

The Case of the Black Dust:

Identifying and Correcting Spurious Elemental Carbon in the
Chemical Speciation Network

A Data Advisory audiobook by
Sean Raffuse, Alex Murrain,
Joshua Rohrer, and Anthony
Kawamoto

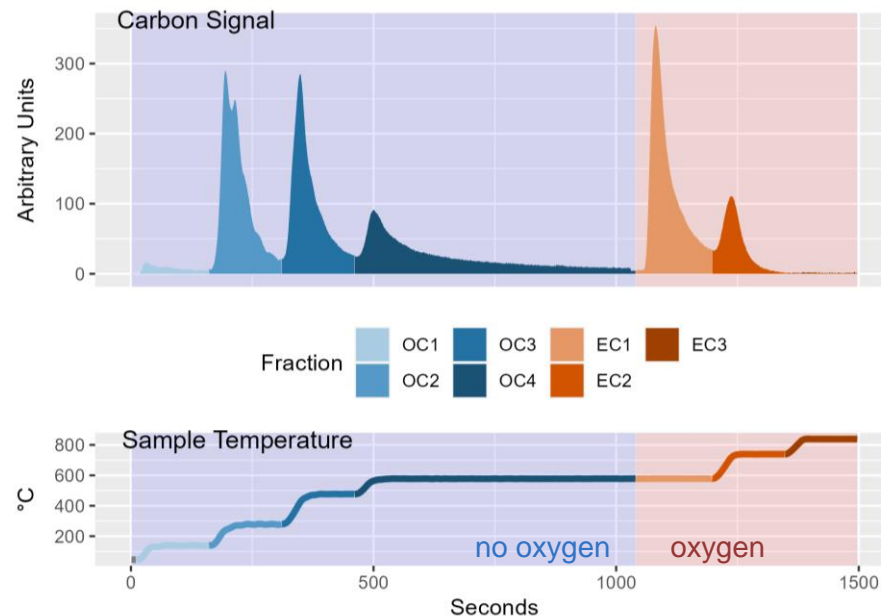
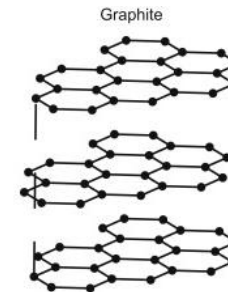
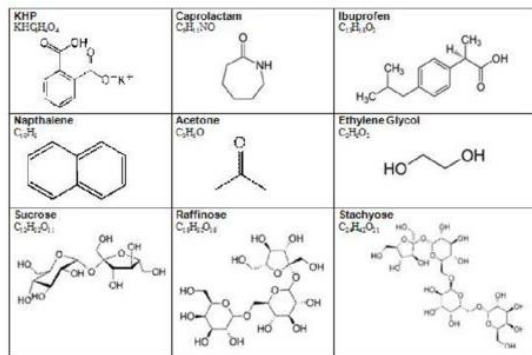
Air Quality Research Center
UC Davis

2024 National Ambient Air Monitoring Conference, August 12-15, New Orleans

Thermal/Optical Analysis

Thermal Analysis

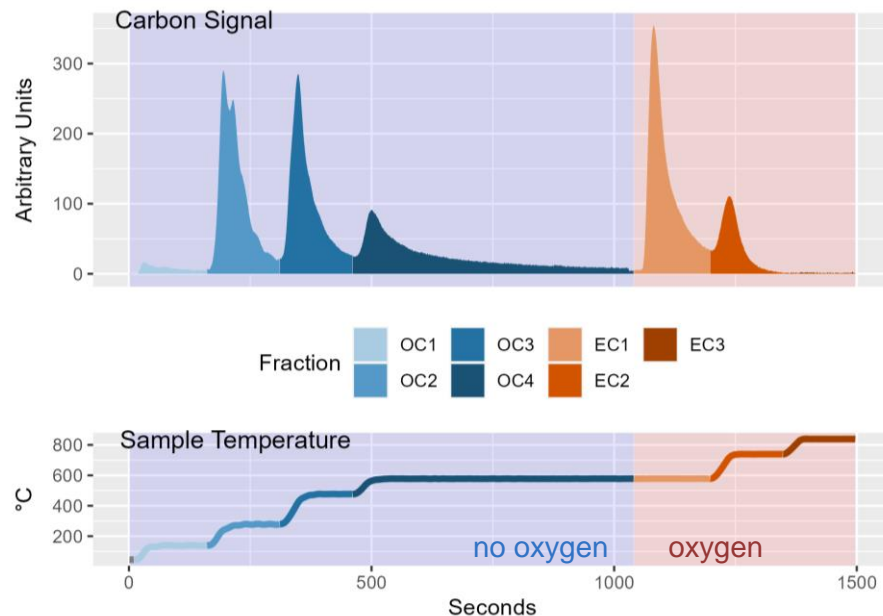
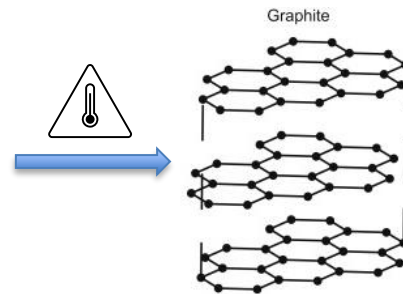
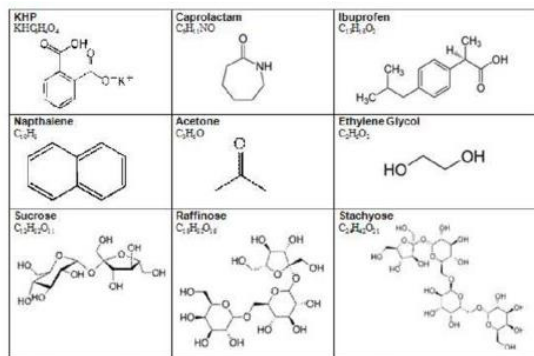
1. Heat the sample in the absence of oxygen
 - Organic molecules will volatilize
 - These are all converted to methane and measured
 - Reported as organic carbon (OC)
2. Add oxygen and burn the rest off
 - Graphitic carbon (soot) will burn off
 - These are converted to methane and measured
 - Reported as elemental carbon (EC)



Thermal/Optical Analysis

But there's a complication

- Heating the sample pyrolyzes (chars) some of the organic molecules (i.e., converts them to soot)
- Resulting EC is artificially high, so we need to make a correction
- Generally, OC is colorless and EC is black



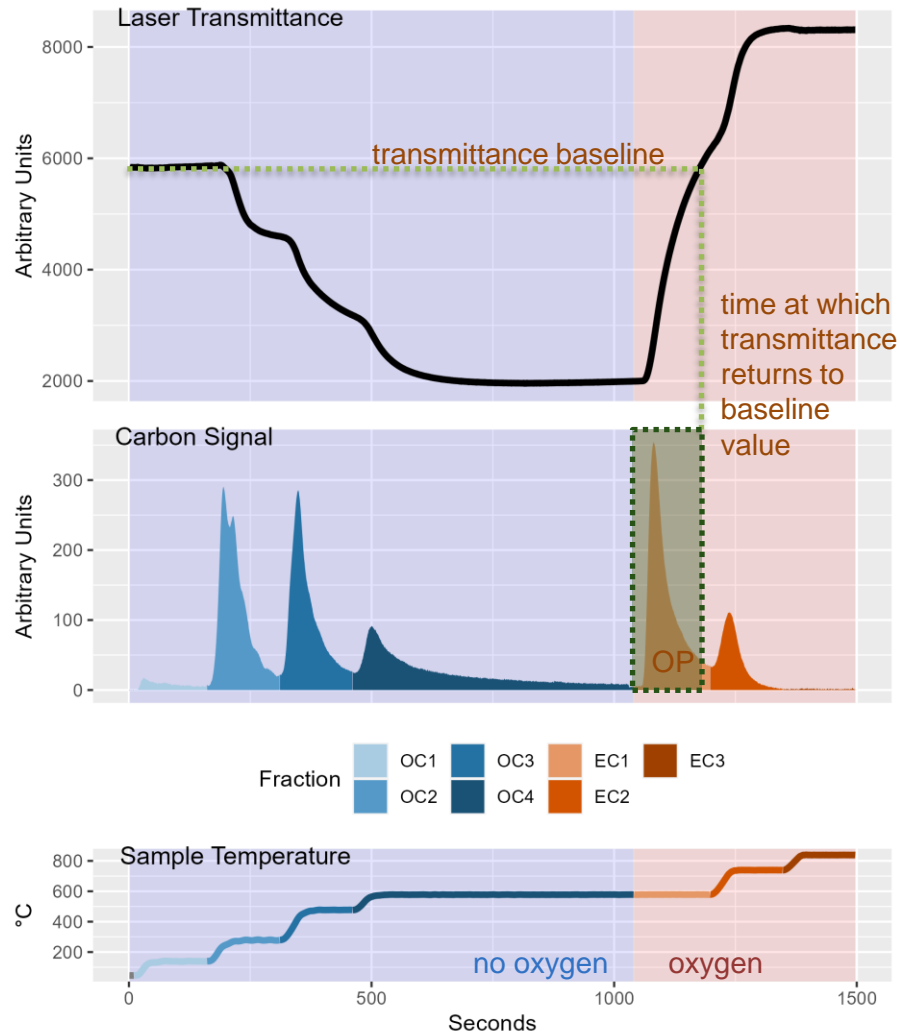
Thermal/Optical Analysis

Optical Analysis

- As the organics char, the sample gets darker
- This is measured with a laser
- When oxygen is added, the soot begins to burn off and the sample gets lighter again
- Once the laser returns to its original signal, we assume the charring we added has been burned off and the rest is now the original soot from the sample
- We refer to this extra added soot as pyrolyzed organics (OP)

$$\text{OC} = \text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OP}$$

$$\text{EC} = \text{EC1} + \text{EC2} - \text{EC3} - \text{OP}$$



Sometimes this doesn't work

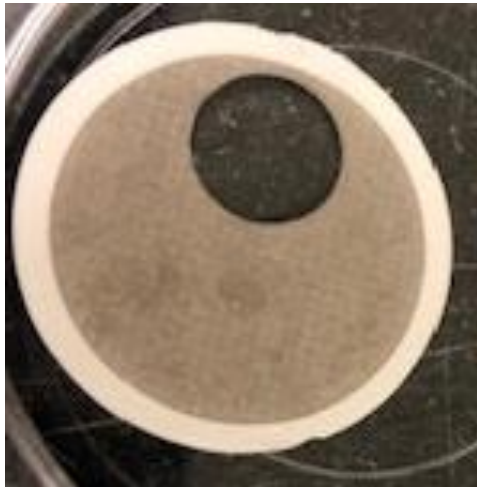
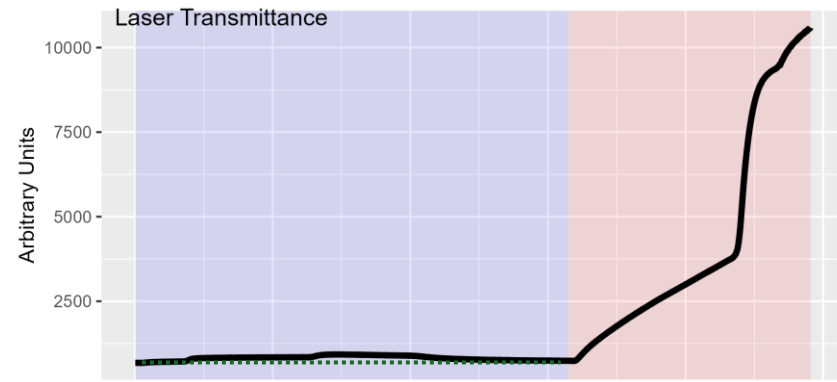
If the sample starts out too dark, the laser cannot see soot being added.



Charring is still happening, but we can't account for it. $OP = 0$ and EC will be artificially high.

UC Davis flagged these with LJ - "Identification Of Analyte Is Acceptable; Reported Value Is An Estimate"





OP > 0



OP = 0

Is it real?

For a few sites, the LJ flag was common

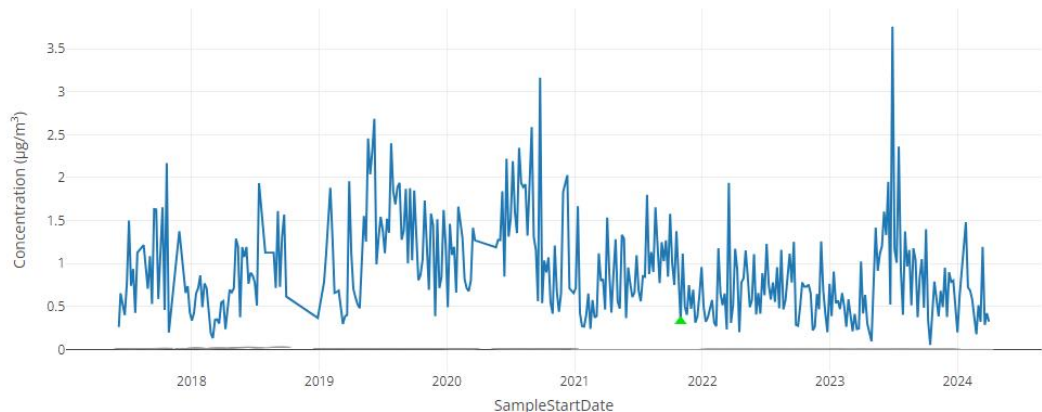
Samples were often too black for the laser to estimate OP

Is this because the site is high in soot?

Because there was no independent comparison, it was impossible to tell.



Show uncertainty





Comments

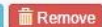
Site: Sampler head rotating during operation causing metallic dust. Wood: Site flagged AL and AN

— Wood 11/8/2022 2:49:38 PM



Site: Contamination from rotating sample head cap. Wood: Site flagged AL, AN, and IL

— Wood 7/13/2022 8:54:19 AM



Sampler intercomparisons

CSN uses two PM_{2.5} samplers at each site

MetOne SASS/SuperSASS

PTFE (Teflon) filter

- elements by X-ray Fluorescence (XRF)

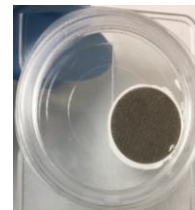
Nylon filter

- ions by Ion Chromatography (IC)

URG 3000N

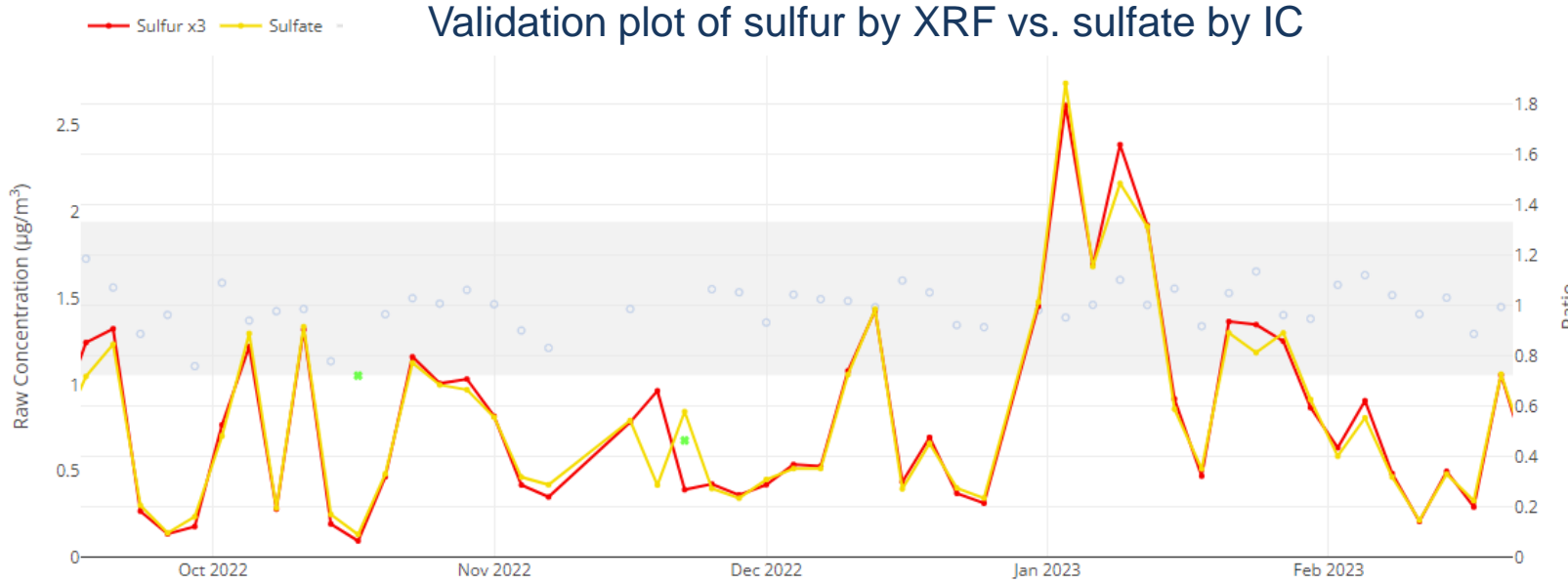
Quartz filter

- carbon by Thermal/Optical Analysis (TOA)



Sampler Intercomparisons

We can validate measurements when we have a companion measurement from a second analytical technique



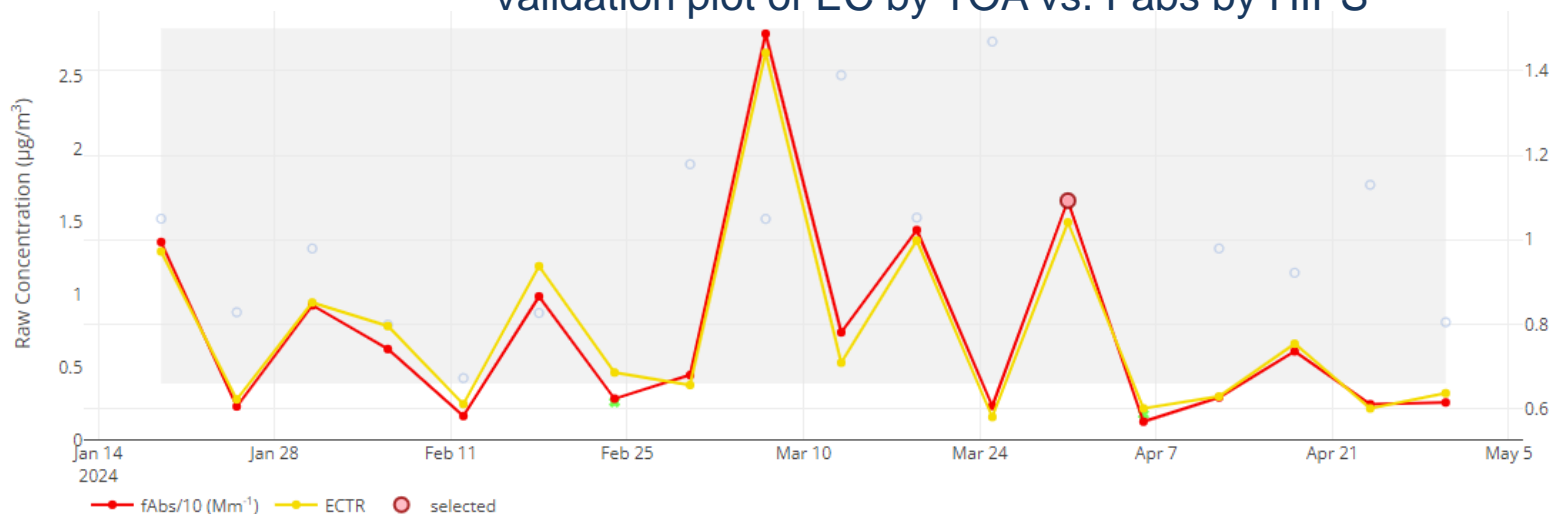
No companion measurement for OC/EC in CSN

But now there is

Hybrid Integrating Plate/Sphere (HIPS)

- Provides filter absorption (Fabs, 63102)
- Analyzed on the PTFE filter from the SASS
- First delivered for May 2022 samples (first analyzed mid-2019)
- Comparable to EC from TOA

Validation plot of EC by TOA vs. Fabs by HIPS



Back to the question: Is it real? Generally, no

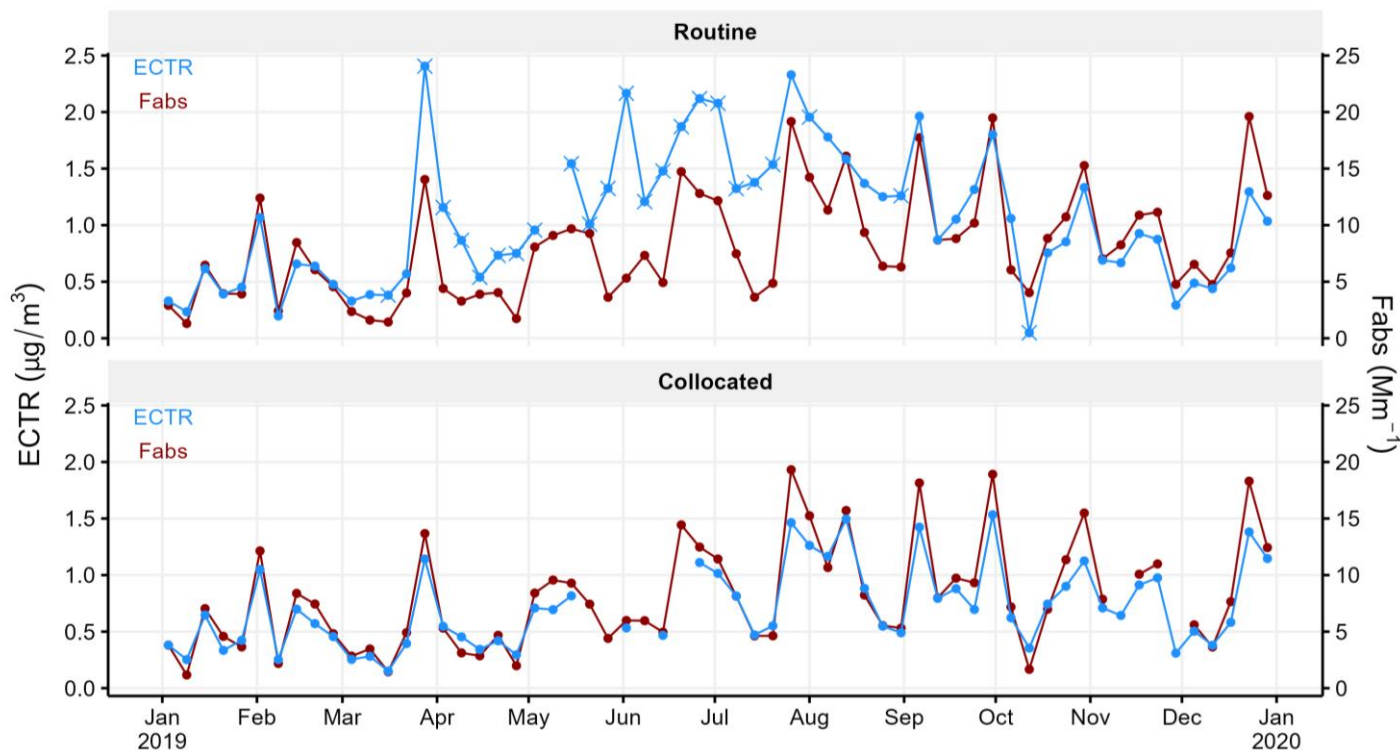
Four filters from four samplers at the same location

EC and Fabs agree well for collocated site

Fabs agrees between routine and collocated

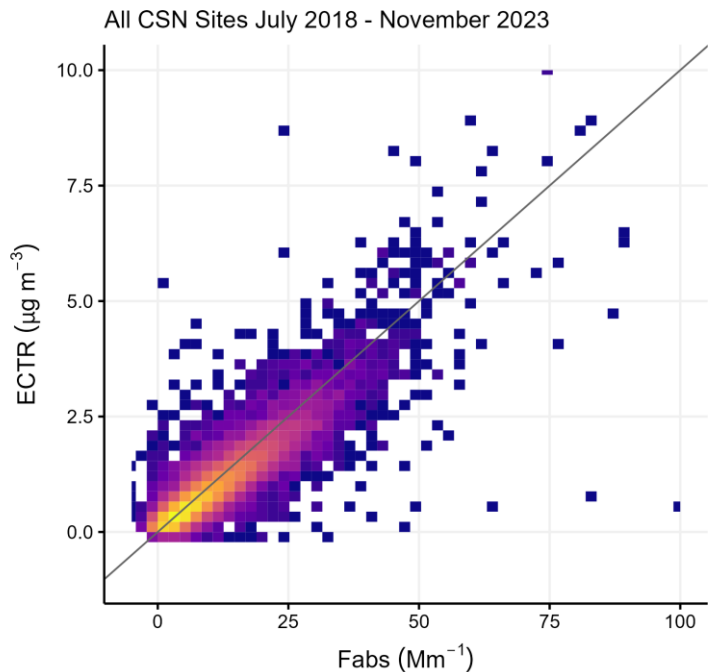
EC at routine site diverges when OP = 0 (shown as x in plot)

If only one filter in four at the same location is black, the sampler is the suspect



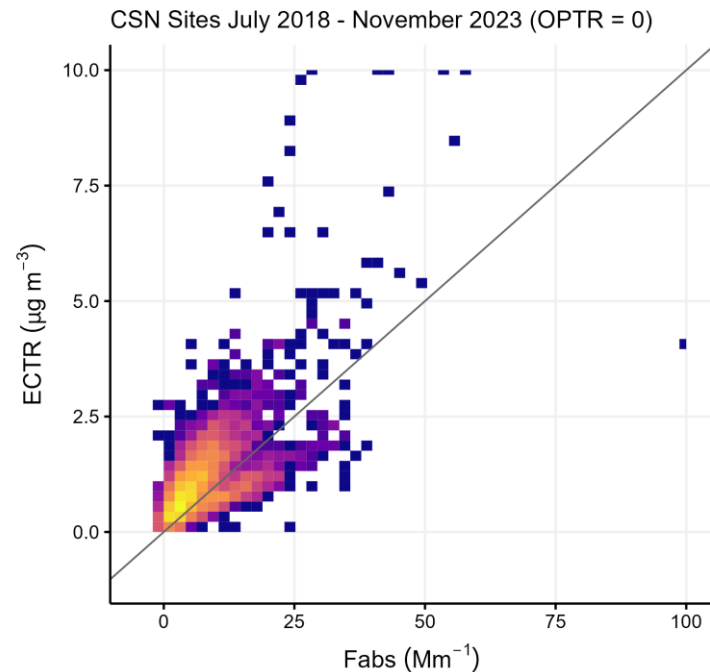
EC vs. Fabs

When OP correction works



Excludes records where uncorrected OPTR = 0

When it doesn't



Includes only records where uncorrected OPTR = 0

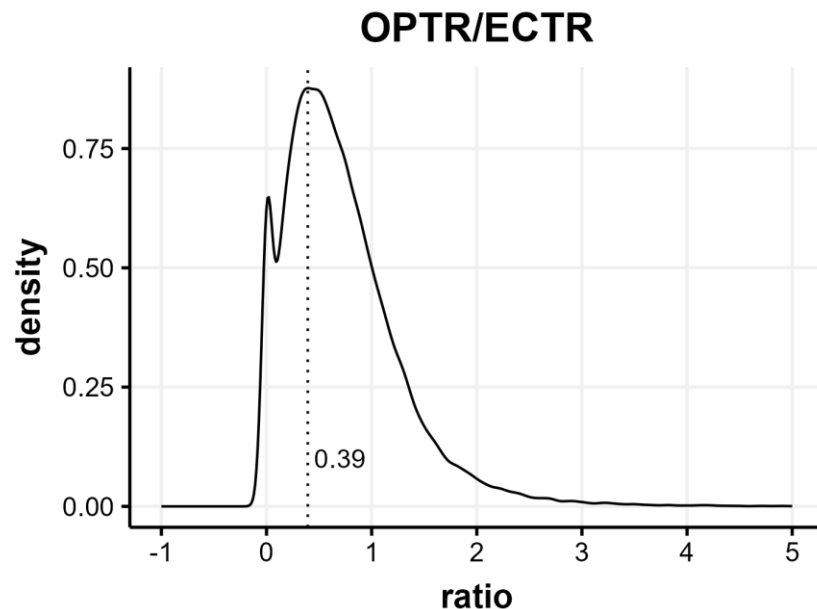
How important is the OP “correction”?

Most commonly, OP ~ 39% of EC
But anywhere in the range of 10 – 200%
is not uncommon!

If this correction cannot be applied, EC
will be overestimated by some large
amount.

This is occurring on ~6% of samples,
most of which appear to be from
malfunctioning samplers.

Ratio of OP to EC across
CSN in the past few years

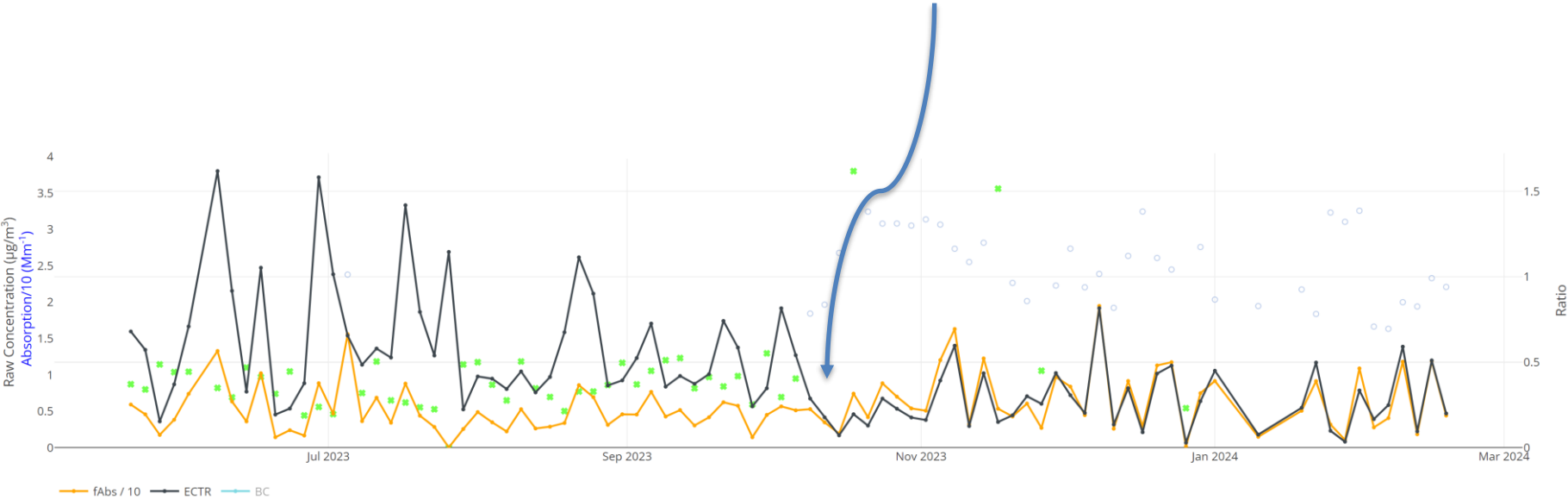


Dealing with the data

- For the EC and OP parameters, when the laser correction does not work, we now apply a null code depending on validation
 - SC (sampler contamination) if the sampler is suspected, Fabs value is low
 - BH (interference) if the Fabs is high, indicating soot collected by both samplers and thus atmospheric
- OC parameters continue to receive the LJ qualifier code (reported value is an estimate)

It's fixable

“Thoroughly cleaned temperature probe compartment and removed all black dust. Replaced internal cyclone and downtube with newly cleaned cyclone and downtube. Found that the sample inlet had a better fit and felt more secure with the replacement downtube (previous downtube may have been worn down by vibration).”



Summary

- If the quartz sample is too black, accurate EC cannot be calculated
- The most common cause of this situation is a malfunctioning sampler
- Regular maintenance and cleaning can help avoid this
- Be on the lookout for “SC” null codes (“sampler contamination”)
- See the data advisory for more information

Preventative Maintenance

It is recommended that URG 3000N samplers should be inspected and cleaned on an annual basis, specifically the inlet cap, downtube, inlet tee and cyclone assembly.

1. Remove cap from downtube, downtube from inlet tee, and inlet tee from frame.
2. Rinse with water, wipe, and blow dry. Do not use WD-40 or other non-water solutions.
3. Reassemble and reattach cyclone, inlet tee, downtube, and inlet cap. Inlet cap should fit tight around the top of the downtube. If fit is not tight (i.e., cap is easily removed from, or rotates around, downtube with light force), replace the o-ring and/or downtube.

https://www.epa.gov/system/files/documents/2024-06/f07-data-advisory_csn_ec_2024-05-23_508.pdf