Interagency Monitoring of Protected Visual Environments (IMPROVE)

Annual Quality Assurance Report

Sample Dates:

January 1, 2021 through December 31, 2021

Prepared for:
National Park Service
Denver, CO 80225

NPS Contract No. 140P2121D0004

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December 12th, 2023

UCDAVIS
AIR QUALITY RESEARCH CENTER

TABLE OF CONTENTS

1. INTRODUCTION

The University of California, Davis (UCD) Air Quality Research Center (AQRC) reviews quality assurance (QA) activities annually 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 resource for ongoing UCD QA efforts.

The graphics shown in this report are a small subset of the many QA evaluations 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 houses 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, 2021 through December 31, 2021.

2. SUMMARY OF LABORATORY AND DATA QUALITY ISSUES

2.1 AQRC Lab and Sample Handling

In the previous 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. The following details impacts from the move that carryover into this reporting period.

2.1.1 Gravimetric Lab Move

A second, new MTL weighing system including a new ultra-balance was ordered and installed in 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. 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.

All samples from this reporting period were weighed on the MTL weighing systems after they were installed at Drew Ave. While two weighing chambers are in use, each network filter's pre- and post-sampling gravimetric measurement is recorded on the same balance. This protocol starts with samplings dates in late February 2021.

After data collection and investigation, it was determined that the weighing chambers cannot sufficiently control the relative humidity (RH) when ambient exceeds 65%. On 08/02/2022, modifications to the gravimetric laboratory were made to enclose the two weighing chambers, isolating them from the rest of the laboratory's HVAC system. A dehumidifier is placed within the enclosure to reduce the effects of occasional high RH experienced throughout the rest of the laboratory. This also allows for a more predictable ambient environment for the weighing chambers. RH and temperatures both inside and outside of the enclosure are recorded at 5-minute intervals and are monitored with daily QC.

2.2 X-ray Fluorescence Laboratory

2.2.1 X-ray Intensity Loss on XRF-5

In November 2021, annual preventative maintenance and calibration were performed on XRF-5. As part of this preventative maintenance the CaF2 target was replaced. After replacement the instrument was plagued by vacuum leaks and low X-ray intensity which delayed the calibration. After several attempts, the manufacturer service technician was able to repair the vacuum leaks and corrected the low intensity by repositioning the CaF2 target. Recalibration was finally completed in early February 2022. No IMPROVE samples were being analyzed on this instrument during this incident. All QC checks were passed after the calibration was completed and XRF-5 resumed IMPROVE sample analysis on February 12, 2022.

Data Impact: None.

2.2.2 X-ray Intensity Loss on XRF-2

On April 6, 2022, XRF-2 underwent service by the manufacturer on the sample chamber and cap. Following this service visit there was a general loss of X-ray intensity for the CaF2 target under which Na – Cl are measured. The intensity drop was less than 5% and was not noticed until the monthly SRM QC sample was measured on April 21, 2022. Because the aluminum and potassium values for this SRM were already very near the lower acceptance limit, the slight drop in X-ray intensities cause the concentrations of these elements to drop below acceptable levels and the QC check failed. Analysis was immediately stopped on the instrument and the manufacturer returned to repair the CaF2 target on May 2, 2022. Sample analysis resumed on May 6, 2022 after QC tests confirmed the instrument was operating within specifications for all elements. Additionally, the SRM that failed the QC because concentrations were near the lower limit was replaced with a new SRM which would be used in subsequent months.

Results for IMPROVE and CSN samples analyzed on XRF-2 from the time the intensity drop occurred after the technician visit on April 6, 2022 and the CaF2 target repair on May 2, 2022 were in question. To assess the impact on the sample results, 5% of samples analyzed between April 6, 2022 and April 21, 2022 when analysis was stopped, were reanalyzed on different XRF analyzers to look for any bias caused by XRF-2's intensity drop. The bias reported from these reanalyses was within expected uncertainty and the results were deemed acceptable. See investigation report IR-0006 for further details.

Data Impact: None.

2.2.3 Deviations to Procedures

There was one deviation to XRF procedures active during this analysis period. DV-0005, was opened on February 25, 2022 and closed on September 9, 2022. This deviation dealt with the temporary stop to replicate analysis for QC, which according to UCD IMPROVE TI 301C, needed to be run on between 2% and 5% of all samples analyzed. The replicate analysis was stopped to catch up with analysis of routine samples due to delays related to COVID-19 restrictions, the laboratory move in late 2020, and various XRF instrument maintenance delays. Once sample analysis completion times returned to a preset length of time from the filter sampling date, the replicate analysis was resumed and the deviation was closed on September 9, 2022. See DV-0005 for more details.

Data Impact: None.

2.2.4 Aluminum and Chlorine Interference

During routine validation of the January and February 2021 sample data, some anomalously high aluminum results were found in some samples. When the XRF lab investigated these findings, it was determined that an interference of the aluminum K-alpha line by the chlorine K-alpha-escape peak was not being properly corrected by the calibration of at least one XRF instrument. Because of the lack of reference materials available with suitable chlorine and aluminum concentrations to test this interference, the problem cannot be positively identified in any particular XRF instrument or calibration. However, some general guidelines for identifying results where the aluminum concentration may be misreported due to this interference can be provided. A data advisory is being drafted on this issue and is still being investigated at this time.

2.3 Gravimetric Laboratory

2.3.1 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 (AH1). A second MTL AH500E weighing chamber was purchased and installed directly at the new Drew Ave. laboratory (AH2). At that time, a new XPR6UD5 was installed in AH2, and another XPR6UD5 replaced the balance in AH1. Due to a filter supply shortage, 378 filters had pre-sampling and post-sampling measurements recorded manually. All other measurements were recorded in the AH500E climate-controlled automated weighing systems.

2.3.2 Mass Gain on MTL Filter Field Blanks

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 2-2) and 4D module (coarse particles, PM_{10}; Figure 2-3) are gravimetrically analyzed to monitor contamination levels and balance stability. As seen in Figure 2-2 and Figure 2-3, there is a step increase in $PM_{2.5}$ and PM_{10} measured on field blanks corresponding with the transition from Pall to MTL, indicating that the filters gain mass between pre- and post-weight measurements. In later 2020, including some 2021 samples, the PTFE filter manufacturer was transitioned back from MTL to Pall for a few months due to filter supply shortage, and the $PM_{2.5}$ and PM_{10} mass from field blanks were correspondingly returned to values similar to those before October 2018. 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 our quality specifications.

Figure 2-2: Time series of $PM_{2.5}$ on PTFE filter field blanks, January 1, 2016 through December 31, 2021. 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.

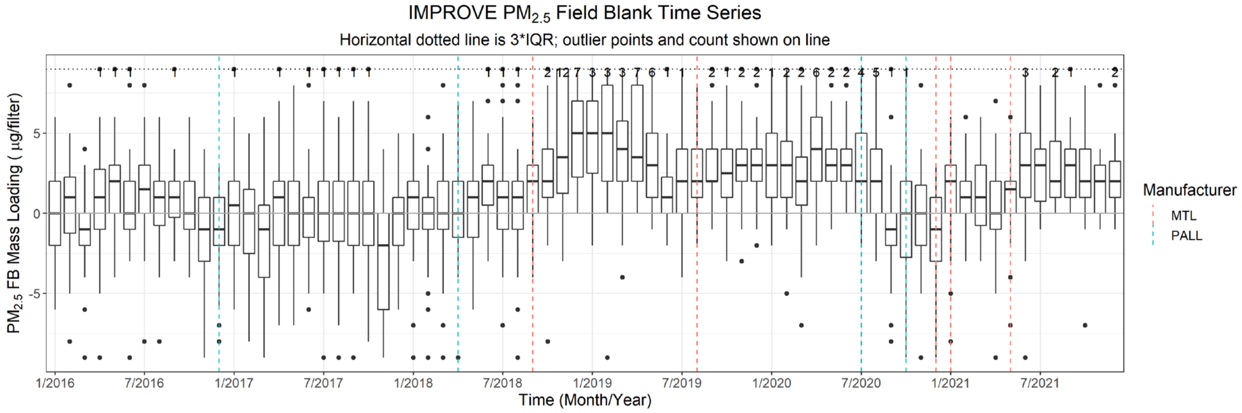
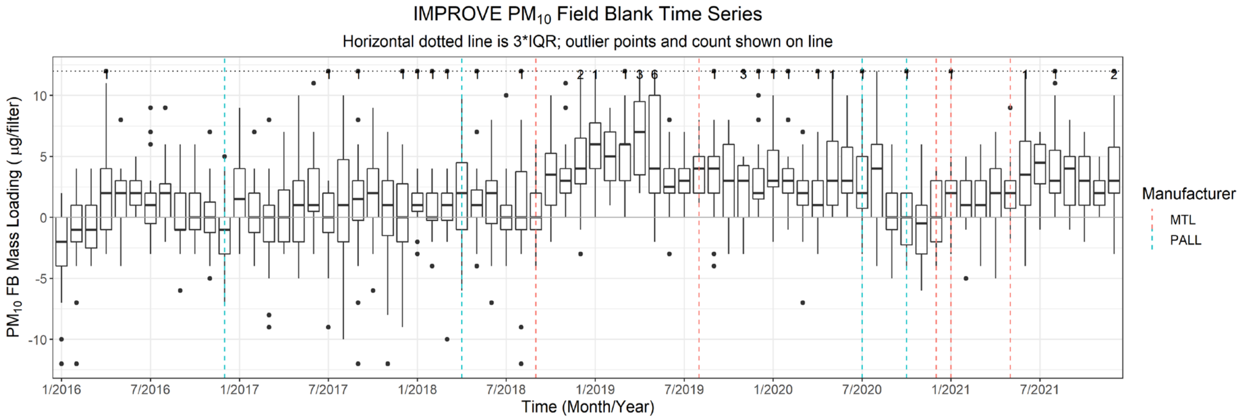


Figure 2-3: Time series of PM_{10} on PTFE filter field blanks, January 1, 2016 through December 31, 2021. Blue vertical lines indicate manufacturer lot transition, where Pall Corporation is the manufacturer. Red vertical line indicates manufacturer transition to Measurement Technology Laboratories (MTL) as manufacturer.



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

2.4.1 HIPS Rebuild to Address Stability

In July 2021, the HIPS instrument was moved to allow for a plumbing repair above the unit. When the unit was returned to its original location, the calibration results began to drift towards the out-of-spec condition. Once that happened, an investigation into why was opened, IR-0001. It was determined that the support base had come loose. Once the base was secured, the calibration results stabilized. A new, more-robust stand was developed and implemented in June 2022. The new mounting system uses a thick aluminum optical breadboard as a solid base and decouples the long laser tube from the system by implementing a fiber optic cable and fiber collimator. This new mounting and laser coupling system has proven to be a more robust design with no further recalibrations due to calibration drift having occurred since its implementation.

2.4.2 HIPS Fiber Collimator Replacement

In August 2022, while reviewing plots for the IMPROVE Steering Committee meeting that year, a discontinuity was discovered in a plot of fabs/ECR. An investigation, IR-0009, was opened to determine the root cause for this discontinuity. Multiple theories were tested and the investigation is still open, but ultimately it was decided that there was no evidence in the data that the HIPS fabs results were erroneous. However, during this investigation, it was apparent that the optical properties of the 90-degree reflective collimator originally fitted to couple the new laser fiber optic cable to the integrating sphere did not match the optical properties of the HIPS system in the previous arrangement - when the laser was directly attached to the integrating sphere.

While there was no indication that the fabs results were inaccurate using this reflective collimator, an alternative was researched as there was more uncertainty in the QC sample results with this collimator. A new focusing lens collimator was purchased and installed in the system to replace the reflective collimator. This allowed the laser spot size on the sample to be adjusted to more closely match the spot size when the laser was directly attached. Testing was performed which confirmed that the new focusing lens collimator more closely matched the optical characteristics of the directly attached laser configuration and it also reduced the additional noise introduced by the reflective collimator. Filters sampled from August 2021 to December 2021 were reanalyzed with the new focusing lens collimator.

2.5 Data Quality

2.5.1 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 2021 there were 17 sites that failed the RHR completeness criteria, as summarized in Table 2-1. Site shutdowns due to COVID-19 impacts continued at some sites in 2021, contributing to a higher number of lost sites. 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 2021.

Site Name	Site Code	Completeness by Quarter (%)				Consecutive Terminal Samples	Annual Completeness (%)
		1st Q	2nd Q	3rd Q	4th Q		
Agua Tibia, CA	AGTI1	7	22	12	10	7	58
Breton National Wildlife Refuge, LA	BRIS1	3	4	12	31	43	59
Cape Cod Natl Seashore, MA	CACO1	11	1	4	25	26	66
Carlsbad Caverns, NM	CAVE1	25	7	6	6	23	64
Egbert Ontario, Ontario	EGBE1	0	3	23	11	19	70
Fort Peck, MT	FOPE1	13	2	2	17	12	72
Hells Canyon, OR	HECA1	5	15	7	7	7	72
Ike's Backbone, AZ	IKBA1	30	24	30	31	71	6
Lava Beds, CA	LABE1	12	1	3	13	11	76
Lake Sugema, IA	LASU2	18	2	3	3	6	79
Northern Cheyenne, MT	NOCH1	0	0	24	31	55	55
Nogales, AZ	NOGA1	25	2	4	3	25	72
San Gabriel, CA	SAGA1	17	14	20	13	12	48
Sequoia National Park, CA	SEQU1	0	0	10	13	14	81
Sipsey, AL	SIPS1	5	8	15	5	9	73
Virgin Islands, Virgin Islands	VIIS1	8	10	6	10	5	72
Wichita Mountain, OK	WIMO1	9	5	8	9	5	75

2.5.2 Data Processing

To handle periods with fewer field blanks or more varied filter lots, the statistics calculation window for field blank has been extended from two months to three months. The database and processing code have been updated to include flagging for specific analyses and individual parameters. This enables preservation of valid data in cases where a filter gets damaged between two different analyses. It also supports invalidating of specific parameters when an analysis is otherwise valid, such as in the case of Zn contamination from the XRF sampling arm.

3. LABORATORY QUALITY CONTROL SUMMARIES

3.1 X-ray Fluorescence Laboratory

The UCD XRF Laboratory received and analyzed PTFE filter samples collected January 1, 2021 through December 31, 2021. 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 October 18, 2021 through October 11, 2022 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.

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**
2021	January	2021-11-06 - 2021-11-14	2021-10-18 - 2022-02-10	2021-10-18 - 2021-11-17	2021-11-07 - 2021-11-16	2021-10-18 - 2021-11-17
2021	February	2021-12-15 - 2022-01-01	2021-12-15 - 2022-02-10	2021-10-31 - 2022-01-03	2021-12-15 - 2022-01-28	2021-11-17 - 2021-11-18
2021	March	2021-12-31 - 2022-02-22	2022-02-06 - 2022-02-24	2022-02-05 - 2022-02-24	2021-12-30 - 2022-02-22	2022-02-12 - 2022-02-24
2021	April	NA	2022-02-24 - 2022-03-13	2022-02-23 - 2022-03-17	2022-01-01 - 2022-01-01	2022-02-23 - 2022-03-17
2021	May	NA	2022-03-17 - 2022-04-11	2022-03-17 - 2022-05-05	NA	2022-03-17 - 2022-04-09
2021	June	NA	2022-04-09 - 2022-04-20	2022-03-18 - 2022-05-25	2022-04-25 - 2022-05-01	2022-04-09 - 2022-05-02
2021	July	2022-05-21 - 2022-06-11	2022-05-06 - 2022-06-11	2022-05-02 - 2022-05-26	2022-05-23 - 2022-06-11	2022-05-21 - 2022-06-11
2021	August	2022-06-11 - 2022-06-26	2022-06-11 - 2022-06-25	NA	2022-06-11 - 2022-06-26	2022-06-11 - 2022-06-26
2021	September	NA	2022-06-25 - 2022-07-13	2022-06-24 - 2022-07-13	NA	2022-06-26 - 2022-07-12
2021	October	NA	2022-07-13 - 2022-08-05	2022-07-13 - 2022-09-08	NA	2022-07-22 - 2022-08-06
2021	November	NA	2022-08-05 - 2022-08-24	2022-08-06 - 2022-08-30	NA	2022-08-17 - 2022-08-29
2021	December	2022-09-14 - 2022-09-21	2022-08-29 - 2022-09-21	2022-08-30 - 2022-09-21	2022-09-13 - 2022-10-11	2022-09-14 - 2022-09-21
2021	All	2021-11-06 - 2022-09-21	2021-10-18 - 2022-09-21	2021-10-18 - 2022-09-21	2021-11-07 - 2022-10-11	2021-10-18 - 2022-09-21

3.1.1 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.

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.

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	Within acceptance limits 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	Within acceptance limits 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	

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.

3.1.2 Laboratory QC Summary

QC tests conducted over the course of this reporting period showed good overall control of the instruments and process. All QC checks passed or were investigated and promptly corrected with no impact to data quality. 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.

The monthly SRM QC check failed acceptance for aluminum and potassium in June 2022. This failure was associated with the SRM currently used for monthly QC, serial number 1720. No other QC samples showed issues with aluminum or potassium at that time. So, a second SRM, serial number 1617 was analyzed in June 2022 with passing results. The previous SRM, serial number 1720, was retired from use as a monthly QC check and the second SRM, serial number 1617, was used in all subsequent monthly QC checks. See section 3.1.6 for details.

There were no other QC check failures to report for this reporting period.

3.1.3 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.

3.1.4 Daily QC Review

At least once daily, when analyzing samples, a PTFE laboratory blank and a UCD produced ME-RM are analyzed. The daily blank and daily ME-RM results are compared to acceptance limits, which are described in SOP 301. If the mass loading exceeds the limit for more than two consecutive days, the blank or ME-RM is cleaned and/or replaced to distinguish between contamination on the QC filter and instrument contamination or issues. 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 QC filter. Whenever an instrumental problem is suspected, all analysis is stopped and all samples analyzed on the instrument since the last passing QC tests are reanalyzed on another instrument.

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

EDXRF Instrument	Calibration Date	Reason for Calibration	Range of Sample Dates Analyzed
XRF-2	2020-11-06	Annual calibration	2021-01-01 – 2021-01-31
XRF-1	2020-11-25	Annual calibration	2021-01-01 – 2021-01-31
XRF-4	2020-11-25	Annual calibration	2021-01-07 – 2021-01-31
XRF-5	2021-06-16	Calibration for new X-ray tube/generator and new CaF2 target	2021-01-01 – 2021-02-15
XRF-3	2021-07-21	Calibration after detector repair and new X-ray tube/generator	2021-01-01 – 2021-02-21
XRF-1	2021-11-24	Annual calibration	2021-02-03 – 2021-03-22
XRF-4	2021-11-24	Annual calibration	2021-02-03 – 2021-06-30
XRF-2	2021-11-26	Annual calibration	2021-01-01 – 2021-12-30
XRF-3	2021-12-02	Annual calibration	2021-02-01 – 2021-07-30
XRF-5	2022-02-11	Annual calibration (delayed due to repairs)	2021-03-02 – 2021-12-30
XRF-1	2022-02-17	Calibration for new X-ray tube/generator	2021-03-02 – 2021-12-30
XRF-3	2022-06-23	Calibration for new X-ray tube/generator	2021-09-01 – 2021-12-30
XRF-4	NA	11/24/2021 calibration corrected for Al/Cl interference	2021-07-03 – 2021-12-30

3.1.4.1 Daily Blank QC

Daily QC blank results during this analysis period showed no QC failures.

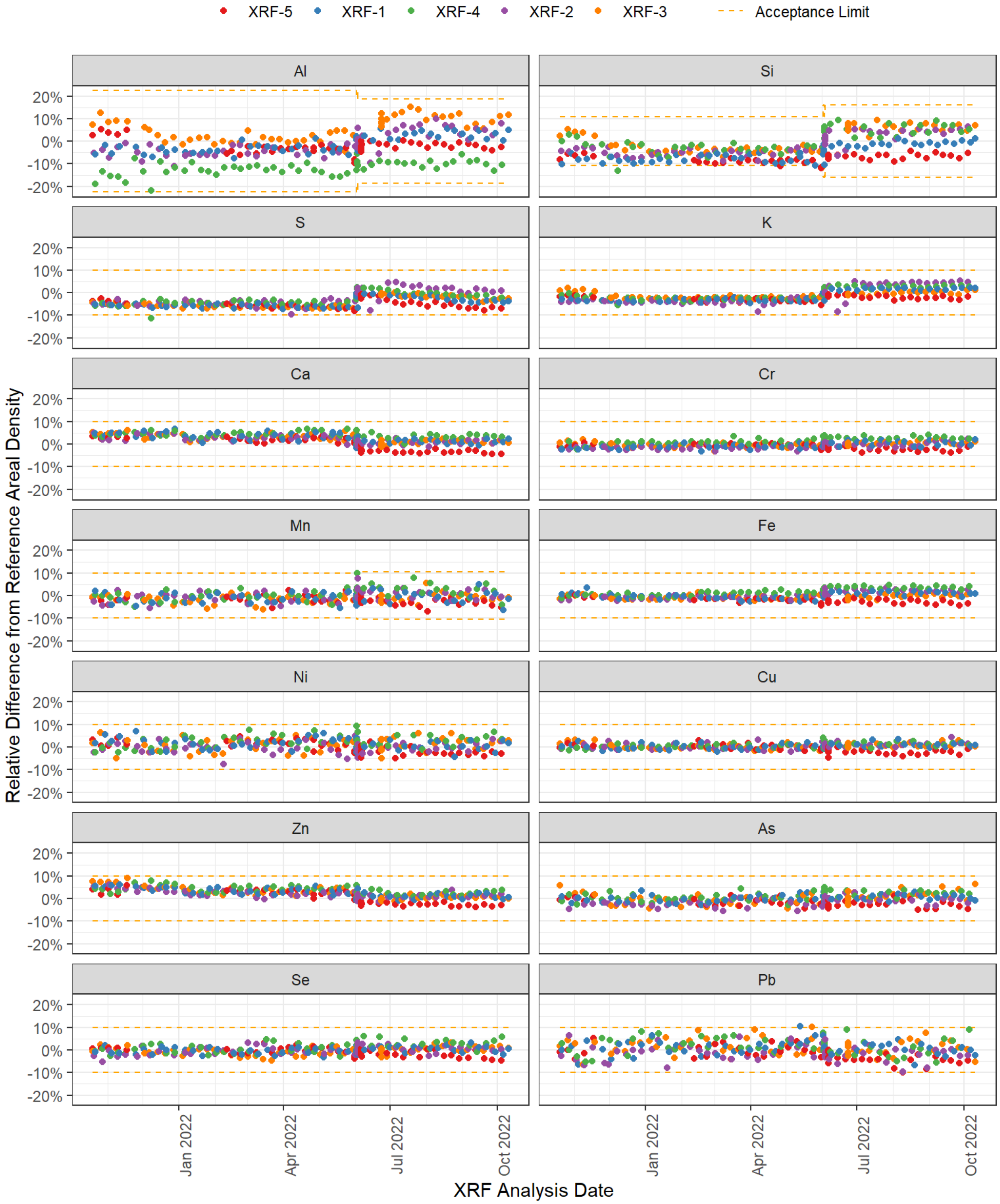
3.1.4.2 Daily ME-RM QC

Daily QC ME-RM results during this analysis period did not have any failures. XRF-5 daily ME-RM QC showed a drop in concentrations linked to a drop in X-ray intensity in early January 2022, but no IMPROVE samples were being analyzed during that time as high-tension generators for the new X-ray tube were being tested and the loss of intensity was related to these repairs. See section 2.2.1 for details.

3.1.5 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 3-1 are weekly ME-RM control charts. There are a few exceedances for Si and Pb, but these do not fail the QC acceptance criteria.

Figure 3-1: EDXRF weekly ME-RM control charts showing a few representative elements. The shift in Al and Si acceptance limits in June 2022 marks the replacement of the weekly ME-RM with a new one. Acceptance limits are recalculated as the elemental loadings are not the same between ME-RMs.



3.1.6 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

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

where x_{ij} is that month's EDXRF result, $\widehat{x_{ij}}$ is the reference value for element, *i*, in filter, *j*, and $U(x_{ij})$ and $U(\widehat{x_{ij}})$ are the uncertainty of that month's result and the reference uncertainty, respectively. Monthly z-scores for each element are calculated as the mean of the z-scores for the 16 reanalysis set filters. The monthly z-score control charts during this analysis period are shown in Figure 3-2. All reanalysis results were within a z-score value of ±1.

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 3-3. There were two QC failures during this analysis period. One occurred for aluminum and potassium on XRF-2 in April 2022. This failure resulted after an overall 5% or less drop in X-ray intensity for elements analyzed with the CaF2 secondary X-ray target. This slight drop occurred after a manufacturer service visit on 4/6/2022 and the SRM QC failure occurred on 4/14/2022. All other QC tests passed. The monthly SRM QC test failed as the monthly results were already near the lower acceptance limit so the slight drop pushed them below the limit. Reanalysis of the SRM on 4/25/2022 passed acceptance for both aluminum and potassium. IMPROVE samples analyzed during the time between the service visit on 4/6/2022 and the passing QC result were reanalyzed on another instrument (XRF-3). The bias between the results on XRF-2 and XRF-3 were within uncertainty and all sample results from XRF-2 were deemed acceptable. See section 2.2.2 and investigation report IR-0006 for details.

The second QC failure occurred for aluminum and potassium in July 2022 on XRF-5. The drop in these concentrations did not correspond to drops in aluminum or potassium concentrations in any other QC samples. So, a second NIST SRM 2783 with serial number 1617 was also analyzed in July 2022 and showed acceptable results. Because of the failure on XRF-5 and the earlier failure on XRF2, NIST SRM 2783 with serial number 1718 was retired from use and replaced with serial number 1617 in subsequent months.

Also, note that the certification for NIST SRM 2783 expired on September 21, 2021. NIST has sold out of stock of this standard and has no replacement air particulate standard. The decision was made to continue using this SRM with an expired certificate as it has shown stability over the two decades since it was first certified and because no suitable replacement exists.

Figure 3-2: Monthly reanalysis control charts.

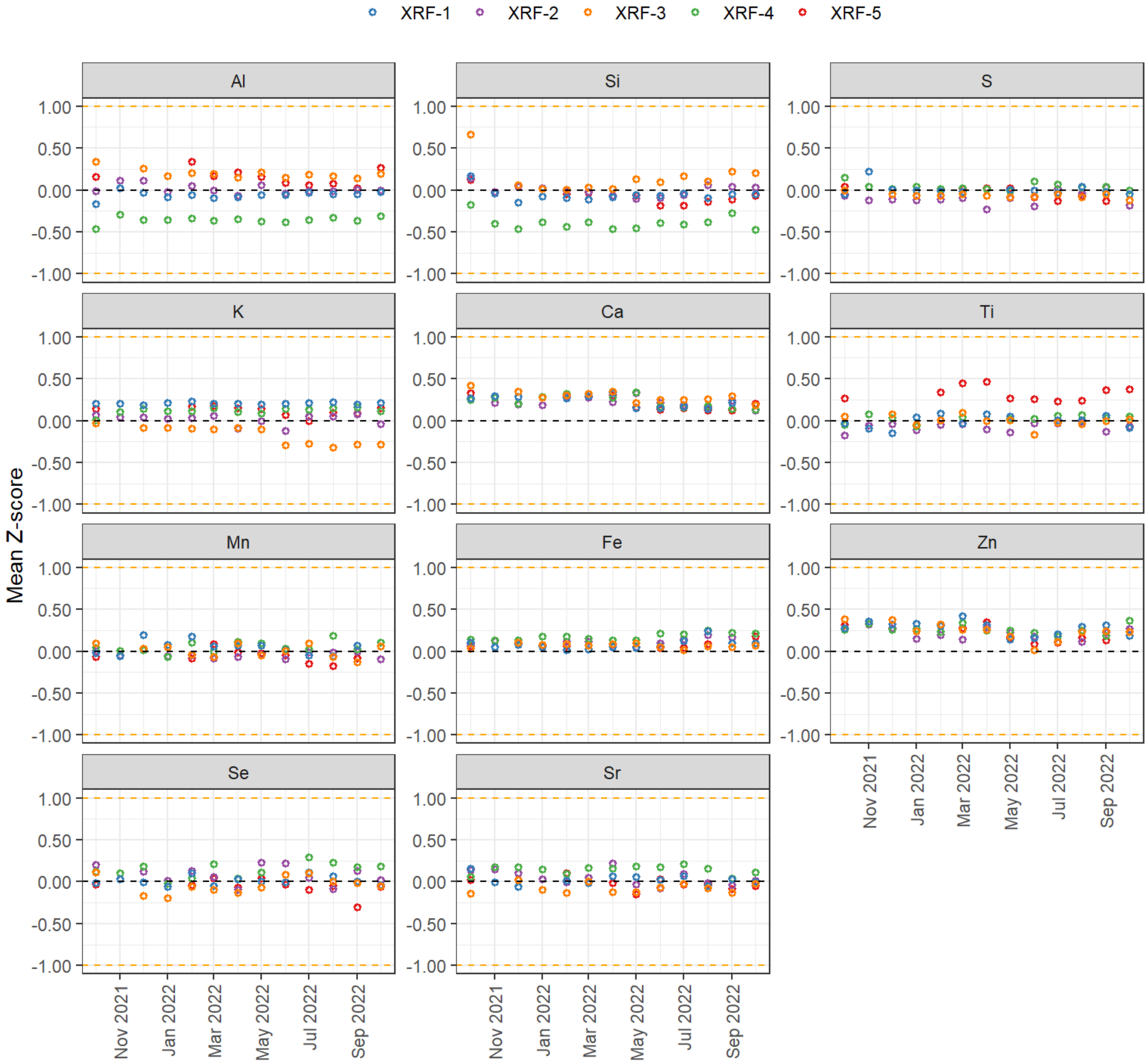
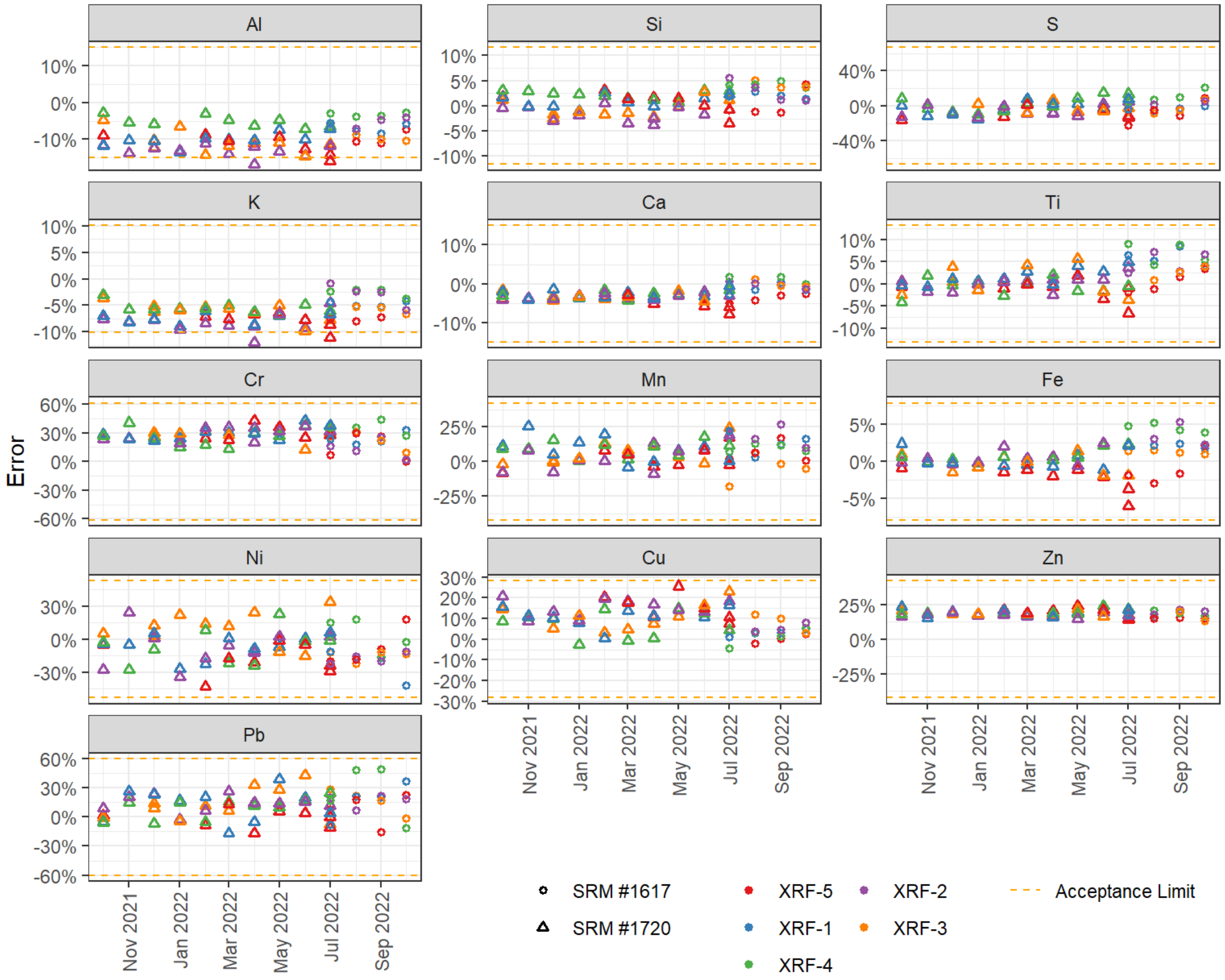


Figure 3-3: Monthly NIST SRM 2783 control charts.



3.2 UCD Gravimetric Laboratory

The gravimetric laboratory is responsible for providing accurate weights of particulate matter aerosol samples collected on PTFE filters. To accomplish this task, PTFE filters are weighed prior to sampling (pre-weigh) and after sampling (post-weigh). The difference provides the mass of any collected sample on the filter.

The gravimetric lab utilizes two Measurement Technology Laboratories (MTL) AH500E temperature and humidity controlled automated weighing chambers for most weighing with a non-climate controlled manual balance (M1) as a backup system. The first MTL AH500E weighing system (AH1) began operation at the previous location of Jungerman Hall (Crocker Nuclear Lab) starting with samples from October 2018 before moving to the new location at 1560 Drew Ave. on February 23, 2021 (see section 2.1.1 for details). The second MTL AH500E weighing system (AH2) began operation on February 1, 2021 at the Drew Ave. lab. Mass results from this analysis period include weights from AH1 while installed in the old lab and the new lab as well as weights from AH2.

3.2.1 Quality Control System

The quality control system is designed to provide confidence in the reported masses of 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 #251A* and are summarized in Table 3-4.

Table 3-4: UCD Gravimetric routine QC activities, criteria, and corrective actions.

Analysis	Frequency	Criterion	Corrective Action
Internal Balance Calibration	Prior to every weighing session	Calibration and check done by MTL chamber software.	• Retry internal calibration. • Further troubleshooting.
Metal Reference Weight Check	At the beginning and every 4 hours during a weighing session.	Two of three metal reference weights must be within acceptance. 100 mg, within ±0.003 mg 200 mg, within ±0.003 mg 400 mg, within ±0.005 mg	• Retry QC of all three weights. • Clean inside balance chamber. • Further cross-instrumental testing.
Controlled-Climate Checks	With every mass measurement	Temperature within 21.5 ± 1 °C RH within 39% ± 1.5%	• Check environmental chamber door is properly closed. • Further troubleshooting.

3.2.2 Laboratory QC Summary

AH1 experience a QC failure on 06/21/2021; the RH recorded higher than acceptable limits. Adjustments were made to the environmental control systems to restore compliance. 14 filters weighed at the times environmental QC failed were reweighed. The re-weigh mass was reported, so there was no impact on the data.

AH1 experience a QC failure on 06/24/2021; the RH recorded higher than acceptable limits. Further adjustments were made to the environmental control systems to restore compliance. 52 filters weighed at the times environmental QC failed were reweighed. The re-weigh mass was reported, so there was no impact on the data.

AH2 experience a QC failure on 07/06/2021; the environmental conditions were not recorded in the MTL database. A system restart resolved a possible communication error. 23 filters weighed at the times when no environmental data was recorded were reweighed. The re-weigh mass was reported, so there was no impact on the data.

AH1 experience a QC failure on 07/29/2021; the RH recorded higher than acceptable limits. For a period of time while routine measurements were taken, the building HVAC system malfunctioned, causing the ambient RH reach ranges that the AH500 cannot correct for. 70 filters weighed at the times environmental QC failed were reweighed. The re-weigh mass was reported, so there was no impact on the data.

AH2 experience a QC failure on 08/10/2021; the RH recorded higher than acceptable limits. Adjustments were made to the environmental control systems to restore compliance. 43 filters weighed at the times environmental QC failed were reweighed. The re-weigh mass was reported, so there was no impact on the data.

AH2 experience a QC failure on 09/20/2021; the 100 mg and 200 mg test weights measured lower than acceptable limits. Investigation found that a 25 mm PTFE filter fell out of its carrier onto the bottom of the balance pan. That filter was removed and the Mettler Toledo balance weighing chamber was cleaned. A subsequent internal adjustment and QC check confirmed that all values are back in compliance. 33 filters weighed at the times QC failed were reweighed. The re-weigh mass was reported, so there was no impact on the data.

AH2 experience a QC failure on 09/25/2021; the 100mg, 200mg, and 400mgtest weights measured lower than acceptable limits. The Mettler Toledo balance weighing chamber was cleaned. A subsequent internal adjustment and QC check confirmed that all values are back in compliance. 78 filters weighed at the times QC failed were reweighed. The re-weigh mass was reported, so there was no impact on the data.

AH1 experience a QC failure on 10/12/2021; the RH recorded lower than acceptable limits. Seasonal adjustments were made to the environmental control systems to restore compliance. 56 filters weighed at the times environmental QC failed were reweighed. The re-weigh mass was reported, so there was no impact on the data.

AH1 experience a QC failure on 10/21/2021; the RH recorded higher than acceptable limits. Further seasonal adjustments were made to the environmental control systems to restore compliance. 52 filters weighed at the times environmental QC failed were reweighed. The re-weigh mass was reported, so there was no impact on the data.

As noted in section 2.1.1, to address the number of environmental failures, we enclosed the weighing chambers in a smaller area with a dedicated dehumidifier. After this change the humidity measured in the chamber is more stable and stays within limits at a higher rate.

3.2.3 Instrument Calibrations

Balance calibrations are performed annually at UCD by Mettler-Toledo; however, additional calibrations may be performed as necessary such as following maintenance or QC failures. Table 3-5 summarizes instrument calibrations for this reporting period.

Table 3-5: Summary of calibrations performed on each balance during this reporting period. M1 is the manual balance, AH1 and AH2 are the MTL automated weighing chambers.

Balance	Calibration Date	Reason for Calibration
M1	2021-03-01	Annual calibration
AH1	2021-03-01	Annual calibration
AH2	2021-03-01	Installation calibration
AH2	2021-04-21	Re-calibration for drift
M1	2022-02-28	Annual calibration
AH1	2022-02-28	Annual calibration
AH2	2022-02-28	Annual calibration

The annual calibrations on March 1, 2021 were performed after AH1 and the manual balance were moved and re-commissioned at the new laboratory at Drew Ave., see section 2.1.1 for more information about the move. The re-calibration of AH2 on April 4, 2021 was because a small drift had been detected in the metal test weights since the calibration in March. The drift was not large enough to fail QC criteria, but Mettler-Toledo attended the lab to calibrate a research balance, and additionally performed an inspection and re-calibration of AH2 at that time.

3.3 UCD Optical Absorption

The optical absorption laboratory is responsible for providing consistent optical absorption factors (Fabs) for aerosol samples collected on PTFE filters. To accomplish this task, the lab utilizes a custom designed and built laser-based hybrid-integrating plate/sphere (HIPS) system to measure a sample's inferred atmospheric absorption optical depth. Analysis of all routine network samples, covering the field sampling period beginning from January 01, 2021 through December 30, 2021. Analyses of these samples were performed November 19, 2021 through June 28, 2023. Calibrations were produced for each lot and after any change to the instrument configuration.

3.3.1 Quality Control System

No standards for light absorption of particulate matter on filter media exist. Therefore, all quality control checks for the HIPS optical absorption instrument are performed on sampled filters. Reference values for these filters are determined by multiple measurements performed over multiple days. Consistency is paramount when no standards exist to check accuracy. To maintain this consistency, the raw detector response to a static set of 14 filters (referred to as the Verification Set) is checked to be within ± 3% of the reference values. Then another static set of 22 filters (the Reanalysis Set) is measured and calibrated results are checked against reference values. Only after these checks pass all acceptance criteria are samples analyzed on the system. A final review of the sample results is performed to check for instrument drift or individual filter issues prior to finalizing the results. HIPS QC tests and acceptance criteria are outlined in Table 3-6.

Table 3-6: UCD HIPS routine QC activities, criteria, and corrective actions.

Analysis	Frequency	Criterion	Corrective Action
Detector Response Verification	Beginning of every day of analysis.	Transmittance and Reflectance signals for all 14 verification set filters are within ±3% of reference values.	- Re-register detectors and re-run verification set. - Further troubleshooting.
Reanalysis Check	Beginning and end of every day of analysis.	Calibrated optical absorption depth (τ) for each reanalysis set filter is within limits. Linear response of τ to reference values has $R^2 > 0.95$ and slope between 0.95 and 1. Mean z-score of τ is between -1 and 1.	- Re-register detectors, re-run verification set, then re-run reanalysis set. - Further troubleshooting.

The Verification Set is used to determine whether the optical system, consisting of the light source, integrating sphere and plate, and detectors are operating as expected. The Reanalysis Set is used to determine if the system can be calibrated correctly. A calibration is generated using field blanks (N=80) from the same manufacturing lots as the Reanalysis Set filters. The field blanks are measured a total of six times, three times each day over two days. The calibration coefficients are taken as the slope and y-intercept of the linear regression of these transmittance and reflectance values. The Reanalysis Set samples are then measured a total of ten times (5 times each over two days). The tau value (optical absorption depth) is calculated from each of the 22 samples using this calibration and the results must lie within ± 2 X uncertainty. The standard deviations for transmittance and reflectance as well as the uncertainty of the linear regression coefficients from the calibration are used to determine the expanded uncertainty of the final Reanalysis Set tau values. The relevant equations are shown below.

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

where τ_{abs} is the field blank corrected absorption optical depth, r is the field blank corrected reflectance value given by $r = -a_1 R/a_0$, with a_0 as the intercept and a_1 is the slope of the linear regression of the field blank results to the line, $r + t = 1$ and t is the field blank corrected transmittance value given by $t = T/a_0$. T and R are the registered (power normalized) transmittance and reflectance measurements reported by the HIPS instrument, respectively.

$$U(\tau_{abs}) = k\sqrt{\left(\frac{u(r)}{1-r}\right)^2 + \left(\frac{u(t)}{t}\right)^2}$$

where,

$$u(r) = \sqrt{\left(\frac{R}{a_0}u(a_1)\right)^2 + \left(\frac{a_1 R}{a_0^2}u(a_0)\right)^2 + \left(\frac{a_1}{a_0}u(R)\right)^2}$$

and

$$u(t) = \sqrt{\left(\frac{1}{T}u(a_0)\right)^2 + \left(\frac{a_0}{T^2}u(T)\right)^2}$$

$u(r)$ and $u(t)$ are the uncertainties of the blank corrected reflectance and transmittance measurements while $u(a_0)$ and $u(a_1)$ are the standard errors in the intercept and slope of the linear regression of field blanks and $u(R)$ and $u(T)$ are the uncertainties of the raw reflectance and transmittance values estimated as the median standard deviation from seven measurements of the reanalysis filters. k is the coverage factor that sets the confidence of the uncertainty. We apply a value of k=2, which corresponds to a 95 % confidence interval.

3.3.2 Laboratory QC Summary

The HIPS instrument has until recently been constructed on a linear rail system. In the new lab space, this design introduced misalignment of the optical path from vibration and inadvertent bumping during normal operation. The HIPS instrument was moved to an optical board to improve stability. The HeNe laser was decoupled from the integrating sphere and connected via a fiber optic patch cable. The linearity of the new optical path was investigated and verified for service using the fiber optic configuration with a 90 degree reflective collimator. Shortly thereafter, a dramatic dip in the comparison of fAbs to ECR was observed between May and June of the 2021 samples, shown in Figure 4-22.

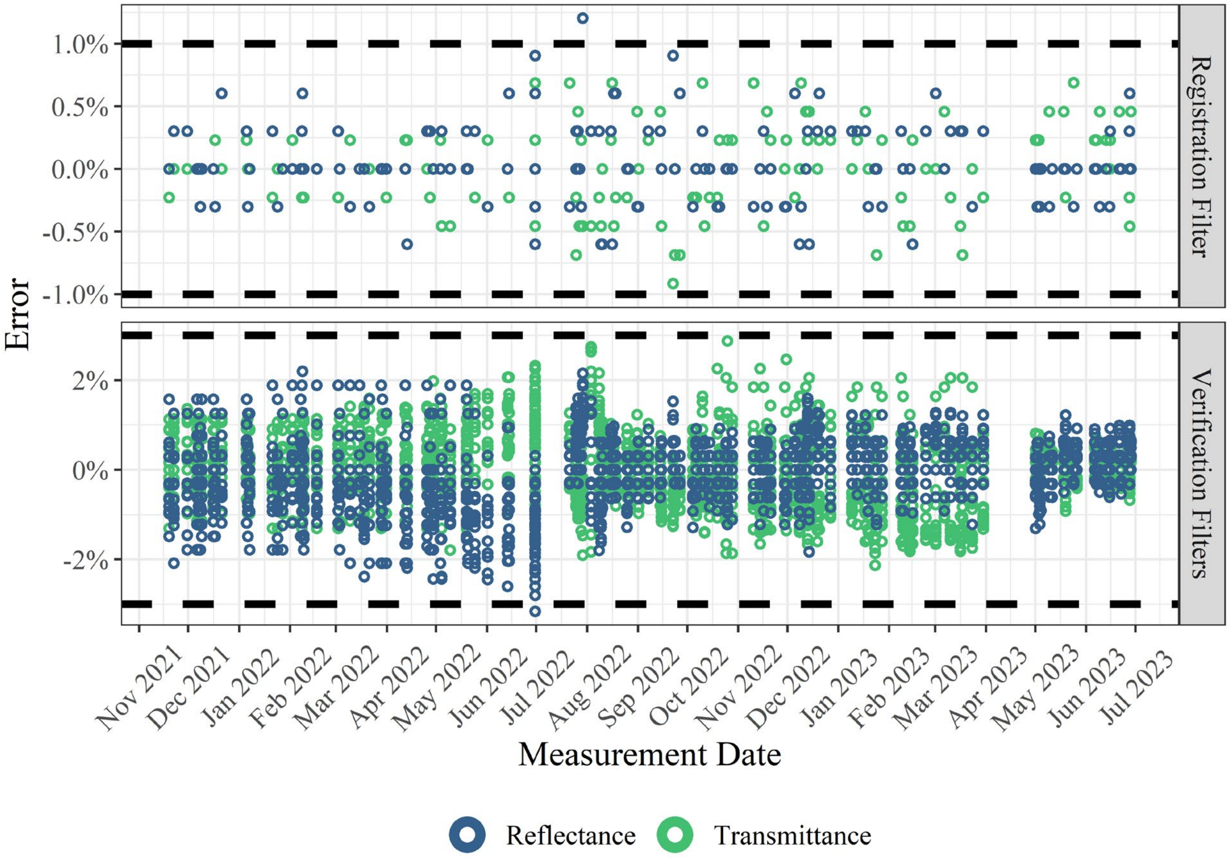
3.3.2.1 fAbs/ECR Ratio Lab Investigation

Multiple threads of investigation were initiated. The decrease observed does not correspond to the change from linear rail to fiber optic and may be related to the change from Pall to MTL PTFE filter manufacturer. That investigation is still ongoing. However, investigators noted that the 90-degree collimator provided a smaller spot size than desired and the uncertainty for QC materials was elevated. To rectify this, a focusing lens/collimator was installed to adjust the beam spot size, which improved intermediate repeatability and decreased QC material error. All 2021 samples originally analyzed with the 90-degree reflective collimator, May through December, were reanalyzed with the new focusing lens collimator.

3.3.3 Detector Response Verification

The Verification Set is used to determine whether the optical system, consisting of the light source, integrating sphere and plate, and detectors are operating as expected. All samples in the Verification Set must lie within ± 3 % of their respective reference values, with one exception. The registration filter (QcSampleId=3), which is used for converting the raw power readings from the detectors to historically consistent normalized values, must lie within ± 1 % of its reference values. The reference values are determined as the mean transmittance and reflectance values from 12 measurements over the course of two days (6 measurements on each day).

Figure 3-6: HIPS verification check results for samples collected in 2021.



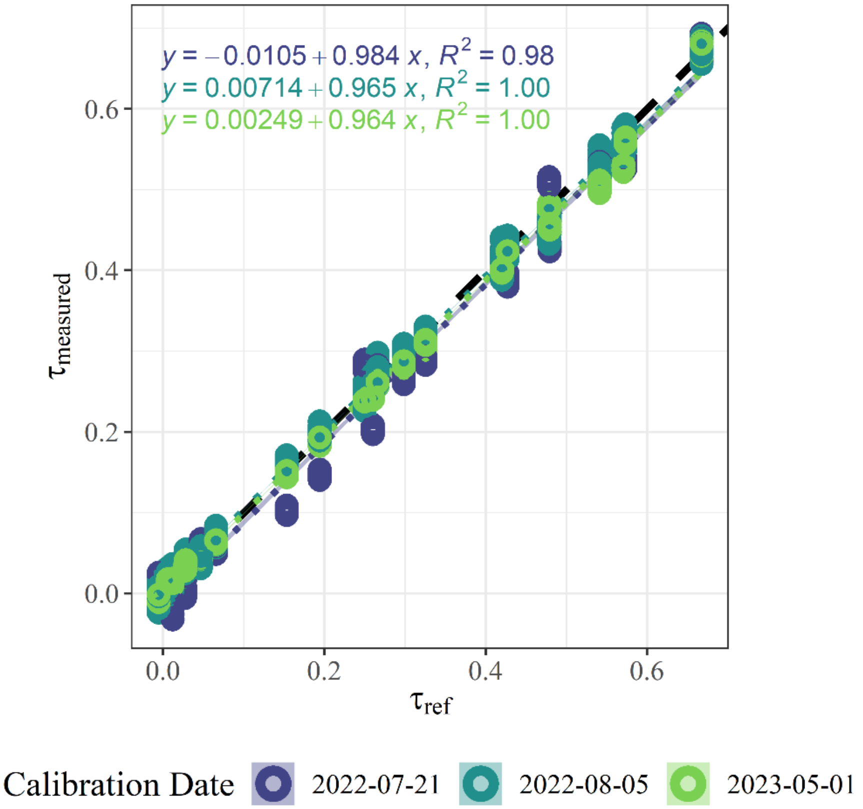
3.3.4 Reanalysis Check

The Reanalysis Set verification check is predicated on a field blank calibration using field blanks representative of the sample filters chosen for reanalysis. This linear calibration is used to calculate the unitless absorption optical depth parameter (τ_{abs}). The measurement results of the Reanalysis Set samples must lie within ± 2 X $U_{\tau_{abs}}$. Additionally, the calibration of the Reanalysis Set must have a linearity, as determined by the coefficient of determination (COD), greater than 0.95. Similarly, the measured τ_{abs} values must correlate with their respective reference values with a COD greater than 0.95 and a slope between 0.95 and 1.0. Calibration of the QC materials are summarized in Table 3.7 below and the comparison of tabs with reference values is shown in Figure 3.7.

Table 3-7: Summary of QC materials calibration results.

Calibration Date	Linearity
2022-07-21	0.968
2022-08-05	0.985
2023-05-01	0.987

Figure 3-7: HIPS linearity check of the Reanalysis Filter set.



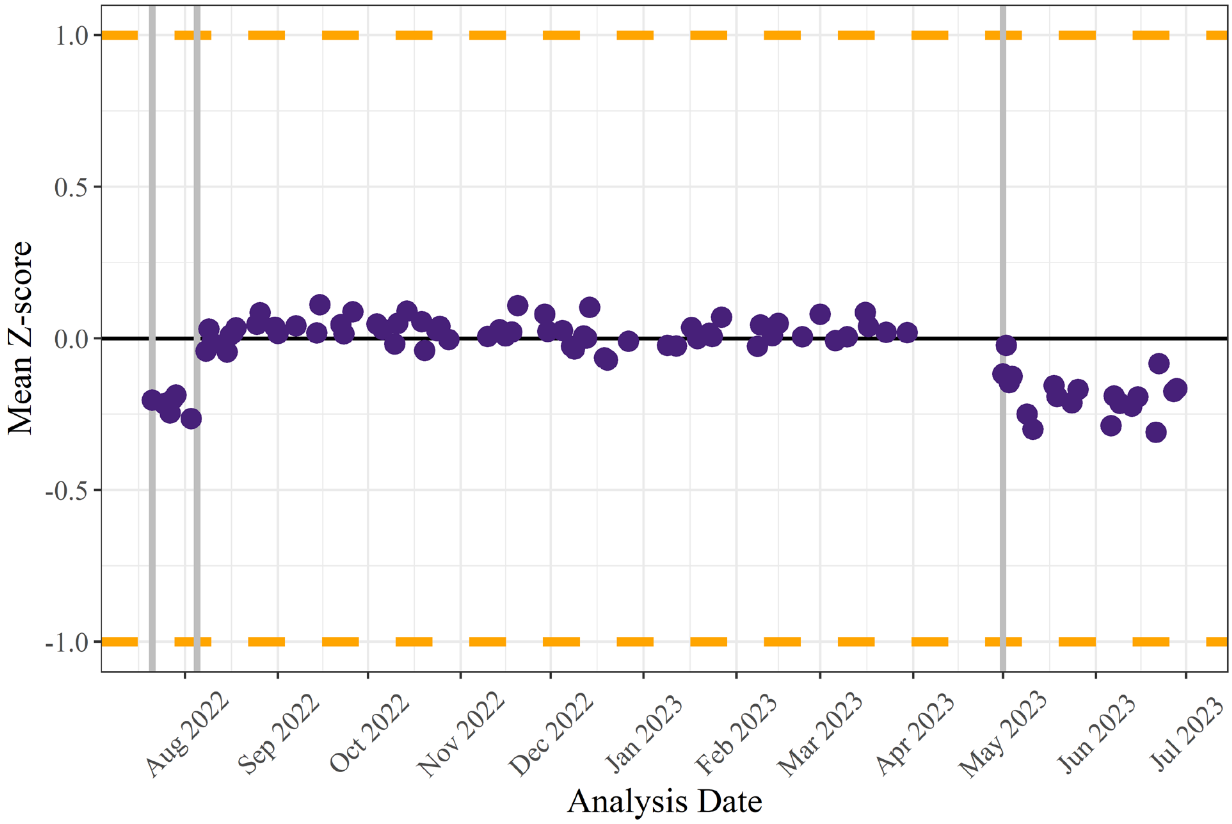
The linearity check passed for all calibrations of the Reanalysis Set. The HIPS instrument had a 100 % passing rate for the reanalysis set measurements within the uncertainty bounds, ± 2 X $U_{\tau_{abs}}$.

The long-term trend of the reanalysis results is monitored using the z-score. The z-score for each reanalysis sample is calculated as

$$z\text{-}score = \frac{\tau_{abs,i} - \tau_{abs,accepted}}{\sqrt{U(\tau_{abs,i})^2 + U(\tau_{abs,accepted})^2}}$$

while the mean z-score is calculated for each day of analysis. Mathematically, $mean\ z\text{-}score = \frac{1}{n}\sum_i z\text{-}score_i$. The absolute value of the mean z-score must remain ≤1 and any sudden shifts in the plotted mean z-score value compared to previous values must be investigated. The mean z-scores from this reporting period are shown below in Figure 3.8.

Figure 3-8: HIPS reanalysis mean z-score. Vertical lines identify calibration dates. Horizontal lines demarcate the QC limits of the z-scores.



3.3.5 Replicate Precision

Replicate analyses are now incorporated into routine laboratory operations. Once a full year of data is available, replicate precision limits will be determined and applied to routine quality control checks. The current replicate measurement results are presented below using the reported fAbs parameter.

The fAbs parameter is calculated using the sample deposit area (3.53 cm^2 for 25mm filters), sample volume (in m^3), and a conversion factor of 100 to convert to inverse megameters (Mm^{-1}).

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

The scaled relative difference (SRD) is the absolute difference of the original and replicate measurements divided by the mean of the two results. A $\sqrt{2}$ term in the numerator accounts for uncertainty in both measurements. Mathematically,

$$SRD = \frac{(Original - Replicate)/\sqrt{2}}{(Original + Replicate)/2}$$

Both the scaled relative difference followed by the absolute differences are presented in Figures 3.9 and 3.10 below.

Figure 3-9: Replicate precision of HIPS results during this reporting period, for sample dates spanning August 02, 2021 to December 12, 2021. The dotted lines locate ±0.2 or 20 %. The vertical line represents the analytical MDL derived from laboratory blanks.

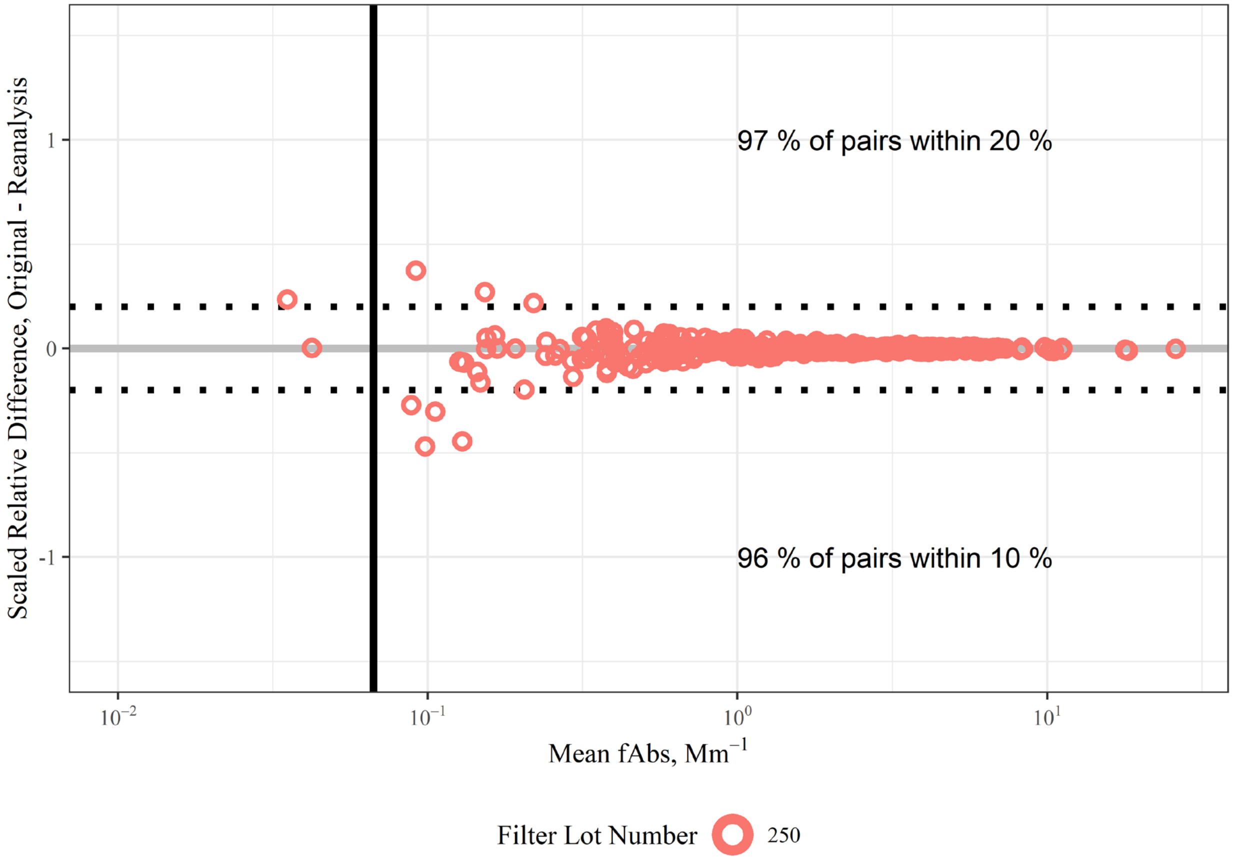
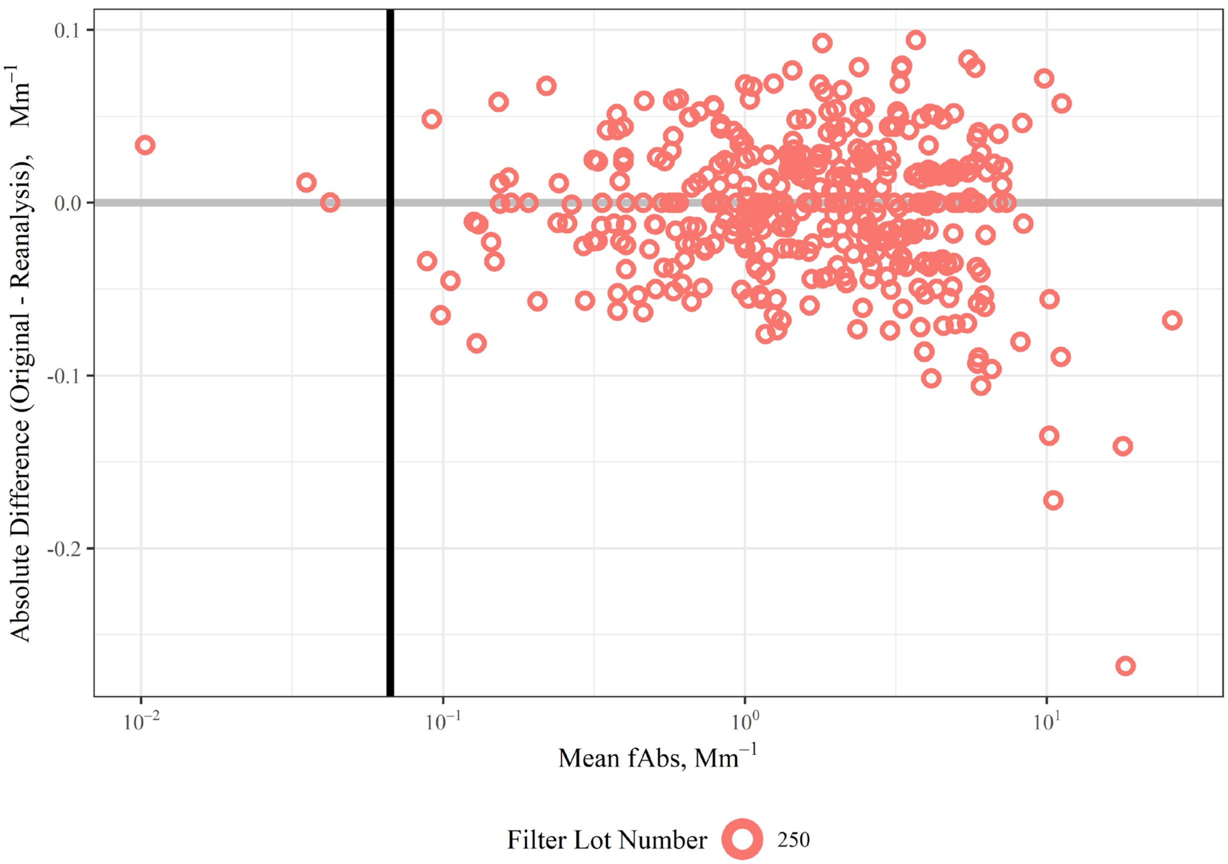


Figure 3-10: Absolute differences (original – reanalysis) of replicate HIPS results during this reporting period, for sample dates spanning August 02, 2021 to December 12, 2021. The vertical line represents the analytical MDL derived from laboratory blanks.



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 and Figure 4-2 show network 90th percentile, median (50th percentile), and 10th percentile concentrations of $PM_{2.5}$ and PM_{10} mass. Figure 4-3 through Figure 4-8 show network 90th percentile, median, and 10th percentile concentrations of organic carbon (OC), elemental carbon (EC), sulfur (S), nitrate (NO_3^-), chloride (Cl^-) and fine soil, which are major $PM_{2.5}$ components for reconstructing $PM_{2.5}$ mass. These plots include the most recent five years of historical network data (2016-2020) to provide context for the current time period under review (January – December 2021).

Network-wide $PM_{2.5}$ and PM_{10} concentrations during 2021 are back to the levels prior to the COVID-19 lockdowns, as evident in the higher median PM concentrations compared to the 2020 values. The 90th percentile concentrations of $PM_{2.5}$, OC, and EC during July and August 2021 exhibit strong signals that are comparable to those in September 2020, indicative of wildfire impacts on network samples.

Figure 4-1: Multi-year time series of network-wide $PM_{2.5}$ concentrations.

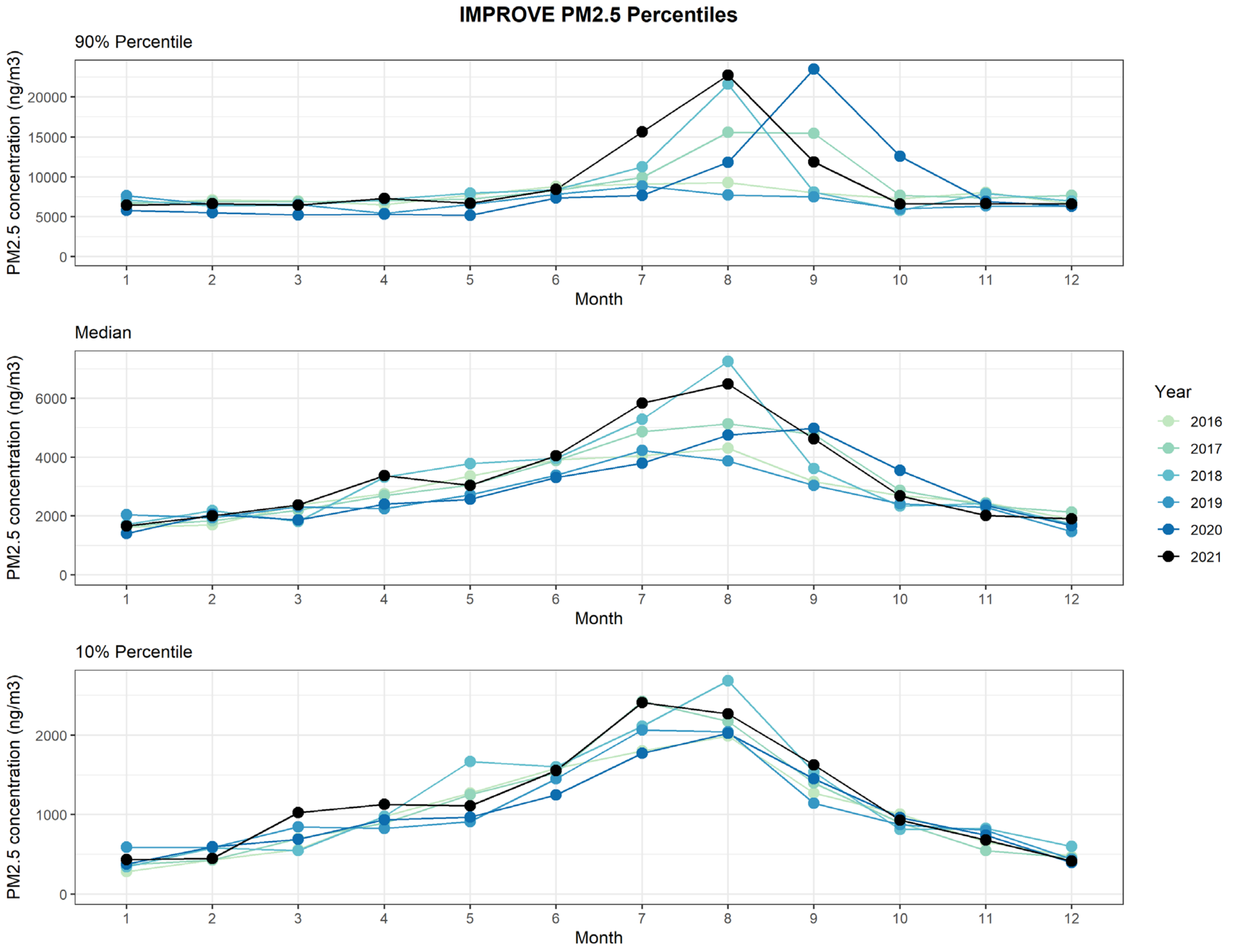


Figure 4-2: Multi-year time series of network-wide PM_{10} concentrations.

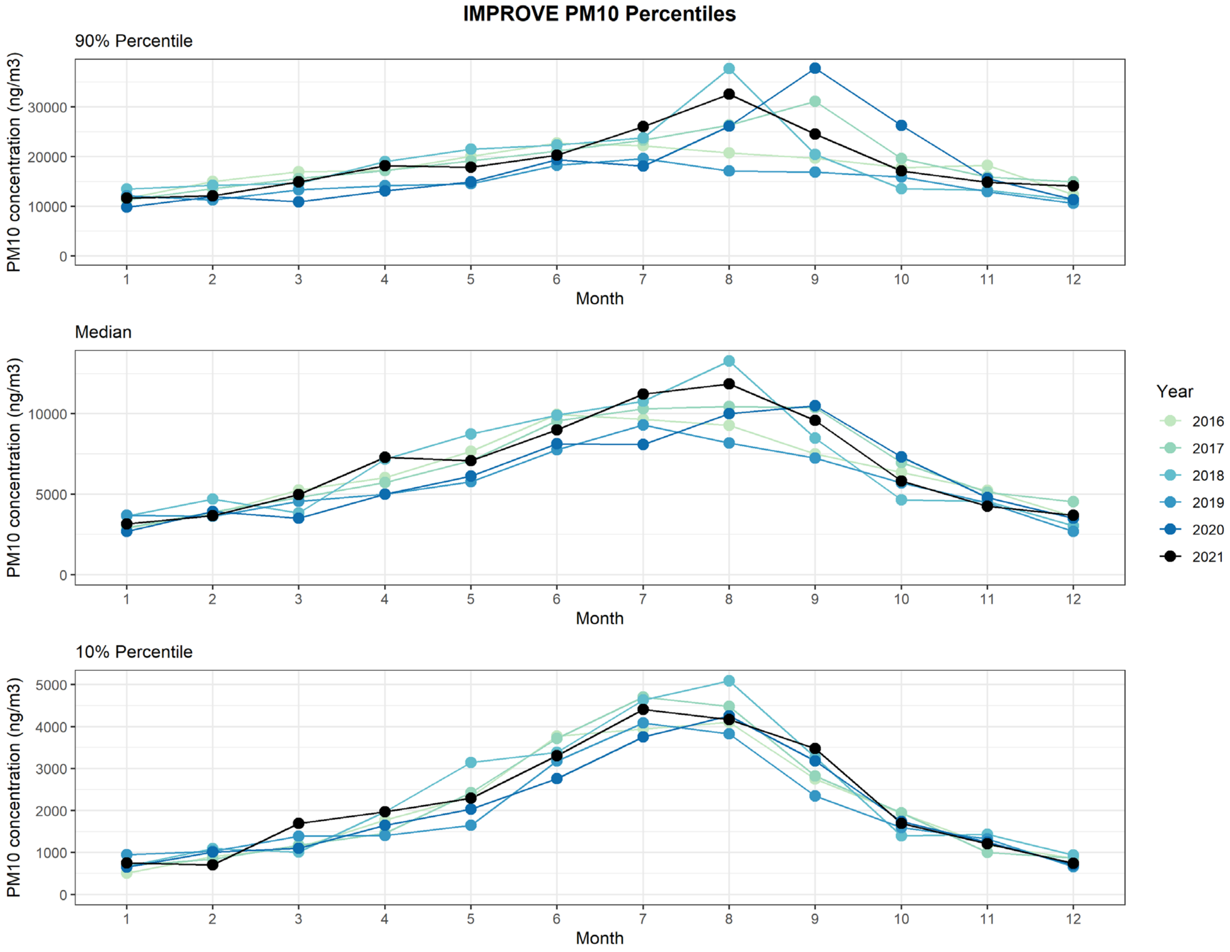


Figure 4-3: Multi-year time series of network-wide thermos-optical reflectance organic carbon (OCR) concentrations.

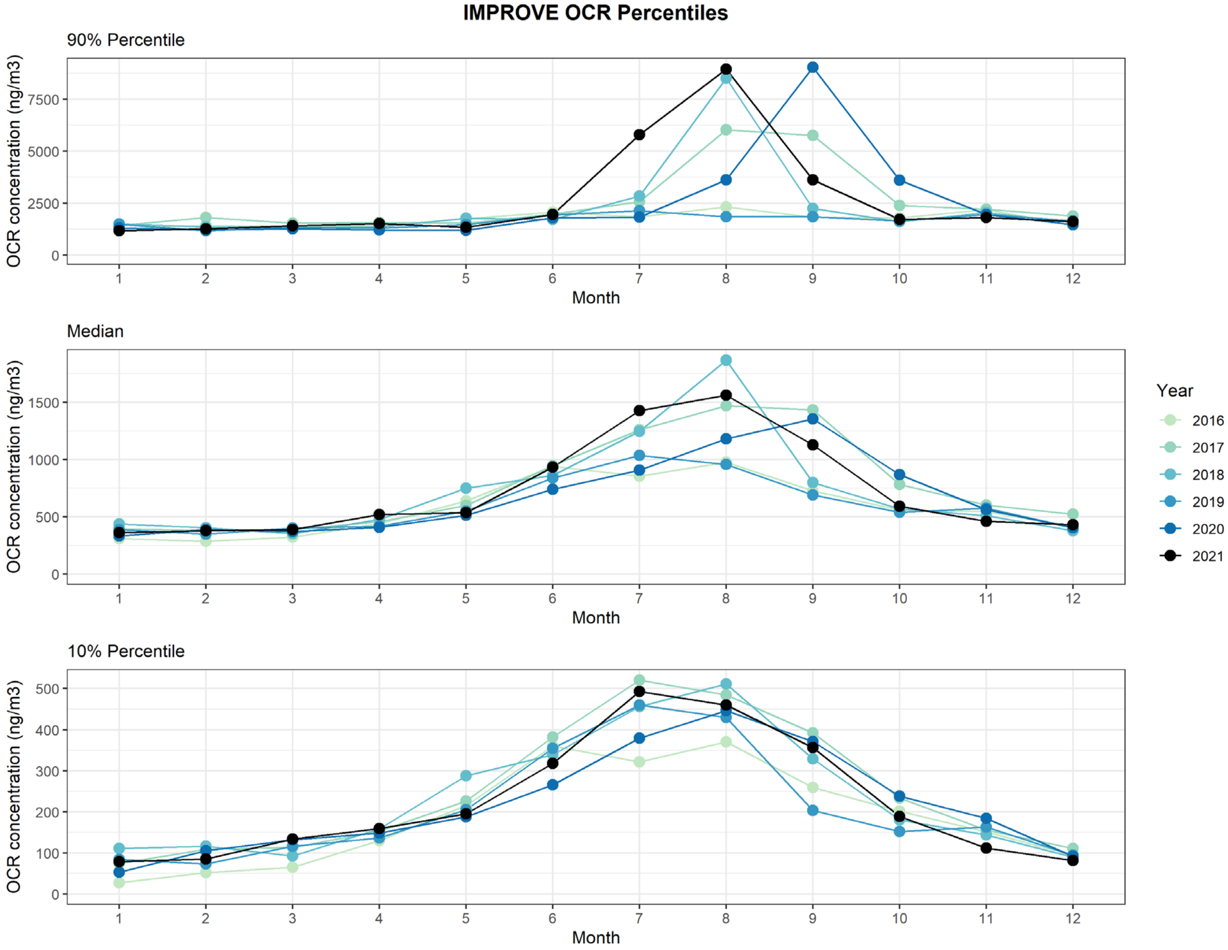
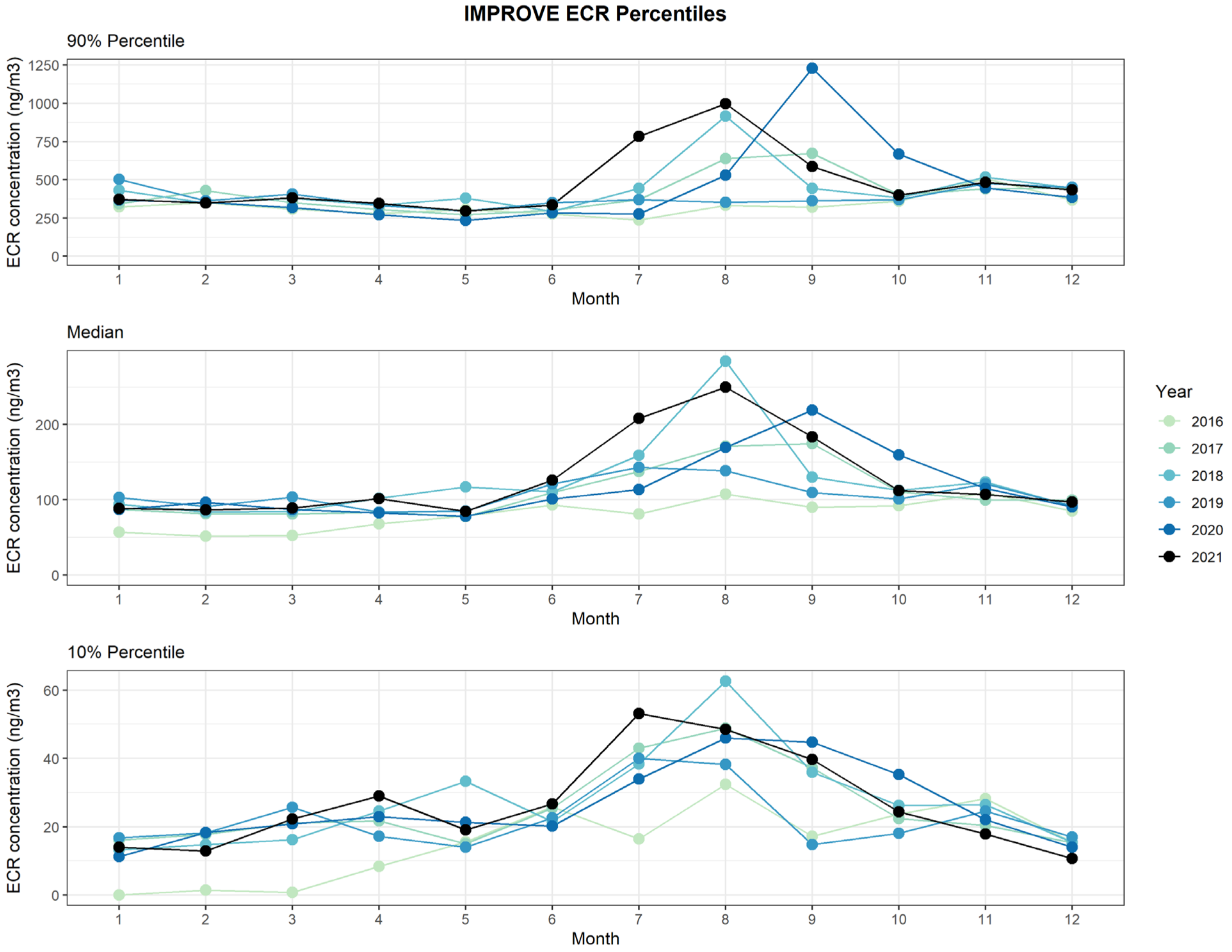


Figure 4-4: Multi-year time series of network-wide thermos-optical reflectance elemental carbon (ECR) concentrations.



Sulfur concentrations during this review period are slightly higher than 2020 and more in line with the 2016-2019 levels (Figure 4-5). This trend is most evident in the 90th percentile concentrations and could be due to reduced sulfur emissions from industrial sources during the COVID-19 lockdown period in 2020. On the other hand, nitrate (Figure 4-6) and chloride (Figure 4-7) concentrations are consistent over the years and do not show any observable impact from the lockdowns.

Figure 4-5: Multi-year time series of network-wide sulfur concentrations.

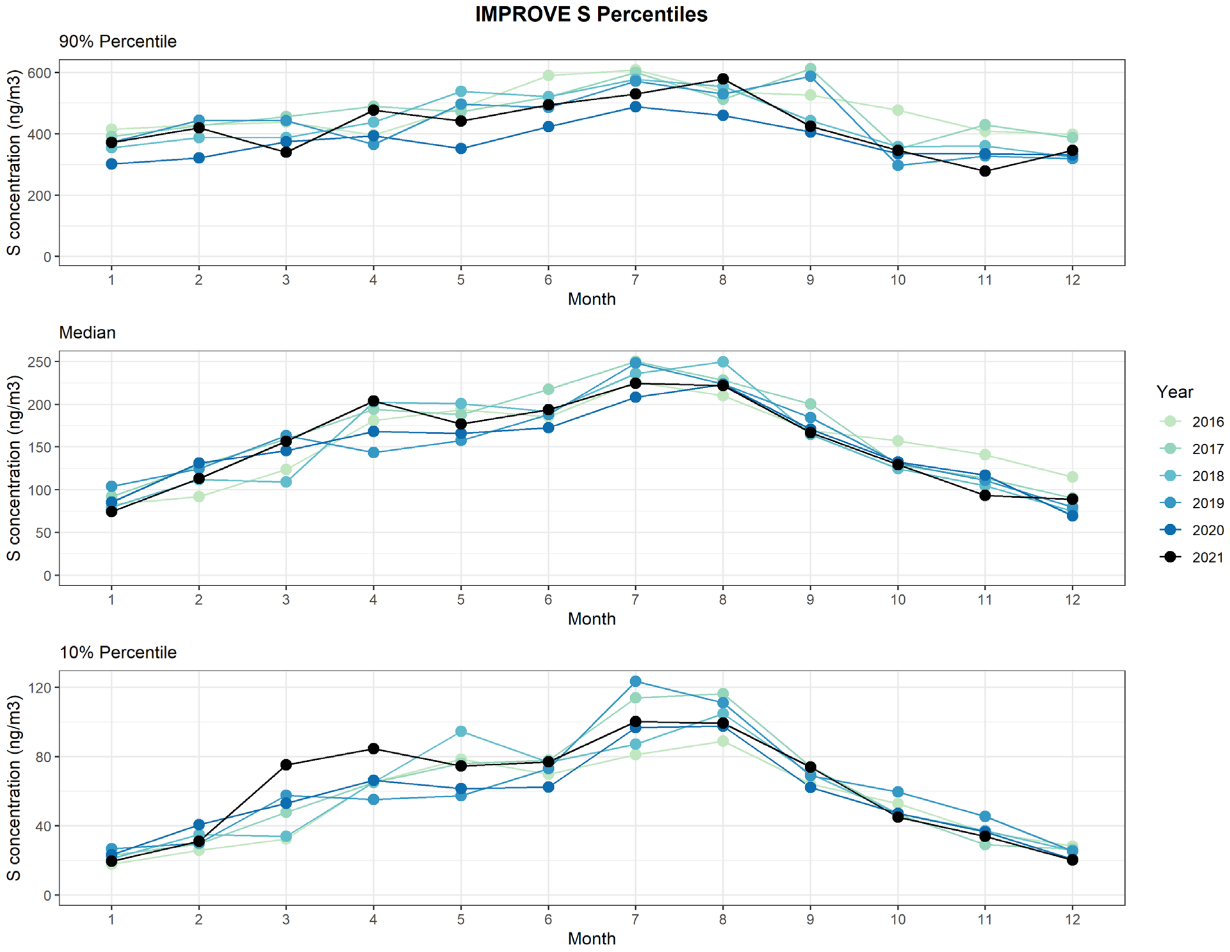


Figure 4-6: Multi-year time series of network-wide nitrate concentrations.

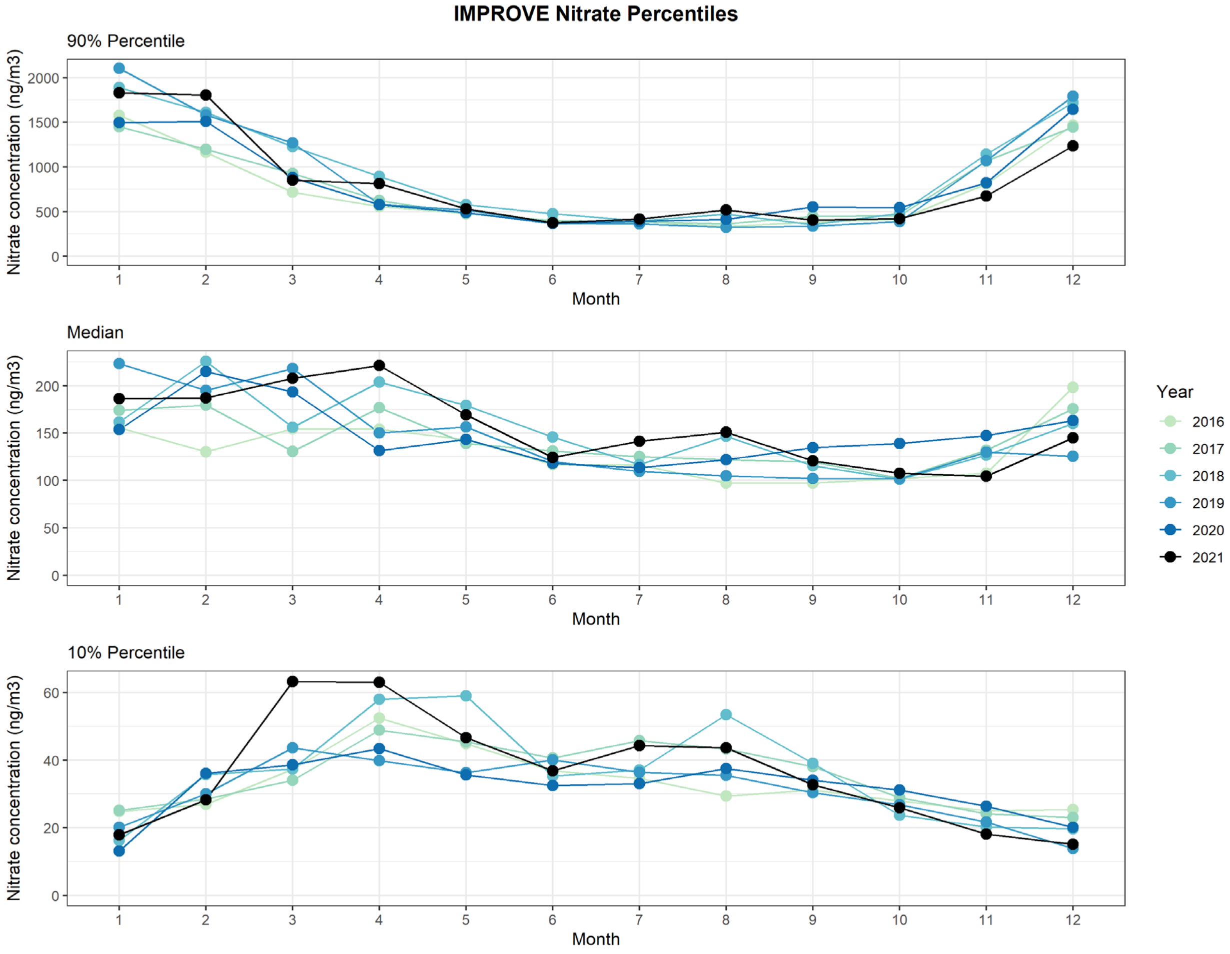
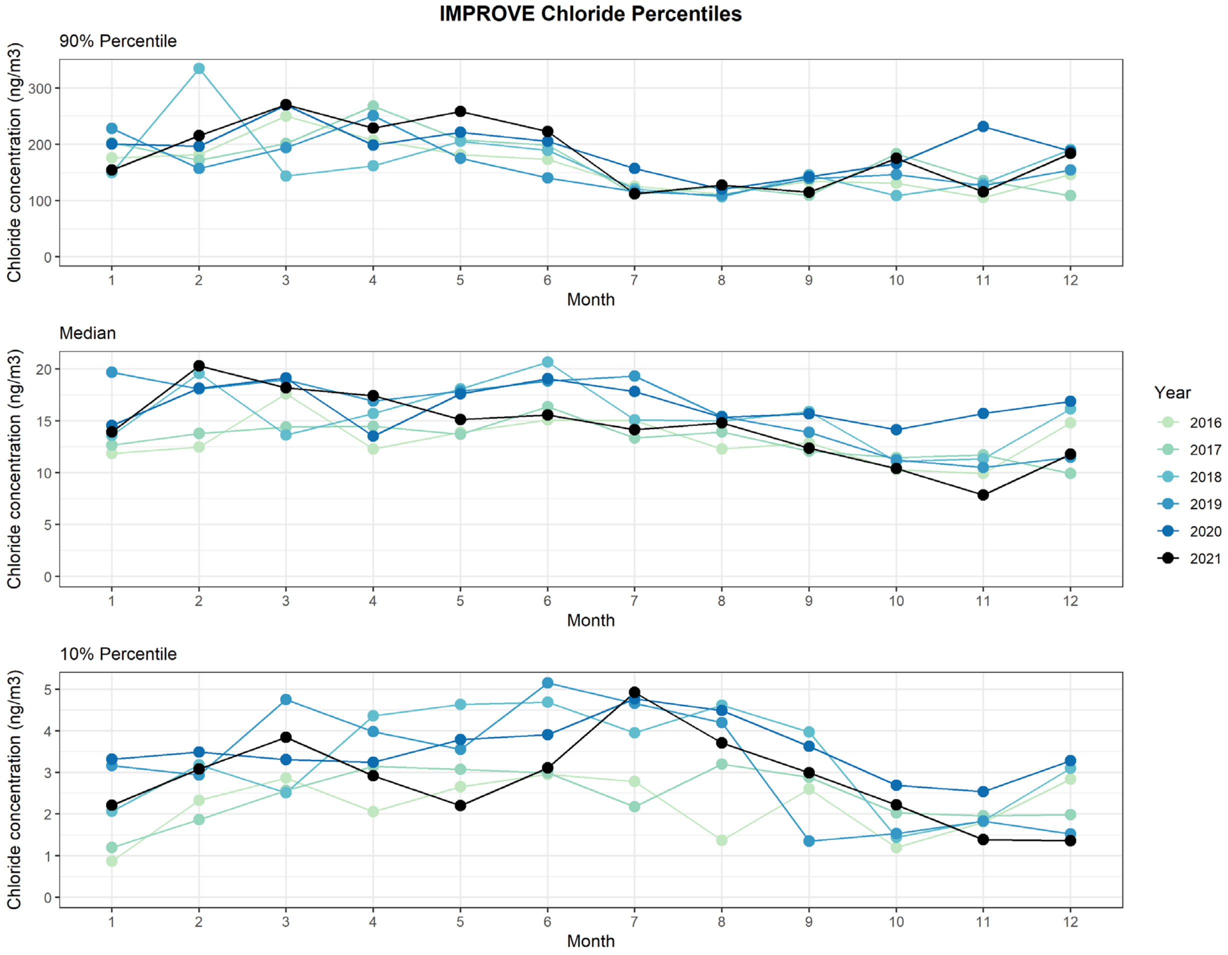


Figure 4-7: Multi-year time series of network-wide chloride (Cl^-) concentrations.



The increasing trend of fine soil concentrations, especially in the 10th percentile, started from the second half of 2020 and extended into 2021. In particular, soil concentrations from March to May 2021 were the highest in recent years across all percentiles.

Composite variable soil is calculated as:

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

The individual crustal elements (i.e., Al, Si, Ca, Fe and Ti) and some other elements such as Mg (Figure 4-9) and Mn (Figure 4-10) exhibited patterns similar to the composite variable.

Figure 4-8: Multi-year time series of network-wide soil concentrations.

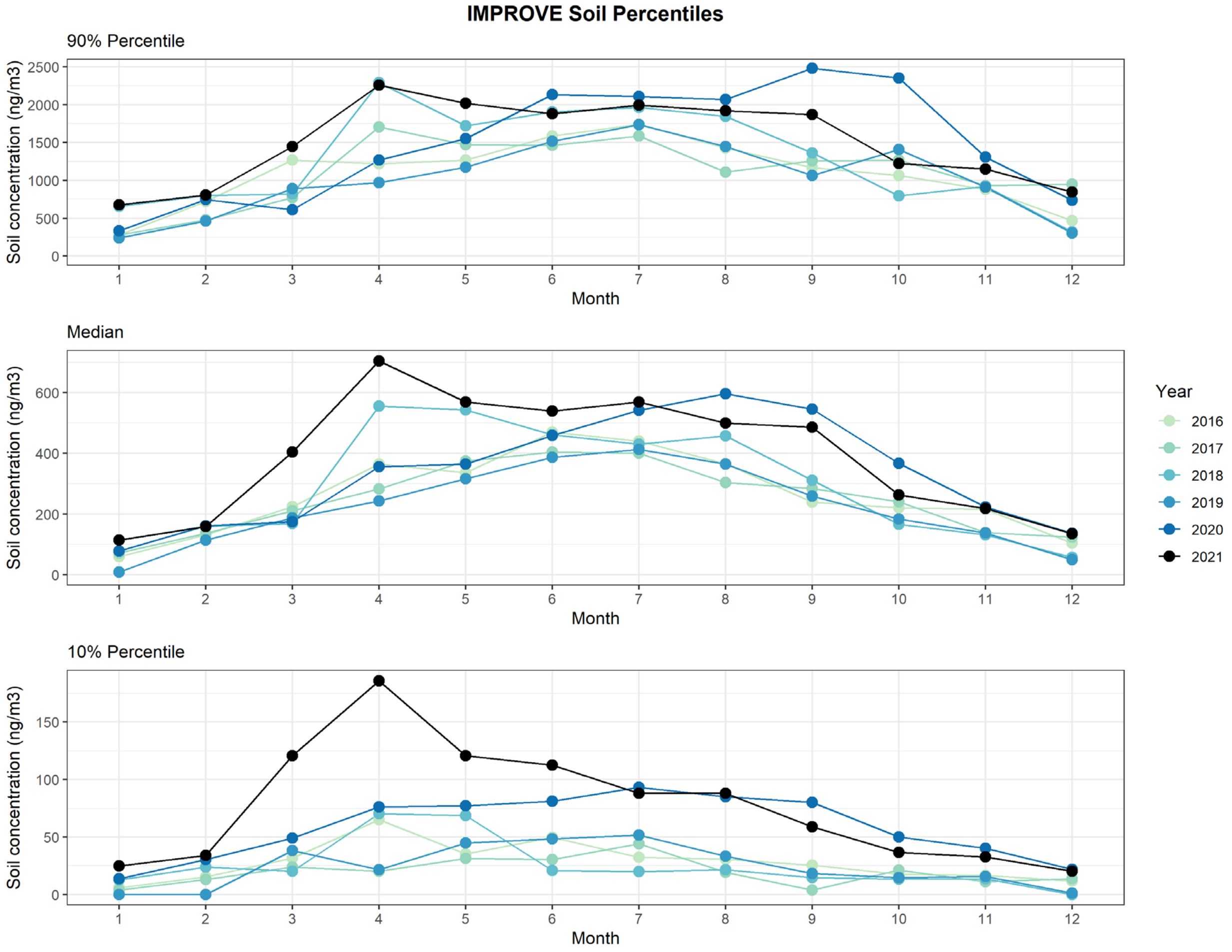


Figure 4-9: Multi-year time series of network-wide Mg concentrations.

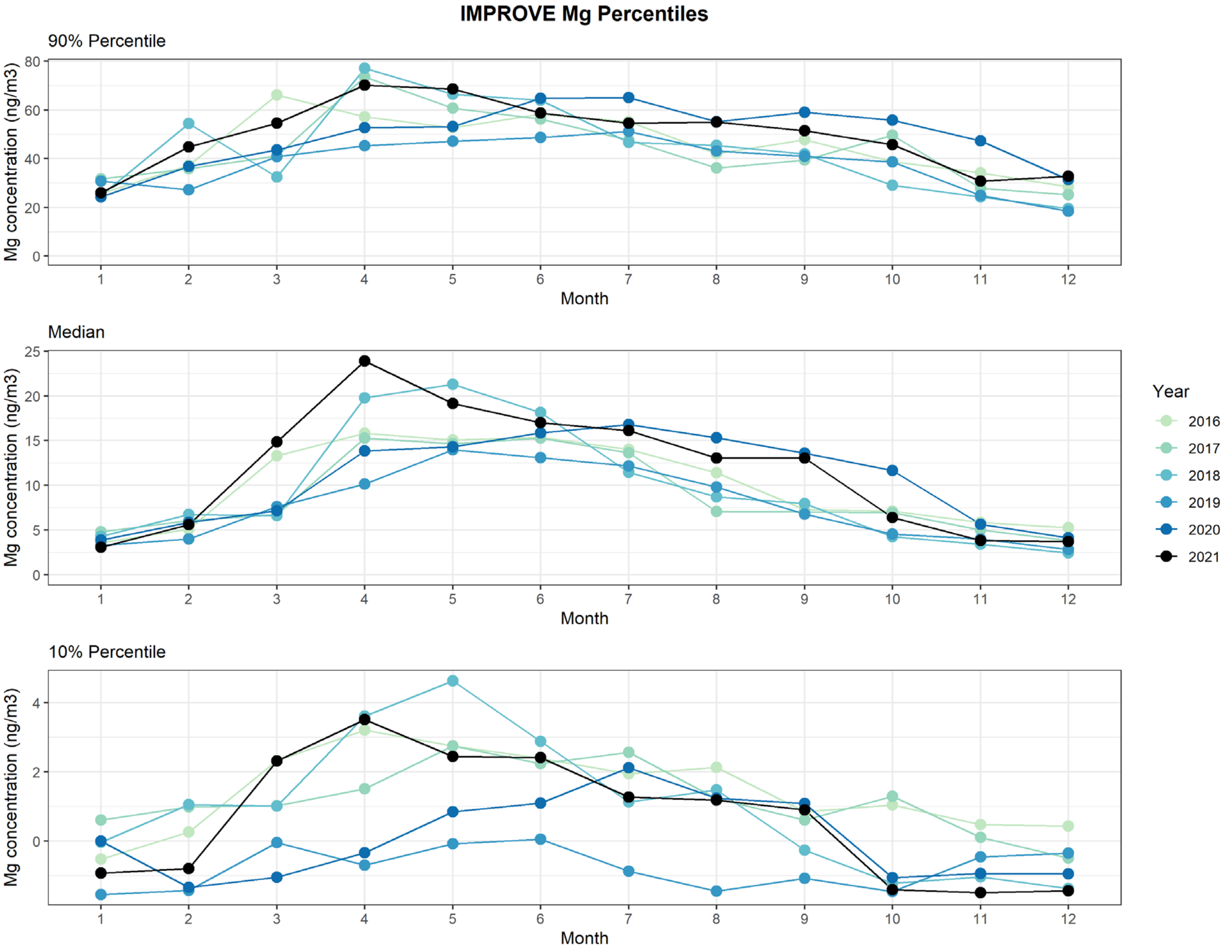
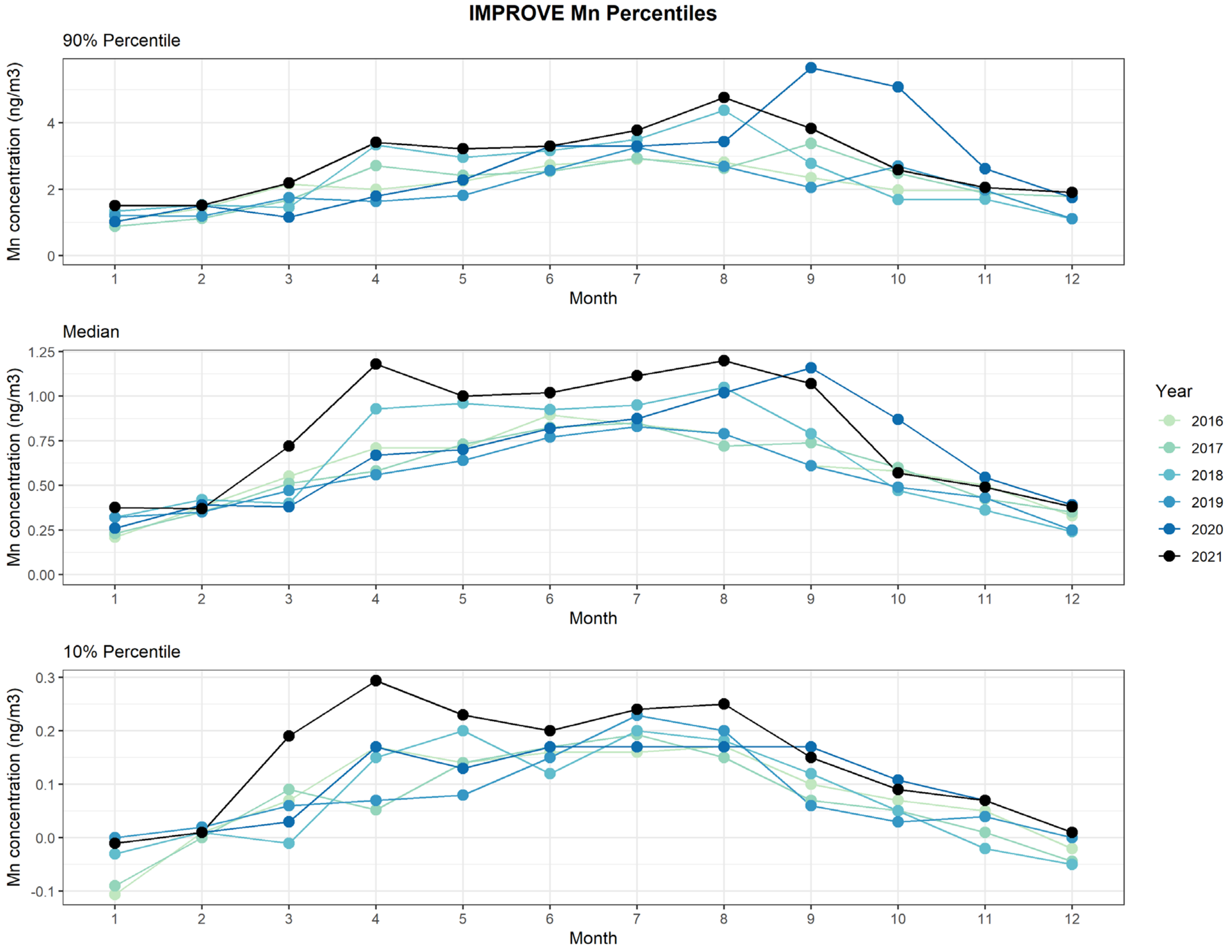


Figure 4-10: Multi-year time series of network-wide Mn concentrations.



The median and 90th percentile concentrations of vanadium (Figure 4-11) during 2021 are lower than previous years. Decreasing vanadium and nickel concentrations were correlated with regulations on marine fuel (Spada et al., 2018). Those regulations have ramped up over the years and may explain the continuing decreases in vandium, although. nickel concentrations during the same period, do not show the same trend (Figure 4-12).

In October 2018, XRF data was processed by taking the (non-blank subtracted) areal densities from the instrument, subtracting the median monthly blank areal density, then processing to concentrations. Prior to that, IMPROVE processed XRF data by taking the raw XRF intensities, subtracting a median monthly blank raw intensity, then applying the supplied calibration factor to produce the Areal Densities which were then processed to concentrations. This change can be seen in the 10th percentile V timeseries where all results after the change were zero.

Figure 4-11: Multi-year time series of network-wide vanadium (V) concentrations.

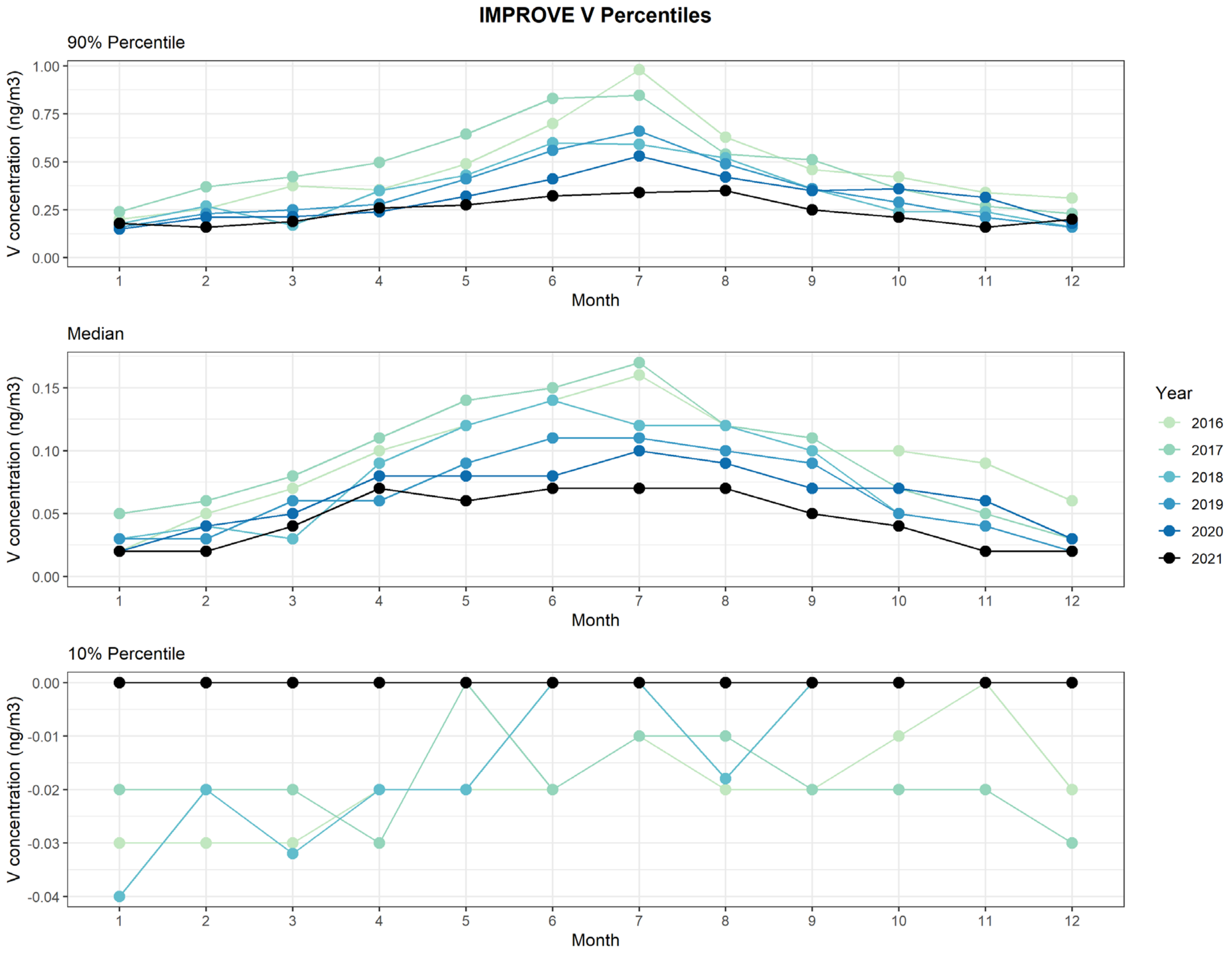
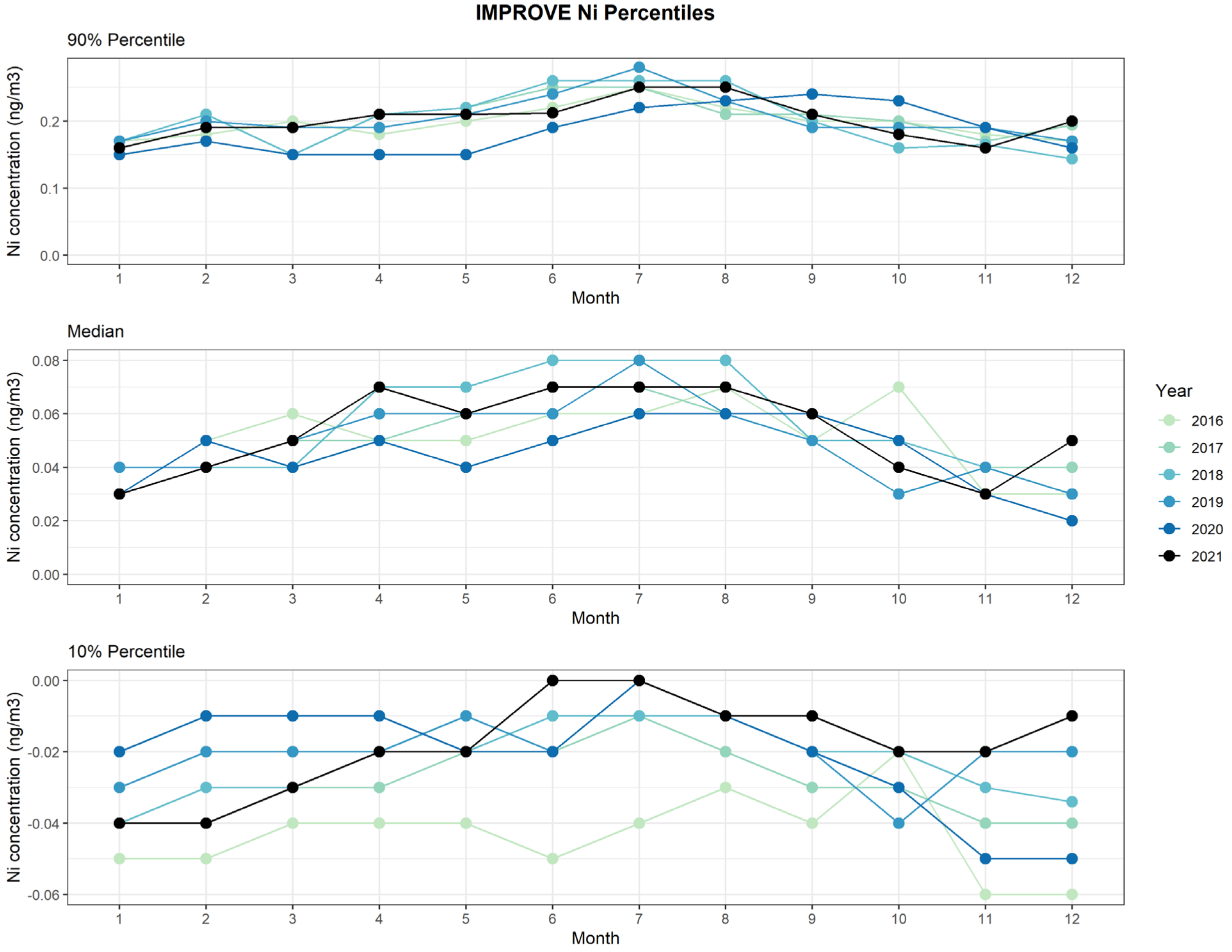


Figure 4-12: Multi-year time series of network-wide nickel (Ni) concentrations.



XRF measurement of arsenic (As) has been impacted by the XRF application change that occurred in Octobor 2018 sampling month (documented in the 2019 QA report). Specifically, As was moved from KBr target at 300 seconds to SrF2 target at 400 seconds. The change in signal was deemed acceptable at the time. Shown in Figure 4-13 and 4-14, the 95th, 90th and 75th percentile concentrations of arsenic had a drastic drop to near zero in October 2018, coinciding with the XRF application change. The 95th percentile concentrations rose back in the month after and stayed at a level close to the measurment MDL until the beginning of 2021, when both 90th and 95th concentrations dropped to near zero again (Figure 4-14).

Figure 4-13: Multi-year time series of network-wide arsenic (As) concentrations.

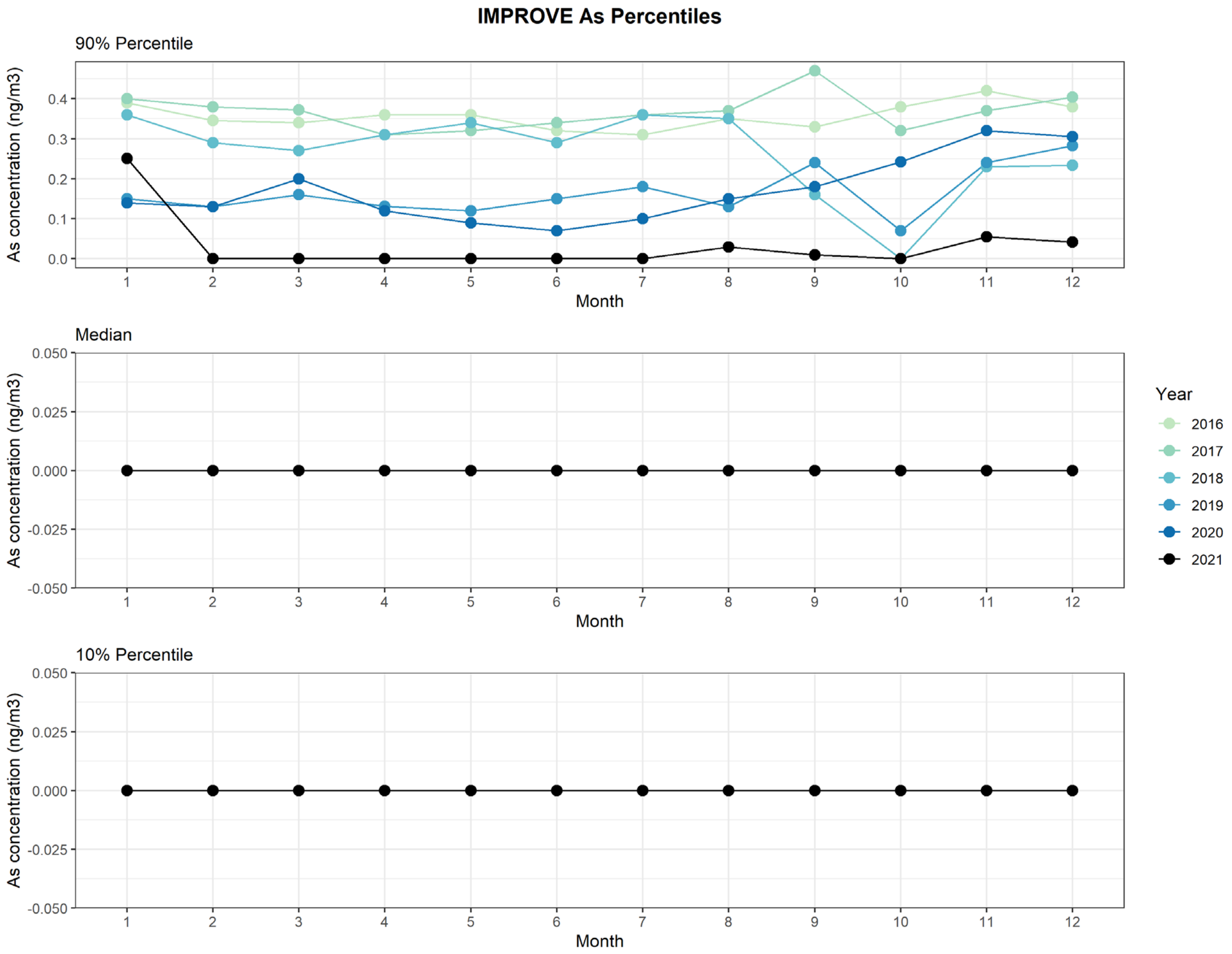
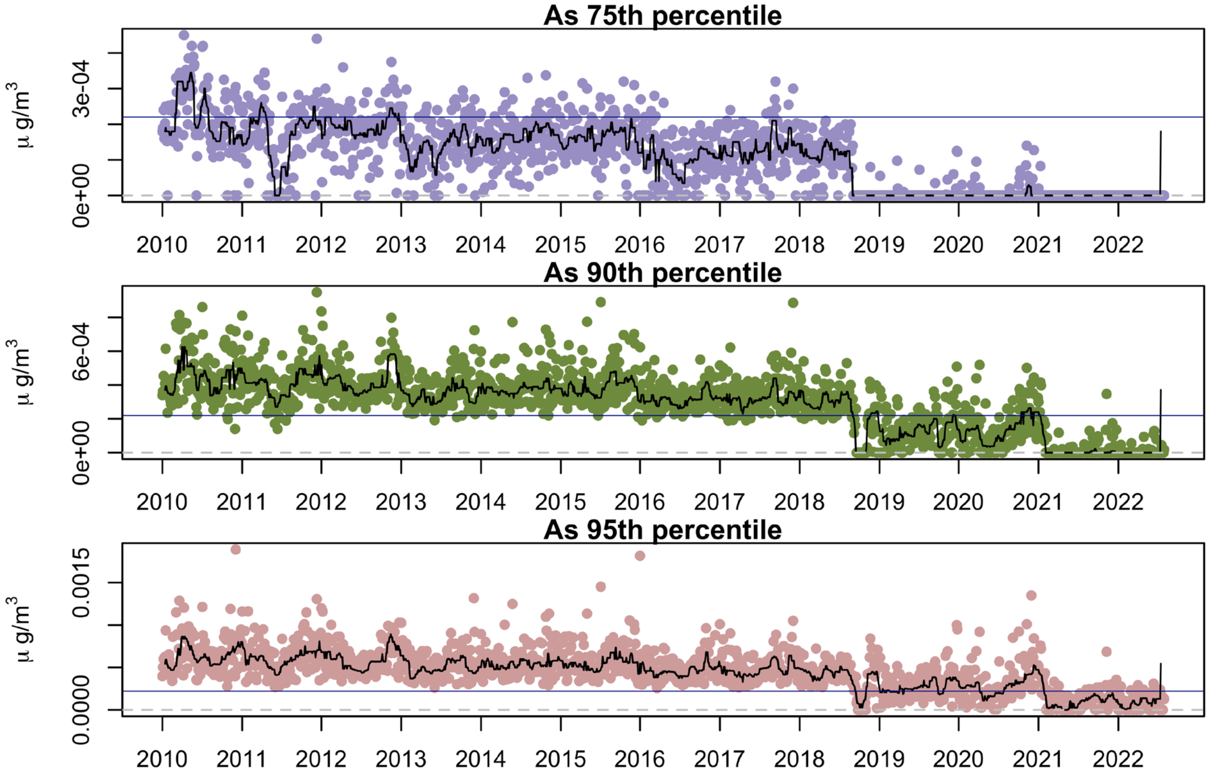


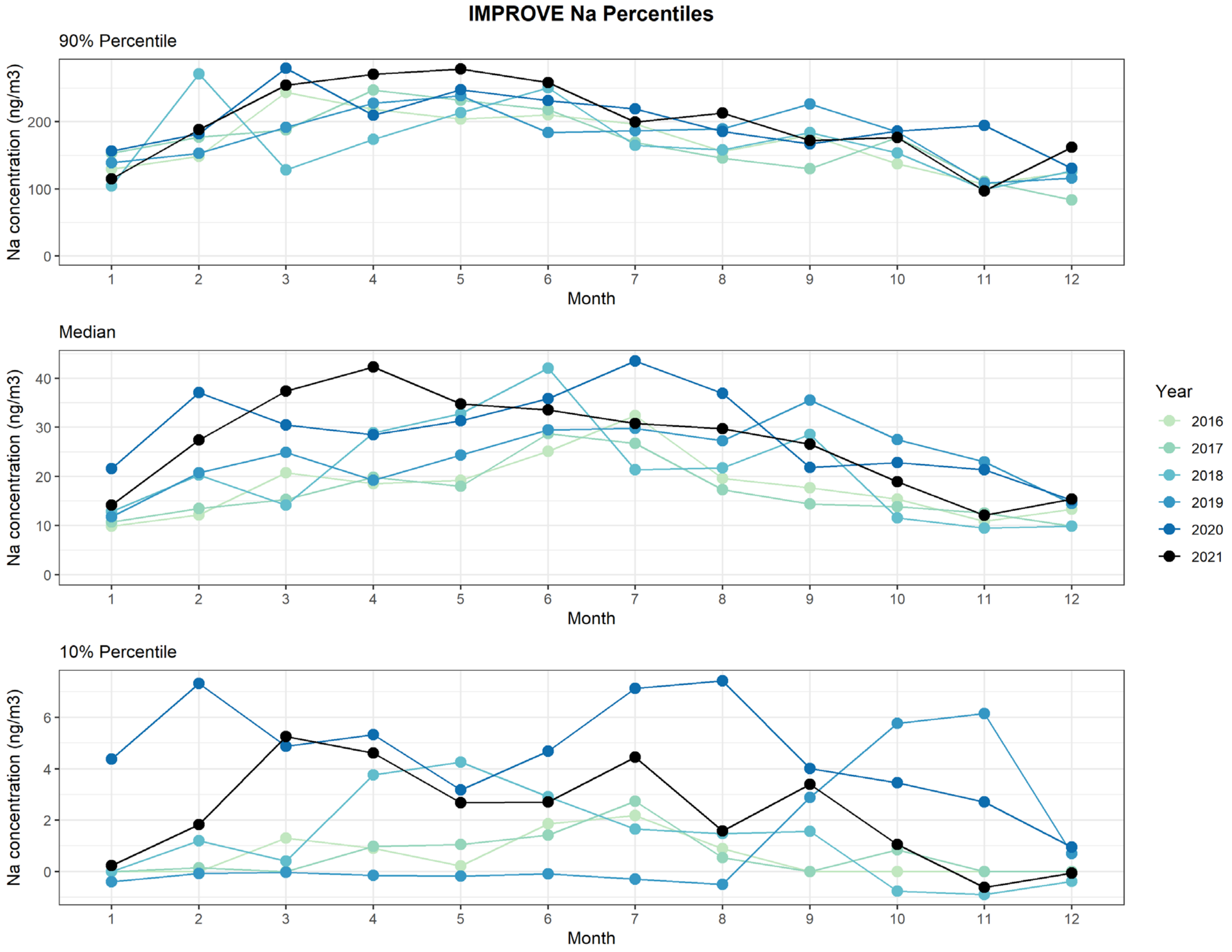
Figure 4-14. Time series of the network daily 75th percentile, 90th percentile and 95th percentile concentrations of arsenic from 2010 to 2022.



In Figure 4-14 above, the solid black line is the 10-point smoothed line for each percentile concentration data. The horizontal thin lines represent the median MDL value for arsenic.

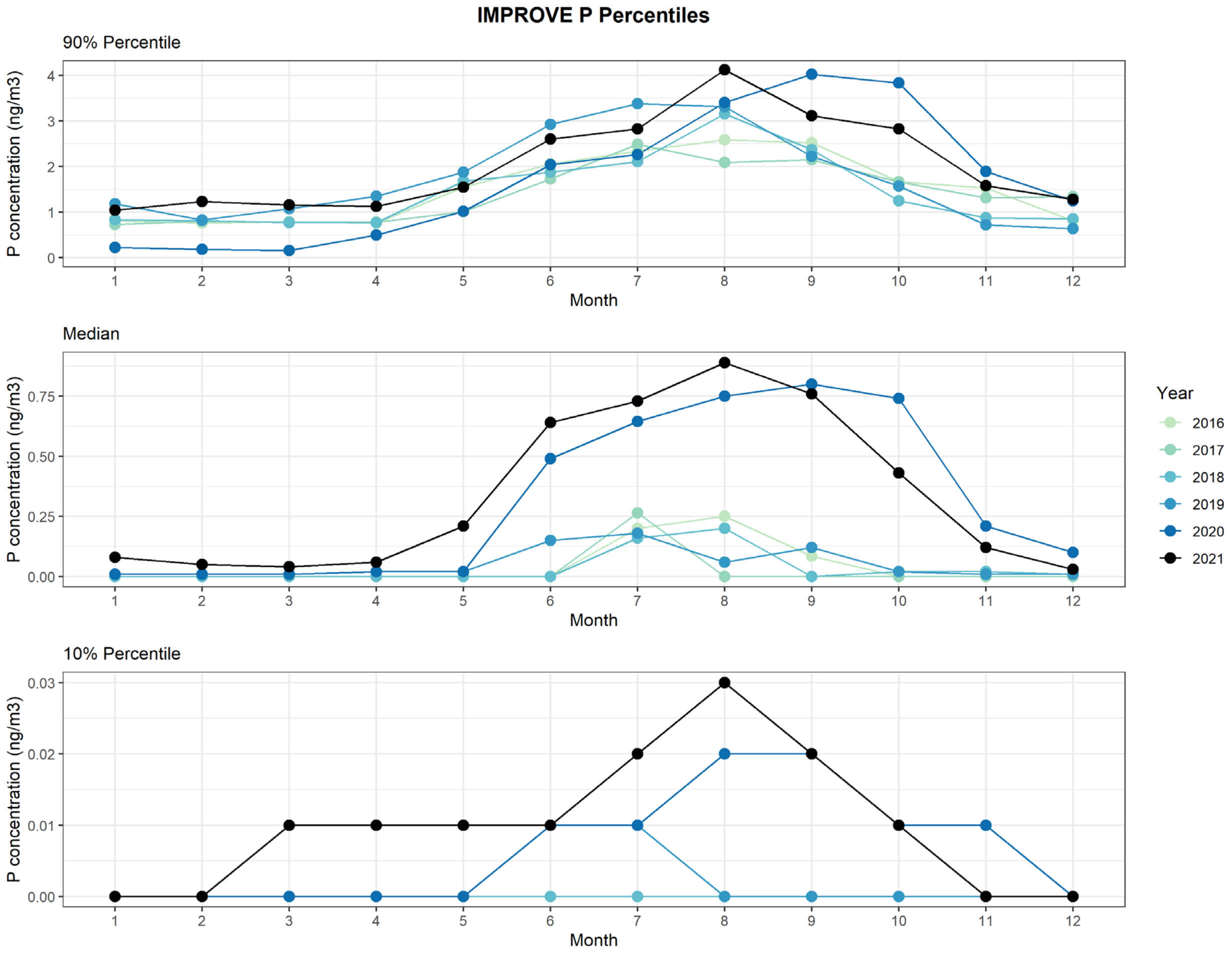
It was noted in the last report that the median and 10th percentile concentrations of sodium (Na) (Figure 4-15) appear to be elevated since September of 2019. The 10th percentile Na concentrations remain high throughout 2020. Such trend is not observed in 2021.

Figure 4-15: Multi-year time series of network-wide sodium (Na) concentrations.



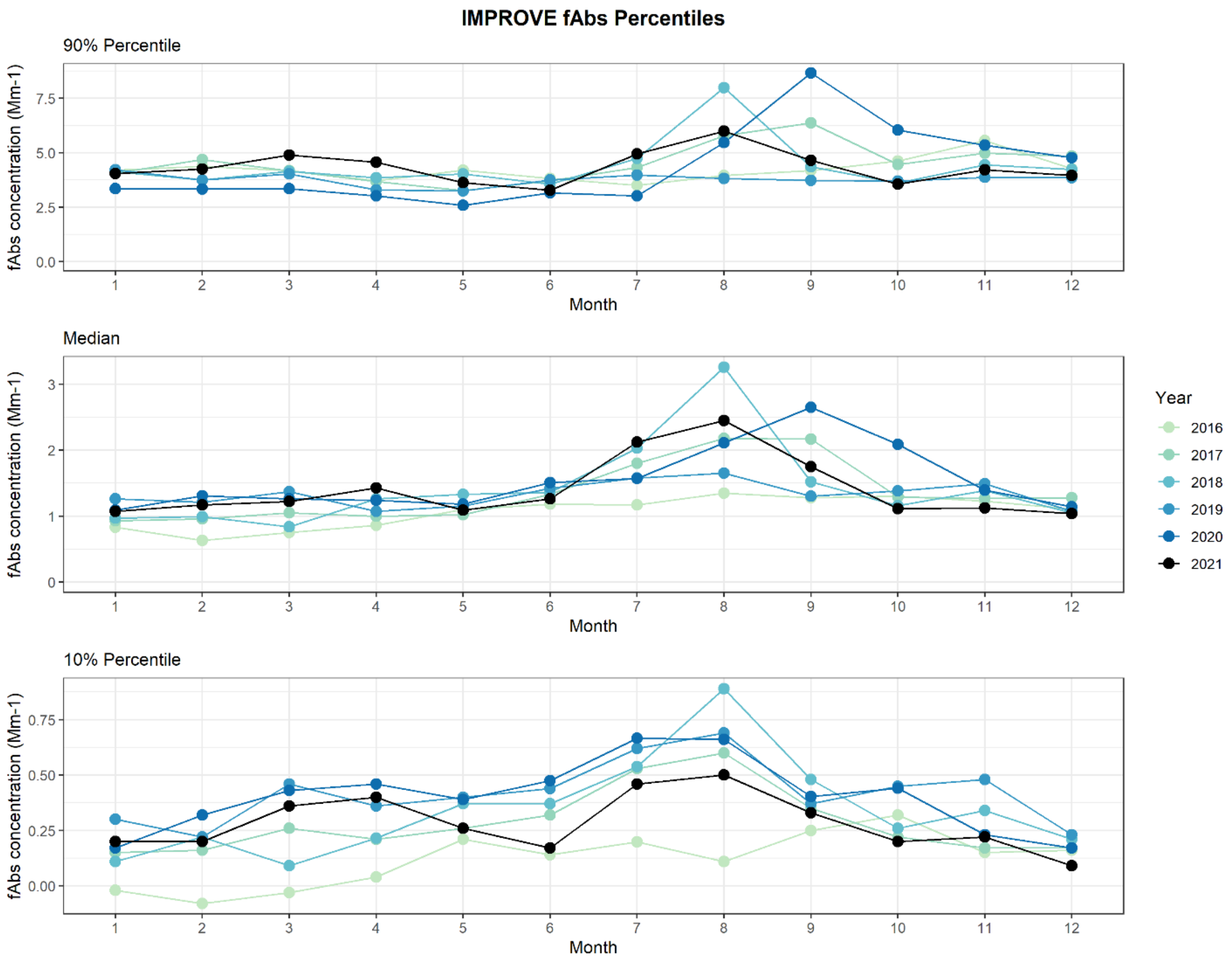
Median phosphorus (P) concentrations were higher than usual from June through October in both 2020 and 2021 (Figure 4-16). Preliminary data analysis suggested the high level of phosphorus is possibly associated with wildfire emissions, and Fresno and Sequoia are the two IMPROVE sites with the highest average phosphorus concentrations. Inter-comparison study between XRF and ICP measurements of phosphorus from summer 2022 samples is being carried out to validate the XRF measurement.

Figure 4-16: Multi-year time series of network-wide phosphorus (P) concentrations.



As explained in Section 3.3, the HIPS instrument was reconfigured starting with data for May 2021. The percentile plot below shows the change did not have a significant impact on network data and followed trends from previous years.

Figure 4-17: Multi-year time series of network-wide phosphorus (fAbs) concentrations.



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.

In the following figures, 4-18 to 4-25, the bars show 25th to 75th percentile range, and the middle line indicates median.

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 $(3\times S)/SO_4$ 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 4-18), suggesting the presence of some sulfur in a non-water-soluble form of sulfate or in a chemical compound other than sulfate. The $(3\times S)/SO_4$ ratio is generally higher during the summer months, although the seasonal cycle of the ratio appears to be less pronounced since 2018 (Figure 4-19). The 2021 monthly median (3×S)/SO_4 ratios were generally higher than those in recent years (Figure 4-18), but were in similar range to earlier years (2011-2016).

Figure 4-18: Multi-year time series of network-wide (3×S)/SO_4 ratios, 2016 through 2021.

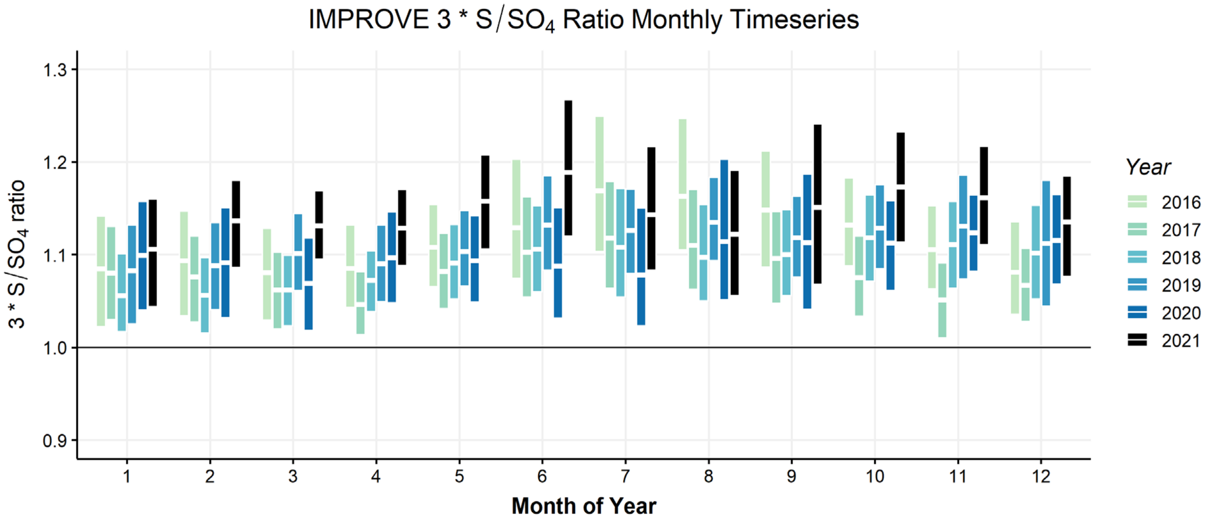
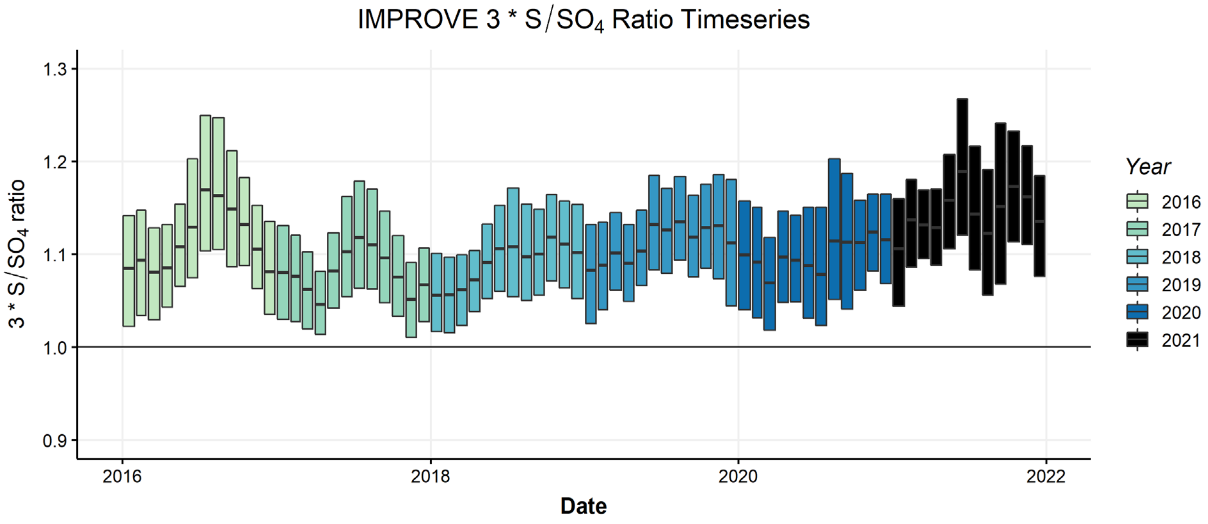


Figure 4-19: Time series of network-wide (3×S)/SO_4 ratios, 2016 through 2021.



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:

$$\mathrm{RCM} = (4.125 \times \mathrm{S}) + (1.29 \times \mathrm{NO_3}^-) + (1.8 \times \mathrm{OCR}) + (\mathrm{ECR}) + (2.2 \times \mathrm{Al} + 2.49 \times \mathrm{Si} + 1.63 \times \mathrm{Ca} + 2.42 \times \mathrm{Fe} + 1.94 \times \mathrm{Ti}) + (1.8 \times \mathrm{chloride})$$

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 4-20). 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 $PM_{2.5}$.

In 2019 and 2020, the RCM/$PM_{2.5}$ ratios are elevated compared to previous years, particularly during the colder months, e.g., in December 2019 through March 2020 and November through December 2020, which have the highest ratios for the years plotted. This observation, together with the upward trend in the ratios observed in those two years, are not continued with the 2021 data (Figure 4-20 and Figure 4-21).

Figure 4-20: Multi-year time series of network-wide RCM/$PM_{2.5}$ ratios, 2016 through 2021.

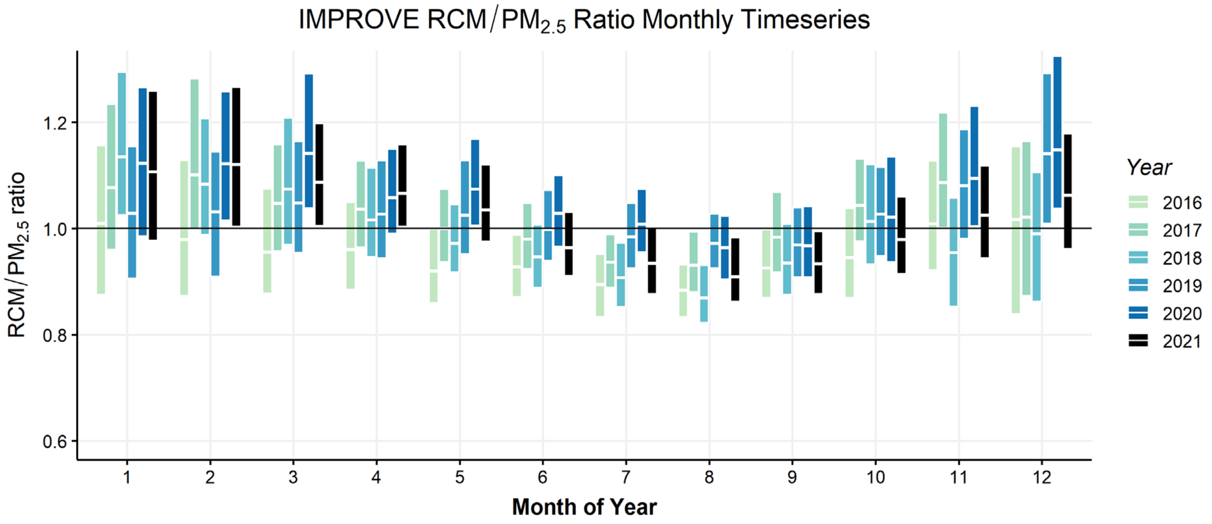
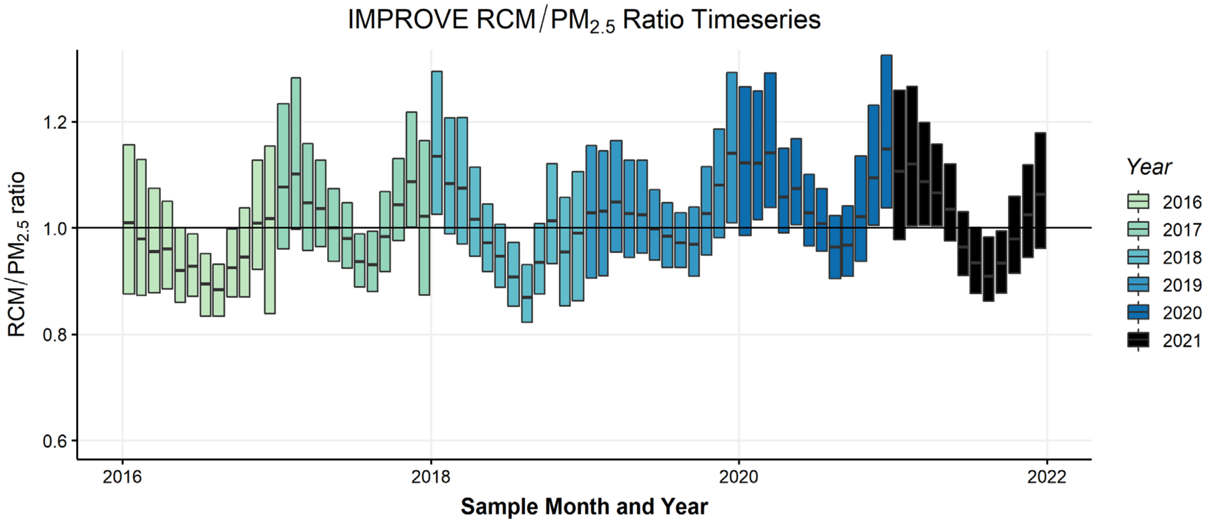


Figure 4-21: Time series of network-wide RCM/$PM_{2.5}$ ratios, 2016 through 2021.



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 ng/m^3) measured by thermal optical analysis (TOA). In the cross-module plots (Figure 4-22, Figure 4-23 and Figure 4-24), fAbs data are multiplied by 100 to bring the fAbs/ECR ratios close to 1 for easier interpretation.

June, July August, and September 2021 fAbs data are low compared to ECR (Figure 4-22 and 4-23). In Figures 4-23 and 4-24, fAbs data are compared with ECT (EC by transmittance) and BC estimated from the TOA laser signals, and these ratios were similarly low during the summer months in 2021. The ratio of BC to ECR in Figure 4-27, both estimated from the quartz filters also are lower in June, July, August, and September 2021, suggesting that the issue is not isolated to the HIPS measurements. The issue of the observed low fAbs values has been investigated through various experiments and reanalysis of the 2021 summer PTFE samples by HIPS. Experiments are ongoing to determine if biases exist between HIPS measurements on the Pall and MTL brand PTFE filters. In addition to investigating the HIPS measurements, EC data are evaluated for consistency by comparing it with the OC measurement because one hypothesis is that EC may be overestimated in the fire-impacted samples due to the inaccurate OC/EC split for heavily-loaded samples. Figure 4-27 shows the time series of the network OCR/ECR ratio from 2016-2021. The OCR/ECR ratios seem to be consistent with previous years in the months of interest.

In the following figures, 4-22 to 4-25, fAbs data are multiplied by 100 to bring the fAbs/ECR ratio close to 1.

Figure 4-22: Multi-year time series of network-wide fAbs/ECR ratios, where fAbs is in Mm^{-1} and elemental carbon by reflectance (ECR) is in ng/m^3, 2016 through 2021.

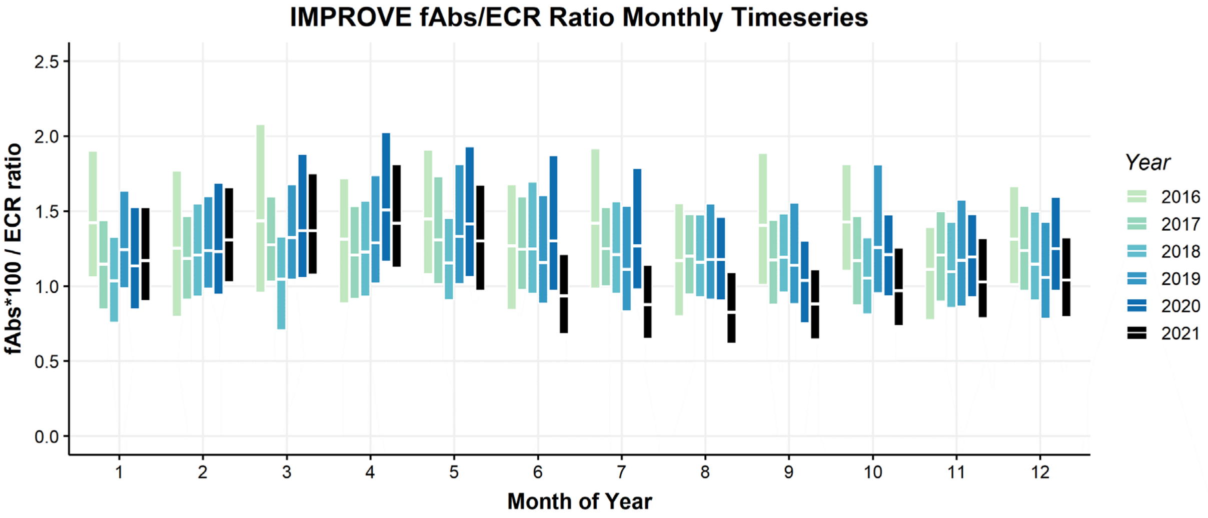


Figure 4-23: Time series of network-wide fAbs/ECR ratios, 2016 through 2021.

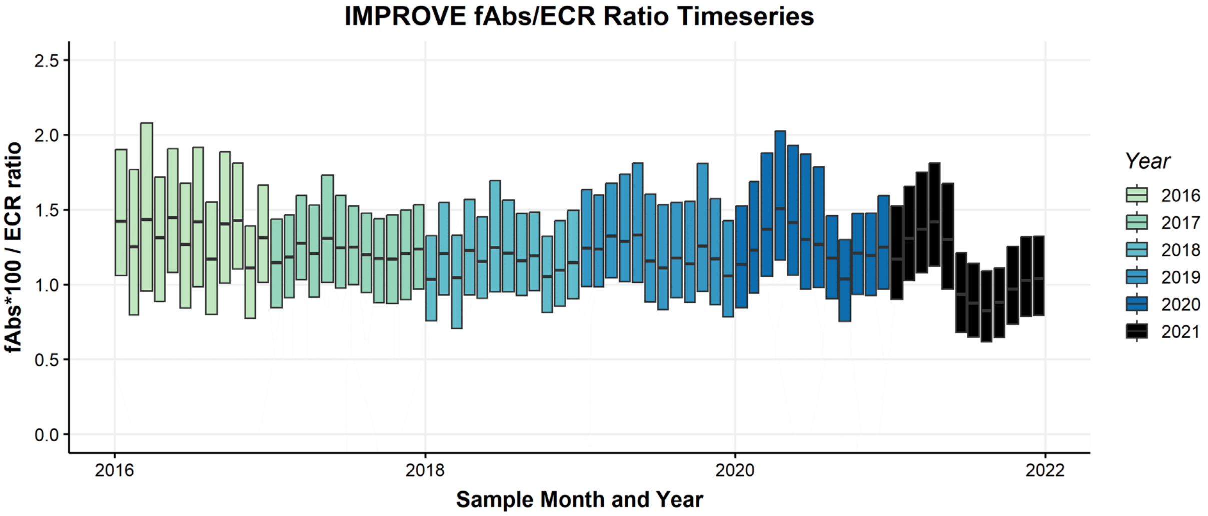


Figure 4-24: Time series of network-wide fAbs/ECT ratios, 2016 through 2021.

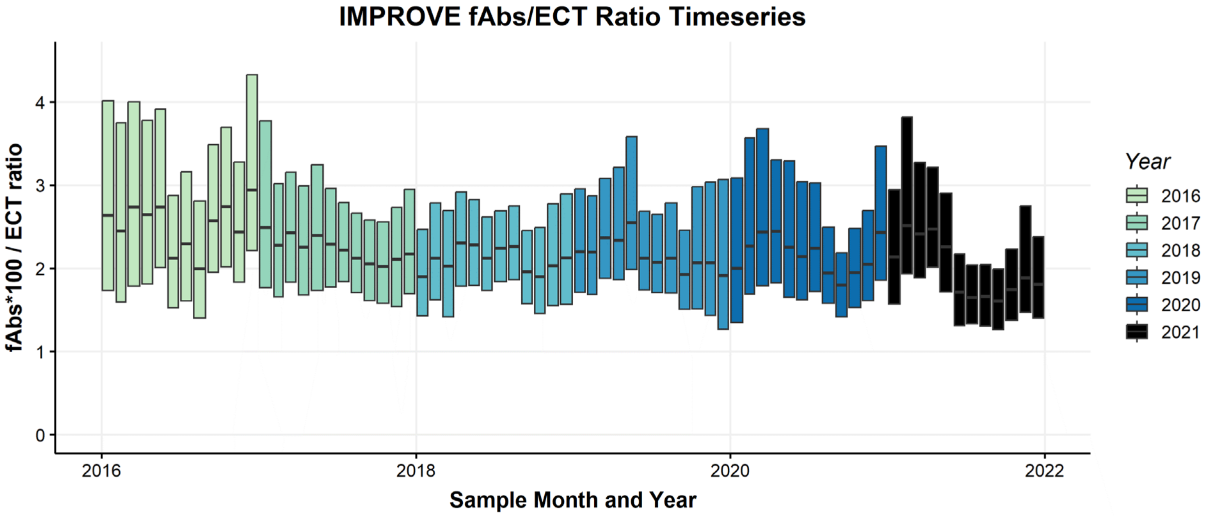


Figure 4-25: Time series of network-wide fAbs/BC ratios, 2016 through 2021.

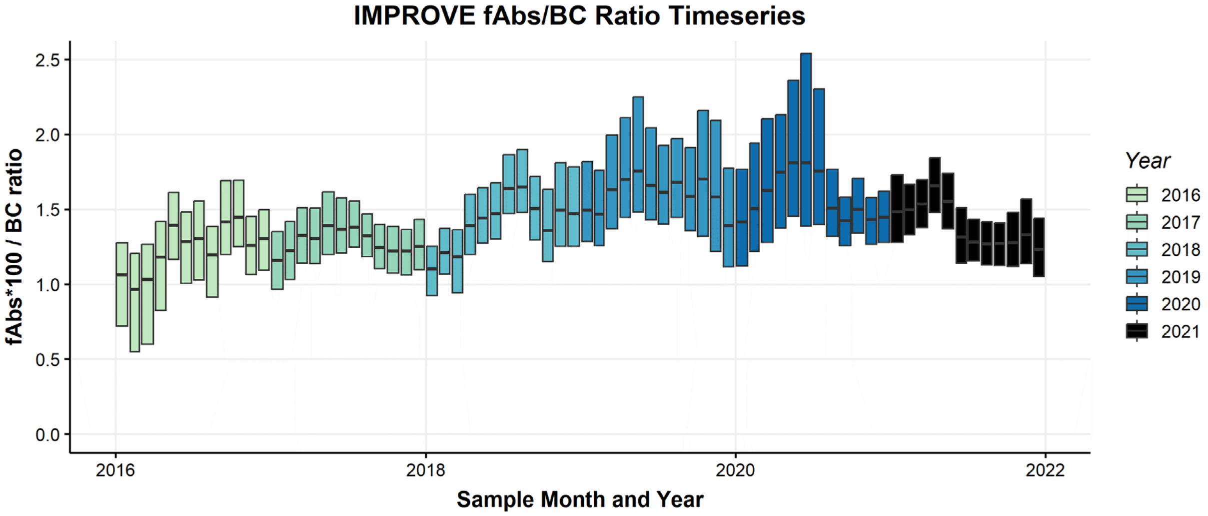


Figure 4-26: Time series of network-wide BC/ECR ratios, both measurements made by TOA on the quartz filters, 2016 through 2021.

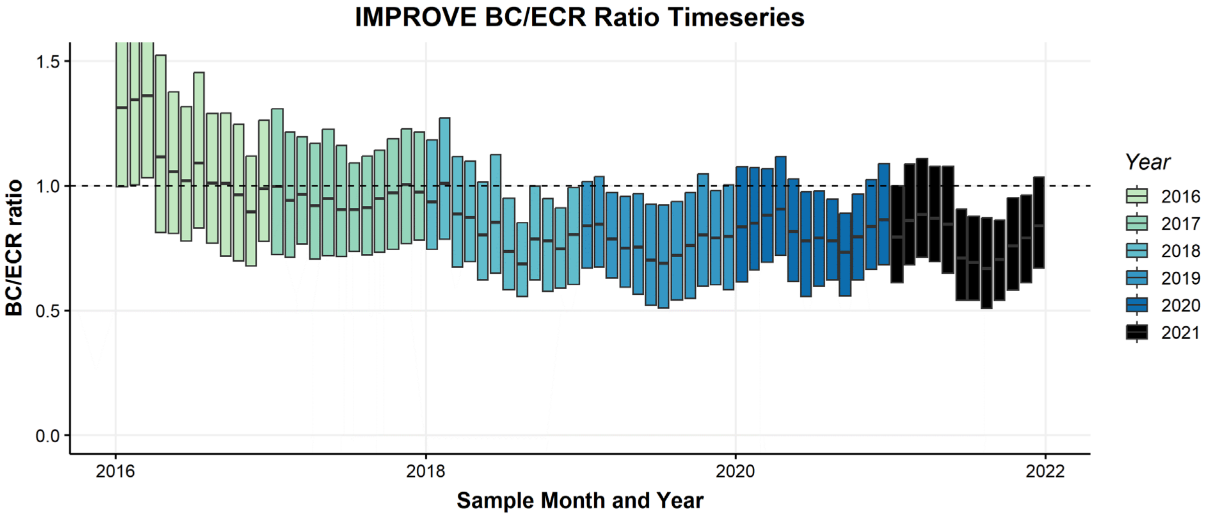
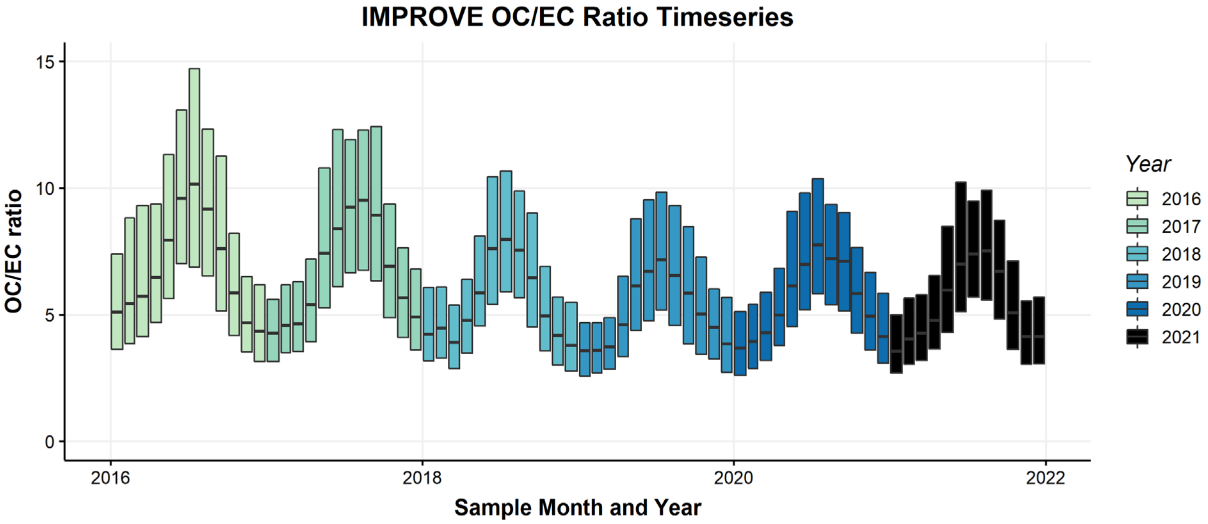


Figure 4-27: Time series of network-wide OCR/ECR ratios, 2016 through 2021.



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 4-28, elements; Figure 4-29, mass; Figure 4-30, ions; Figure 4-31, carbon; Figure 4-32, 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 2021 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)			

In the following figures, 4-28 to 4-32, data from the last two years (2019 &2020) are plotted in grey as reference for the current year. Dotted vertical lines indicate method detection limits.

Figure 4-28: Scaled relative difference for element measurements at sites with collocated modules across the IMPROVE network (2021).

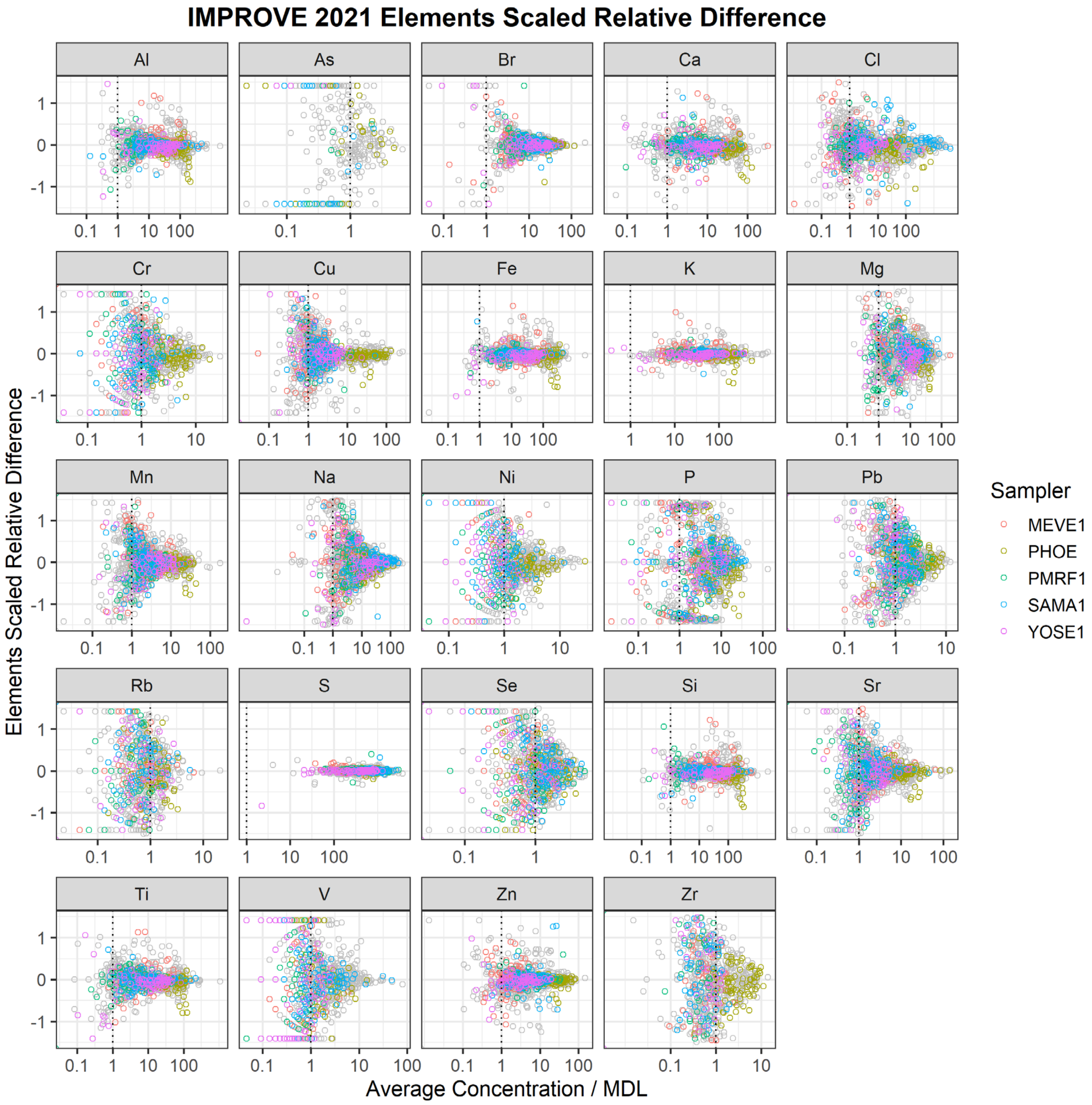


Figure 4-29: Scaled relative difference for PM_{10} and $PM_{2.5}$ at sites with collocated modules across the IMPROVE network (2021).

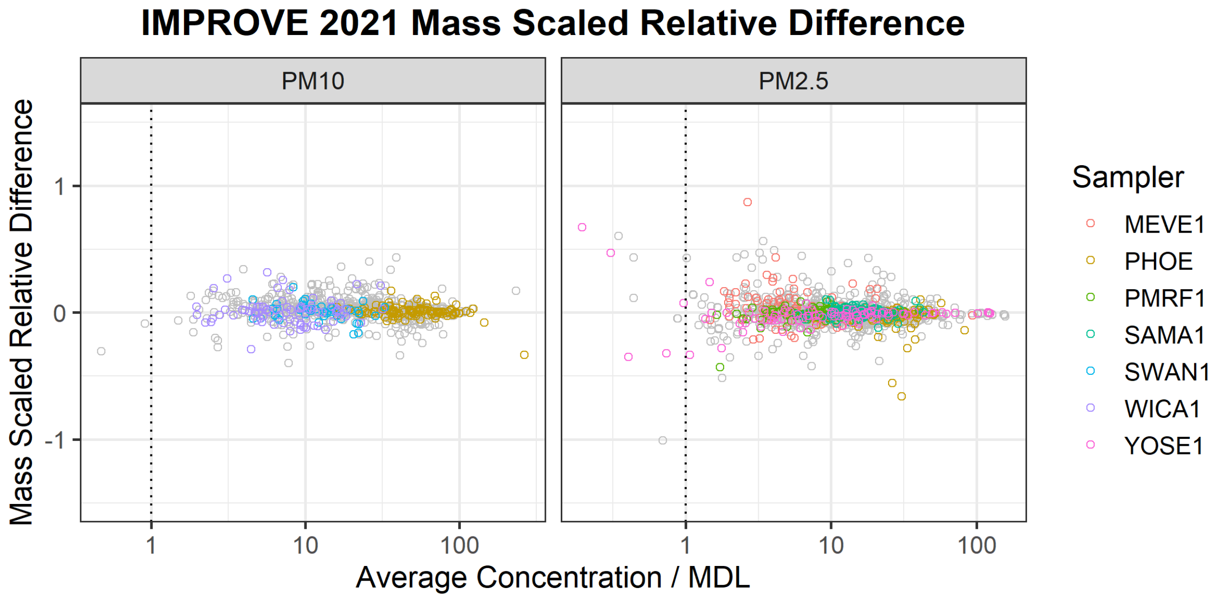
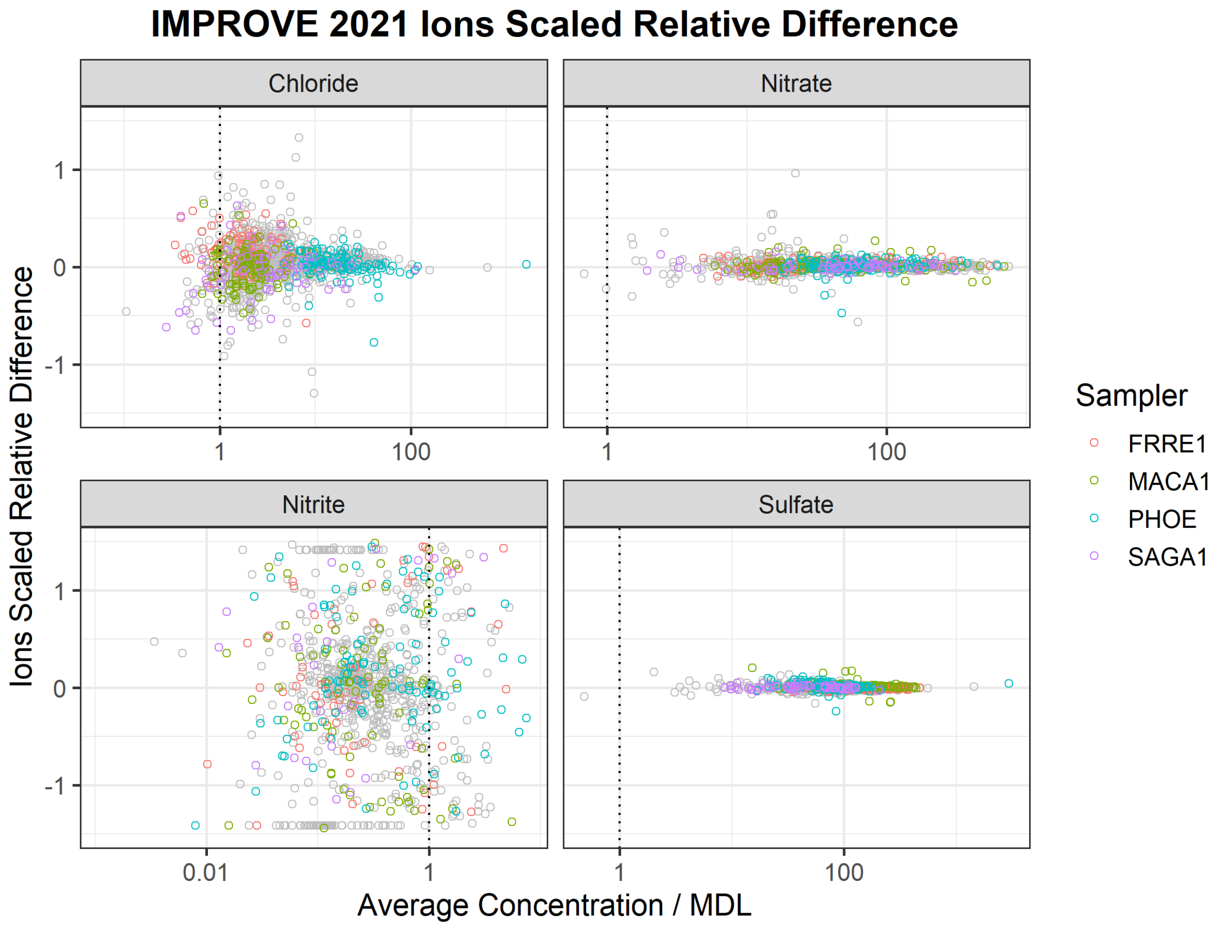


Figure 4-30: Scaled relative difference for ions measurements at sites with collocated modules across the IMPROVE network (2021).



In Figure 4-31 below, 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.

Figure 4-31: Scaled relative difference for carbon measurements at sites with collocated modules across the IMPROVE network (2021).

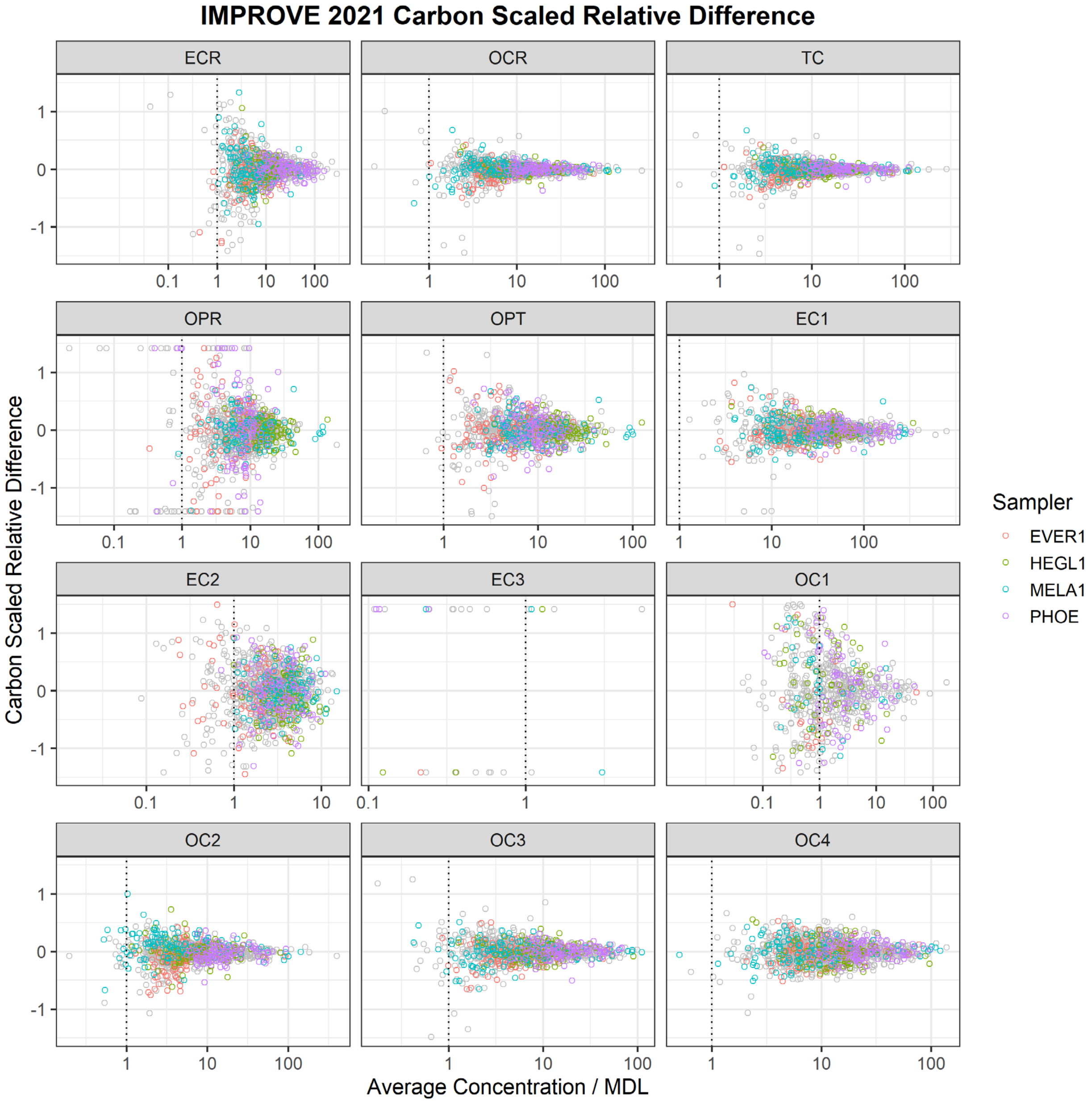
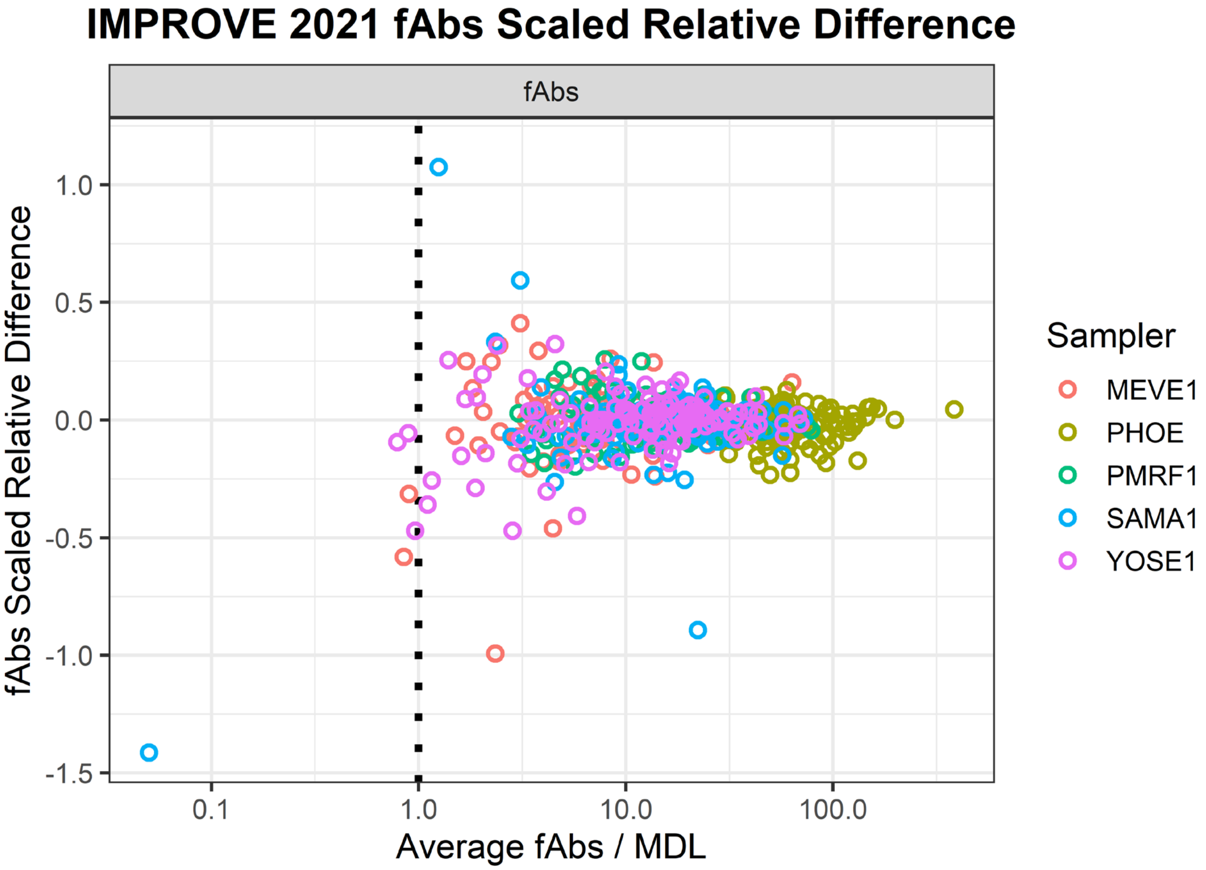


Figure 4-32: Scaled relative difference for optical absorption measurements at sites with collocated modules across the IMPROVE network (2021).



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 2021 IMPROVE data is calculated using data from collocated samples collected 2019-2020 (Table 4-2).

Table 4-2: Fractional uncertainty calculated from collocated samples.

	Fractional Uncertainty Reporting Period				
	2017	**2018**	**2019**	**2020**	**2021**
	Source Data Sample Period				
Species	**2013-2016**	**2016-2017**	**2017-2018**	**2018-2019**	**2019-2020**
Chloride	0.08	0.08	0.09	0.1	0.09
Nitrite	0.25	0.25	0.25	0.25	0.25
Nitrate	0.04	0.04	0.04	0.04	0.04
Sulfate	0.02	0.02	0.03	0.02	0.01
Organic Carbon (OCR)	0.09	0.08	0.07	0.07	0.06
Elemental Carbon (ECR)	0.14	0.14	0.13	0.13	0.14
Total Carbon	0.08	0.07	0.07	0.06	0.06
Organic Carbon (OC1)	0.26	0.23	0.24	0.21	0.17
Organic Carbon (OC2)	0.13	0.11	0.1	0.09	0.09
Organic Carbon (OC3)	0.13	0.13	0.11	0.09	0.09
Organic Carbon (OC4)	0.13	0.13	0.14	0.16	0.16
Organic Pyrolyzed (OPR)	0.16	0.20	0.21	0.2	0.19
Elemental Carbon (EC1)	0.10	0.11	0.11	0.11	0.12
Elemental Carbon (EC2)	0.18	0.19	0.21	0.22	0.22
Elemental Carbon (EC3)	0.25	0.25	0.25	0.25	0.25
Na	0.14	0.14	0.14	0.15	0.16
Mg	0.15	0.15	0.15	0.17	0.2
Al	0.08	0.08	0.09	0.1	0.12
Si	0.07	0.06	0.07	0.09	0.1
P	0.23	0.27	0.3	0.3	0.35
S	0.02	0.02	0.03	0.03	0.03
Cl	0.17	0.14	0.14	0.16	0.18
K	0.04	0.03	0.04	0.05	0.06
Ca	0.06	0.06	0.07	0.09	0.1
Ti	0.09	0.09	0.09	0.11	0.12
V	0.16	0.17	0.17	0.12	0.16
Cr	0.17	0.15	0.17	0.16	0.15
Mn	0.13	0.14	0.13	0.13	0.13
Fe	0.06	0.05	0.06	0.08	0.09
Ni	0.20	0.13	0.14	0.18	0.14
Cu	0.09	0.13	0.1	0.1	0.11
Zn	0.07	0.08	0.08	0.08	0.09
As	0.25	0.25	0.25	0.25	0.25

Se	0.25	0.25	0.25	0.25	0.25
Br	0.11	0.10	0.09	0.09	0.09
Rb	0.25	0.25	0.25	0.25	0.25
Sr	0.13	0.13	0.14	0.14	0.15
Zr	0.25	0.25	0.25	0.25	0.25
Pb	0.16	0.14	0.15	0.25	0.19
$PM_{2.5}$	0.03	0.04	0.04	0.04	0.05
PM_{10}	0.07	0.07	0.08	0.07	0.05
fAbs	0.06	0.06	0.05	0.06	0.07

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 4-33 through Figure 4-36). Transition to new lots occurs over a period of weeks; the shift in field blank concentrations gradually manifest over time rather than abruptly.

The following figures are a timeseries of selected parameters on nylon filter field blanks. January 1, 2017 through December 31, 2021. Vertical lines indicate manufacturer lot transitions.

Figure 4-33: Time series of chloride measured on nylon filter field blanks.

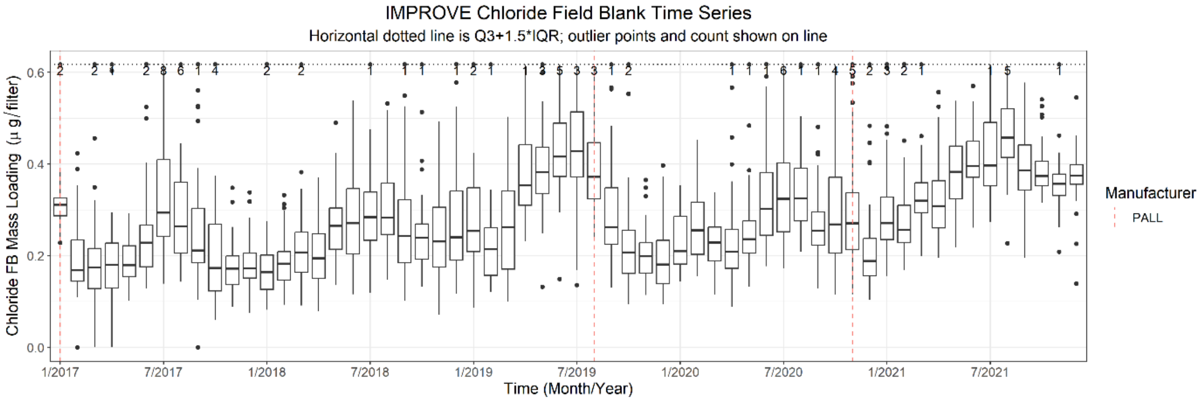


Figure 4-34: Time series of nitrate on nylon filter field blanks.

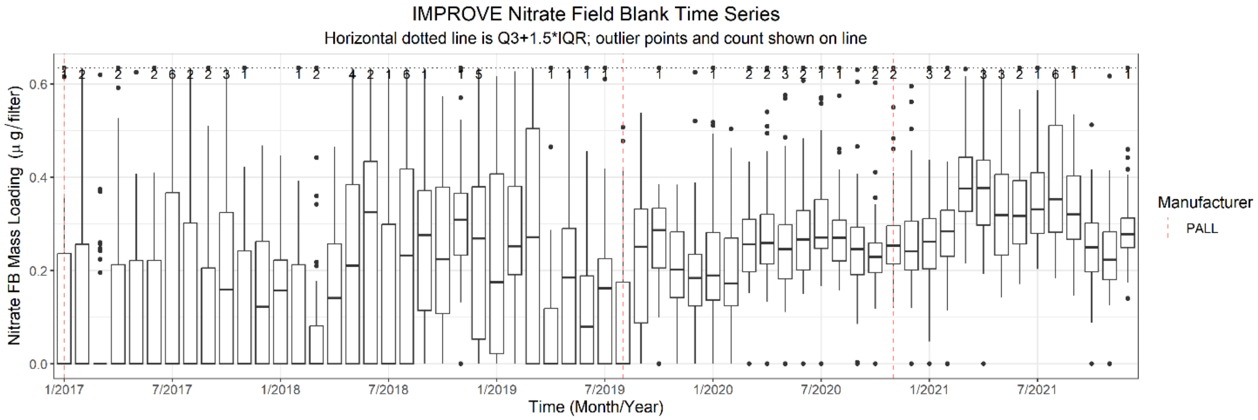


Figure 4-35: Time series of sulfate on nylon filter field blanks.

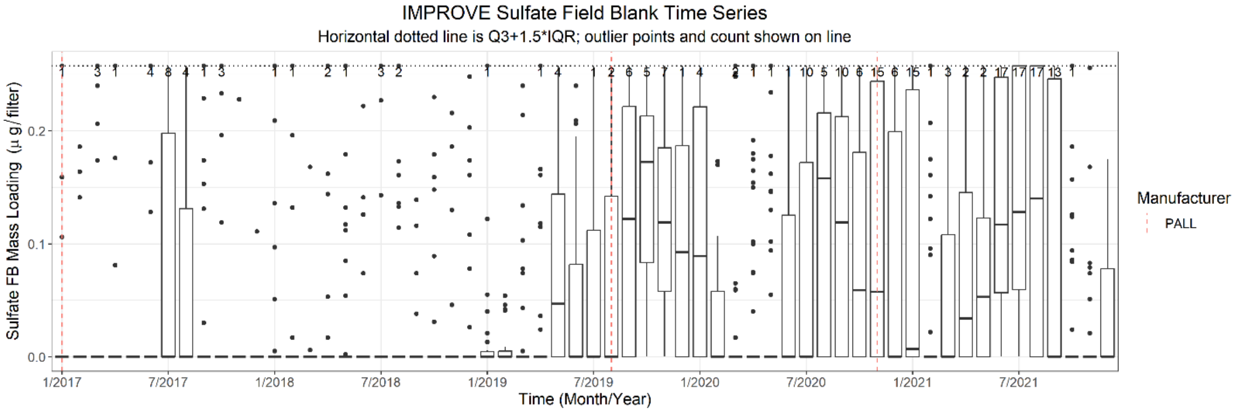
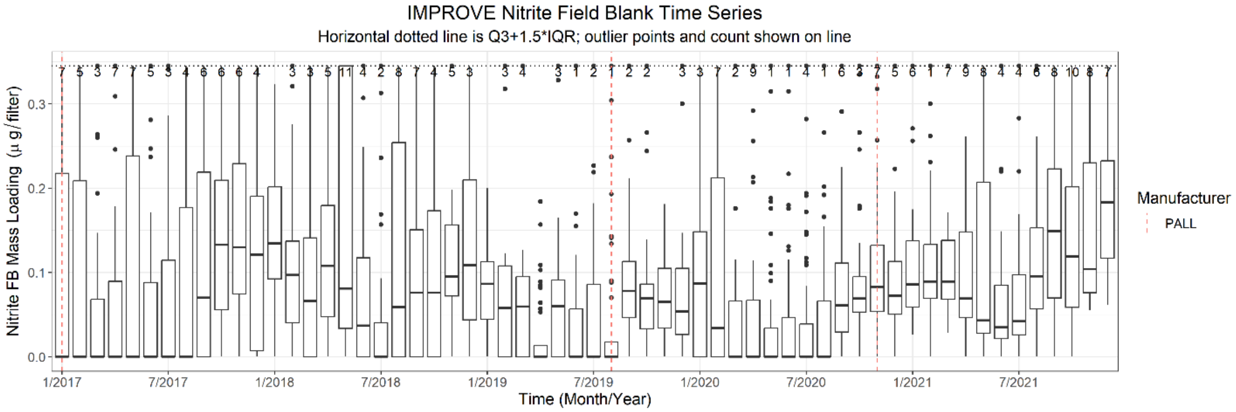


Figure 4-36: Time series of nitrite on nylon filter field blanks.



Quartz filters are pre-fired by DRI. Quartz filter field blanks typically have low concentrations of elemental carbon by reflectance (ECR; Figure 4-36). 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 4-37).

Figure 4-37: Time series of elemental carbon by reflectance (ECR) on quartz filter field blanks.

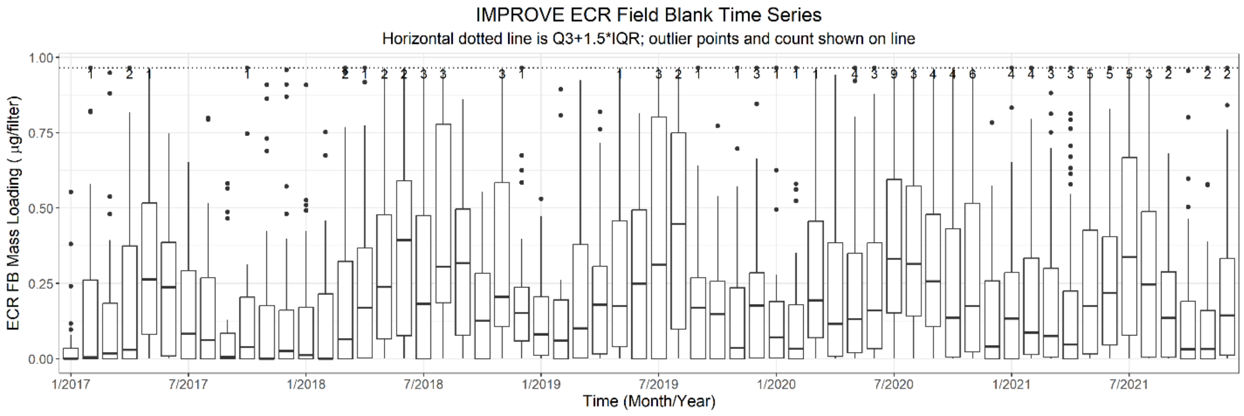
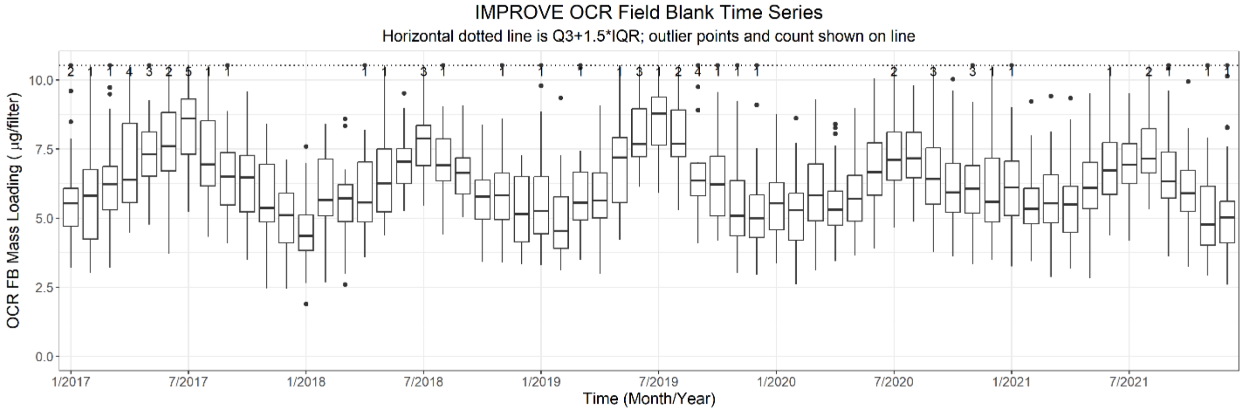


Figure 4-38: Time series of organic carbon by reflectance (OCR) on quartz filter field blanks.



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, K, S, and Ca are shown in Figure 4-39, Figure 4-40, Figure 4-41, and Figure 4-42. 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.

From August 2020 to May 2021, PTFE filter manufacturer was transitioned back from MTL to Pall due to filter supply shortage. During this period, small lots of Pall filters were used without adequate acceptance testing because Pall could not supply the filters in larger lots. Several elements (e.g. Ca, Cl, Fe, K, S, and Ti) exhibited higher mass loadings on blanks (Figure 4-40, Figure 4-41 and Figure 4-42), coinciding with the switch in PTFE filter manufacturer from MTL to Pall. In Figure 4-43, Ca blank mass loadings broken down by filter lot number shows that Pall filters (lot number starting with “FH”) have higher Ca background values than MTL filters. This difference in the levels of blank contamination among filter lots is accounted for by the lot-specific blank subtraction on the sample filters.

In the following figures, 4-39 to 4-44, 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 4-39: Time series of aluminum (Al) on PTFE filter field blanks.

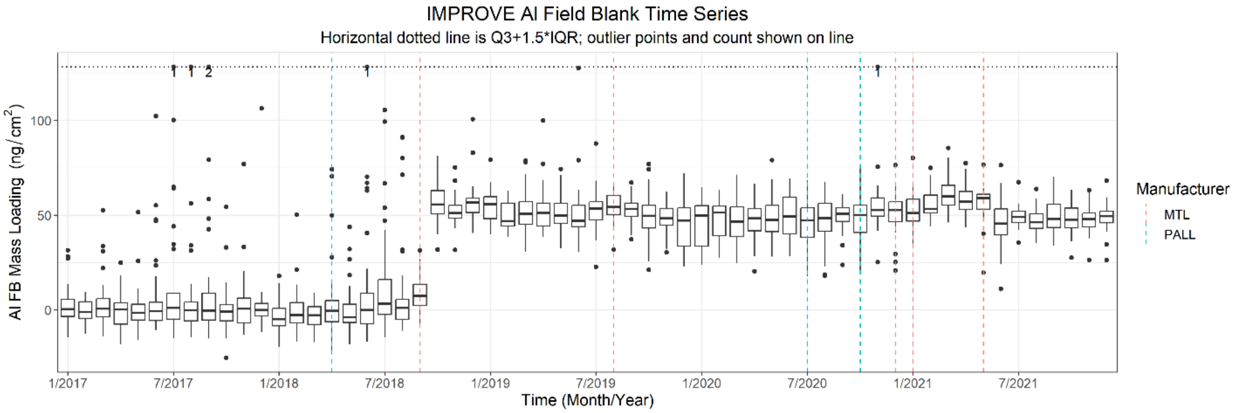


Figure 4-40: Time series of potassium (K) on PTFE filter field blanks.

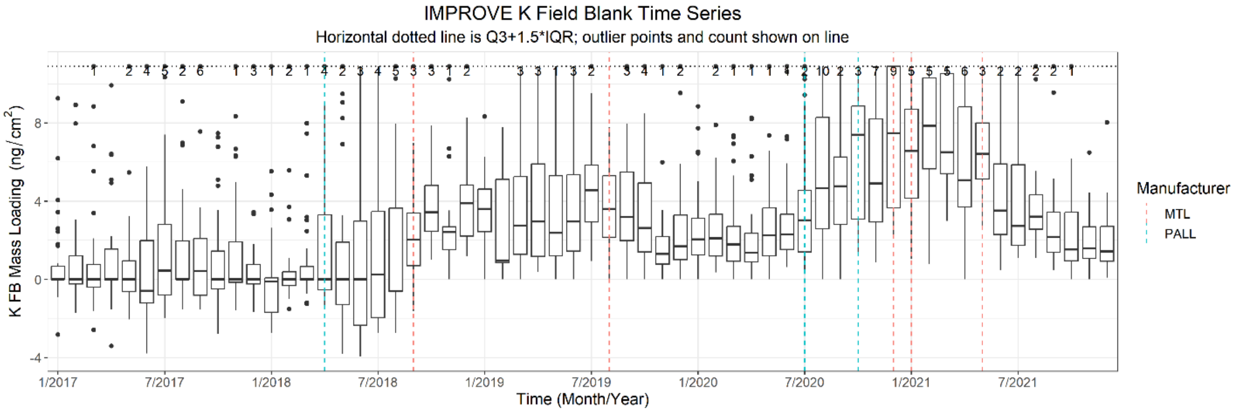


Figure 4-41: Time series of sulfur (S) on PTFE filter field blanks.

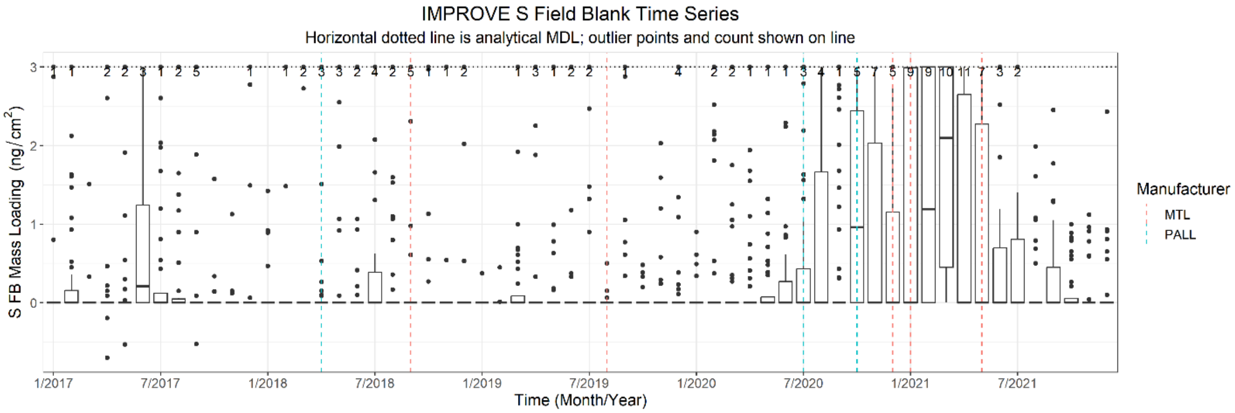


Figure 4-42: Time series of calcium (Ca) on PTFE filter field blanks.

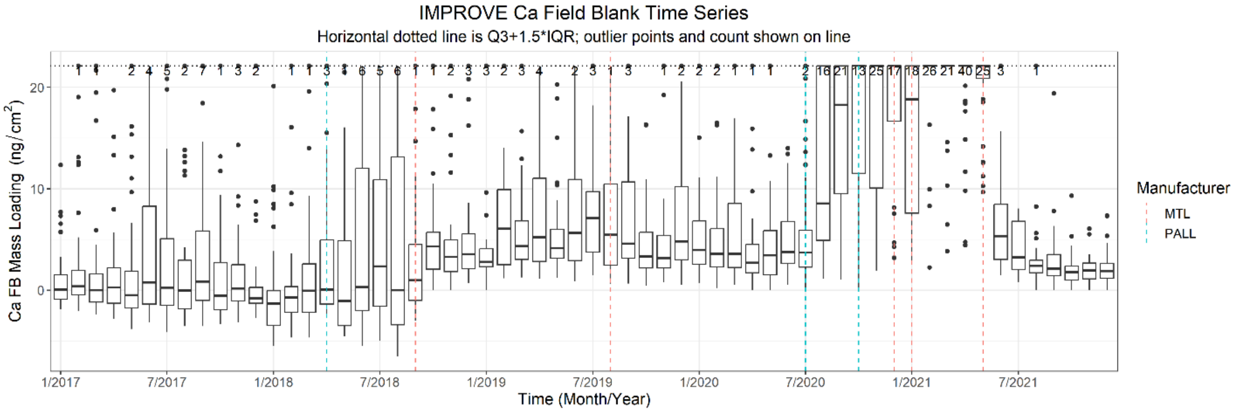


Figure 4-43: Time series of calcium (Ca) mass loadings on PTFE filter field blanks from January 2020 to December 2021. Data are separated by filter lot number (MTL lot: 234, 241a, 248, 250; Pall lot: FH00216740 and FH00227659).

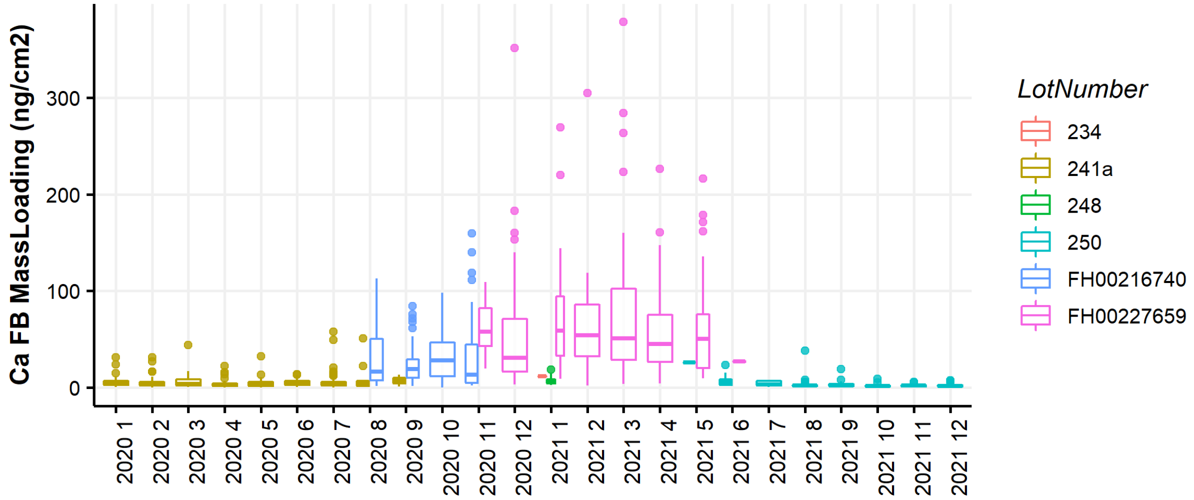
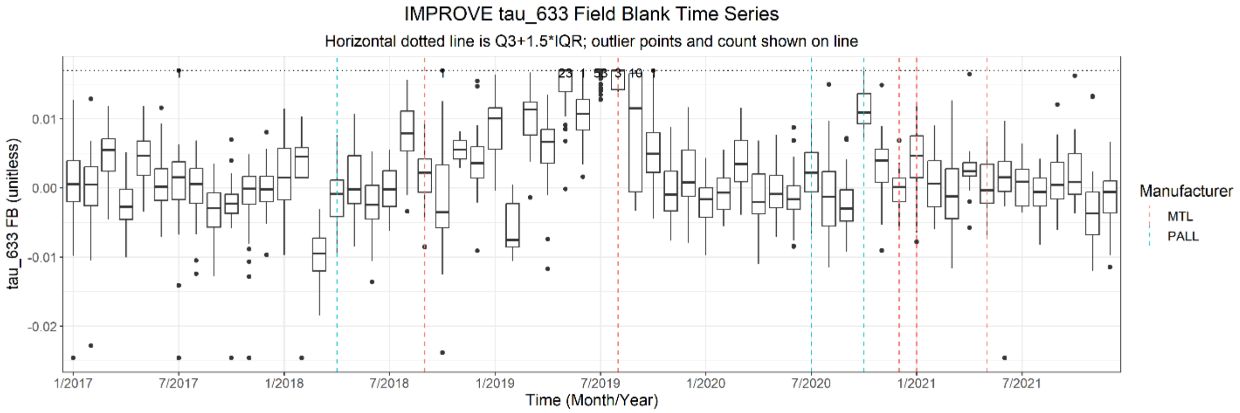


Figure 4-44 shows the Tau_633 measurements by HIPS on the PTFE filter field blanks from the 1A module. As mentioned in the previous IMPROVE Semiannual Quality Assurance Reports and documented in a UCD data advisory (http://vista.cira.colostate.edu/Improve/data-advisories/, posted 4/2019), in April 2018 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 collected January 2017 through February 2018 were analyzed under this calibration. Additionally, in November 2018 a new detector was installed and the instrument was subsequently recalibrated; samples collected beginning March 2018 were analyzed under this calibration.

As noted in Section 2.4.1, the HIPS instrument was reconfigured to use a fiber optical cable and focusing lens collimator. This configuration took effect for May 2021 measurement data.

Figure 4-44: Time series of Tau_633 on PTFE filter field blanks.



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 data from the previous three years for comparison with average MDLs calculated for data from 2021.

Table 4-3: Average method detection limits (MDLs) and percentage of reported data above the MDLs calculated for 2018, 2019, 2020, and 2021 data.

Species	2018		2019		2020		2021	
	Average MDL (ng/m^3)	% Above MDL	Average MDL (ng/m^3)	% Above MDL	Average MDL (ng/m^3)	% Above MDL	Average MDL (ng/m^3)	% Above MDL
Chloride	6	81	7	74	8	76	5	80
Nitrite	20	9	7	11	10	6	20	8
Nitrate	10	98	9	99	8	98	7	99
Sulfate	5	100	6	100	8	100	8	100
Organic Carbon (OCR)	70	97	100	94	90	95	80	96
Elemental Carbon (ECR)	20	90	20	90	20	90	20	90
Total Carbon	80	97	100	95	100	96	80	96
Organic Carbon (OC1)	30	34	30	28	30	28	30	28
Organic Carbon (OC2)	20	92	30	90	20	90	30	88
Organic Carbon (OC3)	40	94	40	90	40	92	30	93
Organic Carbon (OC4)	20	97	20	97	20	96	20	97
Organic Pyrolyzed (OPR)	20	94	20	94	10	93	20	93
Elemental Carbon (EC1)	10	98	10	98	8	98	10	98
Elemental Carbon (EC2)	20	87	20	88	20	85	20	86
Elemental Carbon (EC3)	5	0	5	0	0.3	2	0.3	1
Na	5	80	5	81	5	88	5	81
Mg	3	76	3	70	2	78	2	79
Al	3	92	2	92	2	95	2	95
Si	7	90	4	93	2	96	2	97

Species	2018		2019		2020		2021	
	Average MDL (ng/m^3)	% Above MDL	Average MDL (ng/m^3)	% Above MDL	Average MDL (ng/m^3)	% Above MDL	Average MDL (ng/m^3)	% Above MDL
P	0.2	34	0.2	32	0.2	44	0.2	53
S	0.4	100	0.4	100	0.4	100	0.4	100
Cl	0.4	86	0.3	85	0.5	78	0.8	73
K	1	99	0.9	100	0.8	100	0.8	100
Ca	3	93	2	93	4	90	6	89
Ti	0.4	84	0.3	83	0.2	91	0.2	92
V	0.1	35	0.1	33	0.1	32	0.1	26
Cr	0.1	38	0.1	30	0.1	29	0.2	28
Mn	0.3	67	0.3	65	0.2	77	0.3	79
Fe	2	95	2	95	1	97	1	98
Ni	0.1	25	0.1	24	0.1	21	0.1	22
Cu	0.2	56	0.2	54	0.2	65	0.2	67
Zn	0.2	92	0.4	85	0.3	88	0.5	83
As	0.2	13	0.2	8	0.2	9	0.2	5
Se	0.2	28	0.2	24	0.1	39	0.1	44
Br	0.1	96	0.1	95	0.1	94	0.1	94
Rb	0.2	18	0.2	14	0.2	16	0.2	19
Sr	0.2	53	0.2	46	0.2	62	0.1	68
Zr	1	7	1.3	7	0.8	17	0.9	19
Pb	0.7	33	0.7	27	0.4	45	0.4	53
$PM_{2.5}$	300	98	300	99	300	97	300	97
PM_{10}	400	99	500	98	400	98	400	99
fAbs	0.3	86	0.2	97	0.1	97	0.1	95

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 28, 2024
Quarterly Site Status Report	February 14, 2024 (2023 Q4) May 14, 2024 (2024 Q1) August 14, 2024 (2024 Q2) November 14, 2024 (2024 Q3)
Mid-Year Quality Assurance Update	October 2024

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, 2021through December 31, 2021.

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 2021 data (January 2021 through December 2021) was redelivered to NPS – including a summary of changes made – on November 18,2022, and subsequently made available on the FED and AQS databases.

Table 5-2: Summary of data deliveries, January1, 2021 through December 31, 2021.

Data (Month Samples Collected)	FED/AQS Delivery Date
January-21	February 25, 2022
February-21	February 25, 2022
March-21	April 5, 2022
April-21	April 19, 2022
May-21	May 13, 2022
June-21	June 10, 2022
July-21	July 18, 2022
August-21	August 8, 2022
September-21	September 6, 2022
October-21	September 16, 2022
November-21	September 21, 2022
December-21	October 21, 2022

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, 2021 through December 31, 2021.

Table 6-1: Summary of major repair items shipped to IMPROVE sites, 1/1/2021 through 12/31/2021.

Item	Quantity	Sites
Pump	194	ACAD (2), ATLA (1), BADL (1), BAND (3), BIRM (1), BLIS (1), BOAP (2), BOND (2), BOWA (4), BRID (4), BRIG (1), BRIS (4), CABA (2), CABI (1), CACO (1), CANY (3), CEBL (2), COHU (1), CORI (1), DOME (2), EVER (1), FCPC (3), FG (11), FOPE (2), FRES (2), FRRE (2), GAMO (1), GRBA (2), GRGU (1), GRRI (2), GRSA (1), GRSM (3), HACR (2), HAVO (1), HECA (2), HEGL (4), ISLE (2), JARB (1), JARI (1), KALM (1), KPBO (2), LABE (1), LASU (2), LOND (4), LOST (3), LTCC (1), MACA (3), MAVI

Item	Quantity	Sites
		(1), MELA (1), MEVE (2), MING (1), MOMO (1), MORA (2), MOZI (2), NOAB (1), NOCH (1), NOGA (1), ORPI (1), OWVL (1), PEFO (2), PENO (1), PHOE (1), PHOEV (2), PINN (2), PITT (3), PMRF (4), PORE (1), PRIS (1), PUSO (1), QUCI (4), REDW (4), ROMA (1), ROMO (2), SACR (1), SAGA (1), SAMA (1), SAWT (1), SEQU (2), SHMI (1), SIPS (3), SOGP (2), SULA (2), SWAN (3), TALL (1), THRO (4), TONT (2), TOOL (5), ULBE (1), UPBU (3), VILA (3), VOYA (2), WHIT (1), WHRI (2), WICA (1), WIMO (4), YOSE (1), ZICA (3)
Electronic boxes (Ebox)	47	ACAD (1), AGTI (1), BIBE (1), BIRM (2), BLIS (2), BOAP (3), BRCA (2), BRIS (1), CABI (4), CANY (2), CAVE (2), FRES (1), GLAC (1), GRRI (1), HAVO (1), KAIS (2), MAKA (1), MEAD (1), NEBR (1), OKEF (1), PENO (1), PHOE (1), PINN (1), PMRF (1), SACR (1), SAGU (1), SAWE (1), SENE (1), SHRO (1), TRIN (1), UPBU (1), WEMI (1), WHIT (1), WHPA (1), WHRI (1), ZICA (1)
Controller	33	ATLA (1), BIBE (1), BLIS (1), BOWA (1), BRID (1), CABI (2), CACO (1), CAVE (2), EGBE (1), FRRE (1), GRRI (1), ISLE (1), JARI (1), JOSH (1), LTCC (1), MAKA (1), MEAD (1), MOHO (1), MORA (1), PEFO (1), PORE (2), SAGU (2), SHRO (1), SOGP (1), SYCAII (1), ULBE (1), VIIS (1), VOYA (1), WIMO (1)
Networking Device	22	ATLA (1), CACR (1), CAPI (1), EVER (1), GICL (1), GRRI (1), JARB (1), JARI (1), KPBO (1), MONT (2), NOGA (2), ORPI (1), PENO (1), SACR (1), SAGU (1), SAMA (1), SIME (1), STAR (1), VIIS (1), ZICA (1)
Controller Card	11	CACR (1), CAVE (1), CHIR (1), COHU (1), CRLA (1), GRRI (1), HEGL (2), LASU (1), MELA (1), WHIT (1)
Relay Box	7	BOWA (1), DINO (1), FOPE (1), GRBA (1), PMRF (1), SIPS (1), VOYA (1)
Pump Hose	4	BOND (1), BOWA (1), HECA (1), SOGP (1)
Module	3	BRID (1), MELA (1), SAMA (1)
Module Cable	2	BOAP (1), CAVE (1)
Sierra Inlet	2	SWAN (1), WICA (1)
Temp Probe	2	SYCAII (1), TRCR (1)
Tripplite Surge	2	HAVO (1), YELL (1)
Motor Assembly	1	YELL (1)
PM2.5 Inlet	1	CRLA (1)

6.2 Field Audits

CSU CIRA and local agencies perform 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 and local agencies performed January 1, 2021 through December 31, 2021.

Table 6-2: CSU CIRA field audits 1/1/2021 through 12/31/2021.

Site	Audit Date
VILA1	3/22/2021
PHOE1	5/3/2021
PHOE5	5/3/2021
MING1	5/5/2021
VILA1	5/6/2021
LASU2	5/20/2021
HEGL1	5/26/2021
SAGU1	6/14/2021
SAWE1	6/14/2021
JARB1	7/19/2021
HECA1	7/21/2021
STAR	7/22/2021
CORI1	7/23/2021
MORA	7/26/2021
WHPA	7/26/2021
MOHO1	7/28/2021
THSI1	7/29/2021
CRLA1	8/2/2021
LABE1	8/2/2021
TRIN1	8/4/2021
ROMO2	8/4/2021
LAVO1	8/5/2021
BLIS	8/5/2021
LASU2	8/6/2021
WHRI1	8/8/2021
VILA1	8/12/2021
MOZI1	8/18/2021
SOGP1	10/19/2021
HEGL	10/20/2021
MING1	10/21/2021
PITT1	10/25/2021
MOMO1	10/26/2021
MAVI1	10/28/2021
CACO1	10/29/2021
CABA1	11/1/2021
ACAD1	11/2/2021
PENO1	11/2/2021
GRSA1	11/2/2021
MOOS1	11/3/2021
SHMR1	11/3/2021
PRES1	11/4/2021
GRGU1	11/8/2021
PMRF1	11/8/2021
LOND1	11/10/2021
PACK1	11/10/2021
VILA1	11/10/2021
LYEB1	11/12/2021
DETR1	11/15/2021
LASU2	11/16/2021

6.3 Summary of Site Visits

The UCD Field Group visits IMPROVE network sites biennially to provide routine maintenance and cleaning. Some sites are occasionally visited more frequently to address emergency issues. Table 6-3 summarizes the visits that UCD performed July 1, 2021 through December 31, 2021.

UCD developed new sampler controllers (V4 Controller), deployed them to the entire IMPROVE network except for BYIS1 in South Korea, and continue to add new features by updating firmware/software/hardware. As of December 31, 2021, internet connections to the new controllers at all IMPROVE sites had been established. 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, 1/1/2021 through 12/31/2021.

Site Name	Date Visited	Upgrades	Major Changes
SACR1	3/8/2021	None	
WHIT1	3/9/2021	Upgraded router	
CAVE1	3/10/2021	Upgraded router	New shed at the same location
GUMO1	3/11/2021	Upgraded router	
BIBE1	3/12/2021	None	
GICL1	3/13/2021	None	

Site Name	Date Visited	Upgrades	Major Changes
BOAP1	3/14/2021	None	
PHOE1	3/16/2021	None	
PHOE5	3/16/2021	None	
FRES1	3/22/2021	None	
SEQU1	3/23/2021	None	
LTCC1	3/25/2021	Upgraded router	
TONT1	4/19/2021	Upgraded router	
NOGA1	4/20/2021	Upgraded router	
CHIR1	4/21/2021	Upgraded router	
ORPI1	4/22/2021	Upgraded router	
SAGU1	4/23/2021	Upgraded router	
SAWE1	4/24/2021	Upgraded router	
NEBR1	5/23/2021	None	
BADL1	5/24/2021	Upgraded router	
WICA1	5/25/2021	None	
NOCH1	5/26/2021	None	Site was burnt by a wildfire
THRO1	5/27/2021	None	
LOST1	5/28/2021	None	
MELA1	5/29/2021	Upgraded router	
FOPE1	5/30/2021	Upgraded router	
REDW1	6/21/2021	None	
KALM1	6/22/2021	Upgraded router	
CRLA1	6/23/2021	None	
THSI1	6/24/2021	None	Satellite to Mobile
LAVO1	6/25/2021	None	
GRBA1	6/29/2021	None	
KAIS1	6/29/2021	None	
JARB1	6/30/2021	None	
YOSE1	6/30/2021	None	
CRMO1	7/1/2021	None	
SAWT1	7/2/2021	None	
SULA1	7/3/2021	None	
STAR1	7/5/2021	None	
HECA1	7/6/2021	None	
ZICA1	7/19/2021	None	
BRCA1	7/20/2021	None	
CAPI1	7/21/2021	None	

Site Name	Date Visited	Upgrades	Major Changes
CANY1	7/22/2021	None	
FLTO1	7/23/2021	None	Site was shut down
WHRI1	7/24/2021	Upgraded router	
FOCO1/2	7/26/2021	None	
ROMO1	7/27/2021	None	
DINO1	7/29/2021	None	
MOZI1	7/29/2021	None	
DETR1	8/8/2021	None	
BAND1	8/11/2021	None	
SAPE1	8/12/2021	None	
WHPE1	8/13/2021	None	
JARI1	8/14/2021	Upgraded router	
WEMI1	8/14/2021	Upgraded router	
SHEN1	8/15/2021	None	
SHMI1	8/15/2021	None	Site was shut down
DOSO1	8/16/2021	Upgraded router	
MEVE1	8/16/2021	None	
FRRE1	8/17/2021	None	
GRSA1	8/17/2021	None	
PITT1	8/18/2021	None	New pump housing
QUCI1	8/19/2021	None	
ATLA1	9/8/2021	Upgraded router	
BIRM1	9/9/2021	None	
SIPS1	9/10/2021	None	
KPBO1	9/12/2021	Upgraded router	
MING1	9/12/2021	Upgraded router	
MACA1	9/13/2021	None	
GRSM1	9/14/2021	None	
DENA1	9/15/2021	None	
SHRO1	9/15/2021	Upgraded router	
LIGO1	9/16/2021	Upgraded router	
TRCR1	9/16/2021	None	
COHU1	9/17/2021	None	
SIME1	9/19/2021	None	Add internet connection
HACR1	10/26/2021	None	
HAVO1	10/28/2021	None	
SWAN1	12/6/2021	None	

Site Name	Date Visited	Upgrades	Major Changes
ROMA1	12/8/2021	None	
OKEF1	12/9/2021	None	
EVER1	12/11/2021	None	
CHAS1	12/13/2021	None	
SAMA1	12/14/2021	Upgraded router	
BRIS1	12/17/2021	None	New shelter at the same location

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.