Inter-Comparison of Thermal-Optical Carbon Measurements by Sunset and DRI Analyzers

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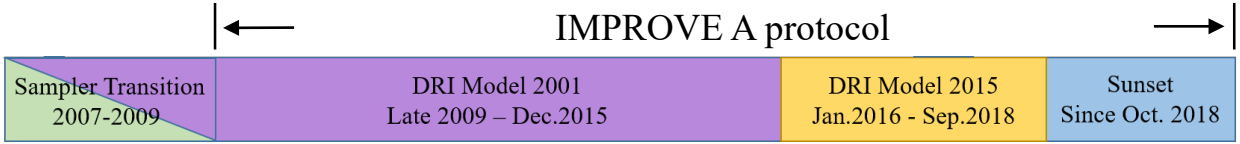
Background/Motivation

- Thermal-Optical Analysis (TOA) is a conventional method for quantifying OC and EC from quartz filter samples.
- Previous TOA inter-comparison studies focus more on inter-protocol comparison (e.g. IMPROVE vs NIOSH).
- CSN TOA switched from using DRI 2015 analyzers (analysis performed by DRI) to Sunset analyzers (analysis performed by UCD) in October 2018.



- The goal of this study is to understand CSN TOA measurement uncertainty and consistency by comparing results from three models of TOA analyzers (Sunset vs. two DRI models).

Main Differences in the Three TOA Analyzer Models

	DRI Model 2001	DRI Model 2015	Sunset Model 5L
Laser Source	Helium-neon (He-Ne) laser at 633 nm	Seven diode lasers at 405, 445, 532, 635, 780, 808, and 980 nm	Single diode laser at 658 nm
Detection	Flame ionization detector (FID) for CH_4	Non-dispersive infrared (NDIR) detector for CO_2	Flame ionization detector (FID) for CH_4
Temperature Calibration	Temperature-indicating liquids (Tempilaq° G) that change optical properties at 121°C, 184°C, 253°C, 510°C, 704°C and 816°C to calibrate oven temperature	Same as DRI Model 2001	A thermocouple at sample position to calibrate oven temperature at 140°C, 280°C, 480°C, 580°C, 740°C and 840°C (IMPROVE_A temperature plateaus)
Optical Configuration	Laser source installed coaxially with the optical detectors; laser beam travels in optical fiber and then through quartz guiding pipe before reaching the sample.	Same as DRI Model 2001	Laser source installed diagonally to the optical detectors with a 45° angle; laser beam travels through quartz oven window in carrier gas before reaching the sample.

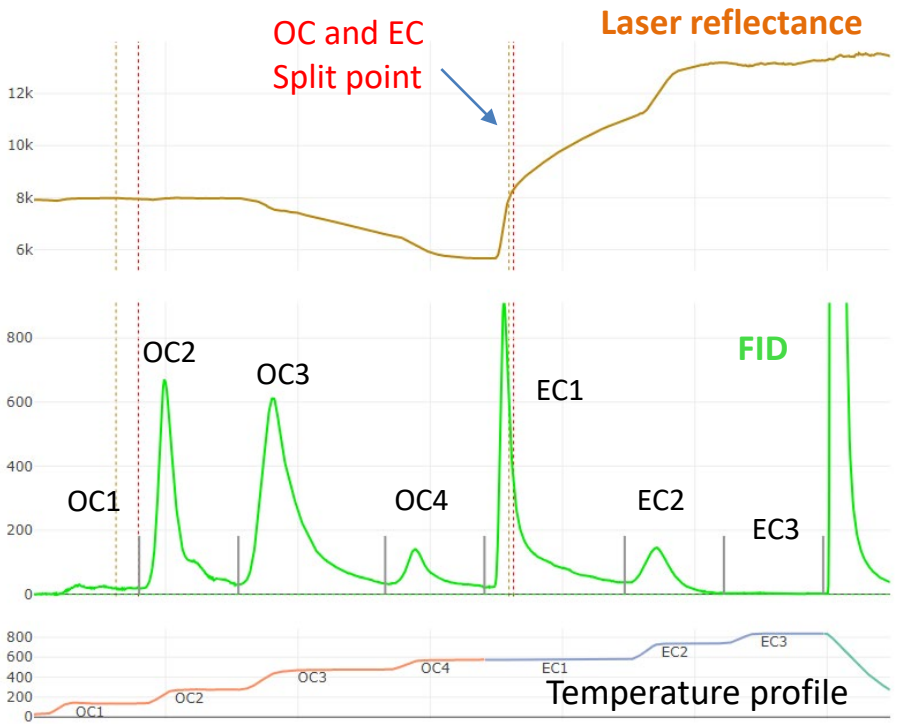
***Software and data processing:**

baseline, peak integration, residence time, laser/temperature dependence, etc.

IMPROVE A Protocol – Reflectance Optical Correction

Temperature Ramp (Duration)	Carrier Gas	Carbon Fraction
Heater off (90 s)	He Purge	----
140 °C (150-580 s)	He	OC1
280 °C (150-580 s)	He	OC2
480 °C (150-580 s)	He	OC3
580 °C (150-580 s)	He	OC4
580 °C (150-580 s)	He/O_2	EC1
740 °C (150-580 s)	He/O_2	EC2
840 °C (150-580 s)	He/O_2	EC3
Heater off (110s)	He/CH_4	----

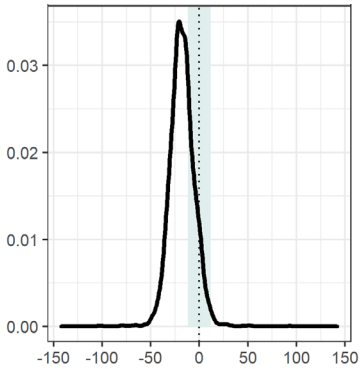
- OC = OC1 + OC2 + OC3 + OC4 + OP
- EC = EC1 + EC2 + EC3 – OP
- TC = OC + EC



Methodology

- Two inter-model comparisons
  1. DRI 2001 vs Sunset (n = 303 archived 2007 CSN samples)
     - DRI analysis in 2008 with DRI 2001 analyzers
     - UCD reanalysis from archive in 2017 – 2018 with Sunset analyzer
  2. Sunset vs DRI 2015 (n = 4073 fresh 2017 CSN samples)
     - UCD initial analysis in 2017 – 2018 with Sunset analyzer
     - DRI reanalysis in 2017 – 2018 with DRI 2015 analyzer
     - Replicate analyses on selected samples
- Scaled Relative Difference (SRD)

$$SRD_i = \frac{([Sunset]_i - [DRI]_i)/\sqrt{2}}{([Sunset]_i + [DRI]_i)/2} \times 100$$



SRD

Within- and Inter-Model Measurement Uncertainty

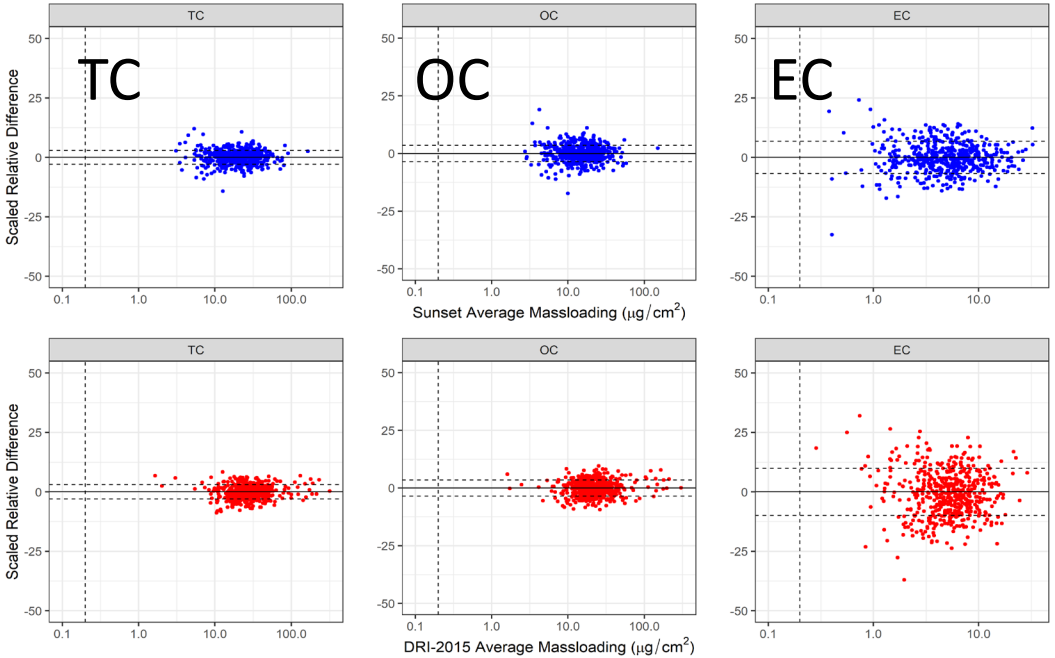
- Replicate analyses by each lab – two punches from one 25 mm filter sample (UCD: *n* = 559; DRI: *n* = 518)

- $$SRD_i = \frac{([Original]_i - [Replicate]_i)/\sqrt{2}}{([Original]_i + [Replicate]_i)/2} \times 100$$
  - Mean $\overline{SRD}$ provides an estimate of replication bias (expected to be negligible)
  - Standard deviation (1σ) of SRD provides an estimate for within-model measurement uncertainty (Unc) of one model type
- Combined inter-model uncertainty

$$Unc_{inter} = \sqrt{(Unc_{DRI})^2 + (Unc_{Sunset})^2}$$

Within- and Inter-Model Measurement Uncertainty

- Inter-model uncertainty provides benchmarks for inter-model comparison

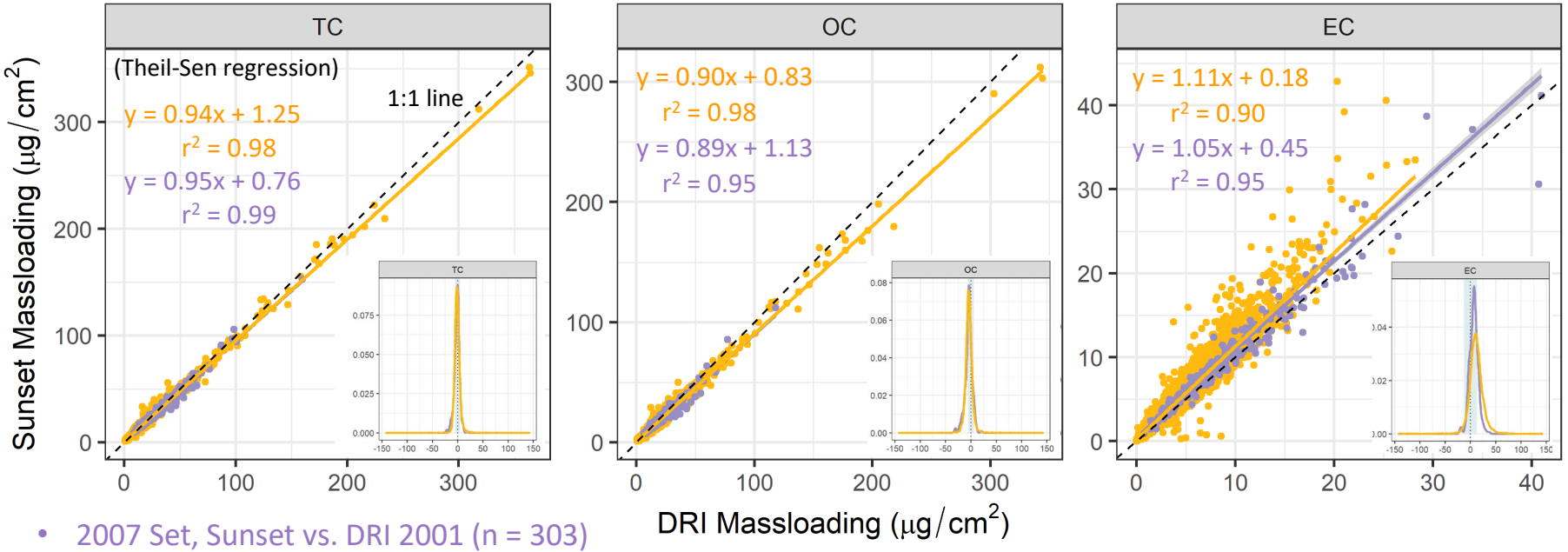


UCD (n=559)

DRI (n=518)

	Combined Uncertainty (%)
TC	4.1
OC	5.0
EC	12
OP	58
OC1	57
OC2	13
OC3	11
OC4	20
EC1	13
EC2	27
EC3	NA

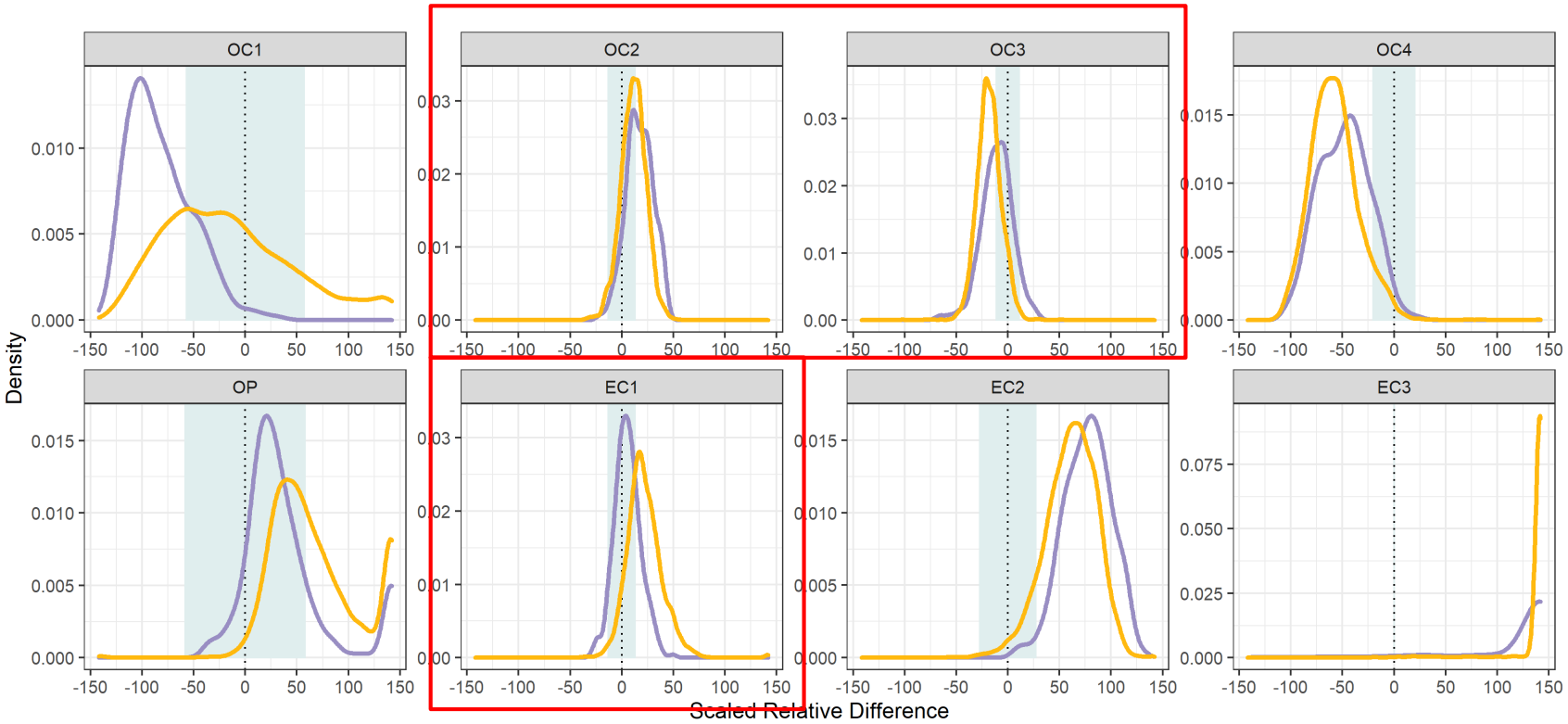
Inter-model Comparison of Bulk Carbon Parameters



- 2007 Set, Sunset vs. DRI 2001 (n = 303)
- 2017 Set, Sunset vs. DRI 2015 (n = 4073)

- Good agreement in both comparisons with strong correlation and slopes close to 1
- Mean $\overline{SRD}$ (inter-model bias) smaller than inter-model uncertainty

Inter-model Comparisons of Carbon Sub-Fractions

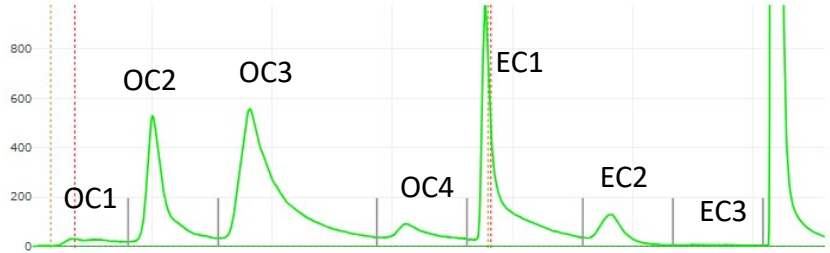


"Carbon Migration"
(e.g. Chow et al., 2007)

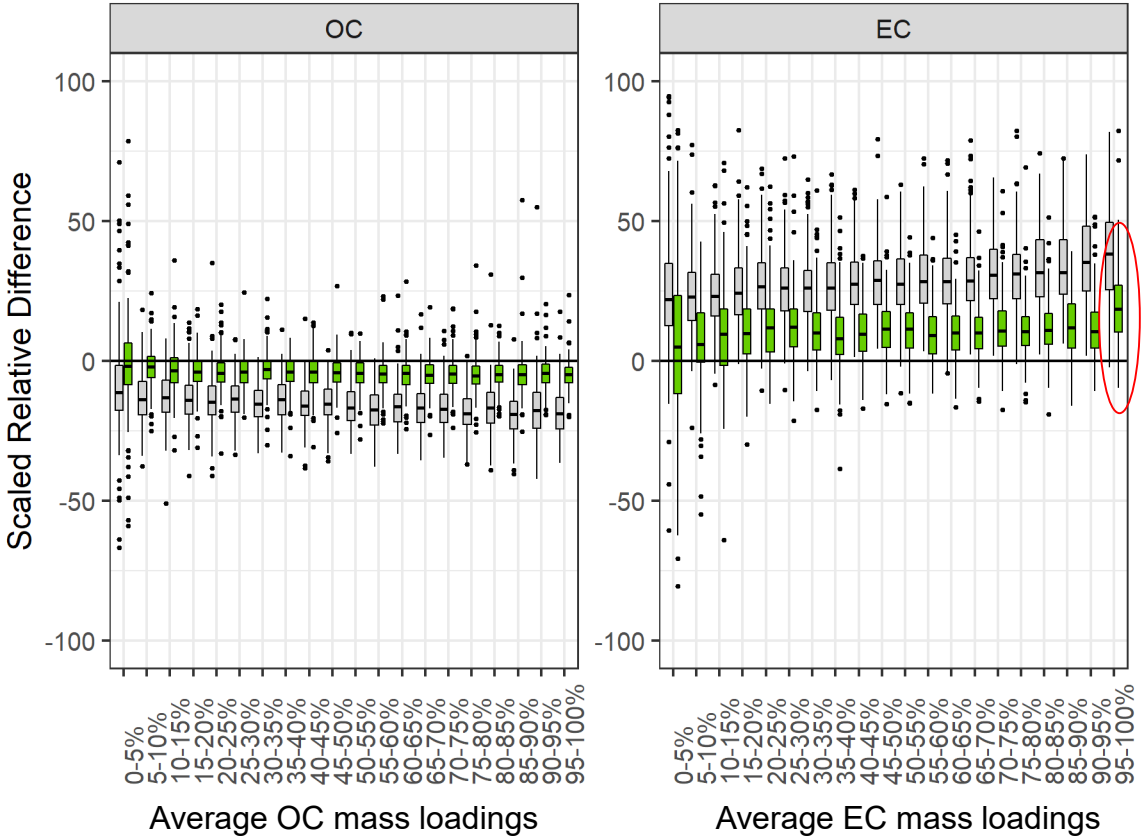
$$SRD_i = \frac{([Sunset]_i - [DRI]_i)/\sqrt{2}}{([Sunset]_i + [DRI]_i/2)} \times 100$$

Possible Reasons for Carbon Migration

- Slight difference in sample temperatures
  - DRI and Sunset analyzers use fundamentally different temperature calibration method.
- Peak integration scheme
  - UCD-Sunset: integrates all carbon signals above baseline (mean of first 10 seconds FID)
  - DRI: peak integration thresholds (differs for FID and NDIR) on top of the baseline
- Residence time
  - IMPROVE A analysis time is concentration-driven; Each step for 150-580 seconds
  - Early advance to the next temperature step may occur with a higher baseline



Optical Correction Reduced Inter-Model Biases in OC and EC



(Sunset vs. DRI 2015 data only)

w/o optical correction

OC_{sum} = OC1+OC2+OC3+OC4

EC_{sum} = EC1+EC2+EC3

w/ optical correction

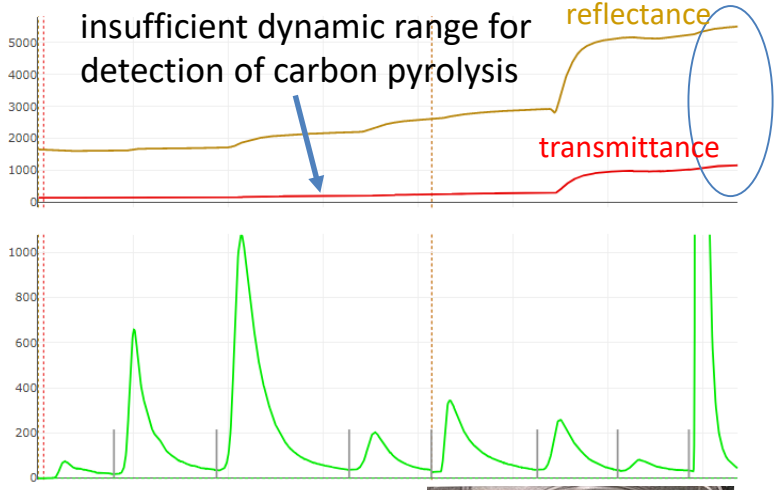
OC = OC1+OC2+OC3+OC4+OP

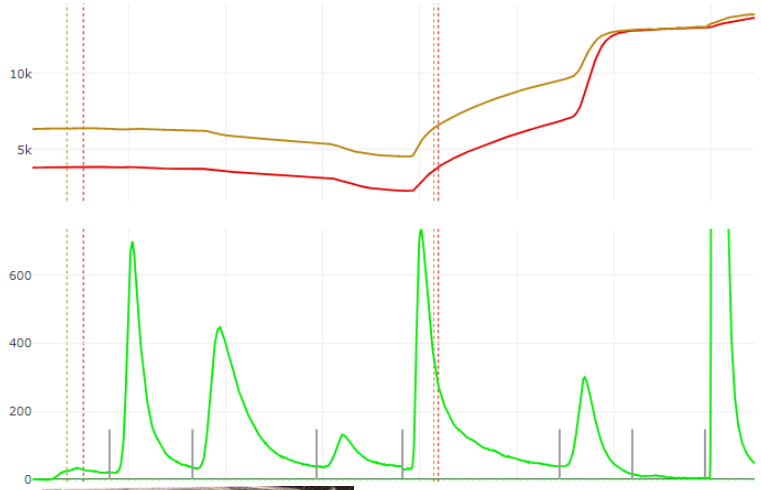
EC = EC1+EC2+EC3-OP

OC_{sum} -> OC	**-16% -> -4.1%**
EC_{sum} -> EC	**29% -> 11%**

Samples with No Optical Correction (Pyrolized OC Not Detected)

Low final reading



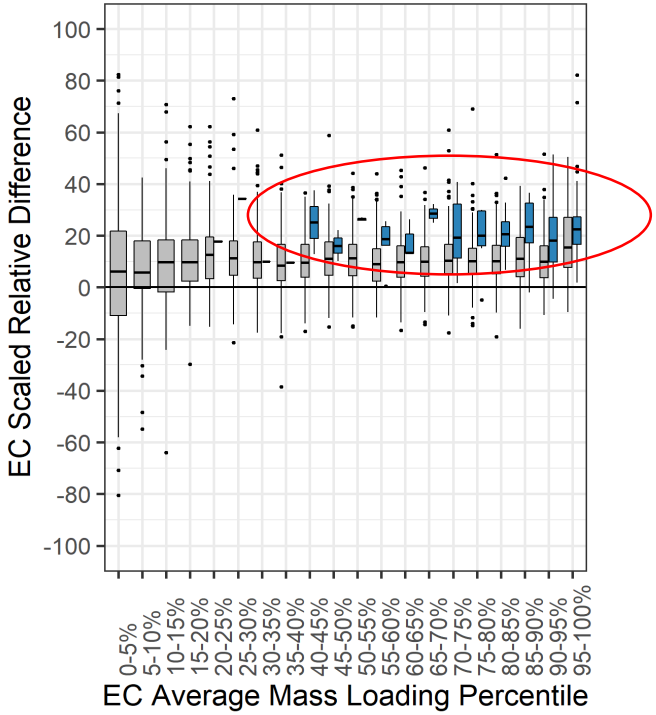


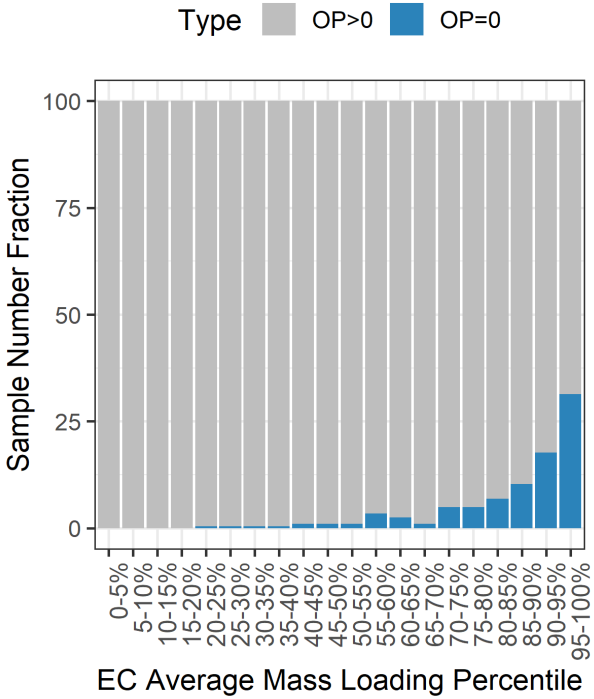
8/13/19 Children's park, AZ
OC = 16.6 µg/cm^2
OP = 0
EC = 6.7 µg/cm^2

8/13/19 Phoenix, AZ
OC = 13.8 µg/cm^2
OP = 2.9 µg/cm^2
EC = 5.6 µg/cm^2

Substantial Inter-Model Biases in EC for Samples with No OP

- Out of the 4073 CSN 2017 samples analyzed, 187 samples (4.6%) have no instrumentally detected OP by both Sunset and DRI 2015.





Conclusion

- TOA measurements are not only protocol dependent, but also instrumentation dependent.
- Good agreement for TC and major carbon fractions OC and EC between DRI and Sunset analyzers; larger and diverse inter-model differences in OC1-OC4 and EC1-EC3 sub-fractions.
- Optical charring correction reduced the inter-model biases in OC and EC relative to those of OC_{sum} and EC_{sum}.
- For extremely dark samples (~5%), inter-model discrepancy in EC was substantial due to erroneous automatic OCEC split.

Any Questions?