

Posting Type	Advisory
Date Submitted	2024-04-23
Subject	Invalid EC due to unresolved laser correction, often as a result of sampler contamination
Project	CSN
Sites	All possible
Sample Period	2007 - present
Parameters	Raw and blank corrected elemental carbon (EC) and pyrolyzed carbon (OP) by reflectance and transmittance (88321, 88380, 88381, 88357, 88328, 88378, 88379, 88388)
Recommendation	Use EC data prior to January 2024 with caution and consider applying OP test.
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Executive Summary

Elemental Carbon by transmittance and/or reflectance (ECTT and ECTR) may be significantly overestimated when the laser correction for method-generated pyrolytic carbon cannot be applied. The most common source of this issue is sampler contamination in CSN, but it also occurs with samples heavily loaded with carbon (e.g., wildfire smoke samples) that overwhelm the Thermal/Optical Analysis (TOA) instrument's ability to perform the laser correction. This issue occurred on about 5% of samples during the 2019-2023 sample period. Beginning with filters collected in 2024, samples with reported raw (uncorrected) pyrolyzed carbon (OPTT or OPTR) of zero, the complementary total EC (ECTT or ECTR) is invalidated and a null code is applied. To determine the appropriate null code for the EC measurements, the filter absorption (Fabs) measurement by Hybrid Integrated Plate/Sphere (HIPS) is examined. For normal valid samples, Fabs and EC tend to have a consistent ratio. If raw OPTT/OPTR is zero and Fabs is low, sampler contamination is expected and the null code SC (sampler contamination) is applied. If Fabs is elevated, suggesting truly high EC in the ambient sample, the BH null code is applied (interference/co-elution/misidentification). The issue also impacts total organic carbon (OCTT and/or OCTR), but to a lesser degree. Those parameters remain valid and are given a qualifier of LJ (identification of analyte is acceptable; reported value is an estimate).

This issue has existed throughout the use of the URG 3000N sampler for quartz filters in the CSN, beginning in 2007. We suggest that users treat the total EC variables with caution and consider screening values where raw OP = 0 before conducting analysis on data collected prior to 2024.

Introduction

The TOA method calculates total OC and EC as follows:

$$\text{OCTR} = \text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OPTR}$$

$$\text{OCTT} = \text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OPTT}$$

$$\text{ECTR} = \text{EC1} + \text{EC2} + \text{EC3} - \text{OPTR}$$

$$\text{ECTT} = \text{EC1} + \text{EC2} + \text{EC3} - \text{OPTT}$$

The organic carbon fractions (OC1, OC2, OC3, and OC4) are analyzed by heating the sample with no oxygen at successively higher temperatures (Figure 1, bottom panel, blue region) following the IMPROVE_A protocol. The evolved carbon is converted to methane and measured (Figure 2, middle panel). Then, oxygen is added and the elemental carbon fractions (EC1, EC2, and EC3) are analyzed by combusting the remaining material off the quartz filter at successively higher temperatures, again measuring the resulting carbon as converted to methane (Figure 1, red region).

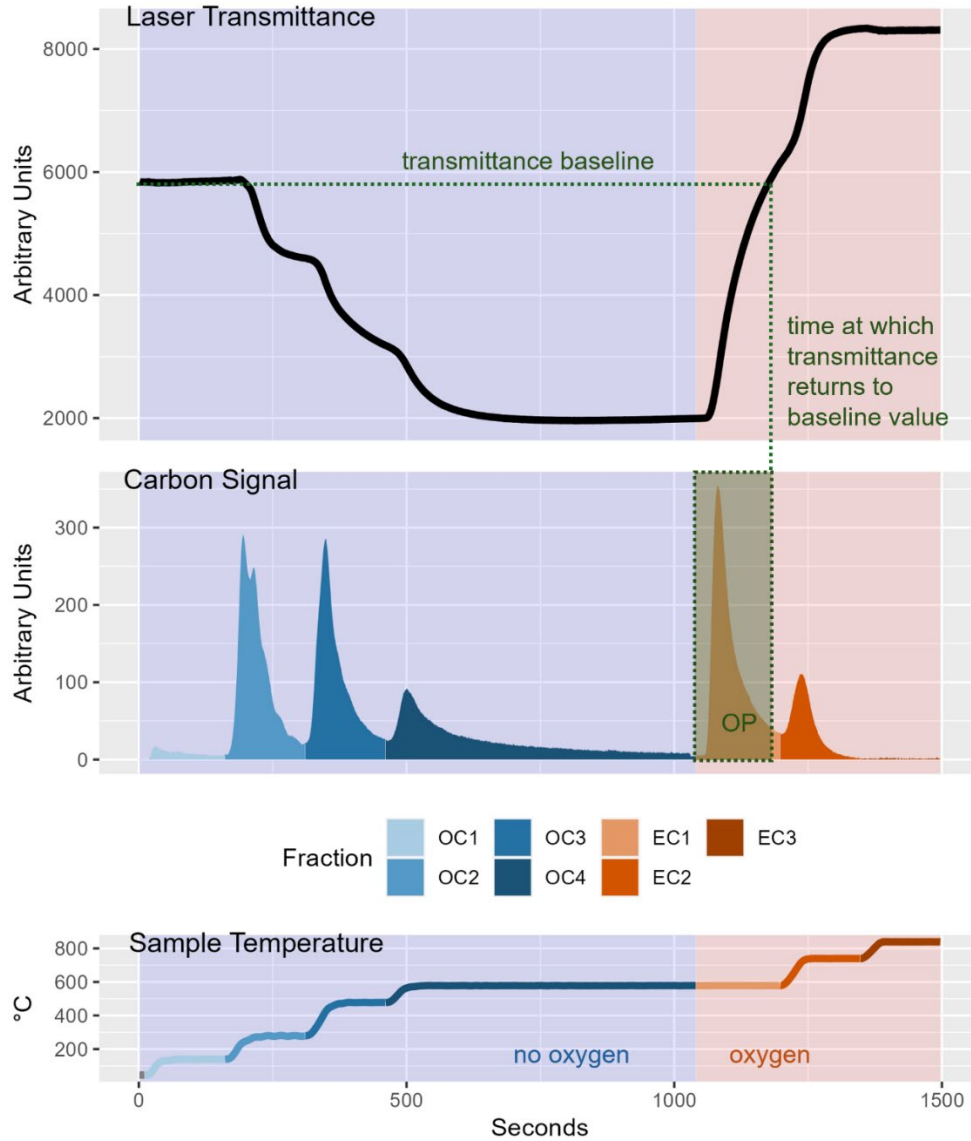


Figure 1. A “thermogram” for TOA analysis of an example CSN filter with a successful laser correction.

During the heating in the no-oxygen phase, some of the deposit becomes pyrolyzed, or charred, and will not evolve until burned in the oxygen phase. To account for this method-generated EC, a correction based on the laser measurements is applied. A laser measures the initial reflectance and transmittance of the sample (Figure 1, top panel). During the no-oxygen phase, as the sample chars, the laser signal (both reflectance and the transmittance) will decrease as the sample gets darker. Then, once oxygen is added, the EC begins to combust and the sample gets lighter. Until the laser signal reaches its initial level, it is assumed that the EC was created during the no-oxygen phase. This is the OP fraction (Figure 1, middle panel, green region); the carbon

measured during this time period is added back to the OC total and subtracted from the EC total as a correction.

Figure 2 shows an example of a laser correction failure. In this case, the initial transmittance is very low (i.e., the sample is very dark). Charring may be occurring during the no-oxygen phase, but it does not reduce the already low transmittance. Because of this, there is no way to estimate the amount of charring on the sample. The OP fraction is zero and no correction is applied to the total OC or EC.

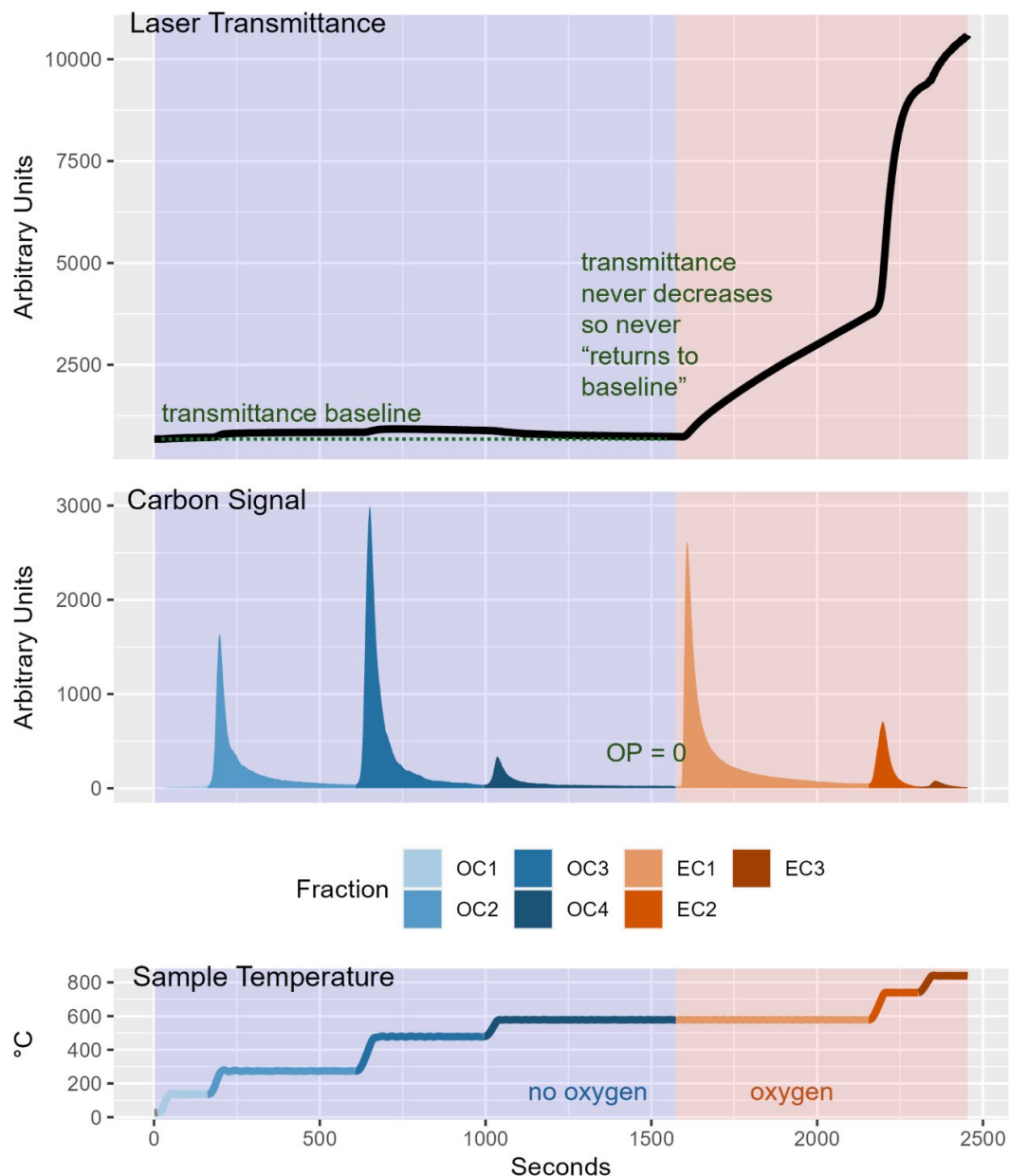


Figure 2. A thermogram for TOA analysis of a CSN filter with no laser correction.

Analysis

The size of the correction

The impact of no laser correction depends on the magnitude of the correction relative to the magnitude of total OC and EC. This varies by sample, and density plots of the ratio of the OP correction to the total EC or OC are shown in Figure 3. The OP correction is generally larger for transmittance than reflectance, but there is a wide distribution. For example, $OPTT/ECTT$ is typically between 0 and 4. That means that the OP value can be up to four times larger than the total EC value. Thus, if this correction cannot be applied, the total EC may be overestimated by 400%, and is most commonly to be overestimated by 80%. Conversely, because OP is added to OC, total OC values will be underestimated when OP is zero, but the relative impact is smaller, between 0 and 60%, with the most common correction around 20%.

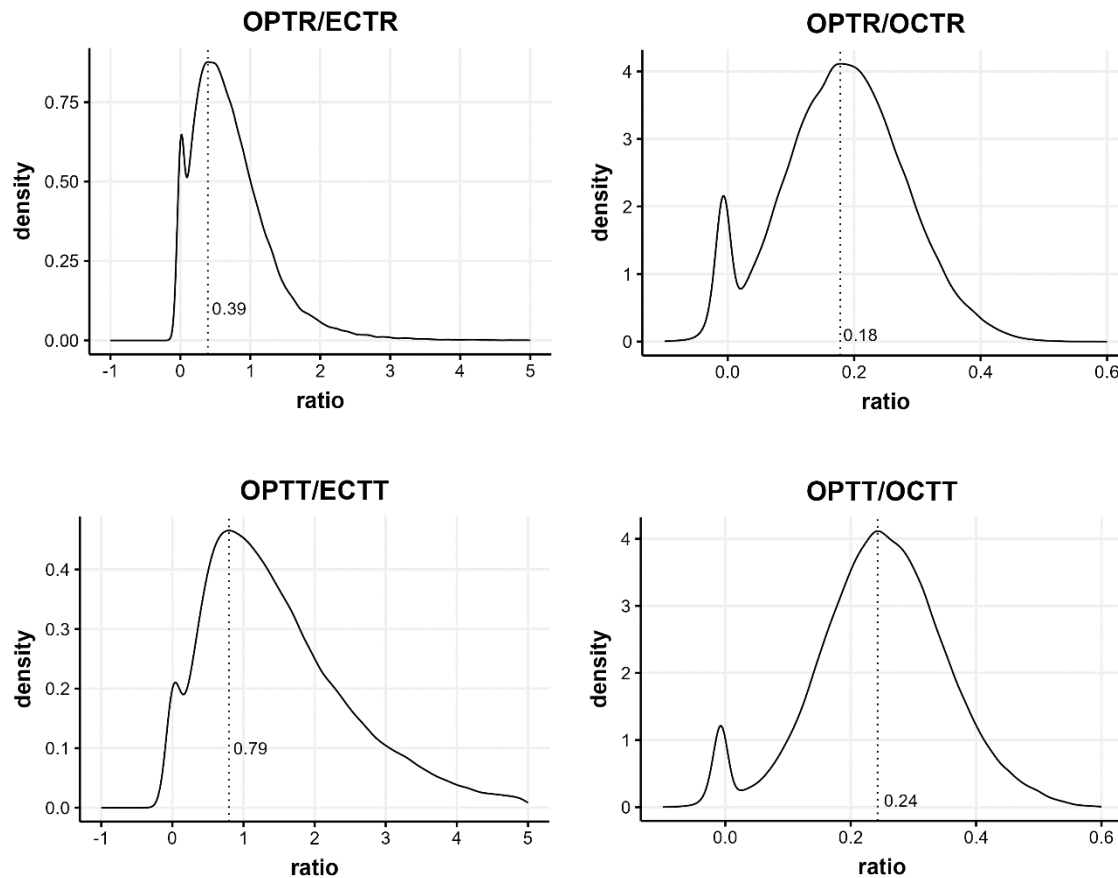


Figure 3. Density plots of the ratio of OP over EC (left) or OC (right) by reflectance (top) and transmittance (bottom). Dotted line indicates the mode.

EC and Fabs

In 2019, UC Davis Air Quality Research Center (UCD) began collecting filter absorption measurements performed on the CSN polytetrafluoroethylene (PTFE, “Teflon”) filters by Hybrid Integrating Plate/Sphere (HIPS). These data were first delivered to AQS beginning with May 2022 samples. Filter absorption is reported as 63102 (Light Absorption Coefficient) in AQS but will be referred to herein as Fabs. Because black carbon (soot) is the prominent source of absorption in most particle samples, Fabs is closely related to elemental carbon (EC) as measured by TOA. Prior to the reporting of Fabs, there was no comparable data that could be used for day-to-day validation of the TOA data. Figure 3 shows the relationship between ECTR and Fabs in CSN when both measurements are valid and the TOA laser correction can be resolved (i.e., OP is not zero, left) or not (right). When the laser correction is successful, Fabs and ECTR are linearly related, with a slope of about 0.1 and an R^2 of 0.81. Conversely, when the laser correction is not successful, the Fabs/ECTR relationship becomes poor, with many of the pairs falling above the 0.1 slope line (i.e., ECTR is higher than expected). ECTR shows a similar relationship to Fabs, but with a slightly different slope (not shown).

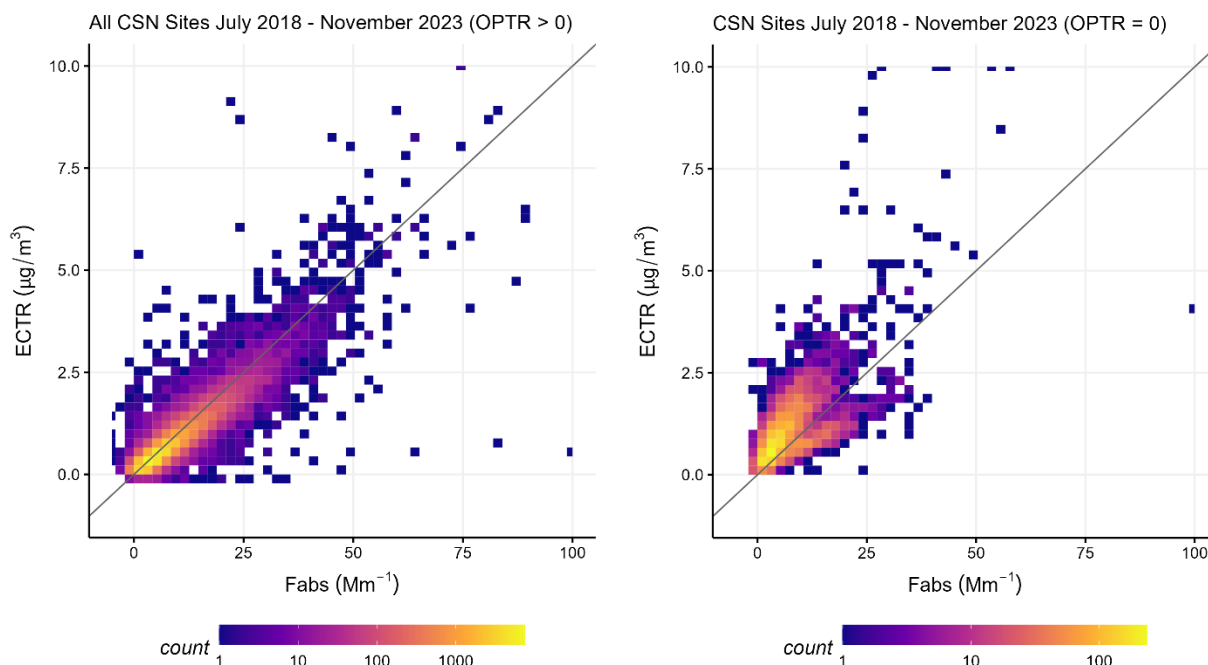


Figure 3. Relationship between ECTR and Fabs in CSN when TOA laser correction is successful (left) or unsuccessful (right). Brighter yellow colors indicate more samples within the square. Note the logarithmic color scale.

Because of the relationship between Fabs and EC, and because they are measured on different samplers, they can be used to validate each other. These inter-analytical method comparisons are a key part of data validation for CSN. When the relationship is not as expected on a given

sampling event, it suggests an issue with one or both measurements. This can be seen by looking at the measurements together in a time series. Figure 4 shows one year of Fabs and ECTR concentrations at the G.T. Craig, Ohio site (39-035-0060). G.T. Craig has both a routine and collocated monitoring setup. During the first two months of 2019, Fabs and ECTR were well correlated for both routine and collocated samples. Between March and August, the relationship at the routine site was degraded, with ECTR much higher than expected for the measured Fabs. Because the ECTR continues to agree with Fabs at the collocated site during this time period, and Fabs is very similar between collocated and routine, the routine ECTR measurement is most likely in error. All TOA measurements where the raw OPTR was zero (i.e., no laser correction) are denoted in the figure with blue X's. Nearly all the routine samples in the period with poor agreement have no laser correction. The ECTR error on these days is significant, with some days high by over 200%.

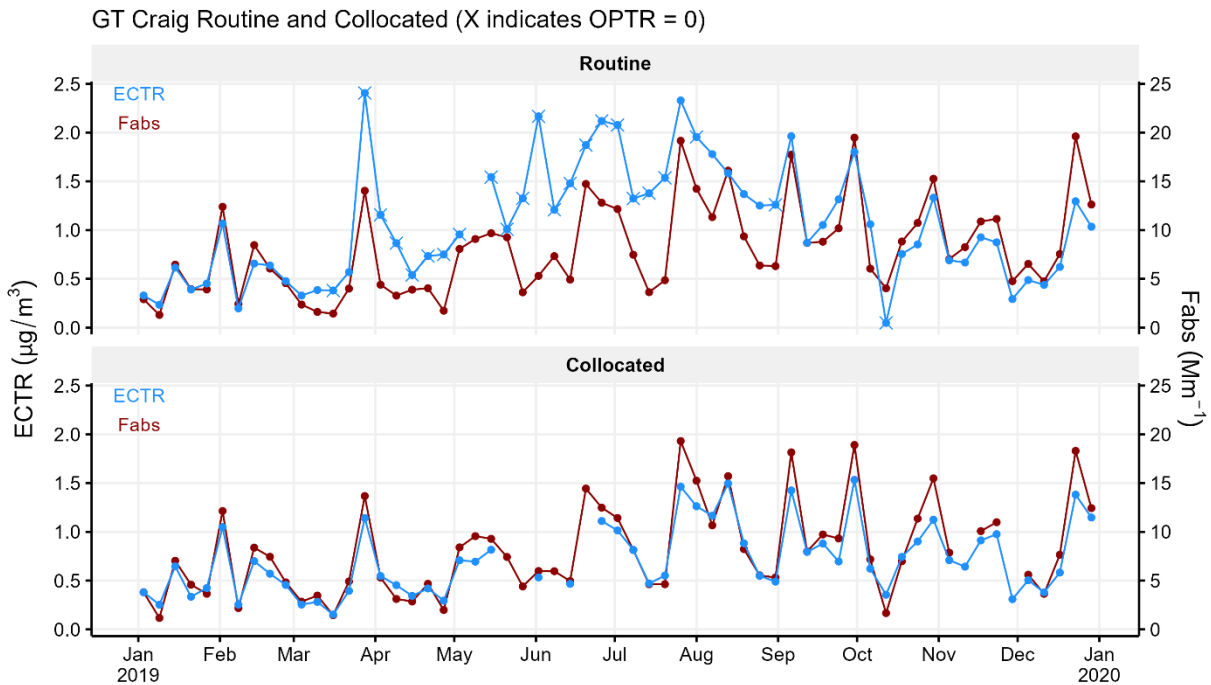


Figure 4. Time series of ECTR and Fabs at G.T. Craig routine and collocated sites for 2019.

Root Cause

The analytical cause of the incorrect EC measurement is related to a saturated laser response. This occurs when there is a very dark deposit on the quartz filter. The dark deposit can come from ambient sampling or a sampler malfunction. Based on the pattern of occurrence and reporting from the field, we conclude that many of the cases in CSN are due to sampler malfunction.

Beginning in 2022, sites began reporting a “black dust” on their quartz filters and in their URG 3000N samplers used to collect quartz samples for TOA. Some sites also reported URG sampler heads rotating during sampling. EC measured from these samples were elevated compared with the Fabs measured from the PTFE samples. The LJ qualifier code was applied to most EC measurements and sites asked questions about the increase in frequency of these qualifier codes.

Figure 5 shows a schematic of the URG 3000N sampler. At one site with recurrent zero OP values, the sampler head was found to have a loose seal with the downtube, which led to rotation while the pump was on. Grease had been used and the o-ring no longer produced a tight seal. Black dust was found in the URG inlet tee and around the cyclone. The quantity of black dust was large enough, it was depositing on the quartz filters during sampling. Figure 6 shows an example of the buildup of black dust.

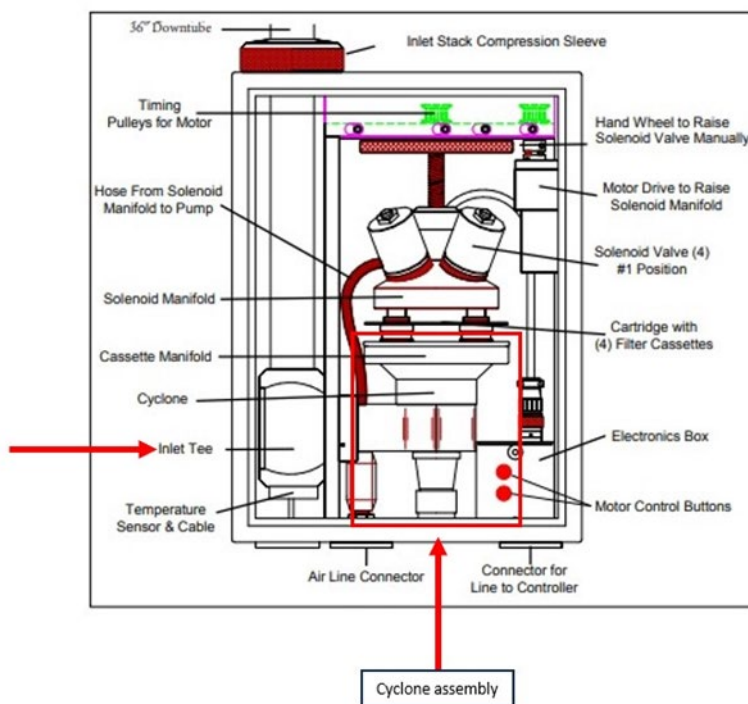


Figure 5. Schematic of URG 3000N sampler body with inlet tee and cyclone assembly highlighted with red arrow. Excerpted from the URG3000N Operations Manual.



Figure 6. Photo of URG 3000N Inlet Tee with “black dust” buildup (taken July 13, 2023).

Corrective and Preventative Actions

Identification and Flagging

UCD has developed validation procedures for identifying cases where the TOA laser signal cannot be resolved and applying the appropriate flags.

- 1) A null code is automatically applied to OPTT and ECTT if $OPTT = 0$. A qualifier code ('LJ') is applied to OCTT.
- 2) A null code is automatically applied to OPTR and ECTR if $OPTR = 0$. A qualifier code ('LJ') is applied to OCTR.
- 3) The Fabs/EC relationship is reviewed for sites flagged in steps 1 or 2 using validation tools such as the screen shown in Figure 7. If the Fabs/EC ratio is consistently low over multiple sampling days at the site relative to historical values, sampler contamination is suspected and the 'SC' null code is applied. If Fabs is also elevated, or other evidence for high concentrations of absorbing particles is observed (e.g., visible wildfire smoke plumes), then sampler contamination is not suspected and the 'BH' null code is applied.

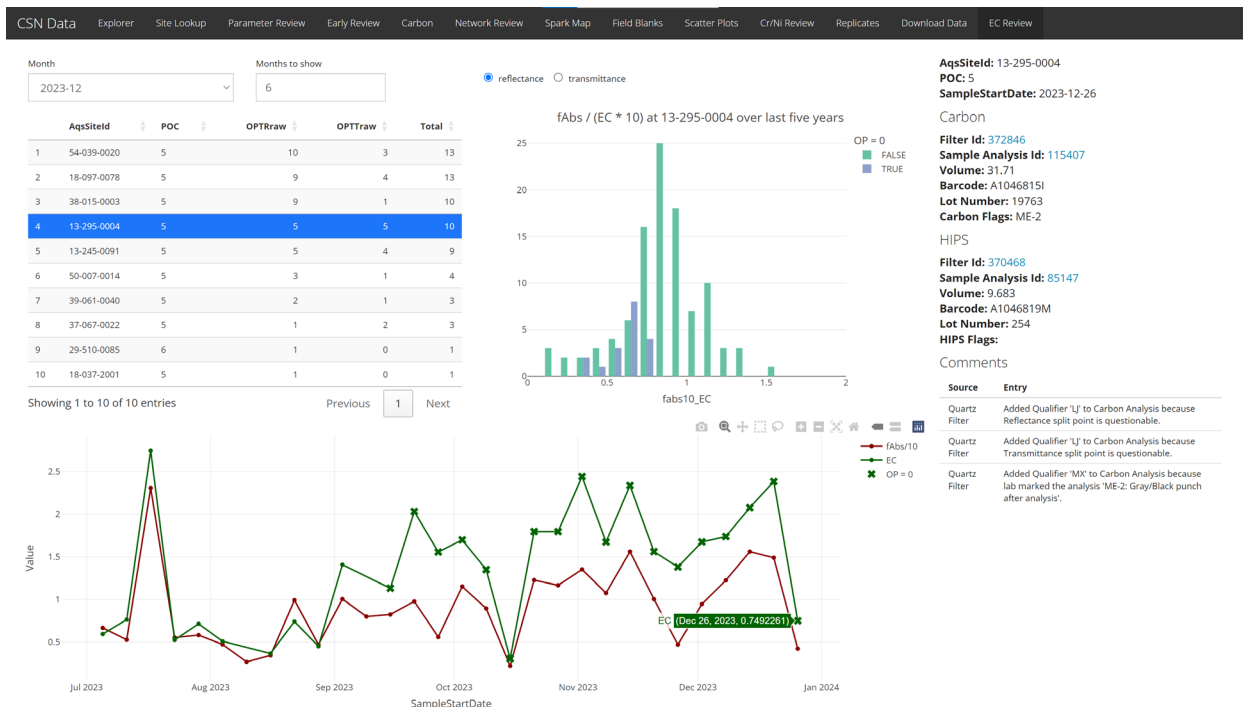


Figure 7. Screenshot of the EC review tool UC Davis validators use to determine appropriate null codes for unresolved TOA laser corrections.

Preventative Maintenance

Although the chemical composition and exact origin of the black dust has not been determined, the issue can be resolved with sampler 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. Figure 7 shows the o-ring of the inlet cap.



Figure 7. Photo of Inlet Cap removed from Downtube with o-ring indicated by red arrow (taken July 13, 2023).