-5 in September, 2020, is due to the loss in intensity discussed in section 2.3.4.

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 3-5. There were no QC failures during this analysis period. However, note the sharp rise in sulfur in November and December, 2019 along with increasing error in Cr and Zn. These increases are related to contamination of the SRM filter. The sudden drastic increase in sulfur was likely a one-time contamination event, the more gradual increases in Cr and Zn were likely slow environmental deposition over time as the SRM was handled and analyzed. In December the SRM which had been in use, serial number 1720, was replaced by another, serial number 1617. The results for the two different SRMs can be seen as different plotted symbols in Figure 3-5.

Figure 3-5: Monthly NIST SRM 2783 control charts.



3.2 UCD Gravimetric Laboratory

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

3.3 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.

Figure 4-1 through Figure 4-10 show 90th percentile, median (50th percentile), and 10th percentile concentrations of select species, with eight years of historical network data (2011-2018) providing context for the current time period under review (2019 – June 2020).

Network-wide $PM_{2.5}$ and PM_{10} concentrations during this review period are in general lower than previous years (Figure 4-1 and 4-2). In particular, the median and 90th PM_{10} concentrations during the springs of 2019 and 2020 are the lowest in the recent 10 years. The low concentrations observed in 2020 may also be related to changes in human activities related to COVID-19. In addition, median and 90th percentile $PM_{2.5}$, PM_{10} and organic carbon (OC) (Figure 4-3) concentrations in August and September of 2019 are significantly lower than those of 2017 and 2018, likely due to the lack of wildfire impact on the network samples.

Figure 4-1: Multi-year time series of network-wide $PM_{2.5}$ concentrations, 2011 through June 2020.

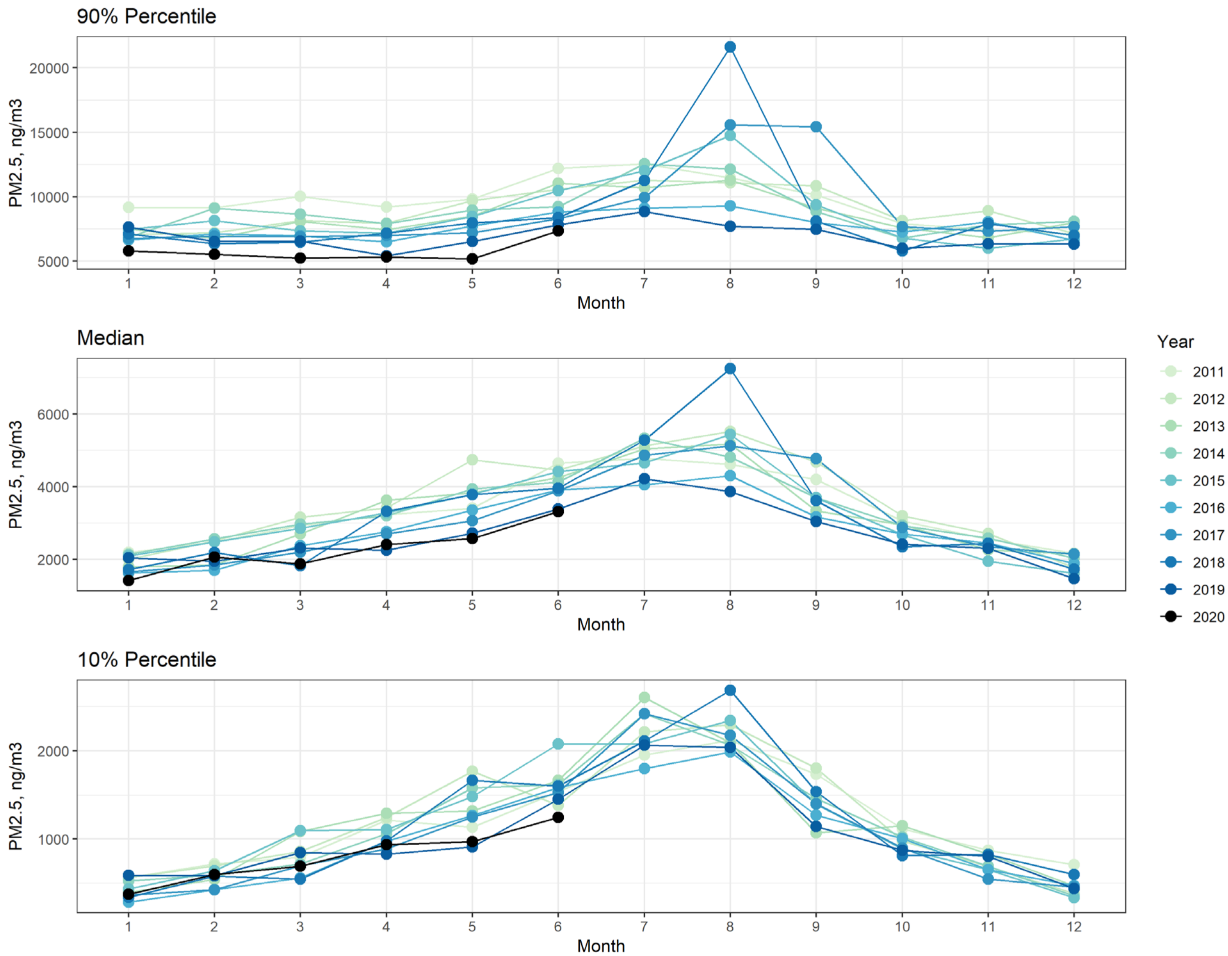


Figure 4-2: Multi-year time series of network-wide PM_{10} concentrations, 2011 through June 2020.

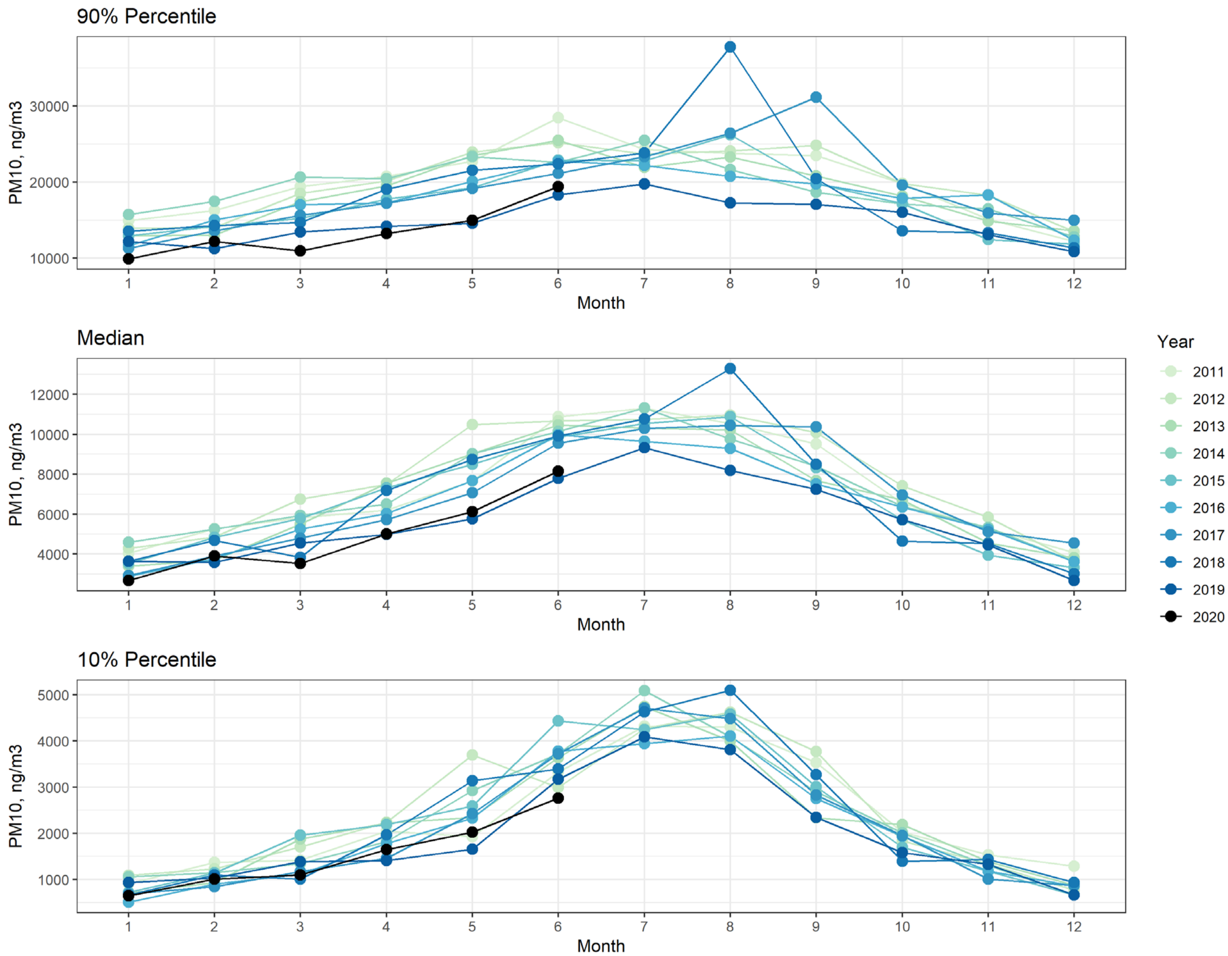
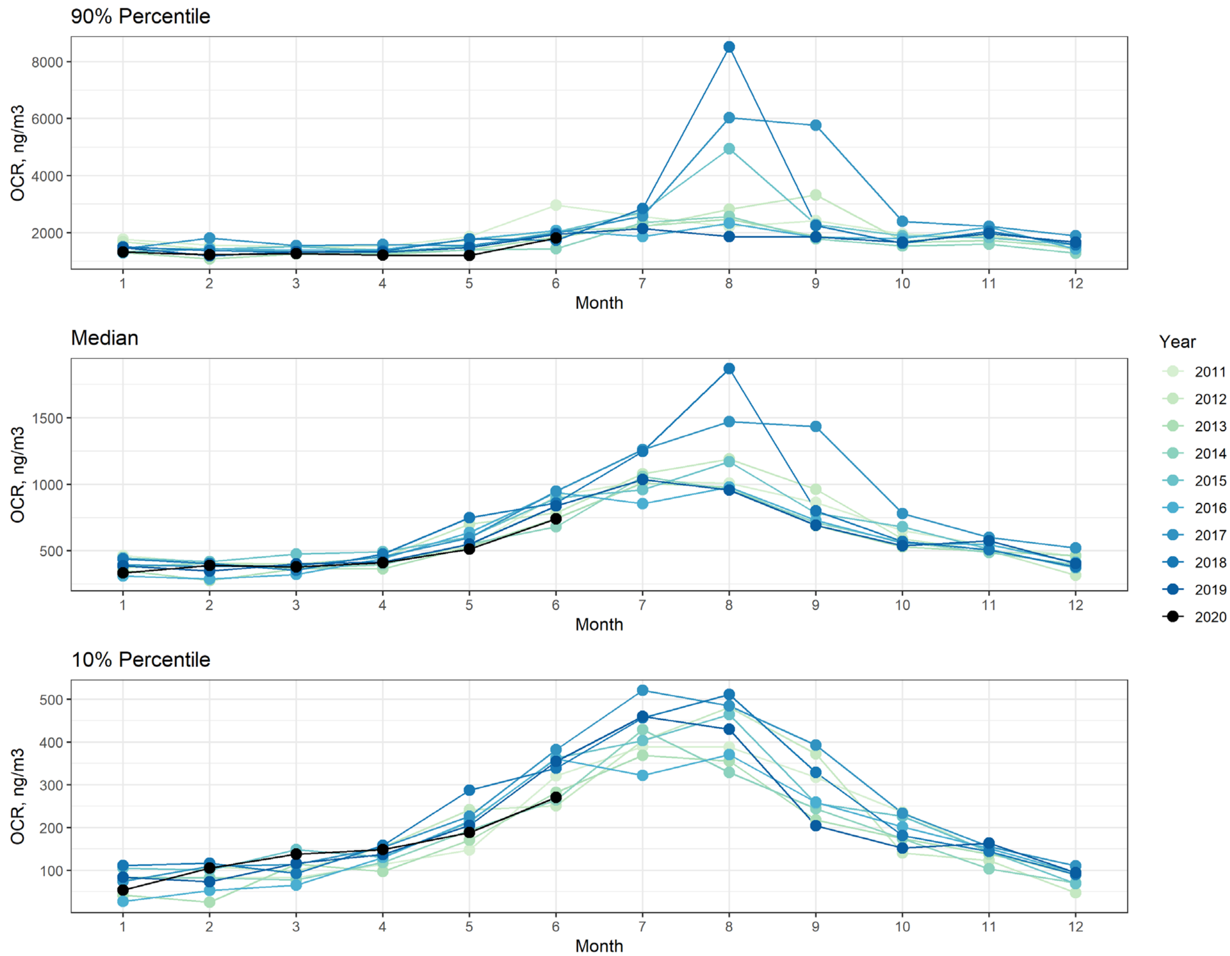


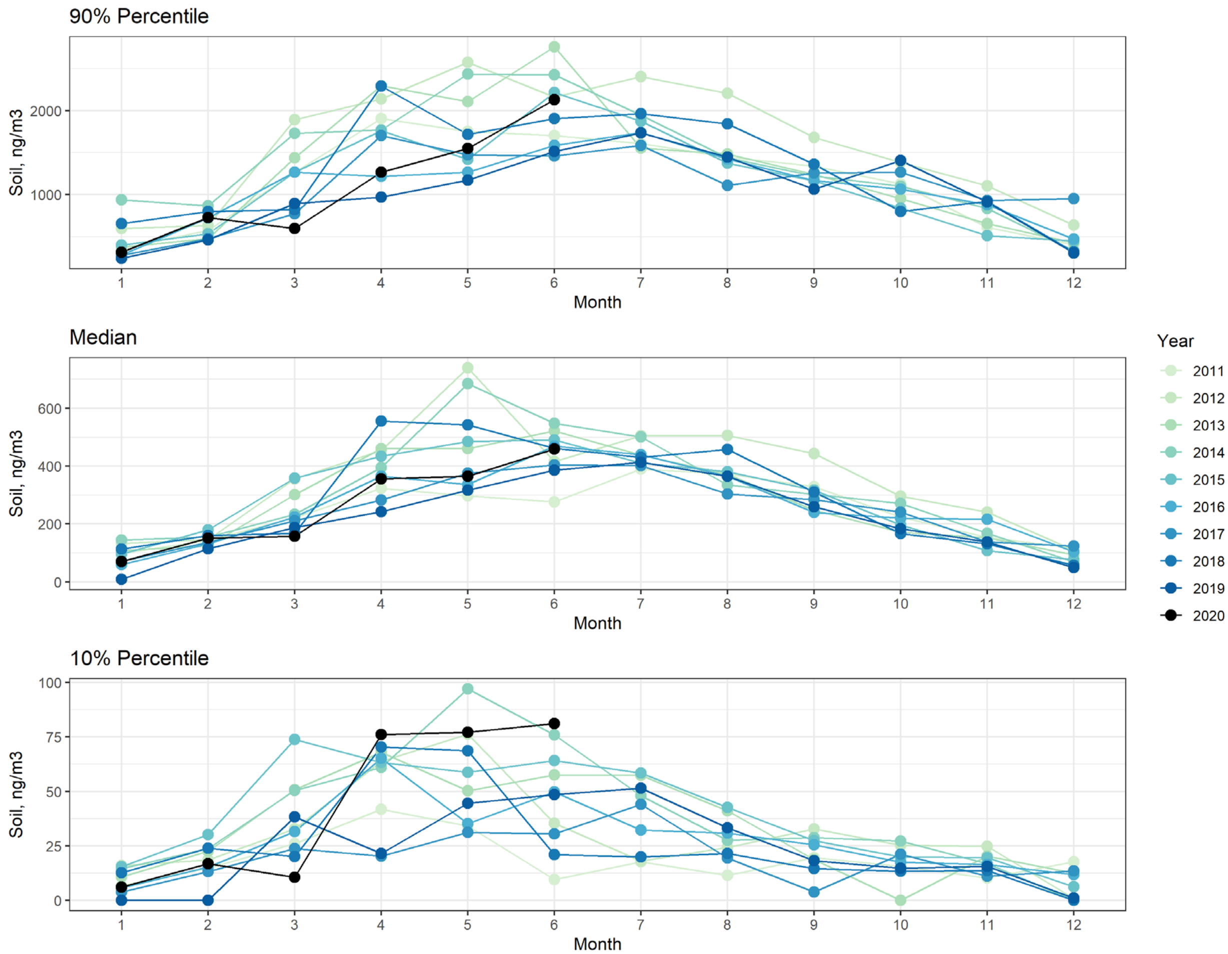
Figure 4-3: Multi-year time series of network-wide thermos-optical reflectance organic carbon (OCR) concentrations, 2011 through June 2020.



Despite the evident decrease in the PM concentrations during March to June of 2019 and 2020, the concentrations of soil (Figure 4-4) remain consistent with previous years. Composite variable soil is calculated as,

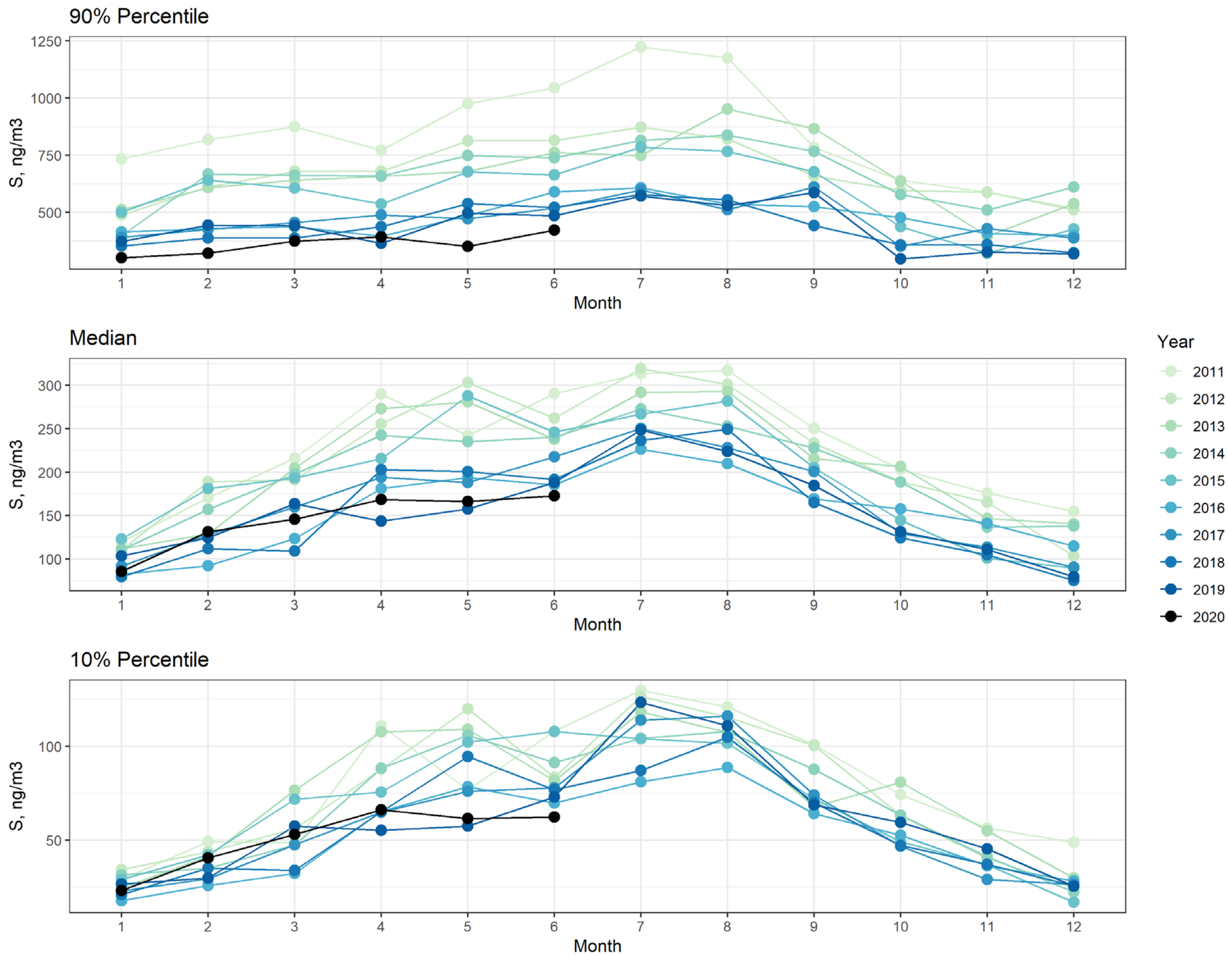
$$SOIL = 2.2 * \max(Al,0) + 2.49 * \max(Si,0) + 1.63 * \max(Ca,0) + 2.42 * \max(Fe,0) + 1.94 * \max(Ti,0)$$

Figure 4-4: Multi-year time series of network-wide soil concentrations, 2011 through June 2020.



Similar to recent previous years (2016-2018), sulfur concentrations during this review period continue to be low and relatively stable compared to the earlier years (2011-2015) (Figure 4-5).

Figure 4-5: Multi-year time series of network-wide sulfur (S) concentrations, 2011 through June 2020.



Concentrations of vanadium (Figure 4-6) and nickel (Figure 4-7) during 2019 are similarly low compared to observations from the previous four years. This is likely a continuation of lower concentrations observed corresponding with regulations on international shipping emissions implemented in January 2015 (Spada et al, 2018). The median and 90th percentile concentrations of vanadium and nickel in May and June of 2020 are the lowest in the recent years, possibly due to reduced marine traffic in response to the COVID-19 pandemic (March et al., 2021).

Figure 4-6: Multi-year time series of network-wide vanadium (V) concentrations, 2011 through June 2020.

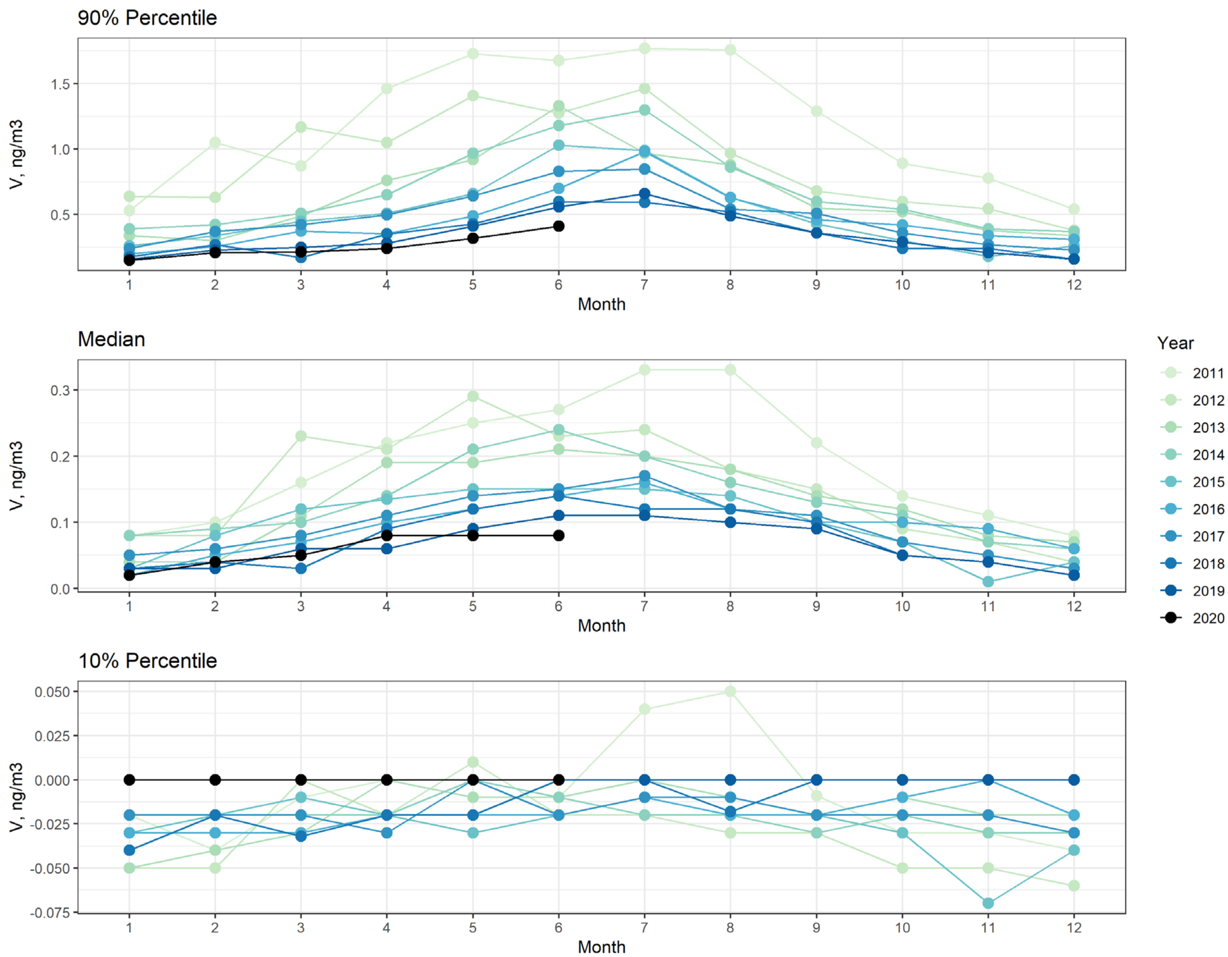
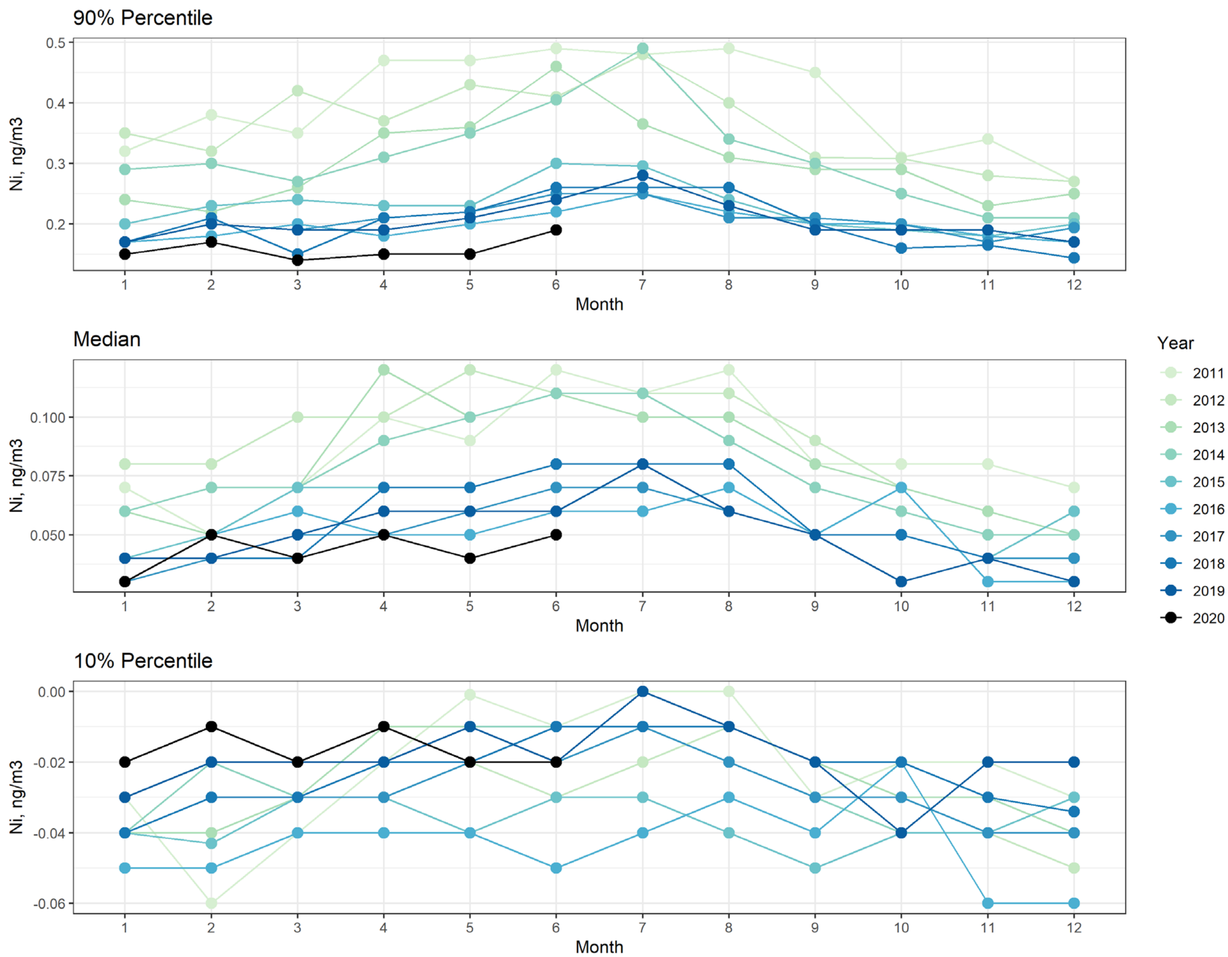


Figure 4-7: Multi-year time series of network-wide nickel (Ni) concentrations, 2011 through June 2020.



The 90th percentile filter absorption coefficients (f_{Abs}) (Figure 4-8) during the first half of 2020 are lower than previous years, whereas the median and 10th percentile f_{Abs} are more in line with the previous year (2019). Similar low 90th percentile concentration in 2020 is not observed for the elemental carbon (ECR) (Figure 4-9). We reviewed the quality control sample results to confirm that there was not an instrument-related issue to explain the low values. We will continue to keep an eye on these f_{Abs} results to make sure this is not a measurement issue.

Figure 4-8: Multi-year time series of network-wide filter absorption coefficient (f_{Abs}), 2011 through June 2020.

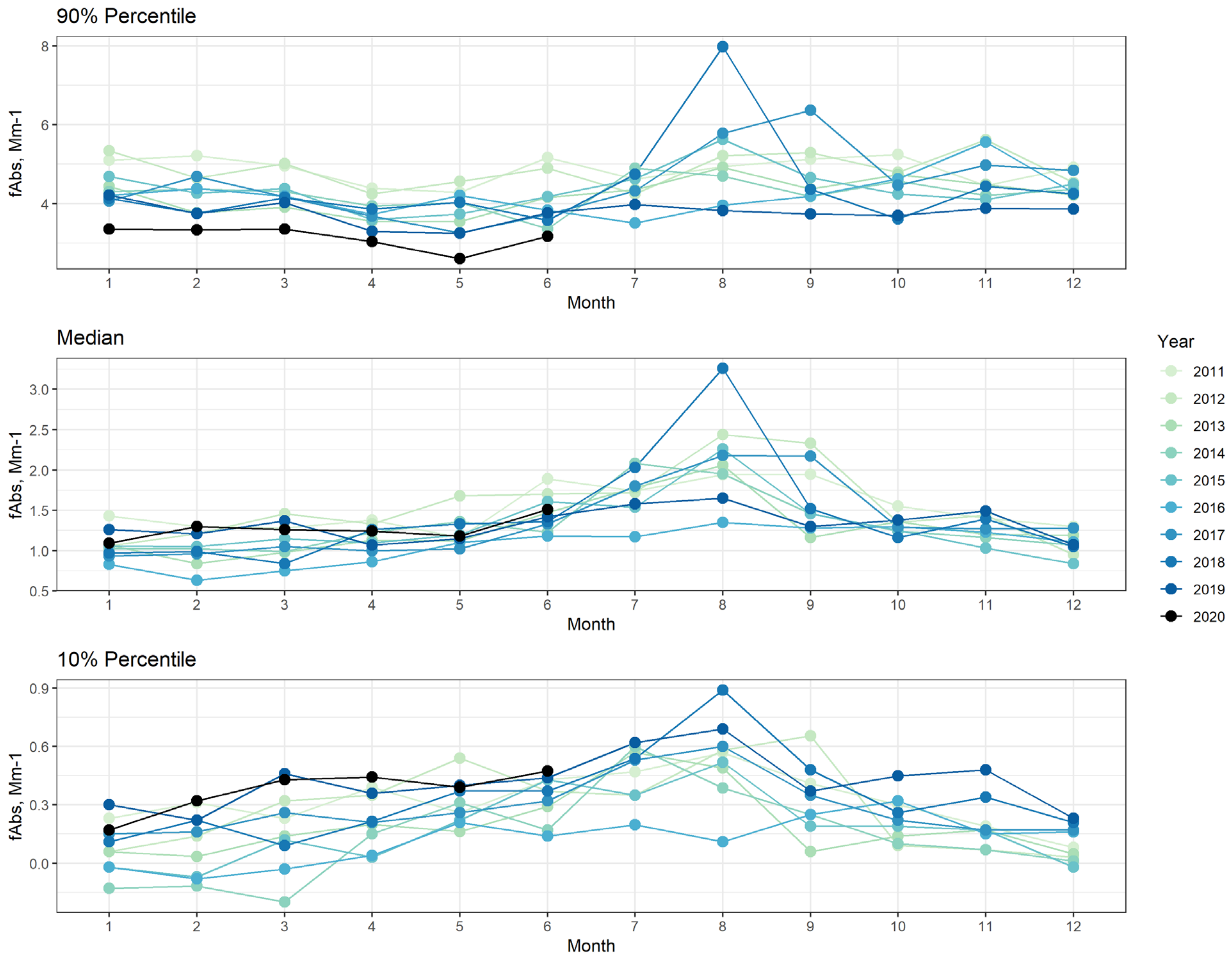
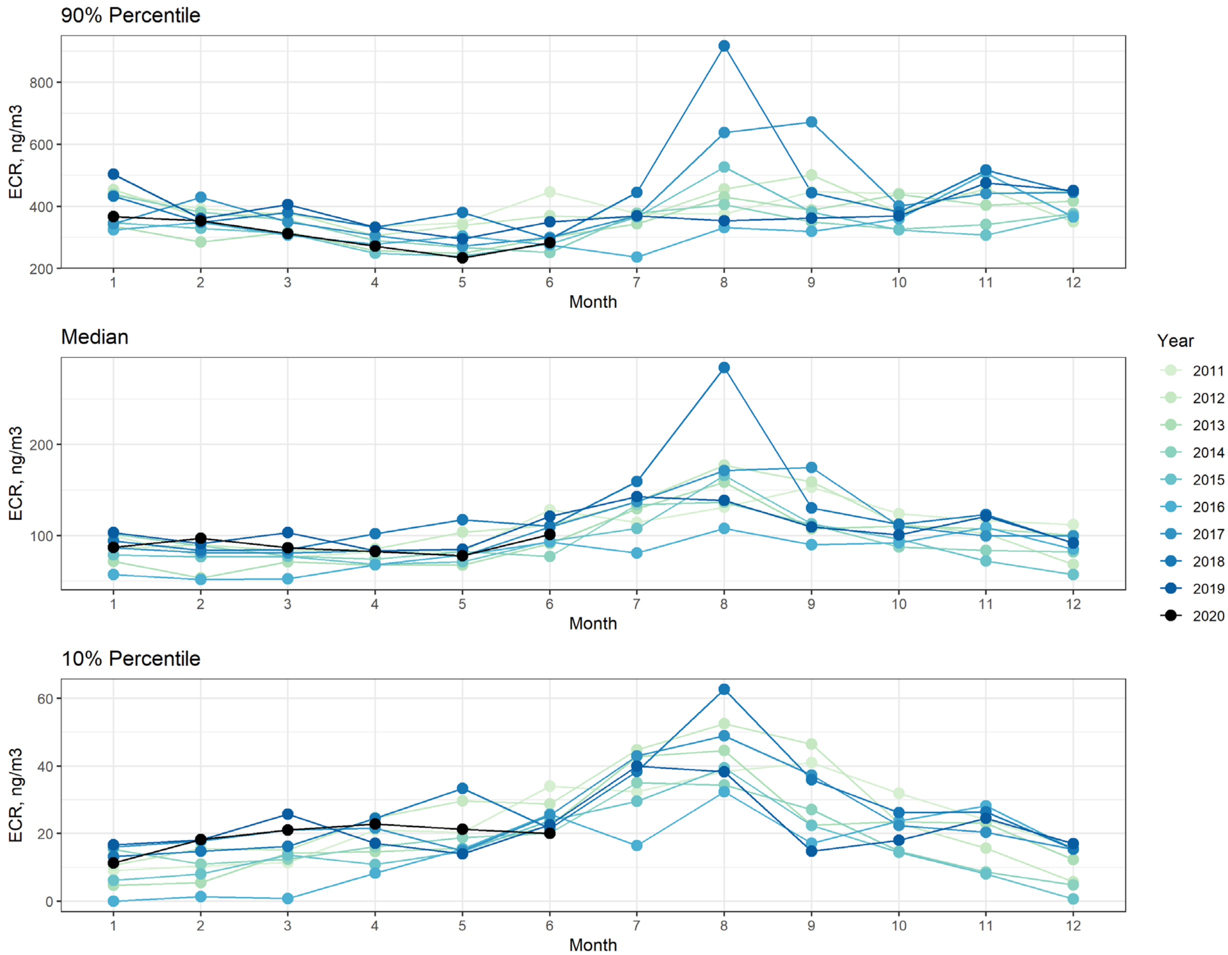
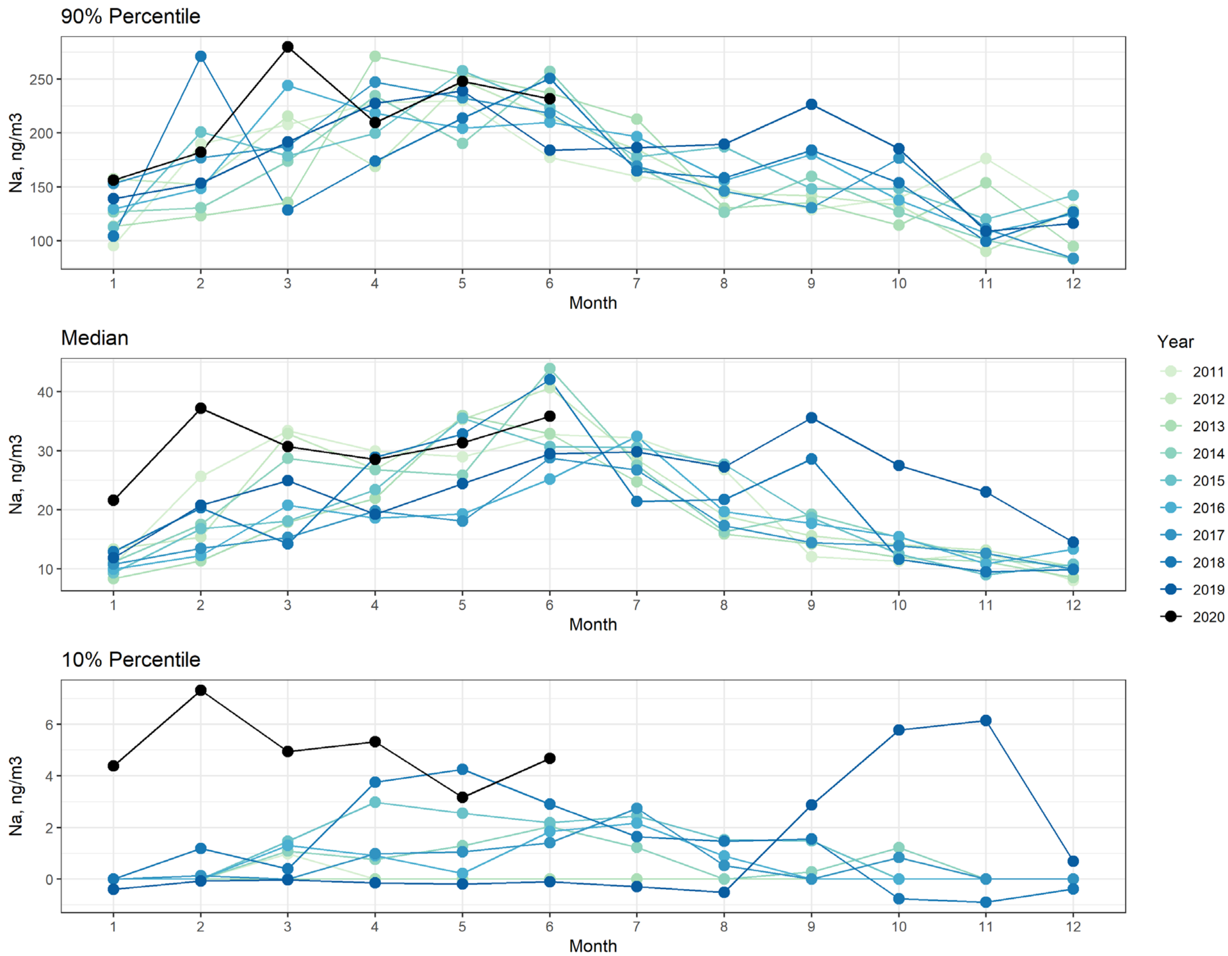


Figure 4-9: Multi-year time series of network-wide thermo-optical reflectance elemental carbon (ECR) concentrations, 2011 through June 2020.



Median and 10th percentile concentrations of sodium (Na) (Figure 4-10) appear to be elevated since September of 2019. The 10th percentile Na concentrations remain high throughout the first half of 2020. The XRF QC checks for Na passed during this period. While an instrument-related change or issue may be responsible for the shift, there is no known cause at this time. We will continue to monitor the Na concentrations.

Figure 4-10: Multi-year time series of network-wide sodium (Na) concentrations, 2011 through June 2020.



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), so the concentration ratio (3×S)/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 4-11), suggesting the presence of some sulfur in a non-water-soluble form of sulfate or in a chemical compound other than sulfate. The (3×S)/SO_4 ratio is generally higher during the summer months.

During 2019 through June 2020 monthly network (3×S)/SO_4 median ratios fell within the range of those previously reported (2011 through 2018). The seasonal cycle of the (3×S)/SO_4 ratio is less pronounced since 2017 compared to earlier years (2011-2016) (Figure 4-12).

Figure 4-11: Multi-year time series of network-wide (3×S)/SO_4 ratios, 2011 through June 2020. Bars show 25th to 75th percentile range, middle line indicates median. Data are grouped by the month in each year.

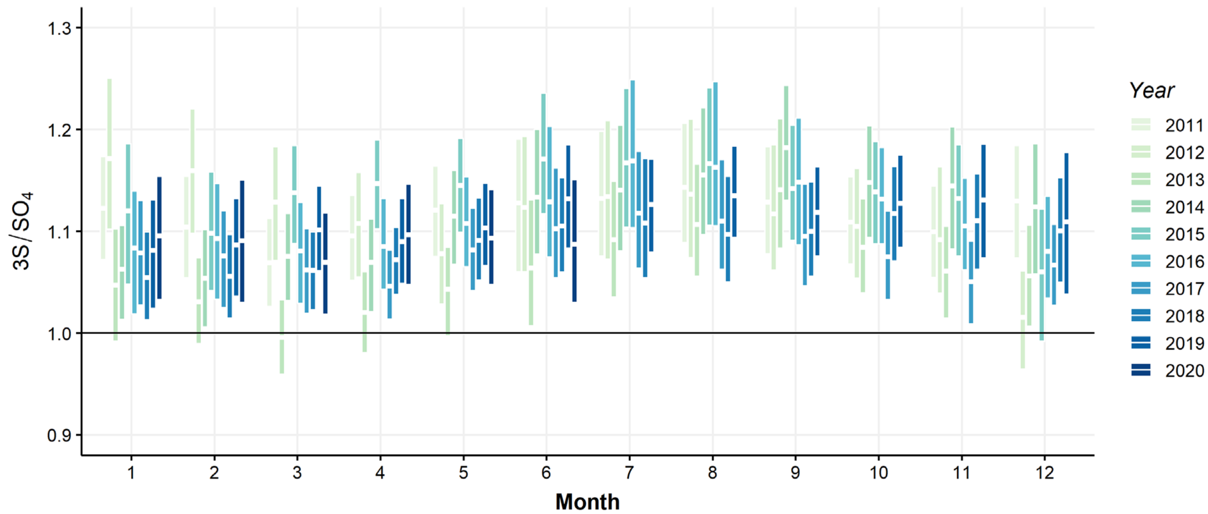
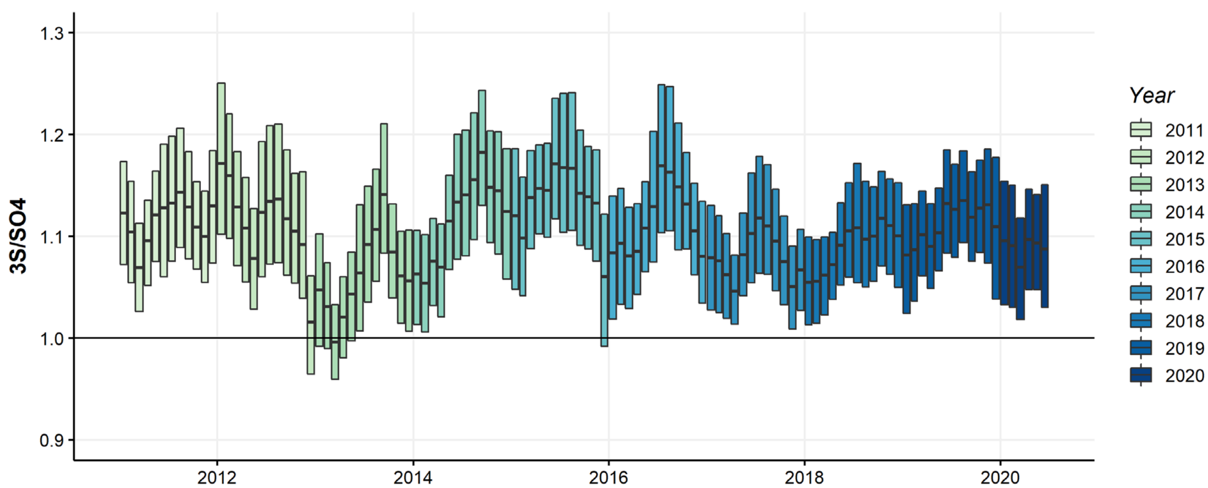


Figure 4-12: Time series of network-wide (3×S)/SO_4 ratios, 2011 through June 2020. Bars show 25th to 75th percentile range, middle line indicates median.



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:

$$RCM = (4.125 \times S) + (1.29 \times NO_3^-) + (1.8 \times OCR) + (ECR) +$$

$$(2.2 \times Al + 2.49 \times Si + 1.63 \times Ca + 2.42 \times Fe + 1.94 \times Ti) + (1.8 \times \text{chloride})$$

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

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 2019 are closer to one, and higher compared to previous years especially between June and August 2019. Since December 2019, the RCM/$PM_{2.5}$ ratios are elevated compared to previous years, particularly in December 2019 and March 2020, which have the highest ratios for the years plotted (Figure 4-13 and 4-14). There is an upward trend in the ratios since 2017, and this trend is pronounced in 2020. It is not clear what drives the RCM/$PM_{2.5}$ ratios high but the increases may be related to changes in the particulate matter composition over the years, possibly affecting the factors in the RCM equation. Alternatively, changes in the measurement techniques, such as the temperature and humidity-controlled weighing chamber, may have affected the mass measurements.

Figure 4-13: Multi-year time series of network-wide RCM/$PM_{2.5}$ ratios, 2011 through June 2020. Bars show 25th to 75th percentile range, middle line indicates median. Data are grouped by the month in each year.

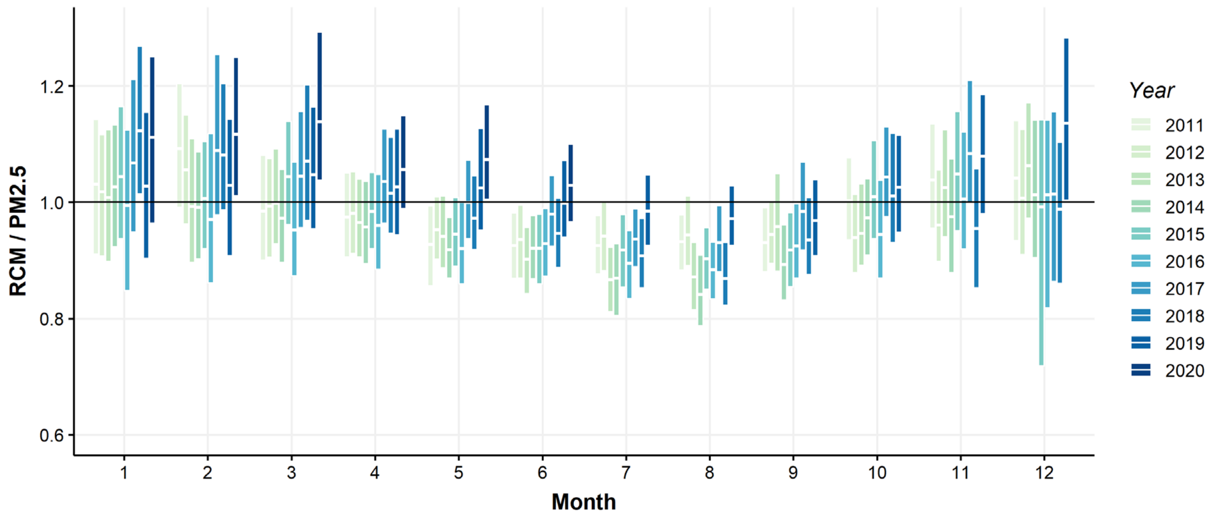
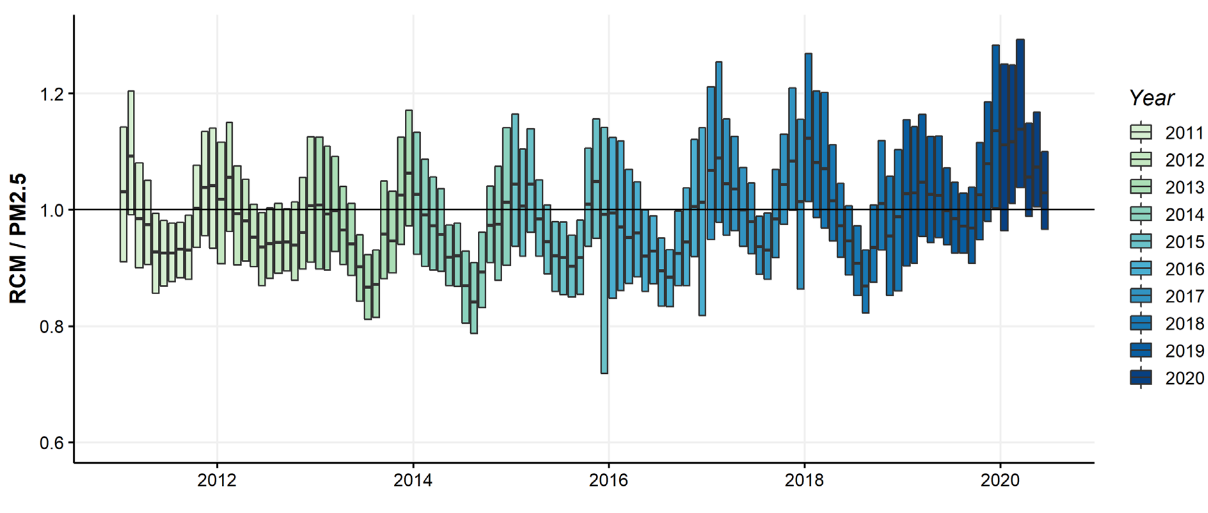


Figure 4-14: Time series of network-wide RCM/$PM_{2.5}$ ratios, 2011 through June 2020. Bars show 25th to 75th percentile range, middle line indicates median.



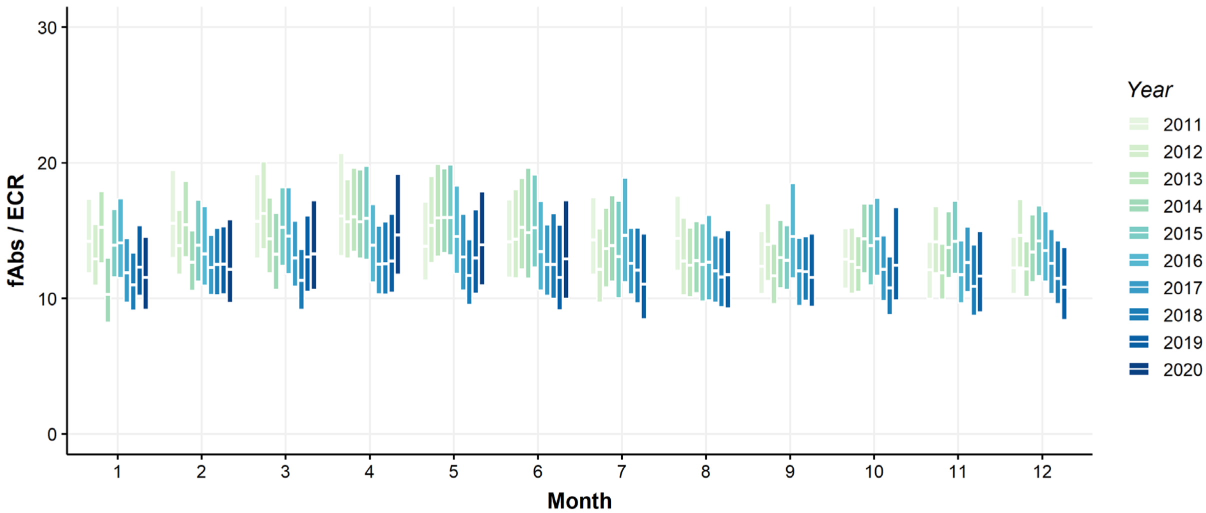
4.1.2.3 Optical Absorption versus Elemental Carbon

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 $\mu g/m^3$) measured by thermal optical analysis (TOA).

The fAbs/ECR ratios during 2019 are similar to years prior to 2018, particularly in January, March, May, and October (Figure 4-15). However, the ratios in June, July, and December 2019 have median values lower than previously observed. The median ratio between March and June

2020 are higher than the previous four years, with the value in April 2020 being more similar to those between 2011 and 2015.

Figure 4-15: Multi-year time series of network-wide fAbs/ECR ratios, where fAbs is in Mm^{-1} and elemental carbon by reflectance (ECR) is in $\mu g/m^3$, 2011 through June 2020. 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 4-16, elements; Figure 4-17, mass; Figure 4-18, ions; Figure 4-19, carbon; Figure 4-20, optical absorption).

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

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 2019 – June 2020 IMPROVE collocated sites.

Module-1A **PTFE / $PM_{2.5}$**	**Module-2B** **Nylon**	**Module-3C** **Quartz**	**Module-4D** **PTFE / PM_{10}**
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 4-16: Scaled relative difference for element measurements at sites with collocated modules across the IMPROVE network (2019 – June 2020). Dotted vertical lines indicate method detection limits.

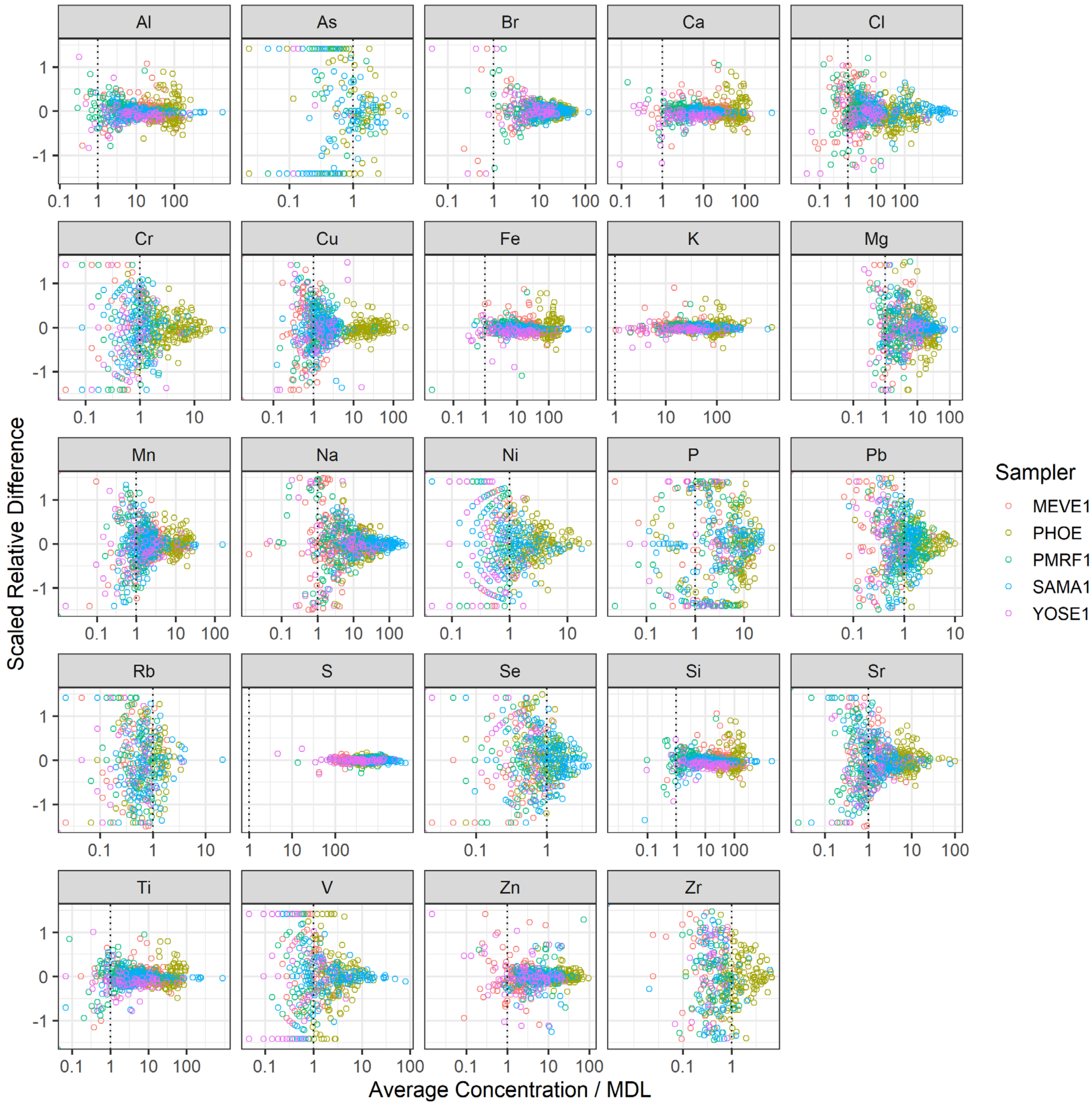


Figure 4-17: Scaled relative difference for PM_{10} and $PM_{2.5}$ at sites with collocated modules across the IMPROVE network (2019 – June 2020). Dotted vertical lines indicate method detection limits.

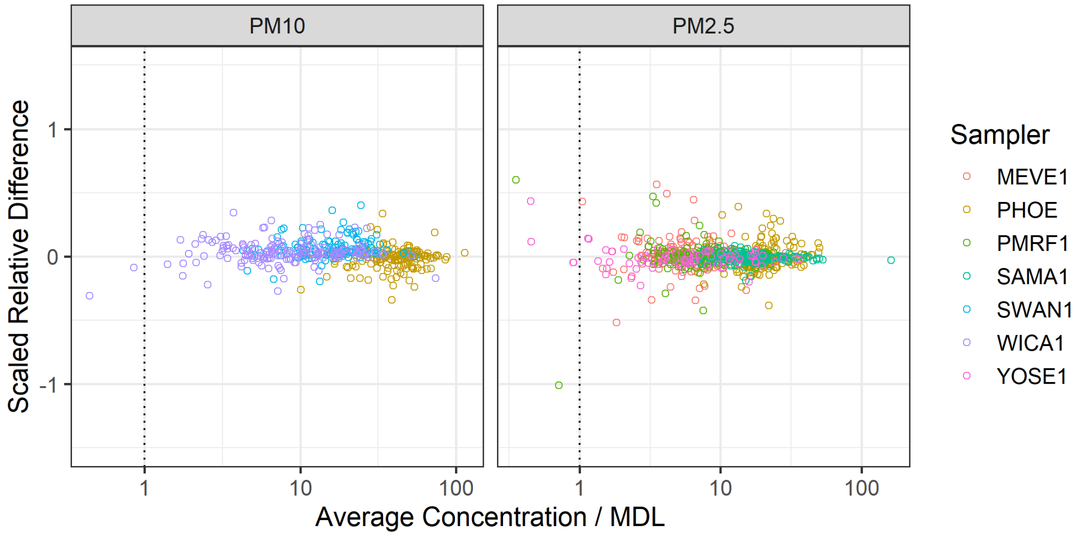


Figure 4-18: Scaled relative difference for ions measurements at sites with collocated modules across the IMPROVE network (2019 – June 2020). Dotted vertical lines indicate method detection limits.

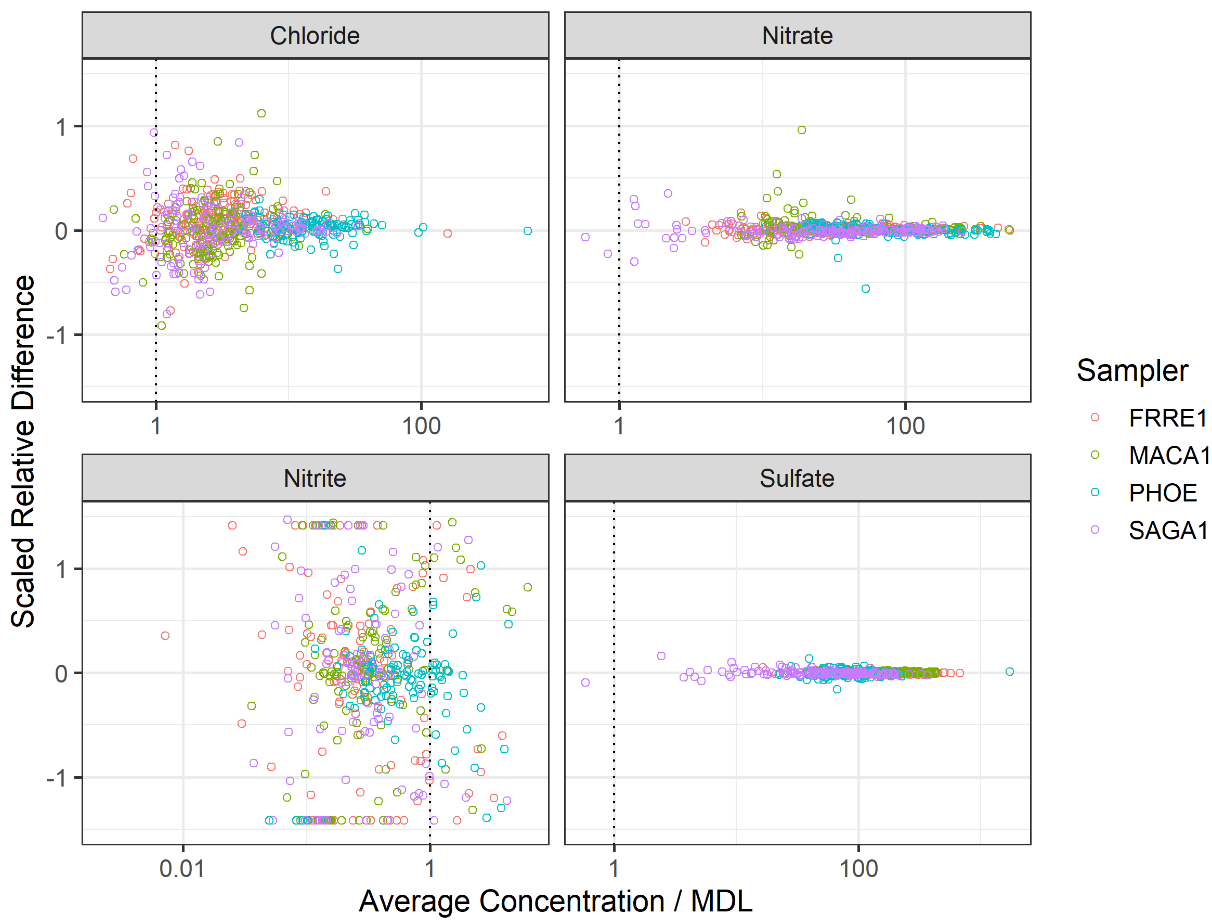


Figure 4-19: Scaled relative difference for carbon measurements at sites with collocated modules across the IMPROVE network (2019 – June 2020). Elemental carbon by reflectance (ECR) fractions are indicated as (1) through (3), organic carbon by reflectance (OCR) fractions are indicated as (1) through (4), R indicates measurement by reflectance, and T indicates measurement by transmittance. Dotted vertical lines indicate method detection limits.

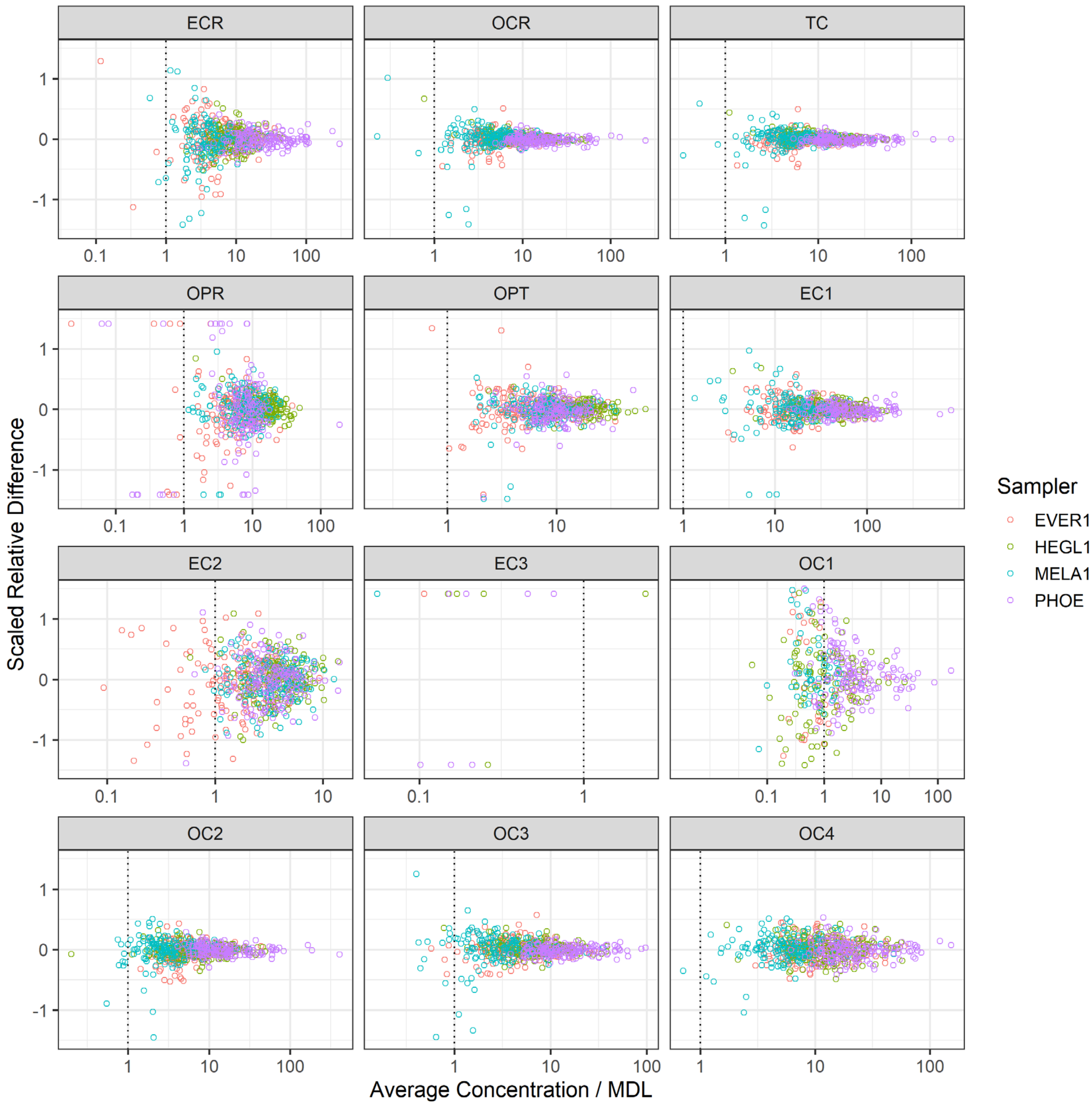
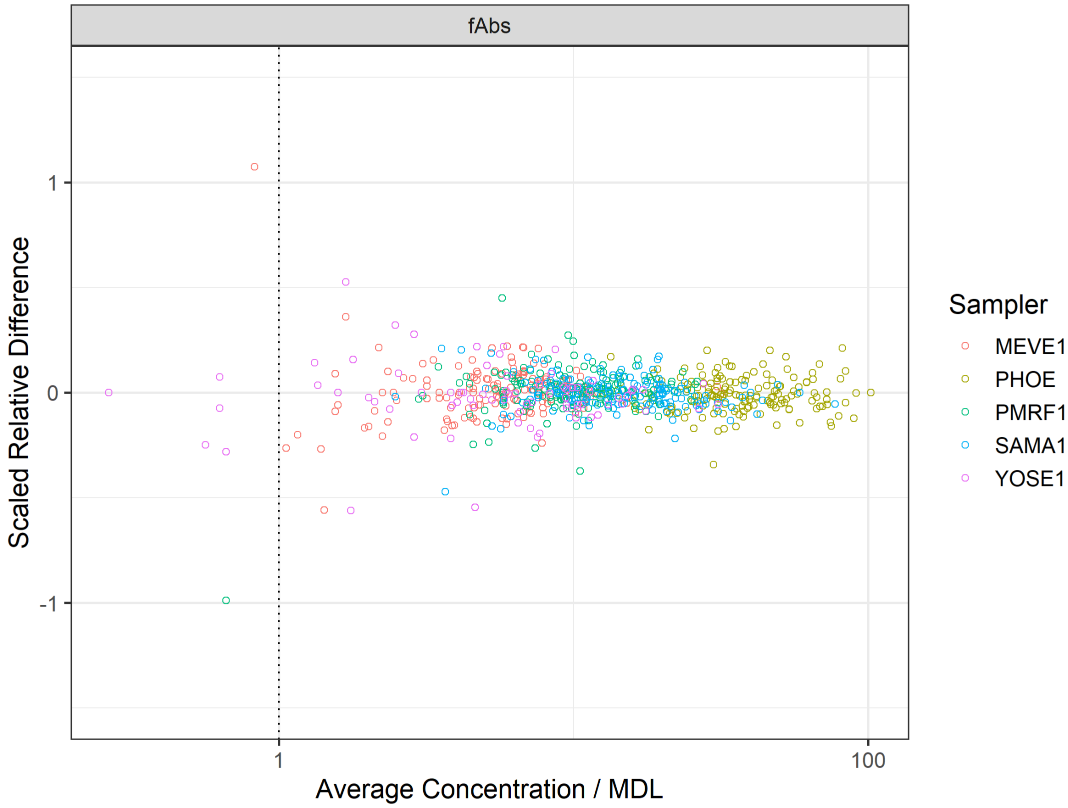


Figure 4-20: Scaled relative difference for optical absorption measurements at sites with collocated modules across the IMPROVE network (2019 – June 2020). Dotted vertical line indicates method detection limit.



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.

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

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 2019 IMPROVE data is calculated using data from collocated samples collected 2017-2018 and the fractional uncertainty for the 2020 IMPROVE data is calculated using data from collocated samples collected 2018-2019 (Table 4-2).

Table 4-2: Fractional uncertainty calculated from collocated samples collected 2013-2016 (reported for 2017 IMPROVE data), 2016-2017 (reported for 2018 IMPROVE data), 2017-2018 (reported for 2019 IMPROVE data), and 2018-2019 (reported for 2020 IMPROVE data).

	Fractional Uncertainty Reporting Period			
	2017	**2018**	**2019**	**2020**
	Source data sample period			
Species	**2013-2016**	**2016-2017**	**2017-2018**	**2018-2019**
Chloride	0.08	0.08	0.09	0.1
Nitrite	0.25	0.25	0.25	0.25
Nitrate	0.04	0.04	0.04	0.04
Sulfate	0.02	0.02	0.03	0.02
Organic Carbon (OCR)	0.09	0.08	0.07	0.07
Elemental Carbon (ECR)	0.14	0.14	0.13	0.13
Total Carbon	0.08	0.07	0.07	0.06
Organic Carbon (OC1)	0.26	0.23	0.24	0.21
Organic Carbon (OC2)	0.13	0.11	0.1	0.09
Organic Carbon (OC3)	0.13	0.13	0.11	0.09
Organic Carbon (OC4)	0.13	0.13	0.14	0.16
Organic Pyrolyzed (OPR)	0.16	0.20	0.21	0.2
Elemental Carbon (EC1)	0.10	0.11	0.11	0.11
Elemental Carbon (EC2)	0.18	0.19	0.21	0.22
Elemental Carbon (EC3)	0.25	0.25	0.25	0.25
Na	0.14	0.14	0.14	0.15
Mg	0.15	0.15	0.15	0.17
Al	0.08	0.08	0.09	0.1
Si	0.07	0.06	0.07	0.09
P	0.23	0.27	0.3	0.3
S	0.02	0.02	0.03	0.03
Cl	0.17	0.14	0.14	0.16
K	0.04	0.03	0.04	0.05
Ca	0.06	0.06	0.07	0.09
Ti	0.09	0.09	0.09	0.11
V	0.16	0.17	0.17	0.12
Cr	0.17	0.15	0.17	0.16
Mn	0.13	0.14	0.13	0.13
Fe	0.06	0.05	0.06	0.08
Ni	0.20	0.13	0.14	0.18
Cu	0.09	0.13	0.1	0.1

Zn	0.07	0.08	0.08	0.08
As	0.25	0.25	0.25	0.25
Se	0.25	0.25	0.25	0.25
Br	0.11	0.10	0.09	0.09
Rb	0.25	0.25	0.25	0.25
Sr	0.13	0.13	0.14	0.14
Zr	0.25	0.25	0.25	0.25
Pb	0.16	0.14	0.15	0.25
$PM_{2.5}$	0.03	0.04	0.04	0.04
PM_{10}	0.07	0.07	0.08	0.07
fAbs	0.06	0.06	0.05	0.06

4.2 Analytical QC Checks

4.2.1 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 4-21 through Figure 4-24). Transition to new lots occurs over a period of weeks; 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 4-21) and sulfate (Figure 4-23) 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 4-21). 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 4-21: Time series of chloride measured on nylon filter field blanks, January 1, 2011 through June 30, 2020. Red vertical lines indicate manufacturer lot transition.

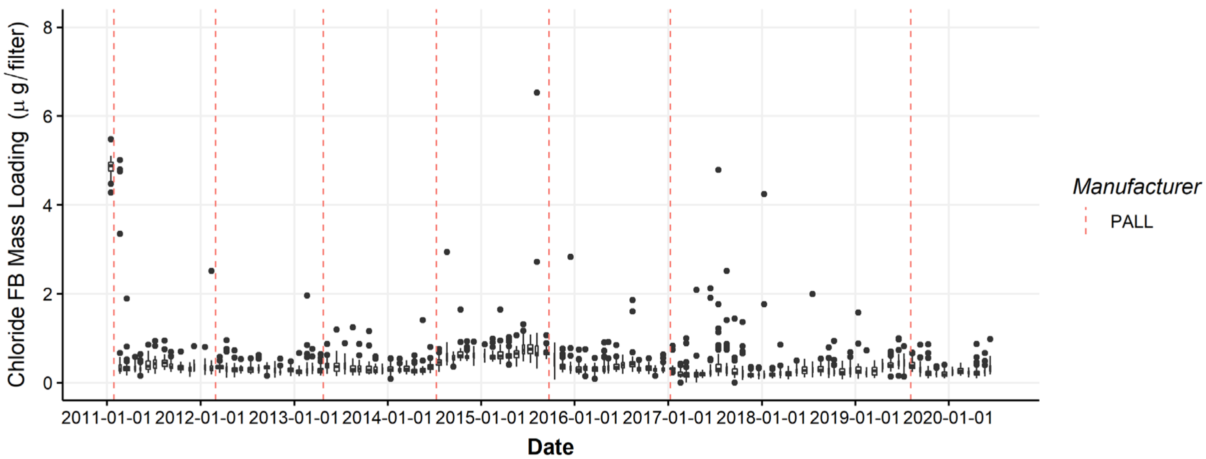


Figure 4-22: Time series of nitrate on nylon filter field blanks, January 1, 2011 through June 30, 2020. Red vertical lines indicate manufacturer lot transition.

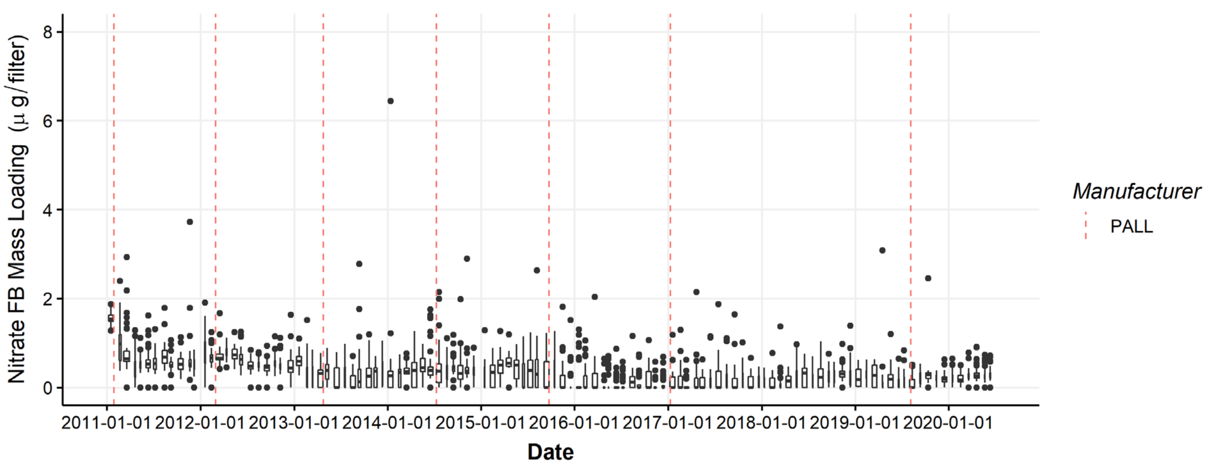


Figure 4-23: Time series of sulfate on nylon filter field blanks, January 1, 2011 through June 30, 2020. Red vertical lines indicate manufacturer lot transition.

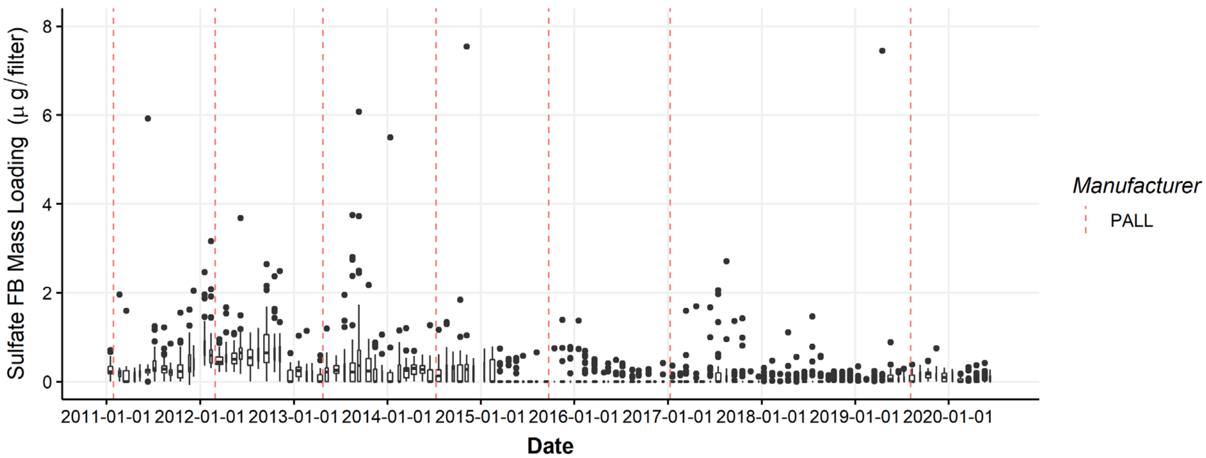
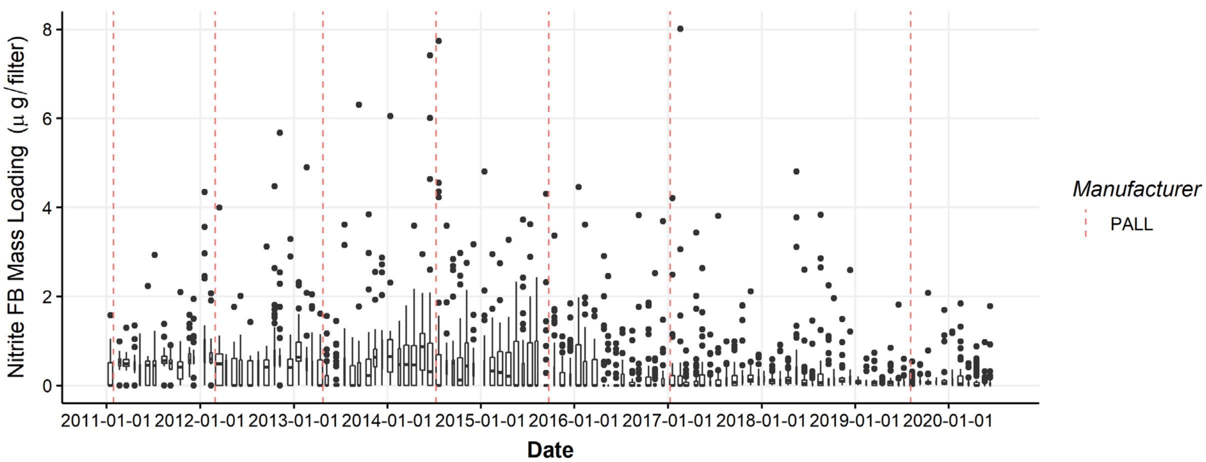


Figure 4-24: Time series of nitrite on nylon filter field blanks, January 1, 2011 through June 30, 2020. Red vertical lines indicate manufacturer lot transition.



Quartz filters are pre-fired by DRI. Quartz filter field blanks typically have low concentrations of elemental carbon by reflectance (ECR; Figure 4-25). 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 µg/filter (Figure 4-26).

Figure 4-25: Time series of elemental carbon by reflectance (ECR) on quartz filter field blanks, January 1, 2011 through June 30, 2020.

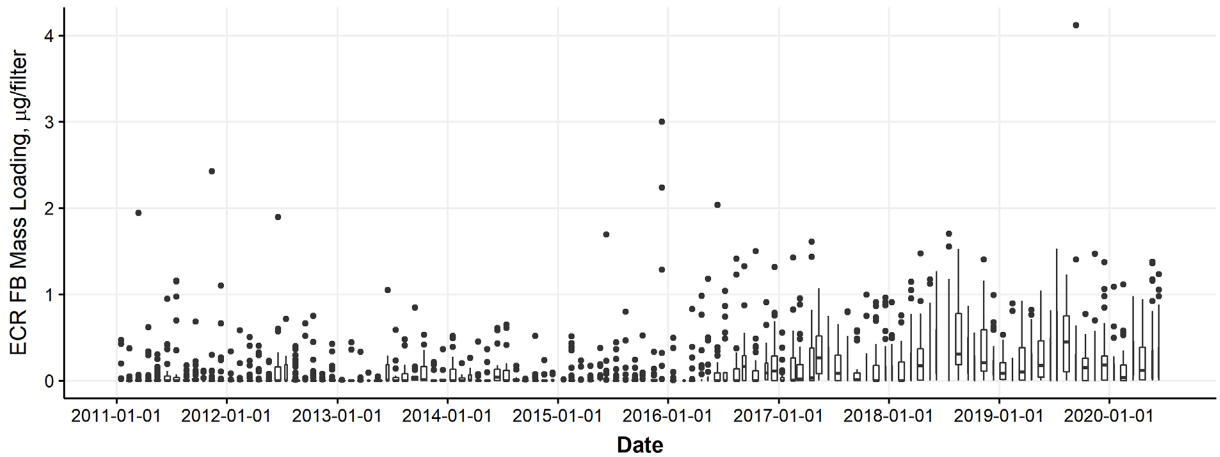
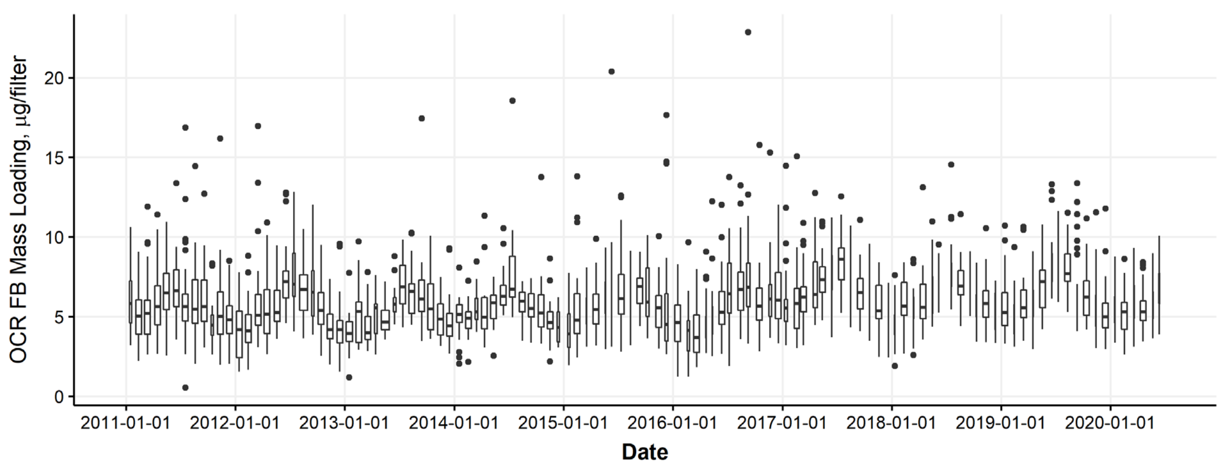


Figure 4-26: Time series of organic carbon by reflectance (OCR) on quartz filter field blanks, January 1, 2011 through June 30, 2020.



PTFE filter field blanks from the 1A module are analyzed by ED-XRF to monitor contamination and consistency in the data processing of elements. The field blank mass loadings of example elements, Al, Ca, K and S, are shown in Figure 4-27, Figure 4-28, Figure 4-29 and Figure 4-30. As expected, shifts occurred in October of 2018 in the field blank mass loadings for several elements (i.e., Al, As, Br, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Rb, Se, Si, Sr, V, Zr), in correspondence with the change in PTFE filter manufacturer from MTL to Pall. This filter manufacturer change coincided with changes in the XRF application documented in the previous report and in the processing code used to report the XRF measurements. That said, the field blank mass loadings for most elements were similar in the Pall and MTL filters, and more importantly, the standard deviations of the loadings were similar. Consistent levels of blank contamination are removed by blank subtraction on the sample filters.

Figure 4-27: Time series of aluminum (Al) on PTFE filter field blanks, January 1, 2011 through June 30, 2020. Blue vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Red vertical line indicates manufacturer transition to Measurement Technology Laboratories (MTL) as manufacturer.

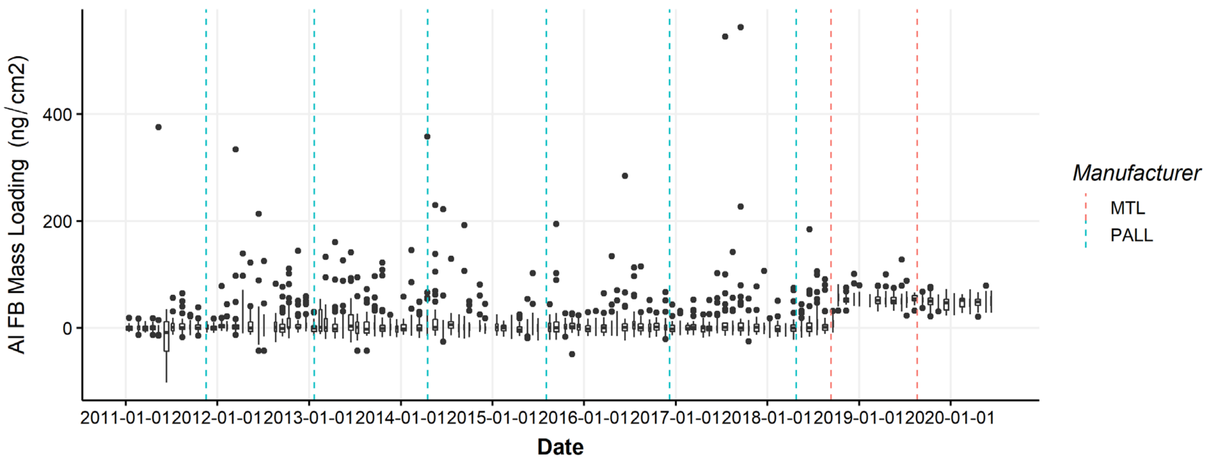


Figure 4-28: Time series of calcium (Ca) on PTFE filter field blanks, January 1, 2011 through June 30, 2020. Blue vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Red vertical line indicates manufacturer transition to Measurement Technology Laboratories (MTL) as manufacturer.

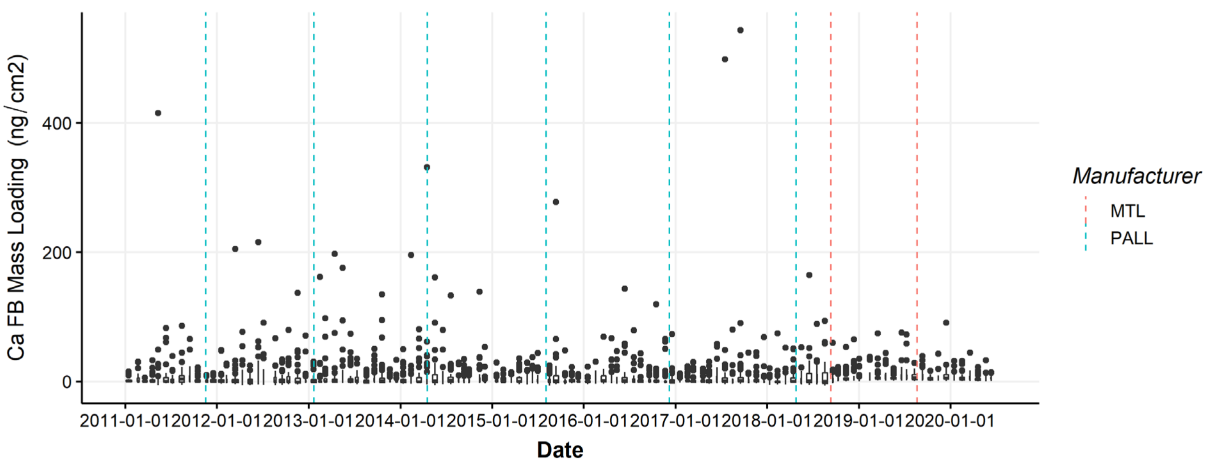


Figure 4-29: Time series of potassium (K) on PTFE filter field blanks, January 1, 2011 through June 30, 2020. Blue vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Red vertical line indicates manufacturer transition to Measurement Technology Laboratories (MTL) as manufacturer.

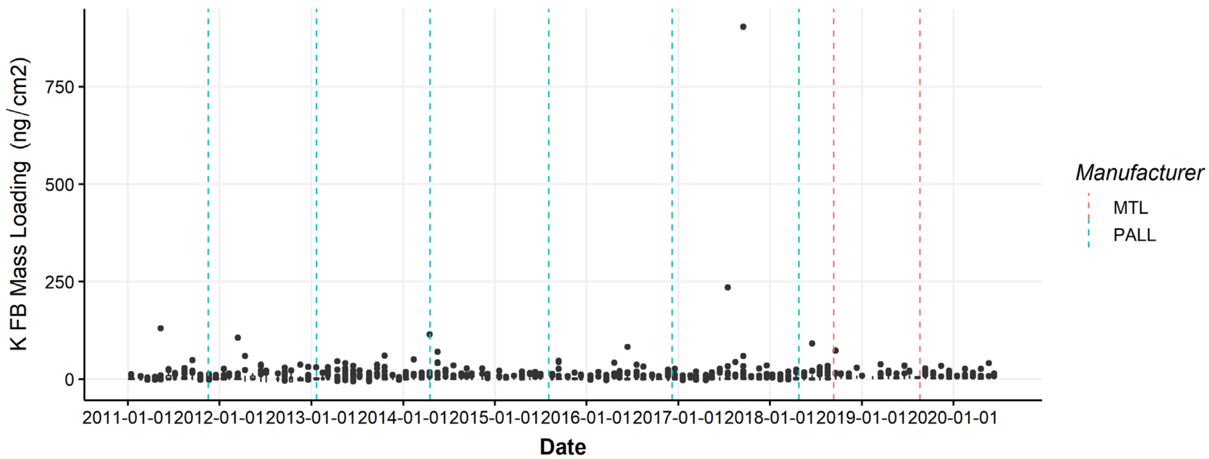


Figure 4-30: Time series of sulfur (S) on PTFE filter field blanks, January 1, 2011 through June 30, 2020. Blue vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Red vertical line indicates manufacturer transition to Measurement Technology Laboratories (MTL) as manufacturer.

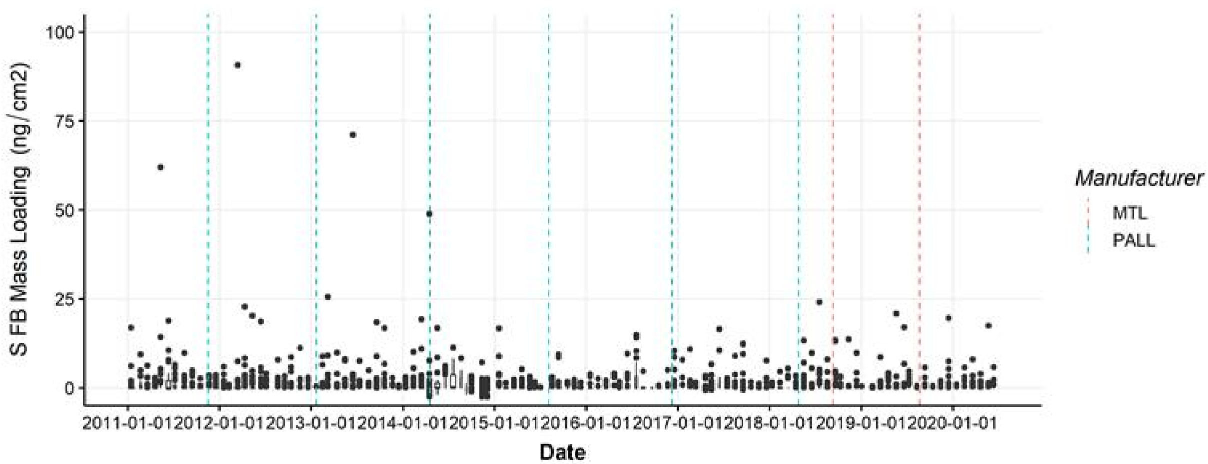
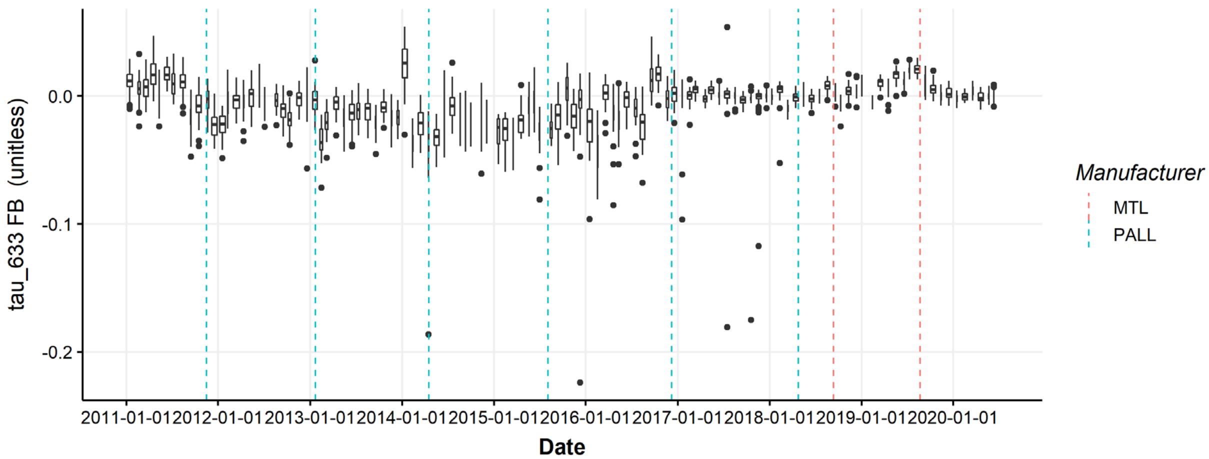


Figure 4-31 shows the Tau_633 measurements by HIPS on the PTFE filter field blanks from the 1A module. As mentioned in the previous IMPROVE Semiannual Quality Assurance Reports and documented in a UCD data advisory (http://vista.cira.colostate.edu/Improve/data-advisories/, posted 4/2019), in April 2018 the HIPS integrating sphere was changed from the legacy 2-inch Spectraflect-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. In response to the abovementioned changes, field blank Tau_633 data since January 2017 show much tighter distribution around 0 compared to previous years (Figure 4-33).

Figure 4-31: Time series of Tau_633 on PTFE filter field blanks, January 1, 2011 through June 30, 2020. Blue vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Red 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× 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 2018, 2019 and 2020 (January through June) data.

Species	2018		2019		2020 (January – June)	
	Average MDL (ng/m^3)	% Above MDL	Average MDL (ng/m^3)	% Above MDL	Average MDL (ng/m^3)	% Above MDL
Chloride	5.6	81	7.46	74	5.16	83
Nitrite	22.1	9	7.1	11	18.8	4
Nitrate	11.27	98	9.33	99	9.21	97
Sulfate	5.28	100	5.95	100	6.24	100
Organic Carbon (OCR)	74.47	97	112.16	94	72.29	94
Elemental Carbon (ECR)	23.5	90	19.7	90	21.37	88
Total Carbon	82.19	97	120.5	95	85.16	95
Organic Carbon (OC1)	27.23	34	33.12	28	24.97	24
Organic Carbon (OC2)	21.89	92	27.83	90	20.95	90
Organic Carbon (OC3)	36.4	94	45.28	90	33.65	91

Organic Carbon (OC4)	16.11	97	17.22	97	14.41	96
Organic Pyrolyzed (OPR)	18.07	94	20.1	94	11.72	92
Elemental Carbon (EC1)	11.08	98	11.53	98	5.76	97
Elemental Carbon (EC2)	15.55	87	17.7	88	15.19	86
Elemental Carbon (EC3)	4.57	0	4.59	0	2.65	1
Na	4.6	80	5.14	81	4.6	91
Mg	2.66	76	2.62	70	2.51	76
Al	3.23	92	1.74	92	1.56	94
Si	6.91	90	3.75	93	2.29	95
P	0.22	34	0.22	32	0.22	23
S	0.36	100	0.35	100	0.27	100
Cl	0.35	86	0.26	85	0.35	80
K	1.08	99	0.88	100	0.58	99
Ca	2.78	93	2.5	93	1.68	94
Ti	0.35	84	0.33	83	0.24	85
V	0.11	35	0.11	33	0.11	28
Cr	0.11	38	0.12	30	0.11	31
Mn	0.33	67	0.33	65	0.28	67
Fe	1.87	95	1.57	95	1.1	95
Ni	0.11	25	0.11	24	0.11	17
Cu	0.22	56	0.22	54	0.18	57
Zn	0.23	92	0.37	85	0.29	86
As	0.22	13	0.22	8	0.22	7
Se	0.22	28	0.22	24	0.2	25
Br	0.14	96	0.11	95	0.11	93
Rb	0.22	18	0.23	14	0.22	12
Sr	0.22	53	0.22	46	0.18	54
Zr	1.31	7	1.33	7	1.09	9
Pb	0.66	33	0.66	27	0.53	38
$PM_{2.5}$	308.56	98	301.38	99	300.31	97
PM_{10}	418.25	99	525.67	98	404.27	98
fAbs	0.33	86	0.18	97	0.1	97

5. Data Management and Reporting

5.1 Documentation

Current standard operations procedures (SOPs) are available at:

http://vista.cira.colostate.edu/Improve/ and

https://airquality.ucdavis.edu/improve-documentation

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

Deliverable	Upcoming Delivery Date
SOPs and TI documents	June 15, 2022
Quarterly Site Status Report	November 15, 2021 (2021 Q3) February 15, 2022 (2021 Q4)
Annual Quality Assurance Report (July through December 2020 data)	February 28, 2022

5.2 Data Deliveries

Summarized in Table 5-2 are dates of which data were delivered to FED and AQS databases for samples collected January 1, 2019 through June 30, 2020.

Data are 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 2019 data (January 2019 through December 2019) was redelivered to NPS – including a summary of changes made – on December 7, 2020, and subsequently made available on the FED and AQS databases.

Table 5-2: Summary of data deliveries, January 1, 2019 through June 30, 2020.

Data (Month Samples Collected)	FED/AQS Delivery Date
January 2019	December 6, 2019
February 2019	December 6, 2019
March 2019	March 4, 2020
April 2019	March 4, 2020
May 2019	April 15, 2020
June 2019	April 15, 2020
July 2019	June 5, 2020
August 2019	June 5, 2020
September 2019	June 29, 2020
October 2019	August 4, 2020
November 2019	August 4, 2020
December 2019	September 9, 2020
January 2020	September 9, 2020
February 2020	October 21, 2020
March 2020	December 17, 2020
April 2020	March 5, 2021
May 2020	April 19, 2021
June 2020	June 29, 2021

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, 2020.

Table 6-1: Summary of major repair items shipped to IMPROVE sites, 1/1/2019 through 6/30/2020.

Item	Quantity	Sites
Pump	227	ACAD1 (x2), ATLA1 (x3), BAND1, BOAP1 (x2), BOND1 (x5), BOWA1 (x7), BRIG1 (x2), BRIS1, CABA1 (x2), CABI1, CACR1 (x2), CANY1 (x4), CAPI1 (x2), CAPI1, CEBL1, CHAS1, CHIR1 (x4), COHU1 (x3), DENA1 (x2), DETR1 (x2), DINO1 (x7), EVER1 (x4), FCPC1 (x2), FOPE1, FRES1 (x4), GICL1, GRGU1, GRRI1, GRSA1 (x5), GRSM1, GUMO1, HECA1 (x3), HOOV1, ISLE1 (x4), JARB1, JARI1, JOSH1, LASU2 (x2), LOND1 (x7), LOST1, LTCC1, MEAD1 (x3), MELA1, MEVE1 (x5), MING1 (x2), MOMO1 (x2), MOOS1 (x2), MOZI1, NEBR1 (x3), NEBR1 (x2), NEBR1, NOAB1, NOCH1 (x2), NOGA1 (x6), OKEF1, ORPI1, PEFO1, PENO1, PHOE1 (x4), PINN1 (x4), PITT1, PORE1 (x2), PRIS1 (x4), PUSO1 (x2), QUCI1, RAFA1 (x4), REDW1 (x3), ROMO1 (x2), SACR1 (x3), SAGO1 (x2), SAGU1 (x2), SAGU1, SAMA1, SAWE1 (x4), SAWT1 (x3), SENE1, SEQU1 (x4), SHMI1, SIPS1, STIL1 (x5), SULA1 (x2), SWAN1, SYCA2 (x5), TALL1, THBA1, THRO1 (x2), TONT1 (x2), TOOL1 (x6), ULBE1, UPBU1 (x2), VIIS1 (x5), VILA1 (x4), WEMI1, WHIT1, WICA1, WIMO1 (x2), YELL2 (x2), ZICA1 (x3)
Electronic boxes	133	AGTI1, ATLA1 (x2), BAND1, BIBE1 (x3), BOAP1 (x2), BRCA1, BRIG1 (x2), BRIS1 (x2), CABI1 (x2), CACO1 (x2), CACR1 (x3), CANY1, CHAS1, CHIR1, COHU, FCPC1, FLAT1 (x4), FRES1 (x5), GAMO1 (x7), GICL1 (x5), GLAC1, GRBA1, GRRI1, GRSA1, GUMO1 (x2), HACR1, HOOV1, LABE1 (x2), LASU2 (x6), LAVO1, LTCC1, MAKA2, MAVI1, MEVE1 (x2), MING1 (x2), MOOS1 (x2), MOZI1, NEBR1, NOAB1 (x5), NOGA1, OKEF1 (x2), OLYM1, OWVL1, PHOE1, PORE1 (x3), ROMO1 (x2), SACR1 (x3), SAGU1, SAPE1 (x2), SAWE1 (x2), SHMI1, SHRO1, SOGP1, STIL1 (x3), SULA1, SYCA2, THBA1, TONT1 (x2), TRIN1, ULBE1 (x2), VILA1 (x10), VOYA2 (x2), WHIT1 (x4), WHPA1 (x2)
Controller	36	AGTI1, BIBE1 (x2), BOLA1, BRIS1, DETR1, EVER1, FLAT1, FRES1 (x4), GAMO1 (x2), GICL1 (x2), GRBA1 (x2), JOSH1, LAVO1, MOOS1, NOAB1, PHOE1, PORE1, RAFA1, ROMO1, SHRO1, SOGP1, STIL1, TALL1, THRO1, TOOL1, VILA1, WHPA1 (x2), YELL2 (x1)
Networking Device	31	BOLA1, BRIS1, CORI1, CRLA1, FRES1, GAMO1, GRBA1, GRBA1, HEGL1, ISLE1, MONT1, NOCH1, ORPI1, PITT1, PORE1, PUSO1, QUCI1 (x2), RAFA1, SAGA1, SAWE1, SENE1, SIME1 (x2), STAR1, THRO1, WHPA1, WHRI1, WIMO1 (x3)

Controller Card	18	HOOV1, GAMO1, CRLA1, STIL1 (X2), NOAB1, NOCA1, UPBU1, TOOL1 (x2), PRIS1, GRSM1, WHIT1, LOND1, DETR1, WHPA1, WHRI1, YELL2
Relay Box	7	SHEN1, BRIS1, EVER1, FLTO1, THBA1, DETR1, DETR1
Module Cable	6	GRSM1PHOE5, NOGA1, PORE1, BRIS1, ROMO1
Temp Probe	4	RAFA1, BOLA1, WHPA1, LASU2
Module	1	LASU2
Motor Assembly	1	PASA1

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, 2020.

Table 6-2: CSU CIRA field audits 1/1/2019 through 6/30/2020.

March 2019	April 2019	May 2019	June 2019	July & August 2019	Sept. 2019	October 2019	Dec. 2019	April 2020	May & June 2020
LASU2	CHIR1	HEGL1	SAGU1	ROMO1	FLTO1	OLYM1	GRSA1	LASU2	PEFO1
VILA1	DOME1	MING1	SAWE1	NOGA1	MOZI1	KALM1	SHMI1	MEAD1	GRCA2
	FRES1	PHOE1	WHRI1			FLAT1	LASU2		SYCA2
	GRCAS1	PHOE5				NOAB1	VILA1		
	HOOV1	LASU2				GLAC1			
	KAIS1	VILA1				CABI1			
	MEAD1					PASA1			
	NOGA1					NOCA1			
	ORPI1					PUSO1			
	OWVL1					SNPA1			
	PINN1					MAKA2			
	SAGA1					REDW1			
	SAGU1					PORE1			
	RAFA1					LTCC1			
	SAWE1					GRBA1			
	SEQU1					DINO1			
	MEVE1								
	SHMI1								

6.3 Summary of Site Visits

The UCD Field Group visits IMPROVE network sites biennially to provide routine maintenance and cleaning. Due to COVID-19, maintenance on IMPROVE sites in 2020 was delayed to the second half of the year. 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, 2020.

UCD has developed new sampler controllers (V4 Controller) and is currently updating new Ebox firmware to version 1.3. Between January 1, 2019 and June 30, 2020 UCD installed 76 V4 controllers (Table 6-3). As of June 30, 2020, V4 controllers had been installed at all IMPROVE sites across the network in the US and Canada. Prior to new controller installation, availability of internet access is evaluated at each site, and in cases where it is not available mobile or satellite internet connections are investigated. As of June 30, 2020, internet connections to all IMPROVE sites had been established except for SIME1 in Alaska and BYIS1 in South Korea. Sites with V4 controllers and internet connections are monitored in real time by UCD technicians, allowing faster follow up and recovery in cases where samples are being lost or equipment has failed.

Table 6-3: UCD field visits to IMPROVE sites, 1/1/2019 through 6/30/2020.

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.	
GUMO1	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.	
QUCI1	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.	
GRBA1	7/9/2019		
ZICA1	7/10/2019	V4 Controller Deployed	
BRCA1	7/11/2019	V4 Controller Deployed	
CANY1	7/12/2019	V4 Controller Deployed	
CAPI1	7/14/2019	V4 Controller Deployed	
FLTO1	7/15/2019	V4 Controller Deployed	
WHRI1	7/16/2019	V4 Controller Deployed	
ROMO2	7/17/2019		
MOZI1	7/18/2019	V4 Controller Deployed	
DINO1	7/19/2019	V4 Controller Deployed	
KPBO1	7/24/2019	V4 Controller Deployed	Cut down vegetation around sampler.
TRCR1	7/25/2019	V4 Controller Deployed	
SIME1	7/25/2019	V4 Controller Deployed	
DENA1	7/26/2019	Installed a test pump for future development	
TOOL1	7/28/2019	Rebuilt sampler stand enclosure.	
NEBR1	8/17/2019	V4 Controller Deployed	
BADL1	8/18/2019	V4 Controller Deployed	
WICA1	8/19/2019	V4 Controller Deployed	
THBA1	8/20/2019	V4 Controller Deployed	
NOCH1	8/21/2019	V4 Controller Deployed	
THRO1	8/22/2019		
MELA1	8/23/2019	V4 Controller Deployed	
FOPE1	8/24/2019	V4 Controller Deployed	
LOST1	8/25/2019	V4 Controller Deployed	
STAR1	9/17/2019	V4 Controller Deployed	
HECA1	9/18/2019	V4 Controller Deployed	
SULA1	9/20/2019	V4 Controller Deployed	
SAWT1	9/21/2019	V4 Controller Deployed Rebuilt pump enclosure	
CRMO1	9/22/2019	V4 Controller Deployed	
JARB1	9/23/2019	V4 Controller Deployed	
SOGP1	10/1/2019	Site install.	Install shorter stacks.

HACR1	10/21/2019	V4 Controller Deployed	
HAVO1	10/23/2019	V4 Controller Deployed Relocated site within compound.	
THSI1	11/6/2019	Rebuilt sampler roof	
LTCC1	12/20/2019		
RENO1	1/22/2020	V4 Controller Deployed	
RENO2	1/22/2020	V4 Controller Deployed	
RENO3	1/22/2020	V4 Controller Deployed	
TRIN1	6/5/2020	Updated Ebox software	
PORE1	6/13/2020	Updated Ebox software	
HOOV1	6/24/2020	Updated Ebox software	
OWVL1	6/25/2020	Updated Ebox software	
DOME1	6/26/2020	Updated Ebox software	

7. References

Spada, N.J., Cheng, X., White, W.H., Hyslop, N.P. (2018). Decreasing Vanadium Footprint of Bunker Fuel Emissions. Environmental Science & Technology, 52 (20): 11528-11534.