UC DAVIS 2025 NETWORK UPDATE

IMPROVE Spring Steering Committee Meeting

2025 Nov 18

Nicole Hyslop, Nicholas Spada, Yongjing Zhao, Indu Sivakumar, Marcus Langston and the whole team

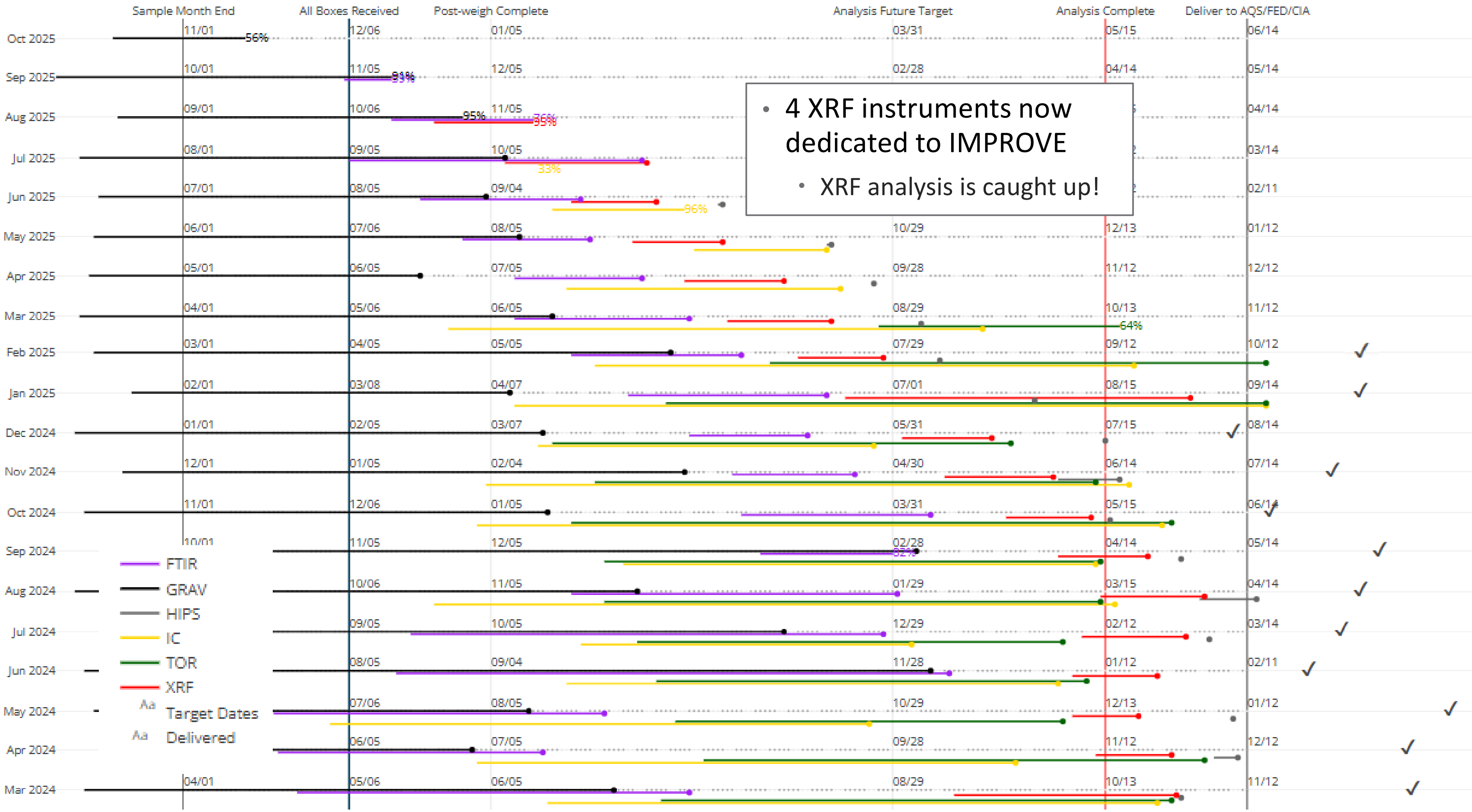
UC DAVIS
AIR QUALITY RESEARCH CENTER

Bandelier National Monument, May 2025

2025 Site Updates

- FL loop delayed by shutdown
- Shelter relocations/rebuilds
  - WIMO1,2 (relocated)
  - GRSA1 (new shelter)
  - BAND1 (rebuilt after blew over)
  - MING1 (shed blew over)
- Back on-line
  - AGTI1
  - MAKA2 is now BAPE1
  - ISLE1 operated by Trent
- Non-operational sites
  - SAGA1 no operator
  - MAKA2 power outage
  - MING1 power outage
  - RAFA1 power problem
  - KAIS1 no operator
  - BALD1 power outage
  - WHPA1 no power, moving

Data Delivery



- 4 XRF instruments now dedicated to IMPROVE
  - XRF analysis is caught up!

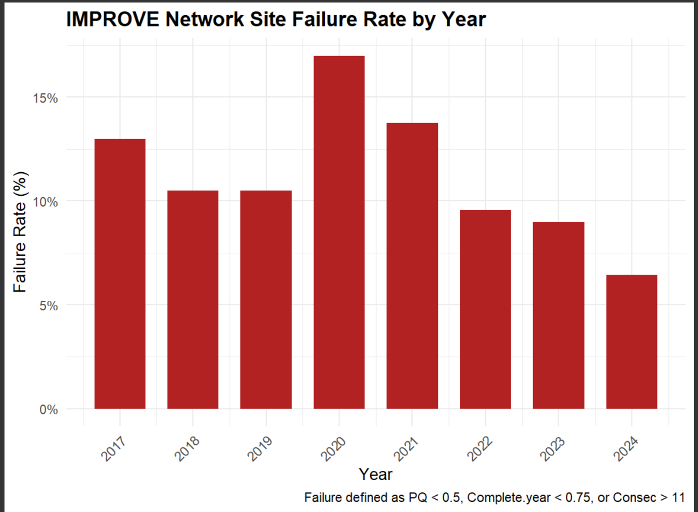
RHR Completeness Failures

2024

1. Agua Tibia, CA (AGTI1): late and no sample changes
2. Gates of the Mountains, MT (GAMO1): inaccessible, relocated to MAPA1
3. Kaiser Wilderness, CA (KAIS1): power out, resumed sampling in October 2024
4. Nebraska National Forest, NE (NEBR1): fire damage, rebuilt October 2024
5. San Rafael, CA (RAFA1): major power problems, looking to move site
6. San Gabriel, CA (SAGA1): no operator
7. UL Bend, MT (ULBE1): no operator, resumed sampling in August 2024
8. Quaker City, OH (QUCI1): spider web in PM_{10} module inlet

2025

- Prior to the government shutdown, 13 sites had failed the RHR criteria
- Government shutdown resulted in an additional 20-21 sites failing the RHR completeness criteria
    - We've got a bit of a mess with the sampling supplies right now that will be sorted out in the next 1-2 months

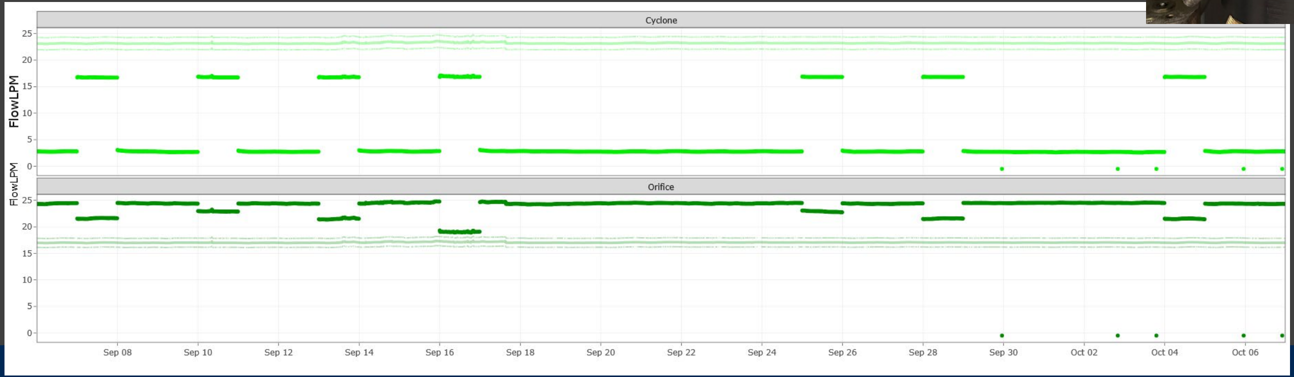


Active Flow Control Field Deployment

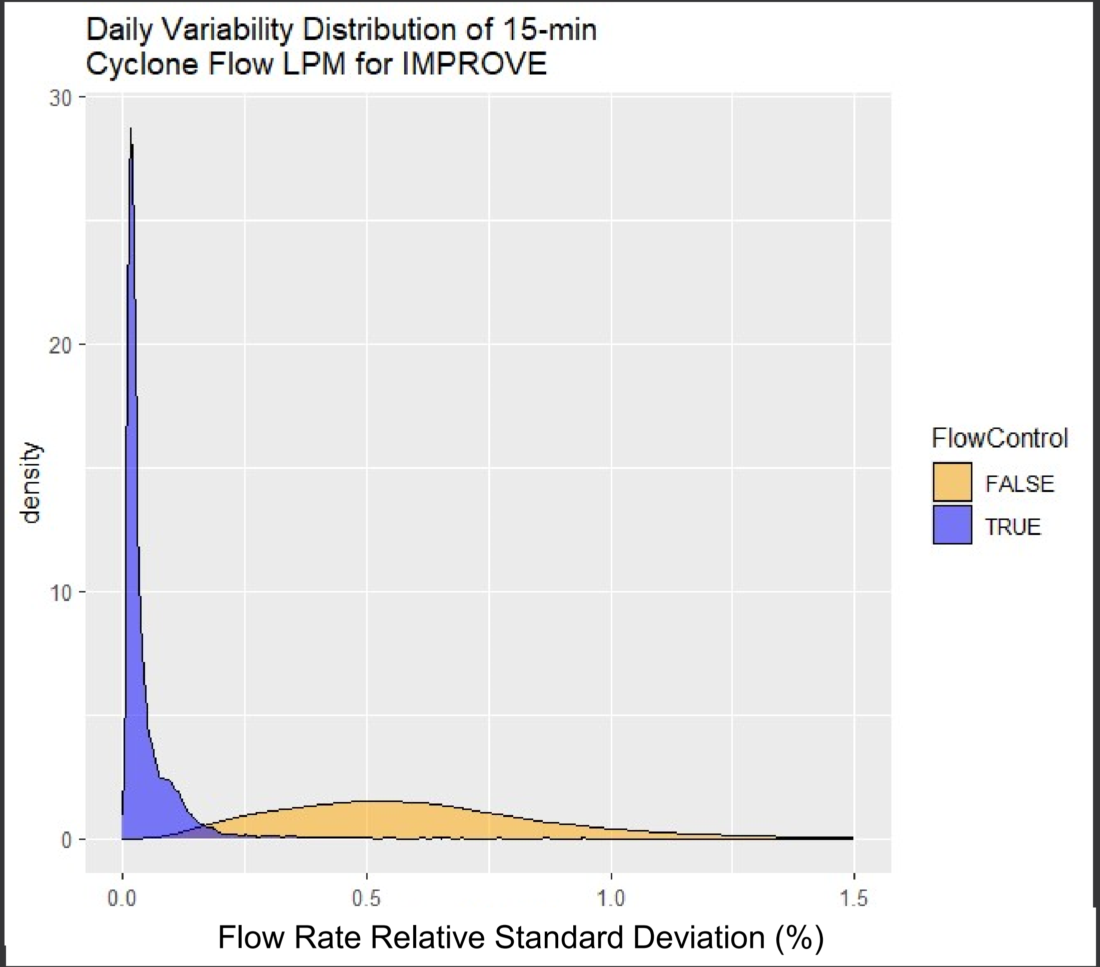
- Deployed active flow control on $PM_{2.5}$ modules to almost entire network
  - Will deploy to Florida sites early next year
- Some minor bugs are still being addressed
- Testing new model AC pumps for PM_{10} modules at some sites
- Testing multiple Venturi flow meters to enable active flow control on PM_{10} modules

Venturi Meter for PM_{10} flow measurement

- Exploring new approach for measuring flow rate on the PM_{10} modules
- Currently PM_{10} module flow rates are determined based on critical flow through a fixed orifice. This measurement technique won't work if we switch to active flow control which requires eliminating the fixed orifice.
- Collecting samples on UCD roof for testing



Active Flow Control Provides More Stable Flow Rates



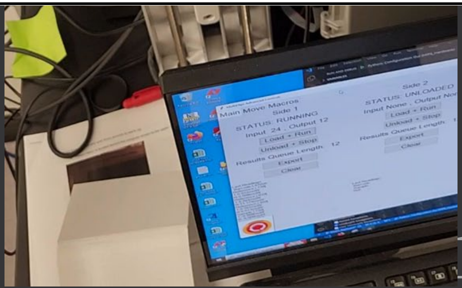
- This may translate to more precise measurements…will explore once all collocated sites have been converted to flow control

Clogging Protocol – Stop sampling

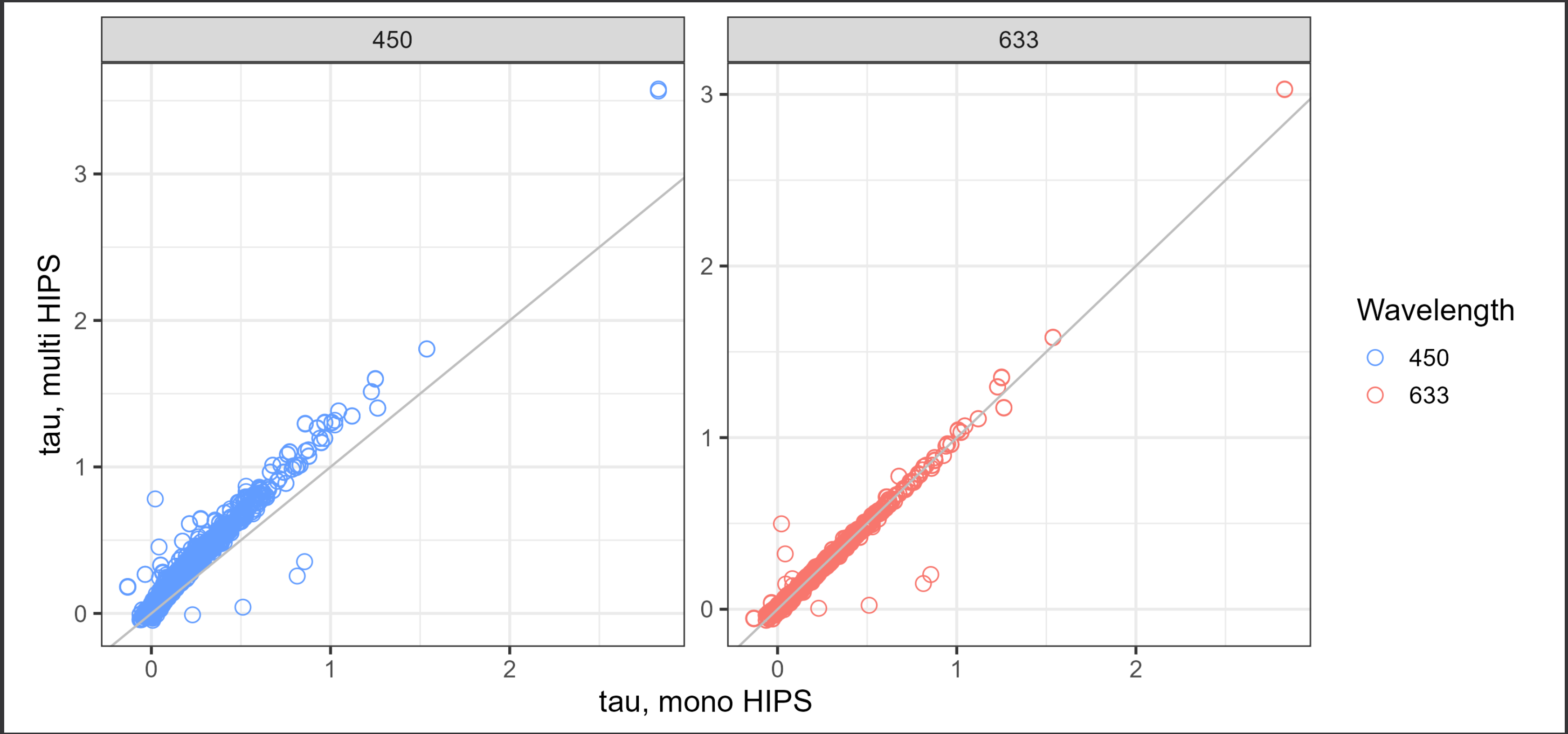
- If flow rate falls below 15 LPM for more than 15 minutes
  - If ≥18 hours into sample
    - Shut off all modules
    - Data are still valid for RHR
  - Else
    - Shut off the clogged module
    - Shut off the companion module for PM coarse calculation (i.e., shut off PM_{10} PTFE if $PM_{2.5}$ PTFE clogs)
    - Data invalid for RHR but delivered with an accurate concentration and a qualifier flag indicating a short sample time
- Short Duration (SD) or Time Out of Bounds (TO) flags applied to samples
  - 34 (0.2%) SD and 14 (0.1%) TO flags out of 18,756 sampling events in 2024
  - 45 (0.3%) SD and 24 (0.1%) TO flags out of 17,538 sampling events so far in 2025
  - Note: These rates are slightly low because flow control is not complete in the network

Multi-wavelength HIPS Refinement

- Existing instrument has one wavelength at 633 nm
- Multi-HIPS has 4 wavelengths at 450, 553, 633, and 730 nm
- Beta testing involved analyzing fraction of IMPR
filters between October 2023 and April 2024
    - 553 nm and 730 nm lasers were repaired followi
- Analyses to-date include:
    - 5,097 IMPROVE samples (2,551 $PM_{2.5}$ & 2,546 P
    - 98 field blanks
    - 1,159 paired pre- and post-sampling measureme
$PM_{2.5}$)
- Refined image collection at multi-HIPS
- Modifying laboratory software to accommodate new analysis pathway
    - Beta testing will resume in January 2025

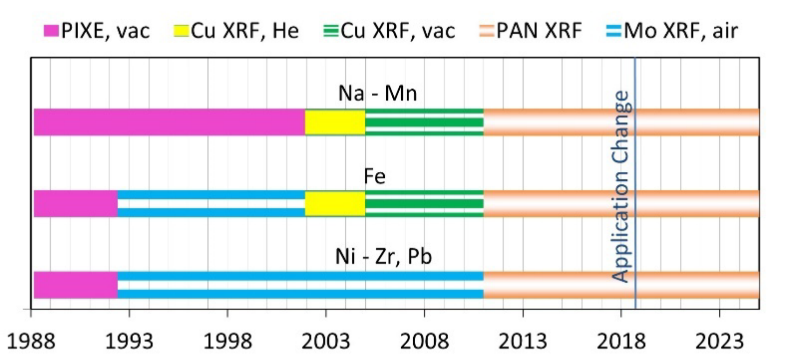


Multi- to mono-HIPS comparison



- 1626 IMPROVE samples (lot 253, Oct23-Feb24 sample dates)

The Future of IMPROVE XRF Analysis



- CSN XRF transition was rougher than expected
  - Not going into details, but it took 3 years
  - Key was developing custom spectral processing software
- IMPROVE path forward is still unclear, but we've made good progress on one approach in the last few months

CSN Element Measurements: XRF Instrument Transition

Nicholas Spada, Jiayuan Wang, Jason Giacomo, Sean Raffuse, Nicole Hyslop

If you want details, let me know

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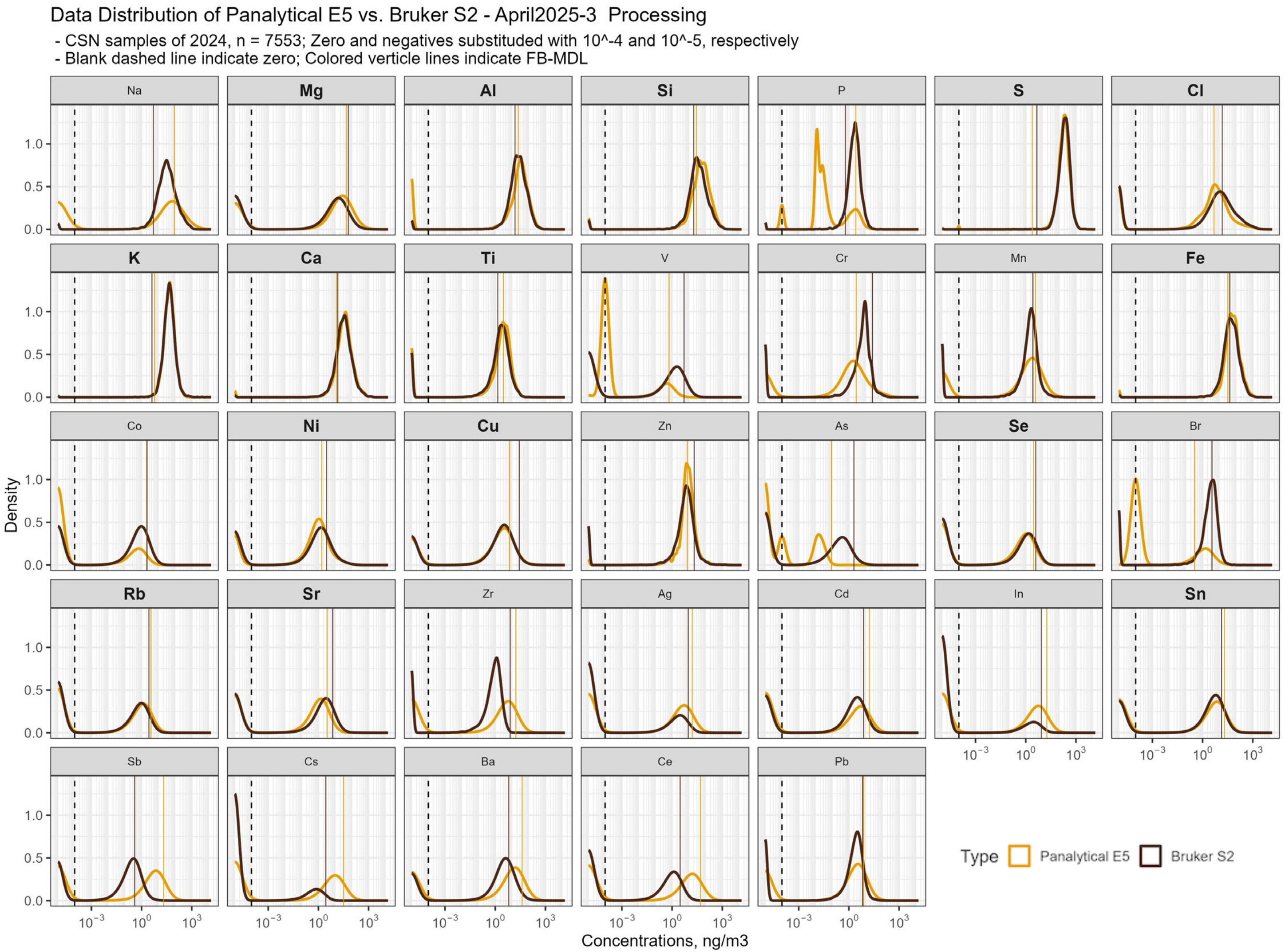
CSN Overview

- Starting with January 2025, CSN samples are analyzed on three new Bruker Puma S2 X-ray Fluorescence (XRF) instruments
  - These instruments replace the five Malvern Panalytical Epsilon 5 XRF instruments that are approaching their end of service
- Prior to deploying these instrument for routine CSN analysis, thousands of 2024 CSN samples were analyzed on both XRF systems for comparison
  - Many elements are infrequently measured above detection by XRF, thus slight changes in detection can result in noticeable changes in the distributions

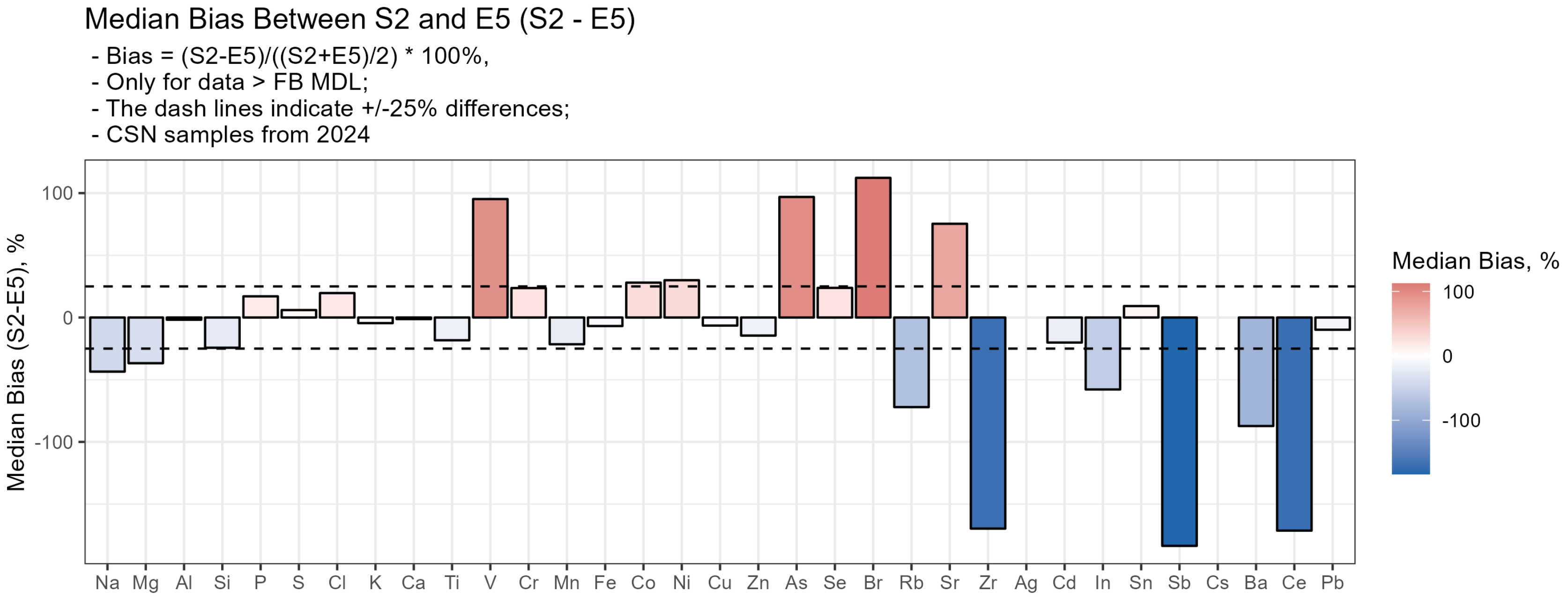
Overview – Data Distribution

- This plot provides an overall view of how S2 and E5 measurements compare.
- 15 elements with **bold** headers, exhibit **overlapping** distributions on both XRFs, suggesting S2 could reliably reproduce E5 measurements for these elements.
- 18 elements exhibit differences. These differences are the result of improved detection in some cases and degraded detection in others.



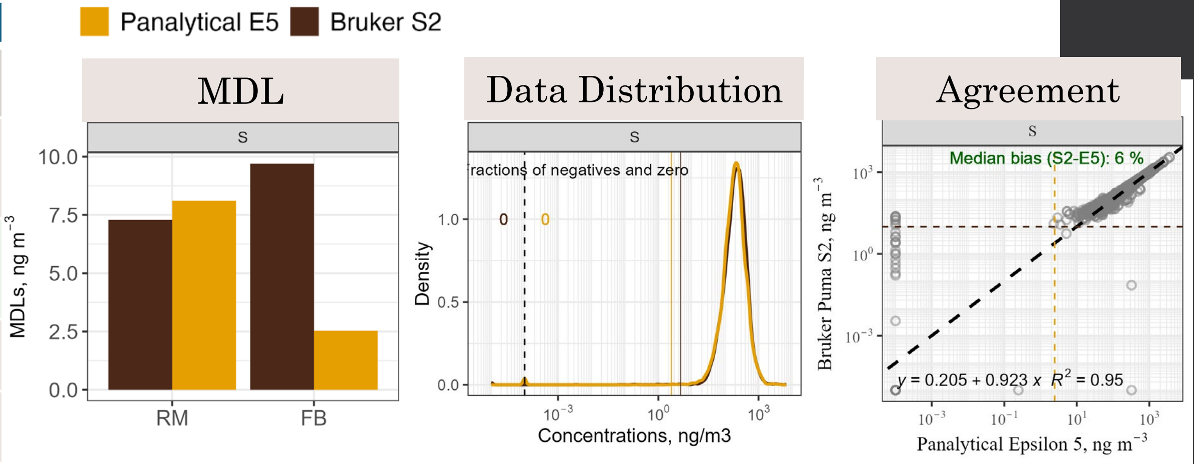
What to Expect with the Bruker S2

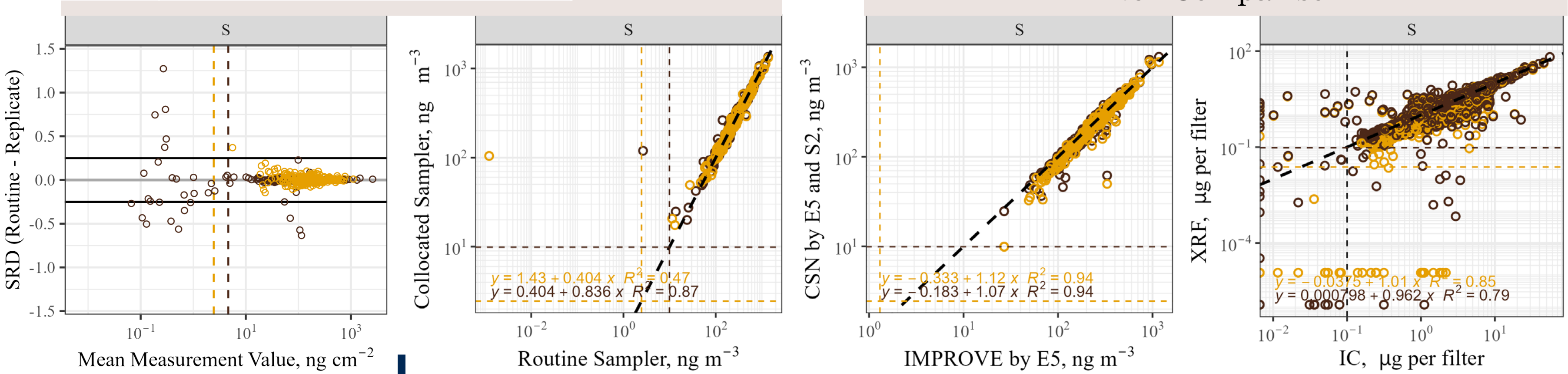
- Bias % = $\frac{S2 - E5}{(S2 + E5)/2} \times 100\%$
- The median bias (differences) are calculated based on data above MDL to focus on the quantitative measurements.
- NOTE: Ag and Cs do not have data above the MDL on either Panalytical E5 or Bruker S2 to calculate the bias.



Sulfur (S)

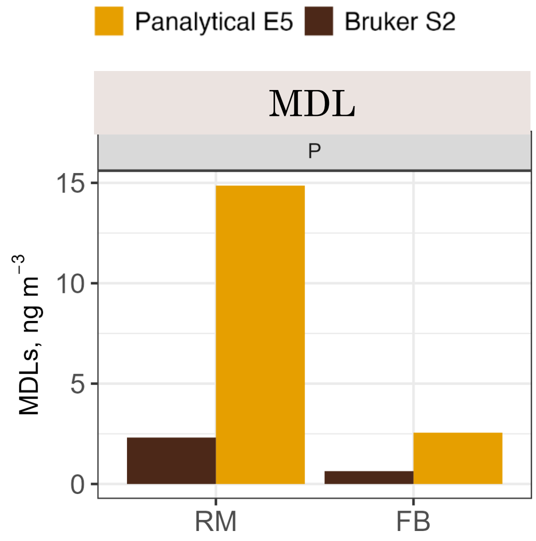
Category		S2 Compares to E5
Sensitivity	MDL	RM ✅ FB ❌ NOTE: E5 FB are frequently zero
	Zeros/ Negatives	✅ 0.15 % vs. 0.46%
Data Distribution & Agreement		• Data Distribution: Almost identical • Median bias (S2-E5): 6%
Precision		• Replicate ✅ • Collocated ≈
Inter-Comparison		• Inter-Network ≈ • Inter-method: XRF vs. IC ≈
Conclusion		S2 **similar** to E5

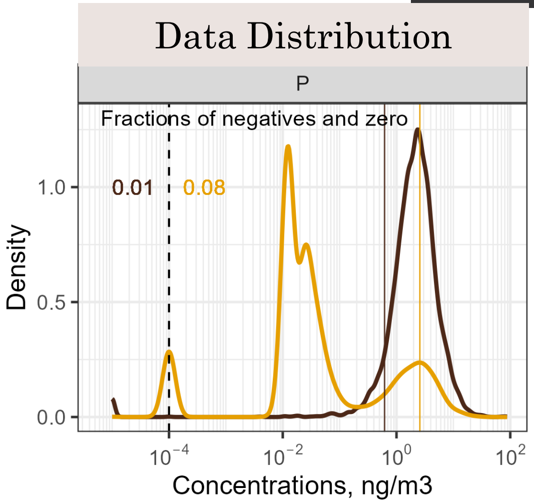


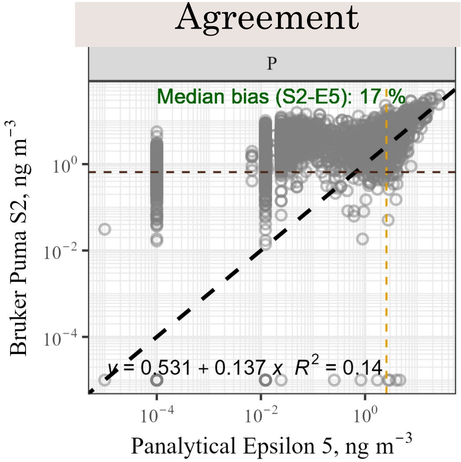


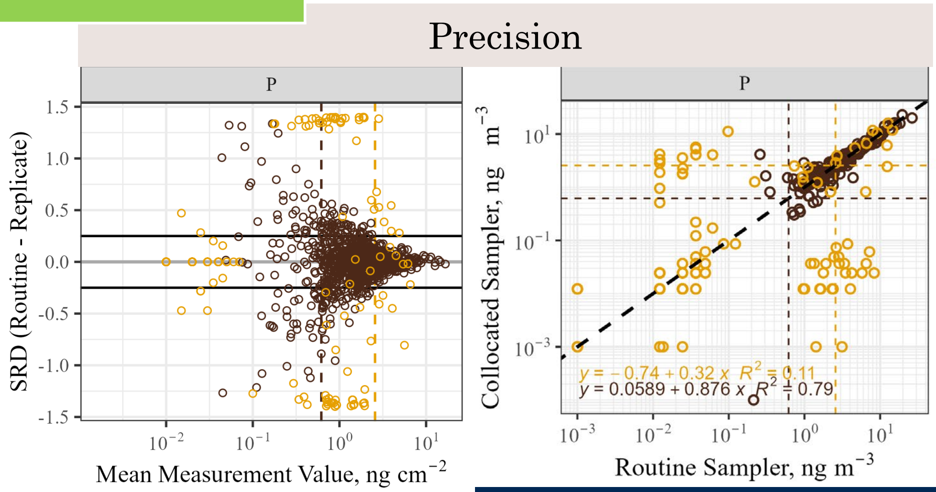
Phosphorus (P)

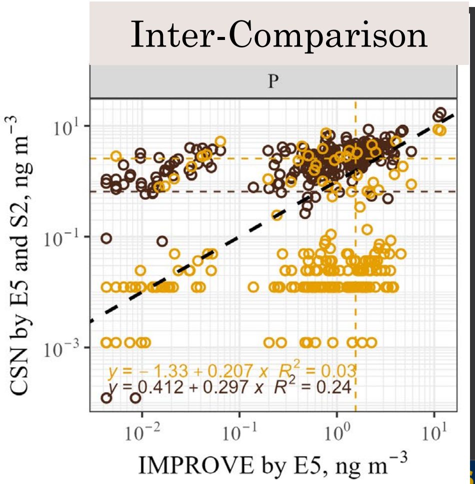
Category		S2 Compares to E5
Sensitivity	MDL	RM ✅ FB ✅
	Zeros/ Negatives	✅ 1% vs. 8 %
Data Distribution & Agreement		• S2 much higher (peak to the right) • Median bias (S2-E5): 17%
Precision		• Replicate ✅ • Collocated ✅
Inter-Comparison		• Inter-Network ✅ • Inter-method: NA
Conclusion		S2 is **better** than E5







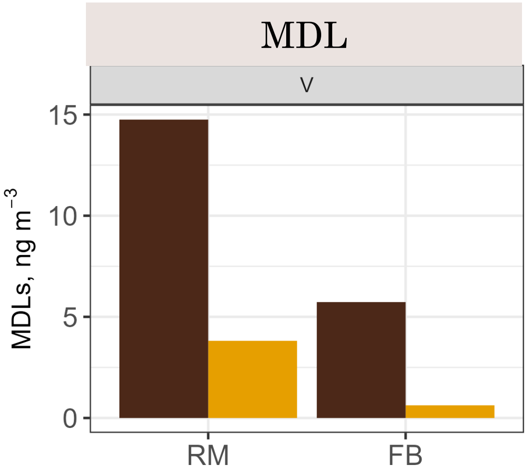


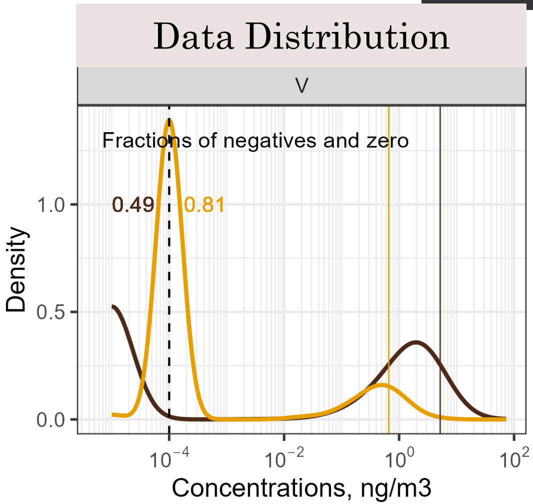


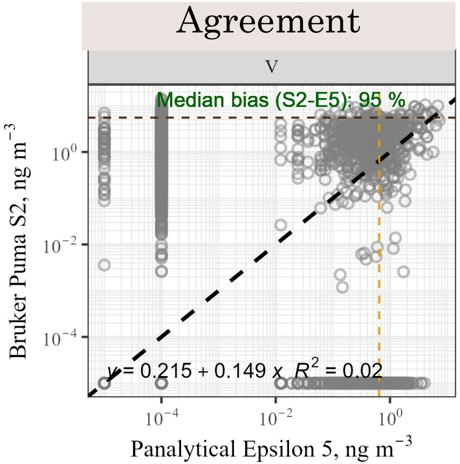
Vanadium (V)

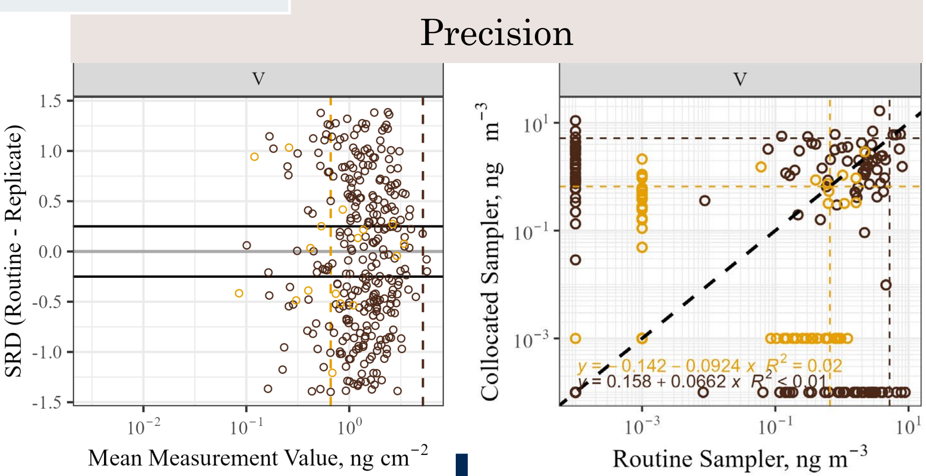
Category		S2 Compares to E5
Sensitivity	MDL	RM ❌ FB ❌
	Zeros/ Negatives	✅ 49% vs. 81%
Data Distribution & Agreement		• Data distribution: S2 measures much higher (to the right) • Median bias (S2-E5): 95%
Precision		• Replicate: Noise • Collocated: Noise
Inter-Comparison		• Inter-network: Noise • Inter-method: NA
Conclusion		S2 more noise than E5

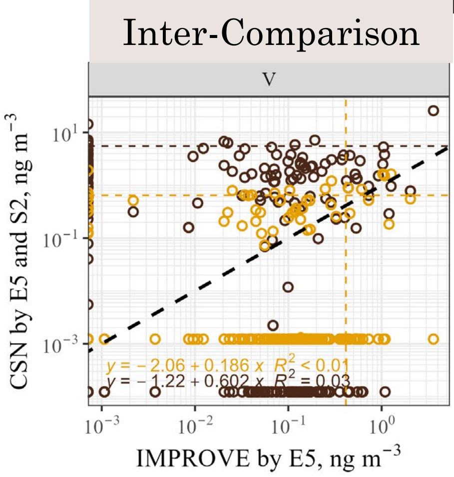
Panalytical E5 Bruker S2







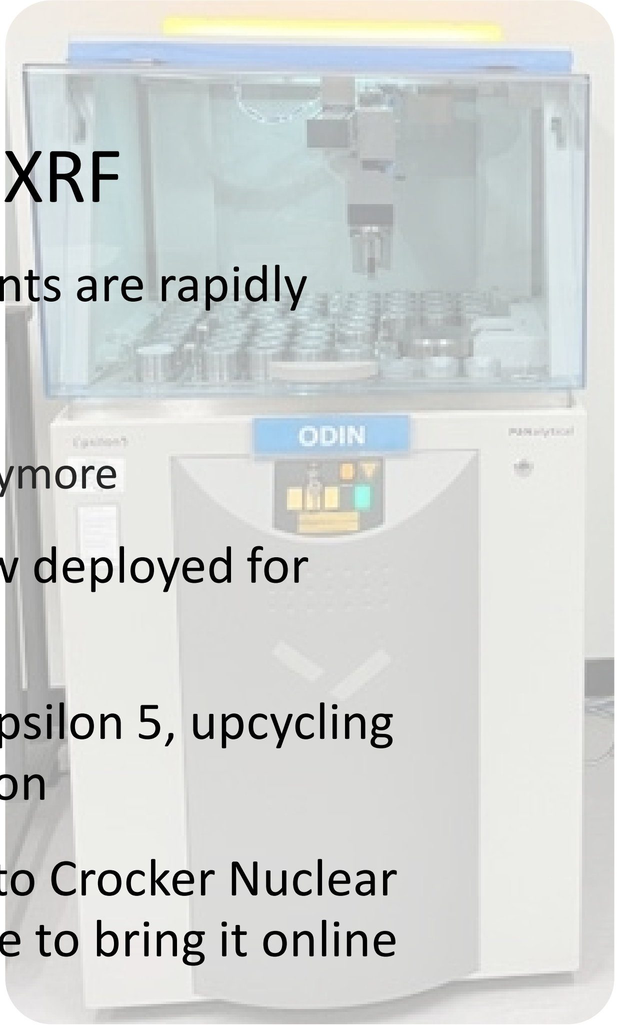




CSN XRF Transition Conclusions

- Most elements are similar across the transition – some are better and some are worse
- S2 Puma instruments require more effort to load and magnetic holders can damage the samples
- Do we want to buy more of these instrument to use for IMPROVE?
  - S2 Puma instruments cannot analyze 25mm IMPROVE samples
    - Have tried developing sample holders with no success so far
  - Alternative approaches are to buy different instruments for IMPROVE or to retrofit the existing Panalytical Epsilon 5 instruments

Project Loki
Rebuilding a Panalytical Epsilon 5 XRF

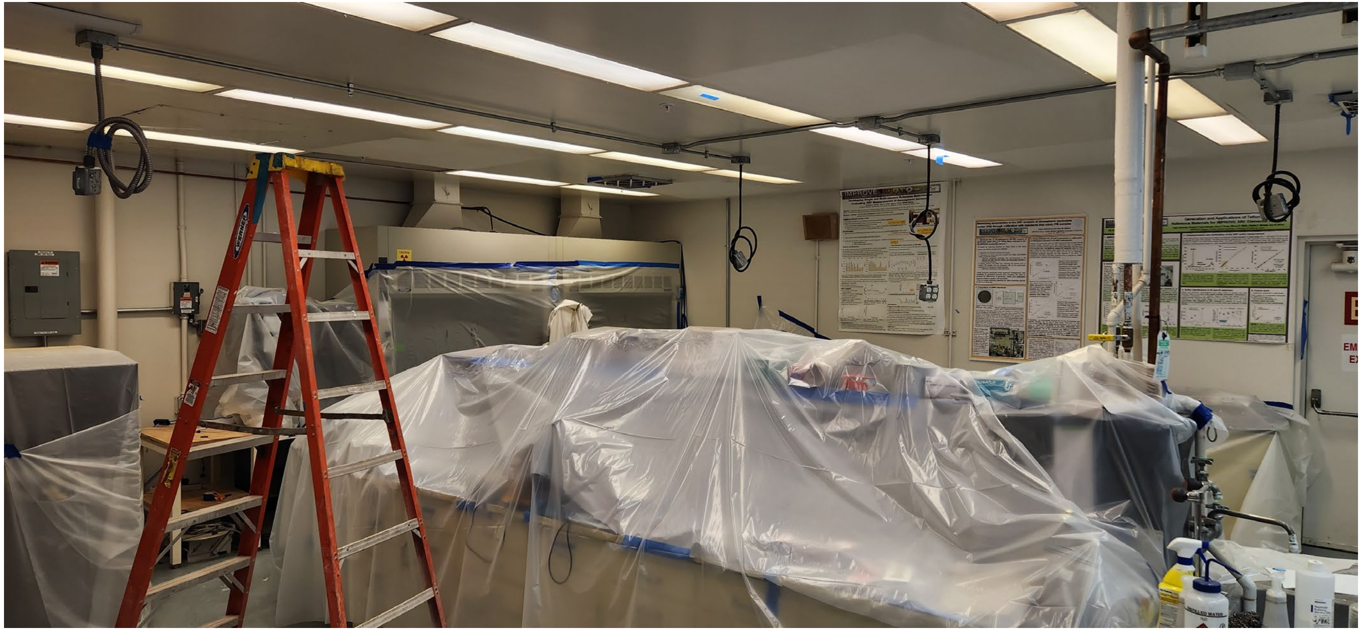


- Our existing Panalytical Epsilon 5 XRF instruments are rapidly approaching end-of-life
  - One of our five instruments is out of commission
  - Some replacement parts are not manufactured anymore
- Three Bruker Puma S2 XRF instruments are now deployed for analysis of CSN samples
- Due to the unique capacity and design of the Epsilon 5, upcycling the existing infrastructure may be a viable option
- Serendipitously, a used Epsilon 5 was donated to Crocker Nuclear Lab and the Panalytical technicians were unable to bring it online

Project Loki - Basic Development Plan

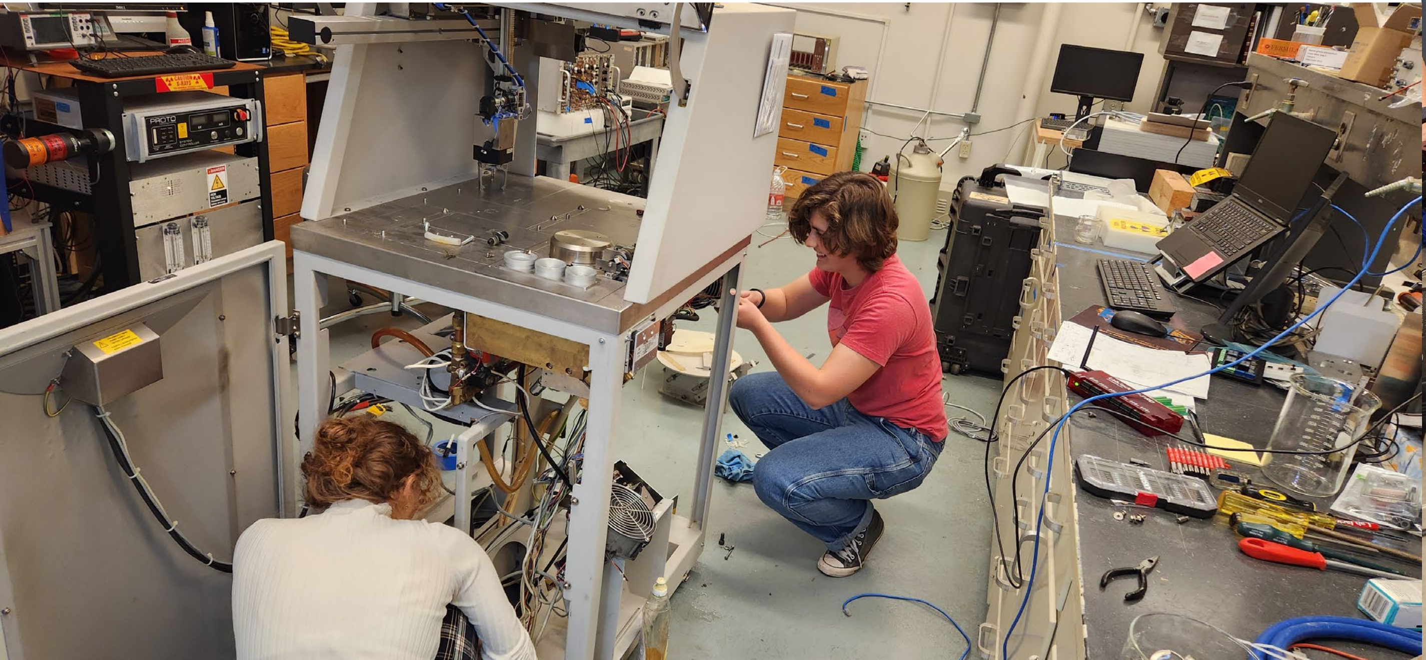
- Strip instrument down to component parts
  - Test/repair secondary systems being retained (cooling, vacuum, optical path including high voltage generator, X-ray tube, and analytical chamber)
  - Remove proprietary Panalytical electronics
- Replace Panalytical electronics with accessible technologies
  - Labjack for X-ray control
  - Ruggeduino for mechatronic control
  - Maxon controllers for robotic arm control
  - Amptek X-123 FAST SDD Spectrometer
- Adapt Multi-Wavelength HIPS firmware
- Install and test core components
  - Cooling: water flow > 1.5 L/min
  - Vacuum: pressure < 10 Pa
  - Optical column: generate and detect X-ray spectra

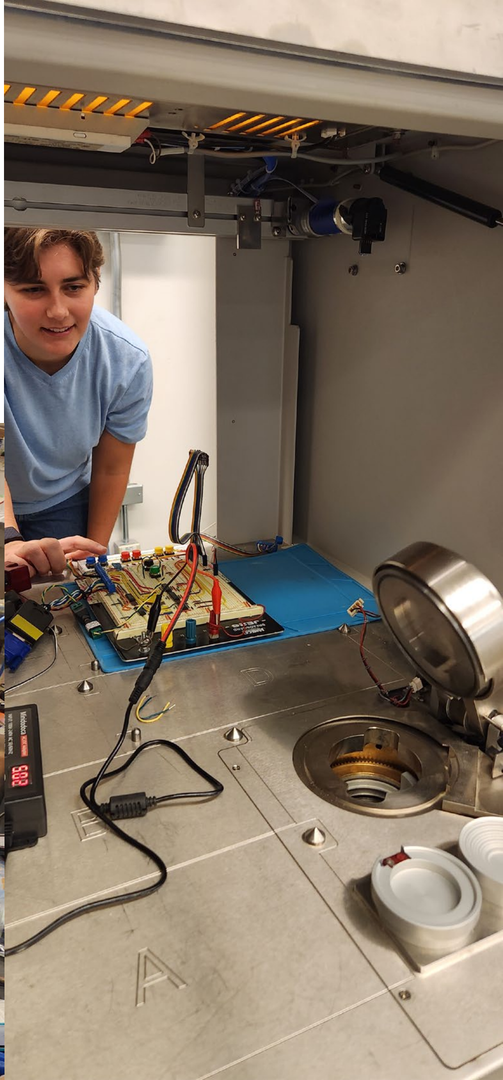
Development was significantly slowed by seismic renovations at CNL
Labs and offices were covered and closed during the intensive construction work

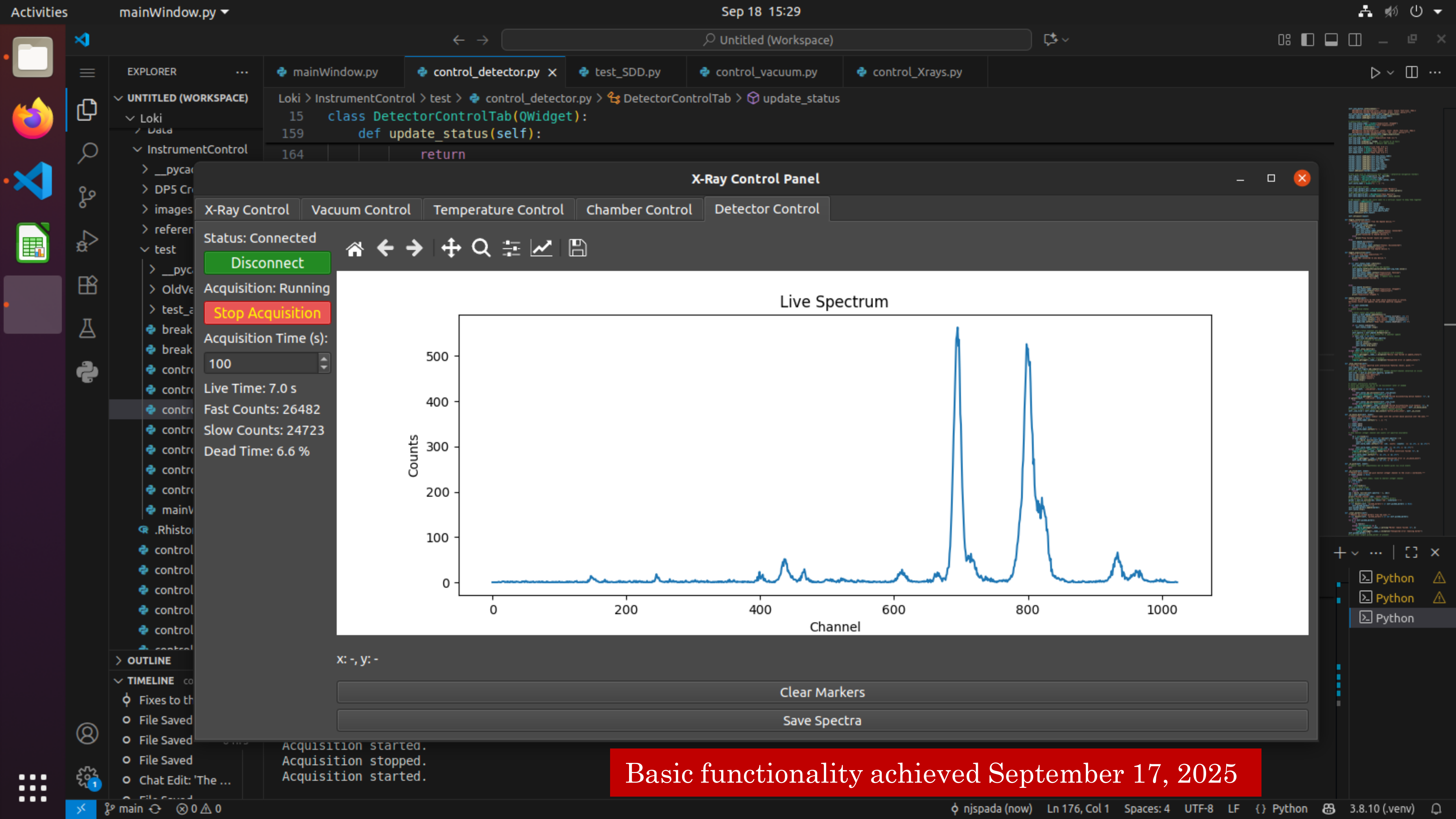


Progress

- A significant amount of the work was performed by student assistants:
    - Madison Nickels (Mechanical Engineering, Class of ‘25)
    - Lada Krat (Art Studio and Anthropology, Class of ‘27)
- Replacement electronics were designed and implemented by volunteer Paul Rundle and Tony Wexler’s project engineer, Chris Wallis
- Firmware was originally developed by Nick Spada and Ilia Potanin for multi-HIPS
- Data reduction algorithm developed by Nick Spada and Rudi De Marco for the Bruker Puma XRF instruments





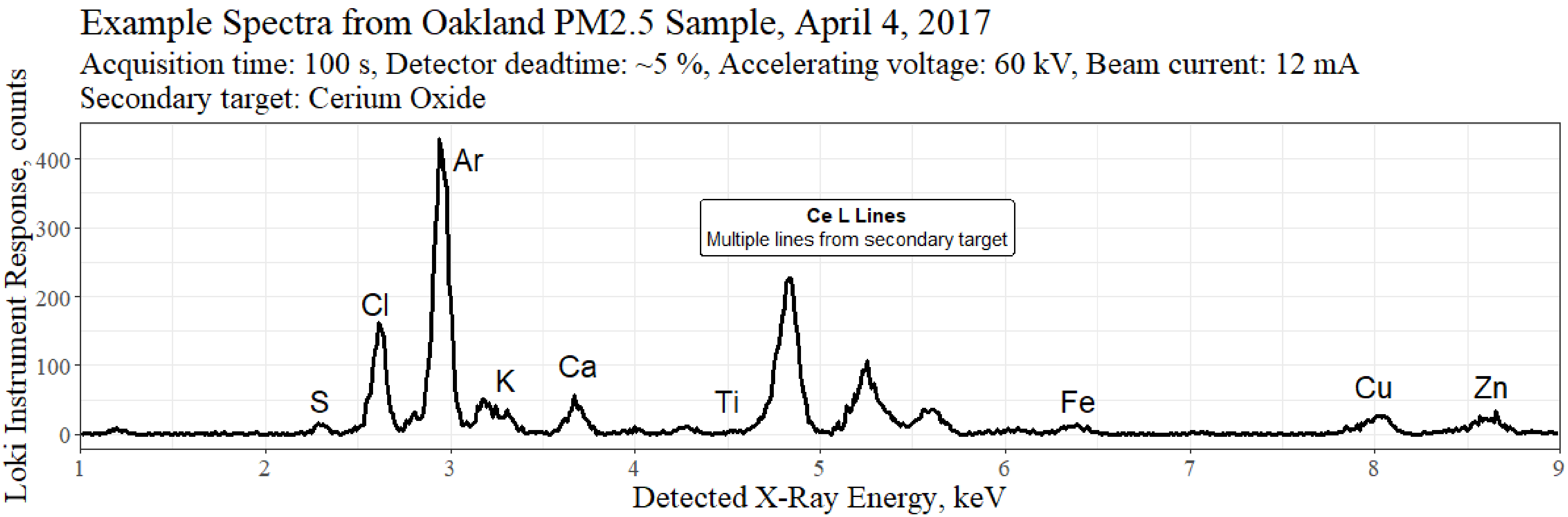


Basic functionality achieved September 17, 2025

X-ray Spectrum

To test the basic functionality of the instrument, six single element reference materials and eight archived special project sampled were analyzed.

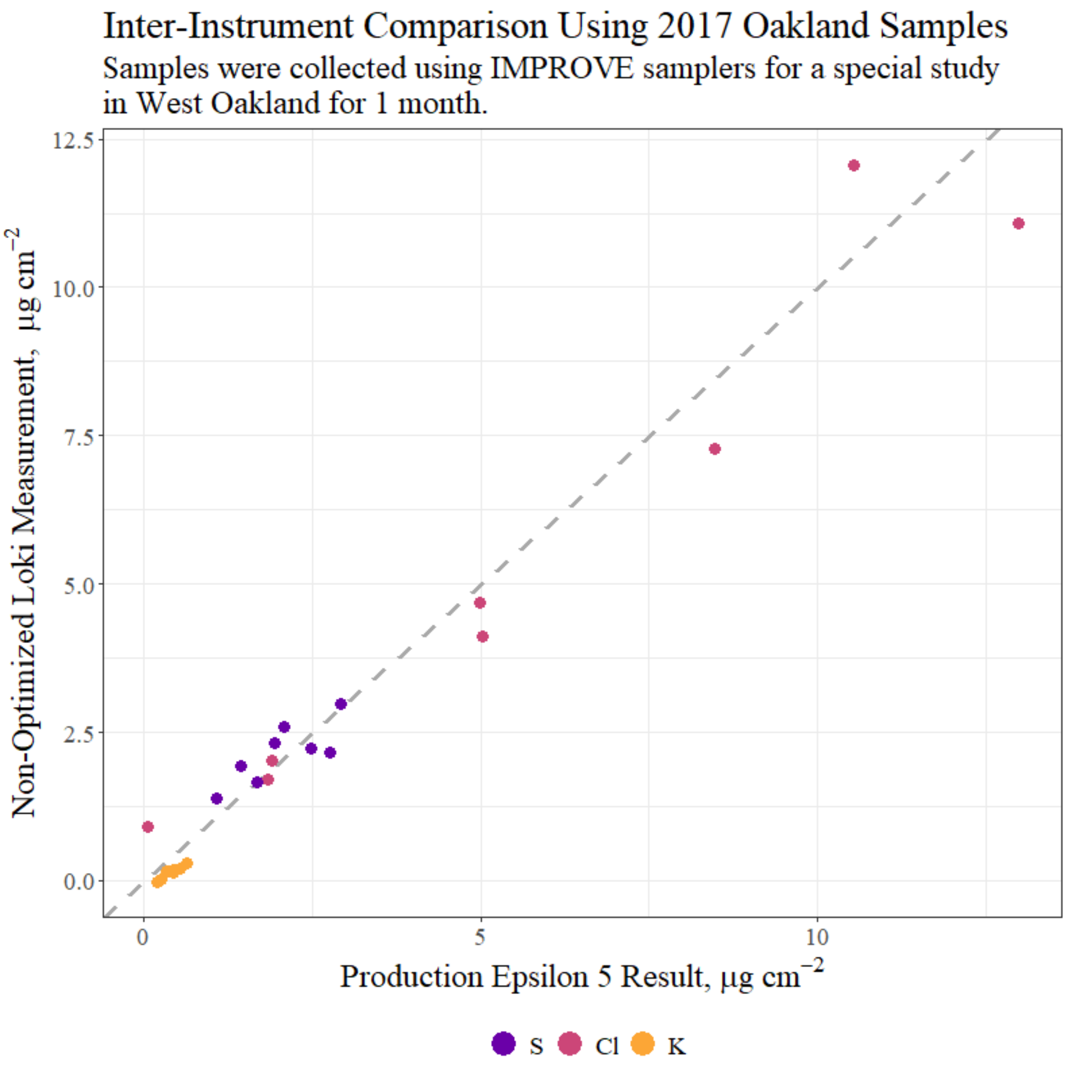
- Using the existing X-ray generator, the secondary target that happened to be in place, and a new detector.
- The secondary target used for this comparison is not used by IMPROVE or CSN. It is simply the current target loaded on the instrument.



Preliminary results show promising reproducibility of the instrument.

Next steps include:

- Activate secondary target wheel
- Generate and test custom circuit boards to improve wire management - ordered
- Implement off-the-shelf controllers for the robotic arm autoloader
- Perform automated experiments to optimize operating conditions for each element using full suite of reference materials
- Perform inter-instrument comparison using both reference materials and samples

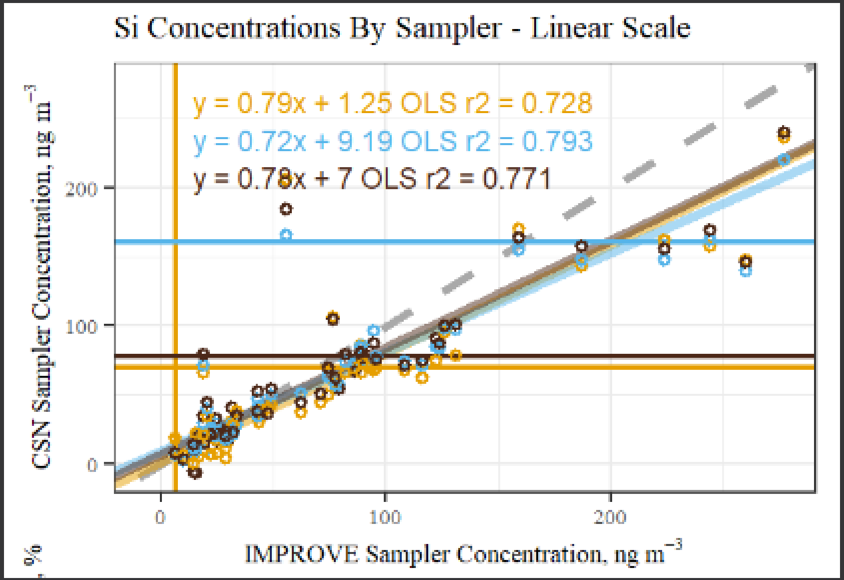


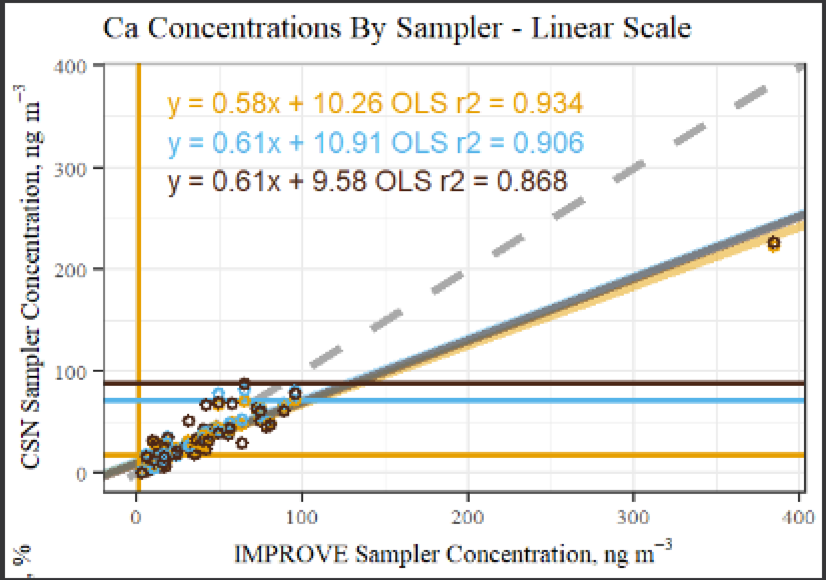
Quality Assurance Activities

- HIPS Light Absorption
- PTFE Filter Properties
- Cyclone cut point

$PM_{2.5}$ Size Cut Concerns

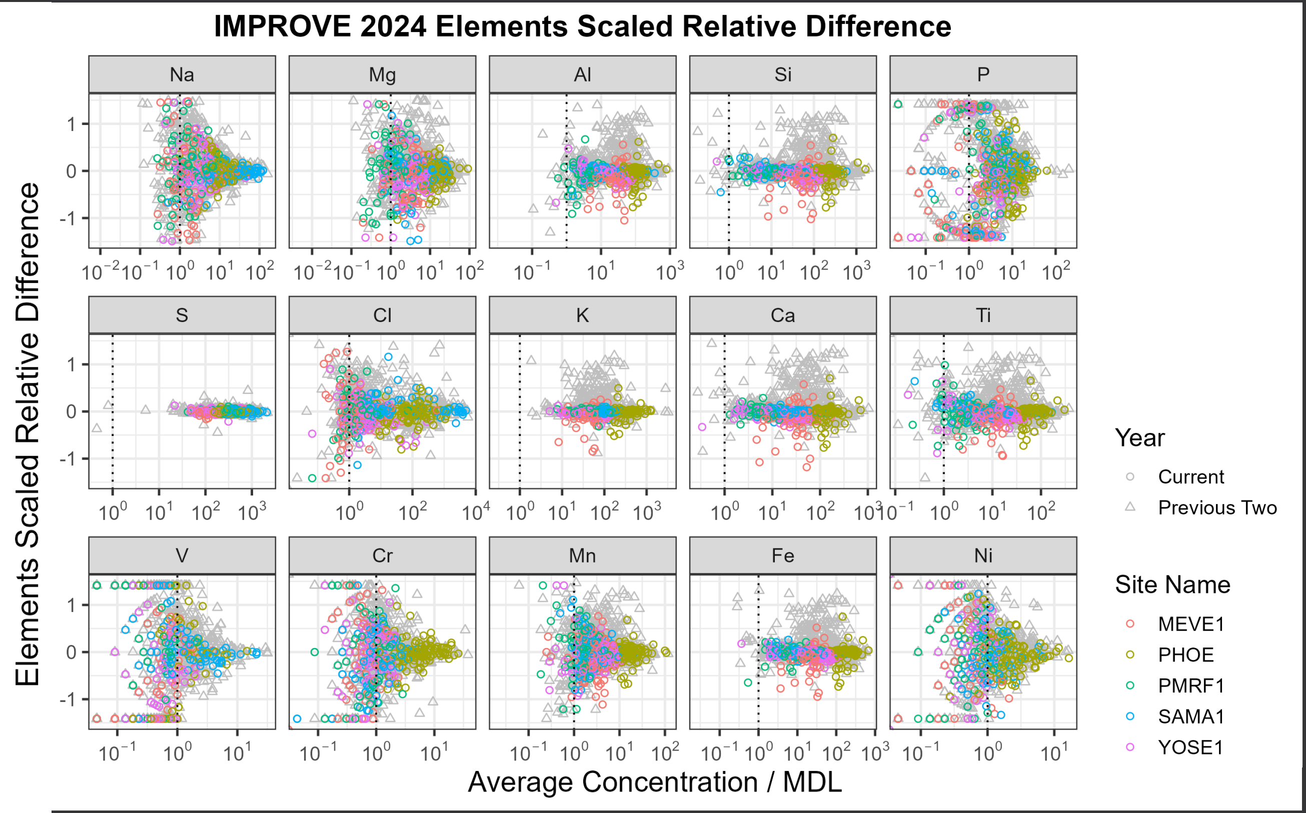
- IMPROVE versus CSN soil concentrations
    - IMPROVE is consistently biased high for soil elements





$PM_{2.5}$ Size Cut Concerns

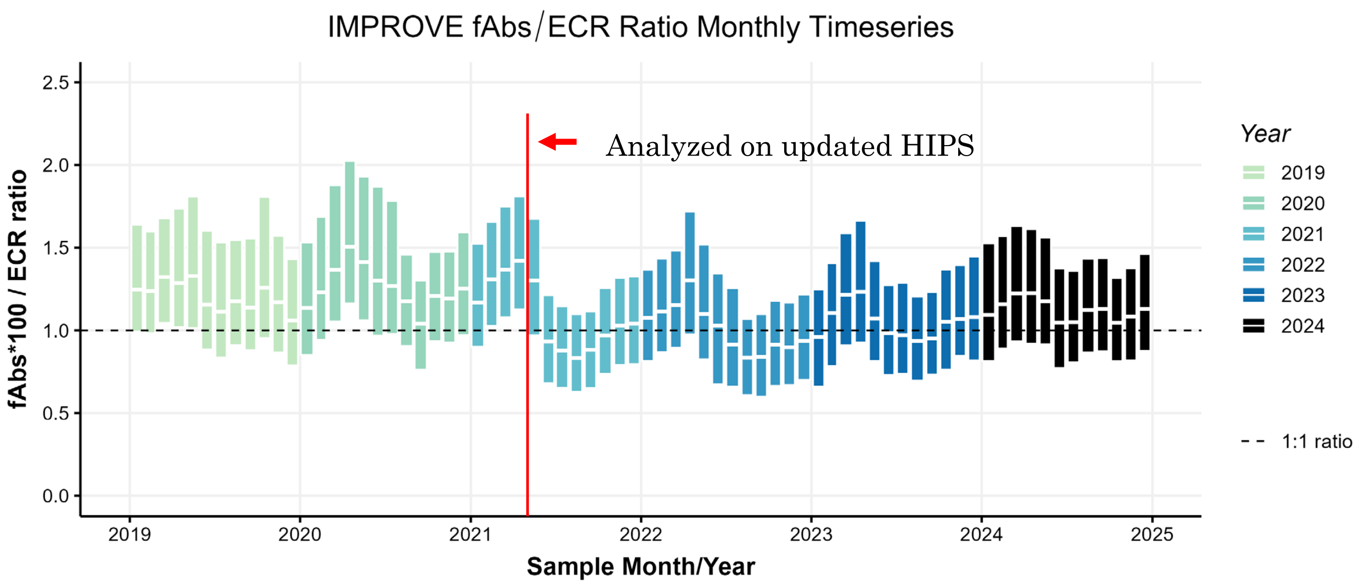
- Poor agreement between soil elements in collocated measurements at soil-dominated sites



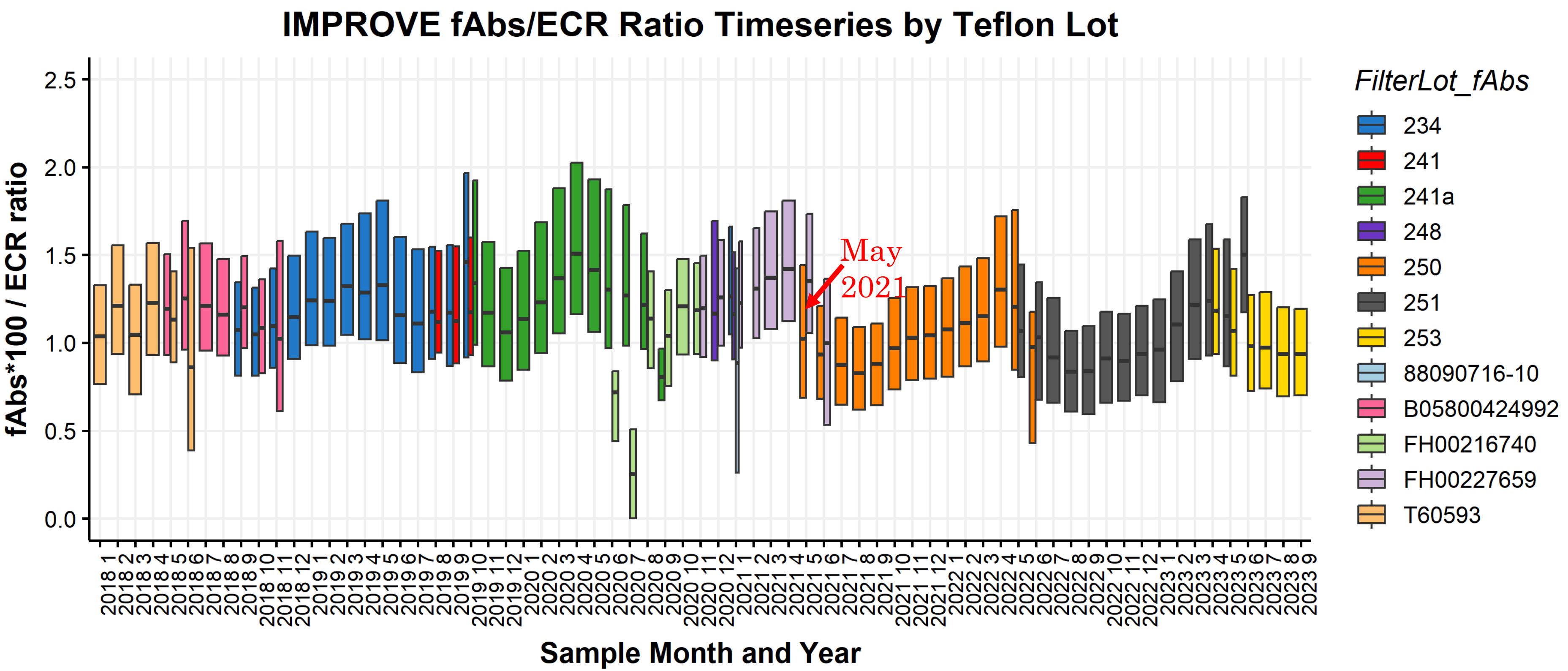
$PM_{2.5}$ Cut Point Test

- Test PM_7 inlet on top of $PM_{2.5}$ stack on collocated Phoenix module (PHOE5)
  - Started in March 2025
  - No data yet

Cross-Module Ratios



- Filter manufacturer changed (Pall to MTL) around May 2021
- New collimating/focusing lens was installed on the HIPS instrument and all samples back to May 2021 were reanalyzed
- Started an experiment to compare HIPS measurements on Pall versus MTL filters

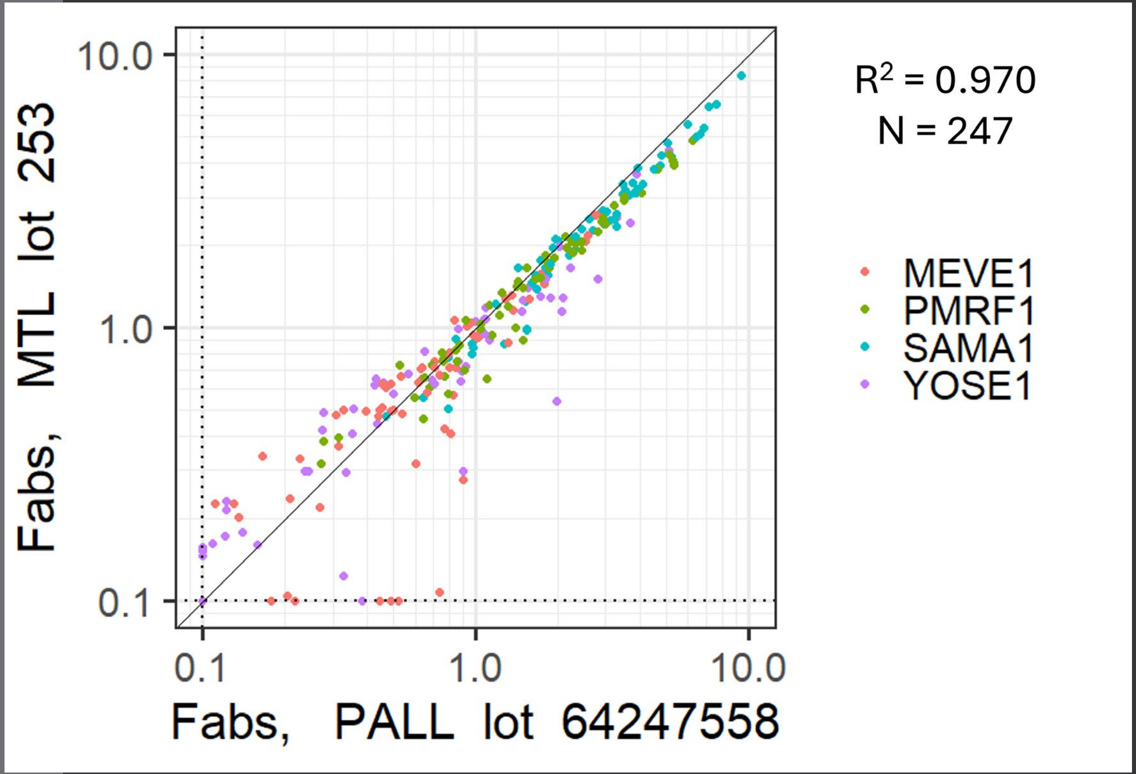


MTL Lot 250: May 2021 – June 2022
MTL Lot 251: May 2022 – June 2023

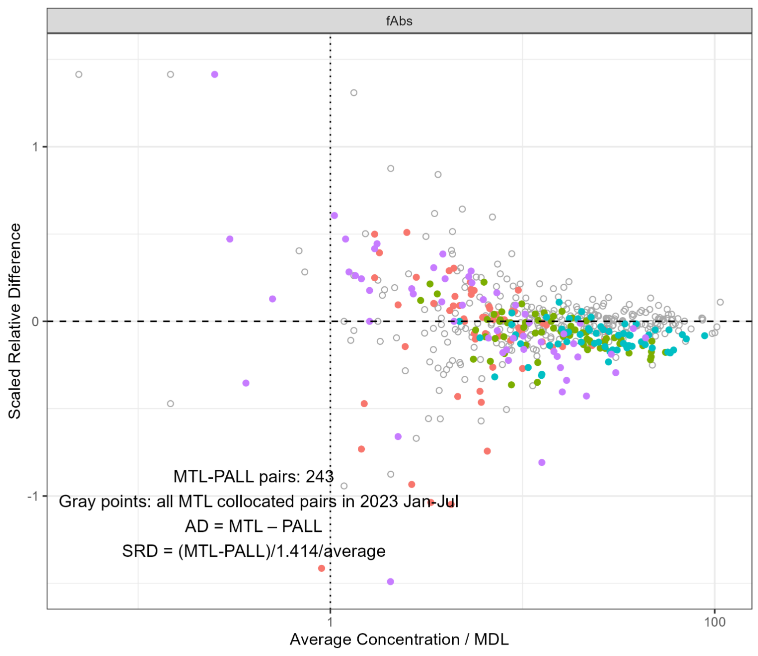
Still Exploring Role of Filters in the Shift

- Collocated Pall and MTL PTFE filters at multiple sites to check if light absorption (HIPS) results are significantly different
    - Samples collected Aug 2023 thru March 2024
- Experiments on both Pall and MTL PTFE filters
    - Optical consistency
        - Analyze by HIPS before and after pulling clean air through filters for 24 hours
        - Results: No change in optical properties detected after pulling clean air through filters

Light Absorption on Pall versus MTL filters

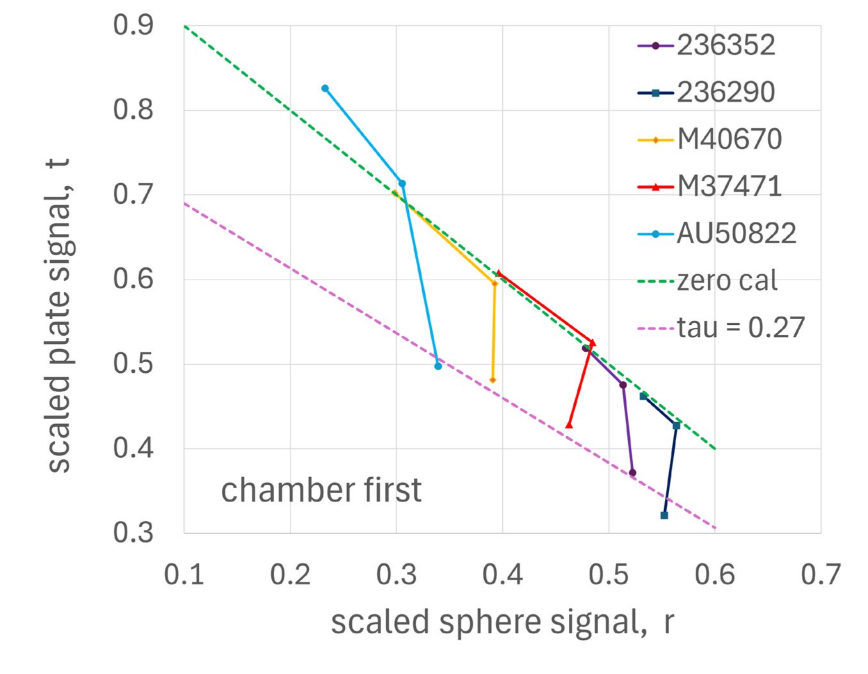


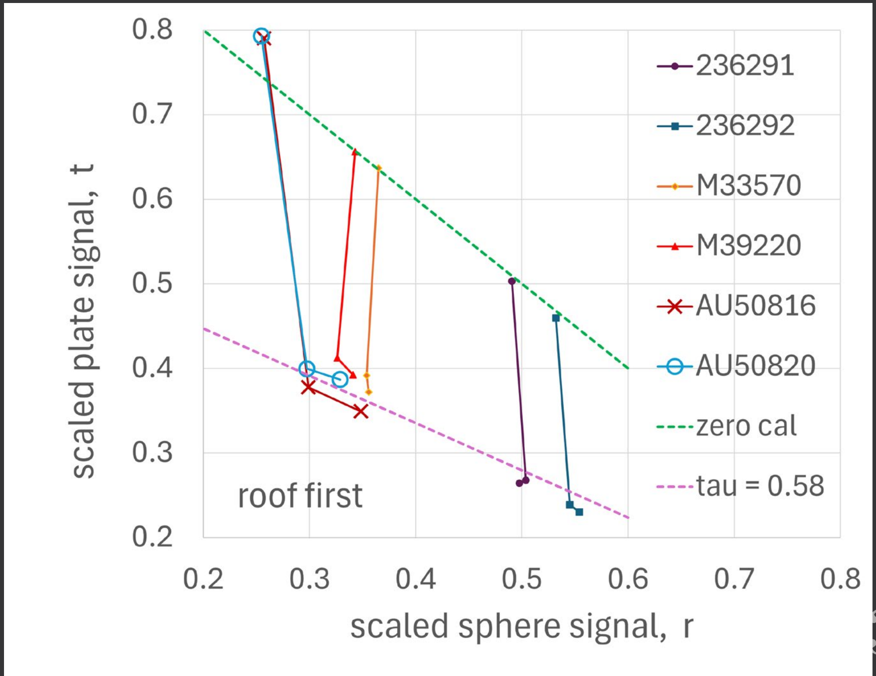
- MTL filters biased low compared to Pall filters



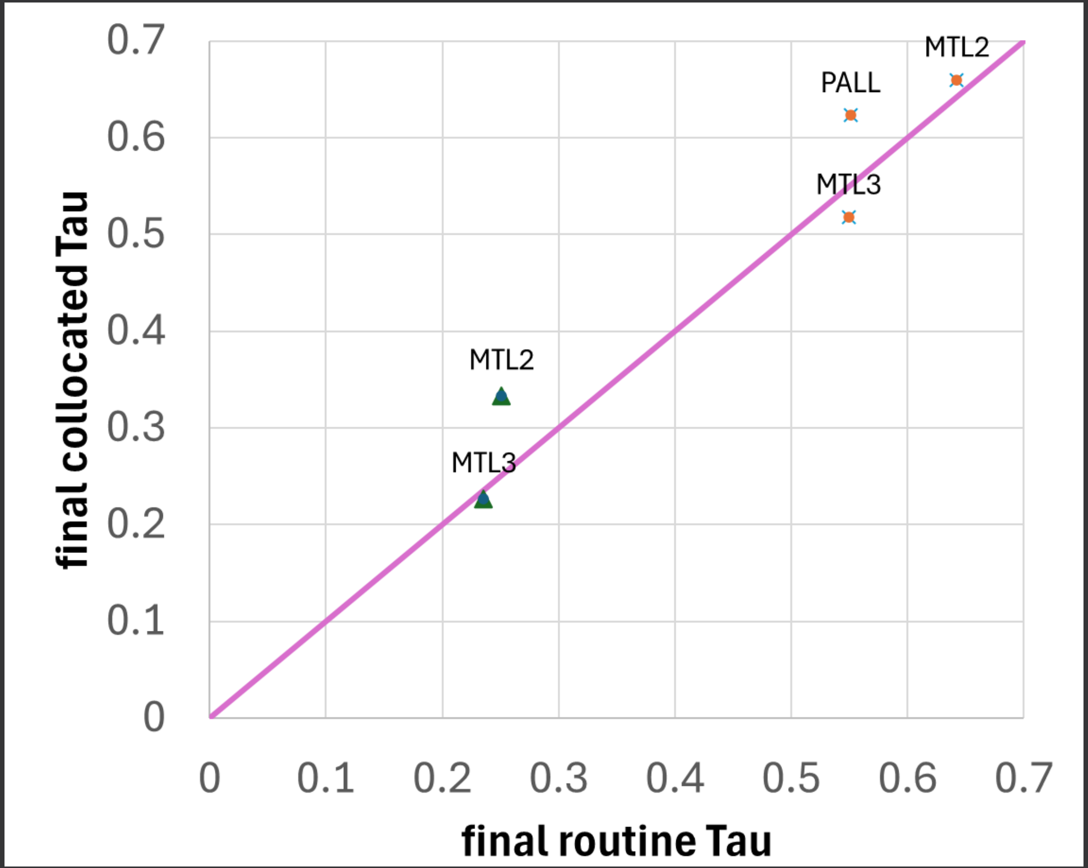
Effect of Scattering Particles on Light Absorption

- Effect of scattering particles on HIPS light absorption
  - Analyze by HIPS before each step
  - Deposit $(NH_4)_2SO_4$ particles before and after ambient sampling



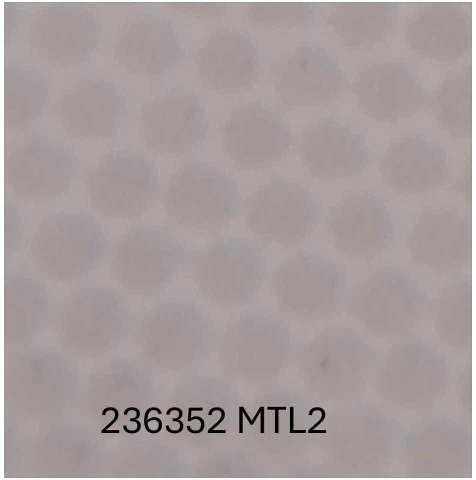


Light Absorption on Pall vs MTL 3 μm and 2 μm pore size filters

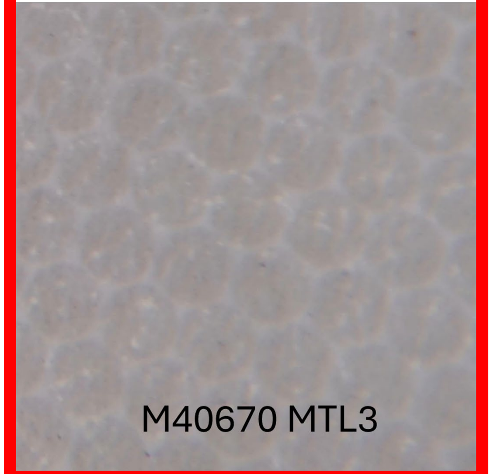


- MTL 3 um pore size filters biased low compared to Pall filters and 2um pore size MTL filters

CHAMBER FIRST

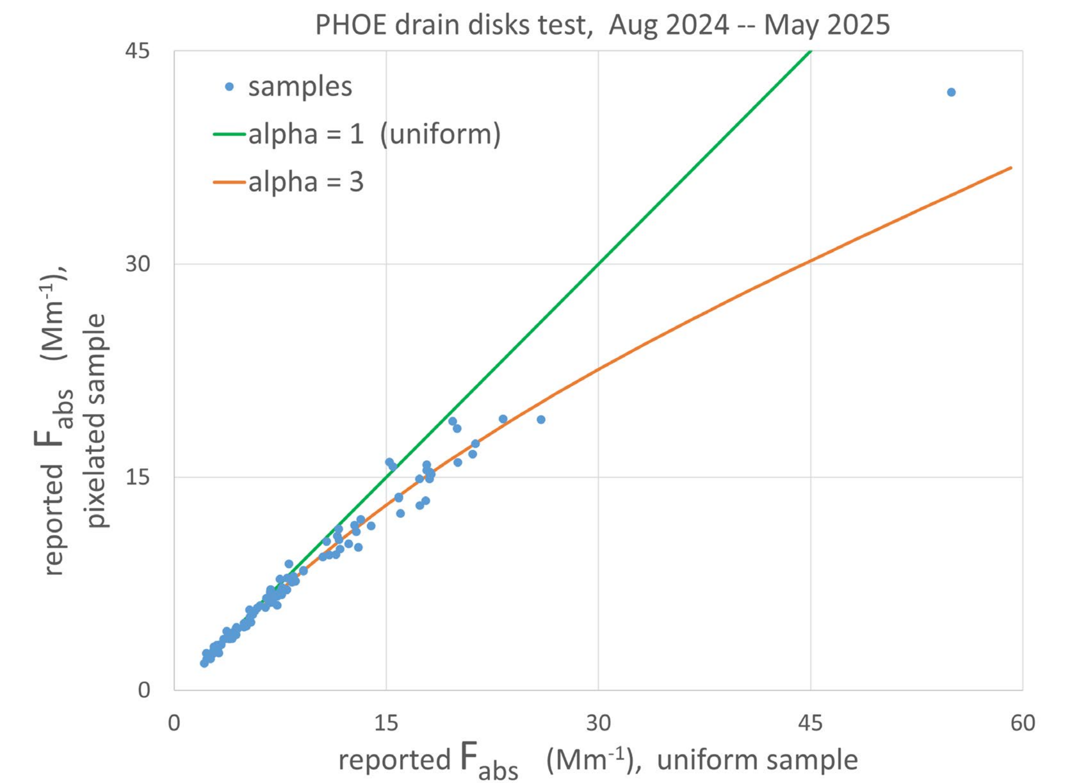


All micrographs are at same setting for lighting, focus, & magnification, with clean copy paper as background.



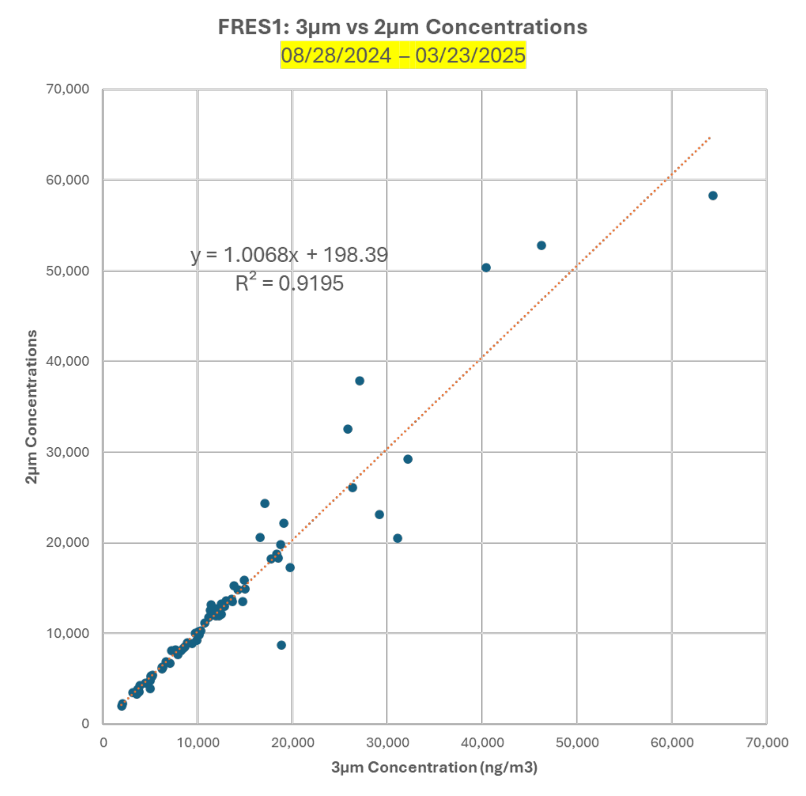
Pixelated Deposits

- Drain disks for collocated $PM_{2.5}$ module versus no drain disk on routine module

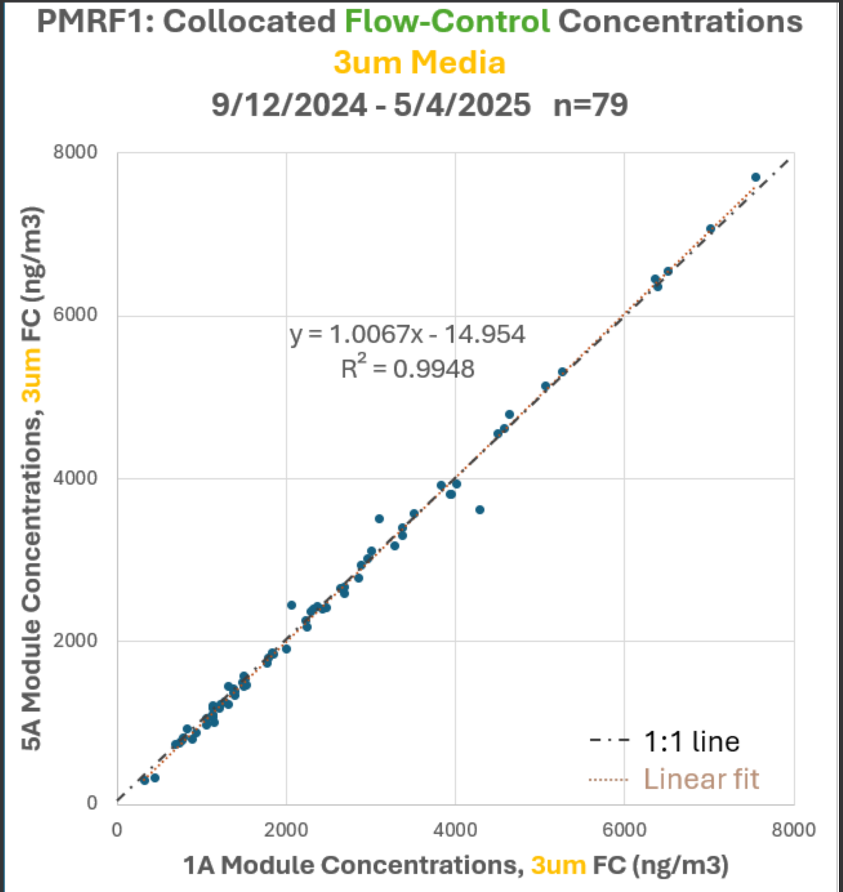


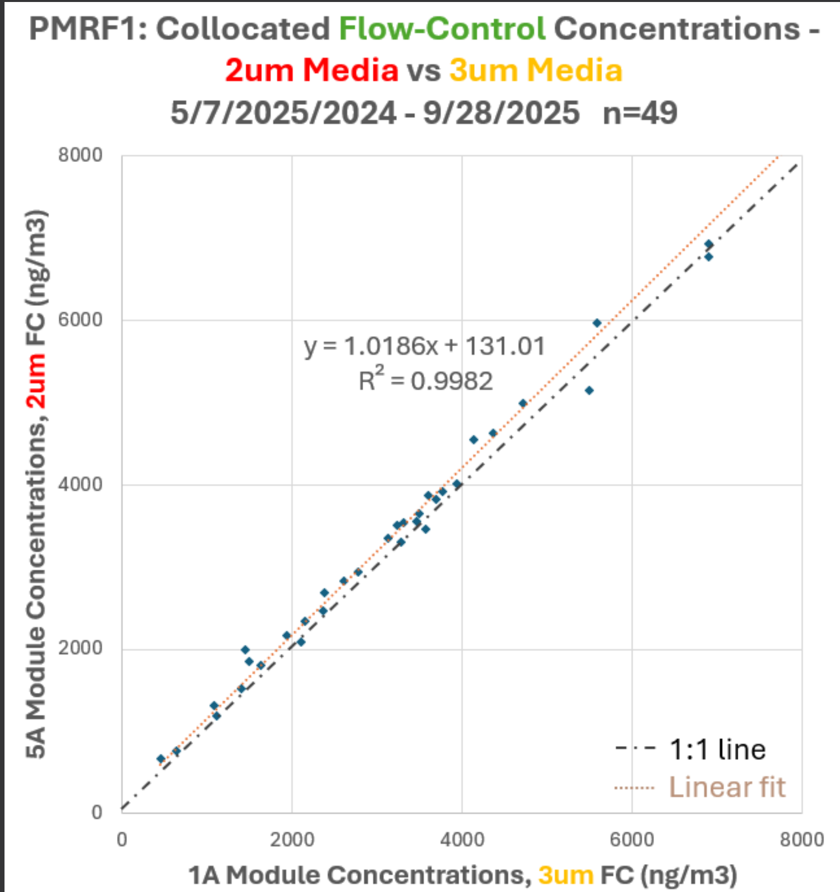
Experiments on PTFE filters: Pore size

- CSN uses 2 µm pore size, IMPROVE uses 3 µm pore size filters
  - Capture efficiency specifications are almost identical, but limited tests suggest otherwise
- Passive flow control could not accommodate 2 µm pore size
- Active flow control allows for higher pressure drop and changes in pressure drop with new lots
- Tested with flow control on roof – worked well and clogged slower than 3 µm filters
- Tested on newly installed collocated module in Fresno, results mixed
- Moved to testing at PMRF1 - excellent collocated precision established



Experiments on PTFE filters: Pore size





Experiments on PTFE filters: Pore size

- PMRF results are very encouraging
- What is the next step?
    - Switch more collocated sites to using 2 um pore size filters?
        - Would degrade collocated precision slightly
    - Switch network to using 2 um pore size filters?
    - Test 2 um pore size filters with drain disks?

Any questions?

New MAPA1 site, Photo credit: Lawrence Tsai