Potential Carbonaceous Aerosol Measurements in IMPROVE

Outline

- Requirements for carbonaceous measurements in long-term routine monitoring programs
- Pros and Cons of
  - Thermal optical reflectance (TOR) – Current method for measuring organic carbon (OC) and light absorbing carbon (LAC)
  - Fourier transform infrared spectroscopy (FTIR) – TOR Hybrid Approach to estimate TOR OC and LAC
  - Total carbon and filter absorption (fabs) to estimate OC and LAC
- Contrast alternative methods

*Note, LAC is what is in the atmosphere. Many refer to filter based measurements of LAC as elemental carbon or EC. Both terms are used.

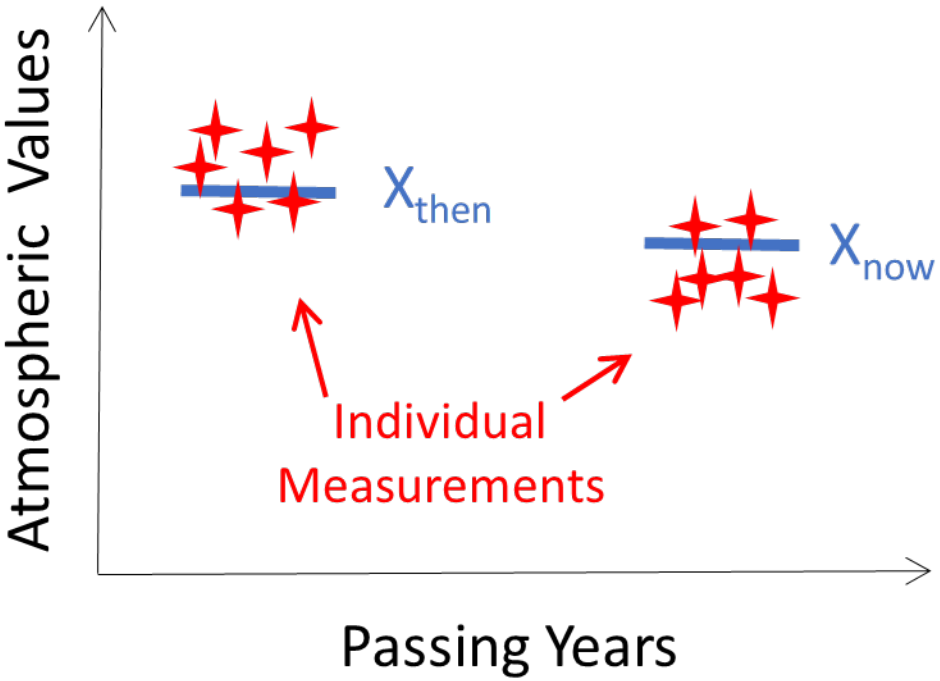
Ideal Requirements for Measuring Particulate Carbon in Long-Term Monitoring Programs

- Applicability to meet network goals
  - Relatable to ambient PM species or properties that meet the network goals
  - Measure low concentrations found in remote environments as well as high concentrations in found in urban centers and biomass burning plumes
- Stability, reproducibility and precision (track long term trends)
  - Ability to calibrate OC and LAC fractions to ensure a consistent and accurate concentration
  - Variables measured should not be sensitive to analytic protocol or instrument type
- Network implementation
  - Cost effective
  - Suitable for use in remote environments.

*Comparable with existing TOR OC and LAC data

Comparability in Organic and Light Absorbing Carbon Measurements

- Carbonaceous aerosols are a complex mixture of compounds with varying physical/chemical/optical properties
- Organic mass and LAC are ill-defined categories of these compounds
- TOR- OC and LAC are surrogates for these classes of carbonaceous aerosols and their relationship to ambient concentrations will change as the carbonaceous aerosol changes with time.
- Measurements such as absorption can be related to TOR-LAC today, but as the composition of PM and physical/chemical/optical properties of carbonaceous aerosols change that relationship would also change.
- More important than long-term comparability is that the measurement are stable and trends are reflective of changes in concentrations and/or properties of the aerosols and not analytical artifacts.



$$\underbrace{x}_{\text{measured value}} = (\underbrace{X}_{\text{atmospheric value}} + \underbrace{\epsilon}_{\textbf{random}\text{ error (noise)}}) \times \overbrace{f_{\substack{cal\\era}}}^{\text{calibration bias, with potential for drift}} \times \overbrace{g\left(\frac{V_{air}}{A_{dep}}X\right)}^{\text{nonlinear response ('loading effect')}} \times \overbrace{S}^{\text{Surrogate factor}}$$

$$\left\{\begin{array}{l} E(\epsilon) = 0 \\ \sqrt{var}(\epsilon) = \sigma_X \end{array}\right.$$

(Expectation & Variance)

What we want: ${X_{now}}/{X_{then}}$. What monitoring can give: ${E(x_{now})}/{E(x_{then})}$.

The problem:

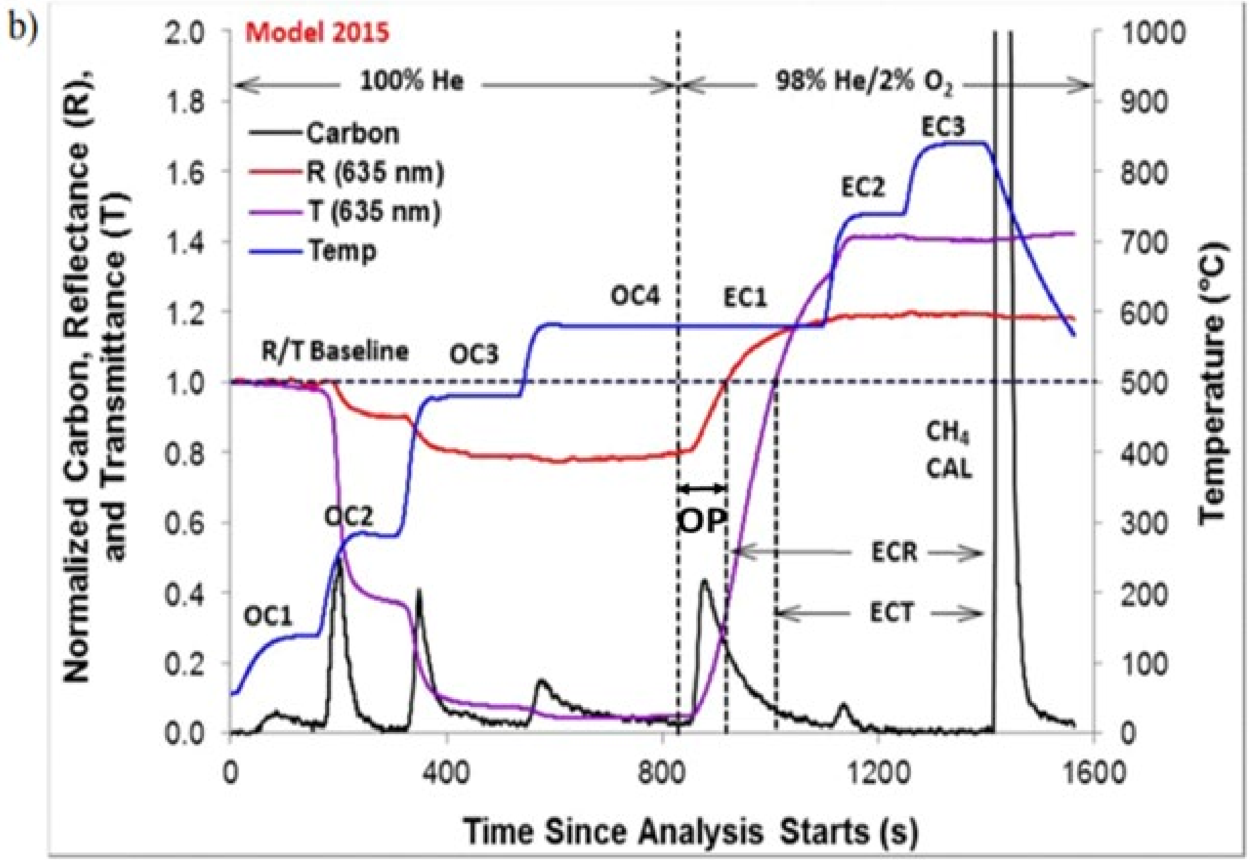
$$X_{now}/X_{then} = E(x_{now})/E(x_{then}) \times f_{then}/f_{now} \times g\left(\frac{V}{A}X_{then}\right)\Big/g\left(\frac{V}{A}X_{now}\right) \times S_{then}/S_{now}$$

Network Goals

- **IMPROVE** primarily supports the Regional Haze Rule
  - Track trends in RHR haze metric
    - Estimate ambient organic mass light scattering
    - Estimate ambient LAC light absorption
- **CSN** primarily supports the fine PM health NAAQS
  - Fine PM composition and trends
    - Estimate ambient organic mass
    - Estimate Ambient LAC

- IMPROVE and CSN
  - Understand the composition of fine PM (reconstruct fine PM)
    - Estimate ambient organic mass (OM)
    - Estimate ambient LAC
  - Spatial and temporal patterns in ambient OM and LAC and relate to changes in precursor emissions and atmospheric processing
    - Focus on long term trends
  - Assess the origin of organic and light absorbing carbon

Thermal Optical Analysis (TOA)



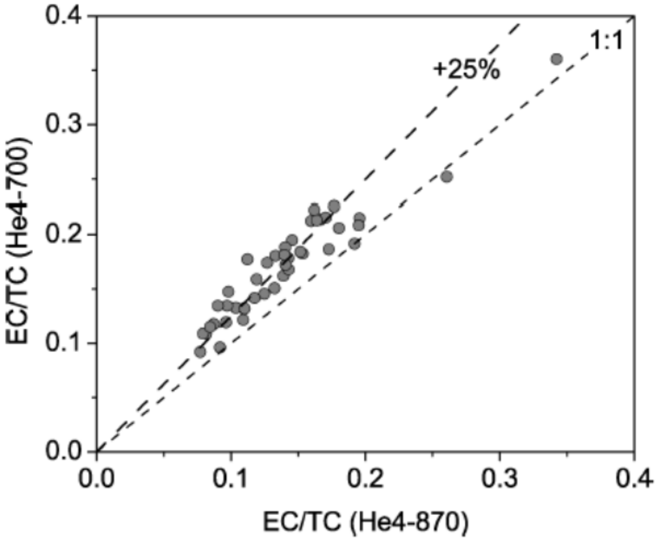
- OP and thus OC/LAC split is ill-defined and can’t be calibrated so we assume
  - All non absorbing-pyrolized OC volatilizes prior LAC (no OC slip)
  - All OP volatilizes prior to LAC **or** OP and LAC have the same mass absorption efficiency (MAE)
  - Aerosol optical properties remain constant during heating
  - The laser signal accounts for all changes in sample absorption

- The OC/LAC split depends on pyrolized carbon (OP)
- OP is not a chemical constituent, but a product of the optical correction and depends on the correction method (R vs T) and optical properties of the sample.

OC/LAC Dependence on TOA Temperature and Optical Protocols

Subramanian et al., 2006

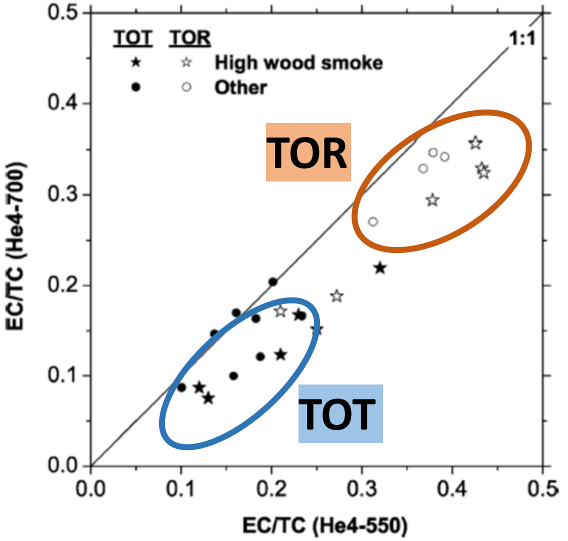
Low temperature



High temperature

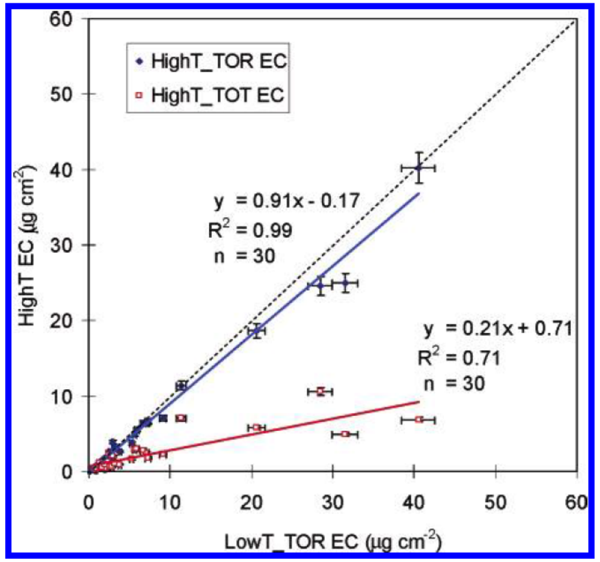
- Low temperatures results in higher LAC

High temperature



Low temperature

- TOR LAC is generally higher than TOT LAC



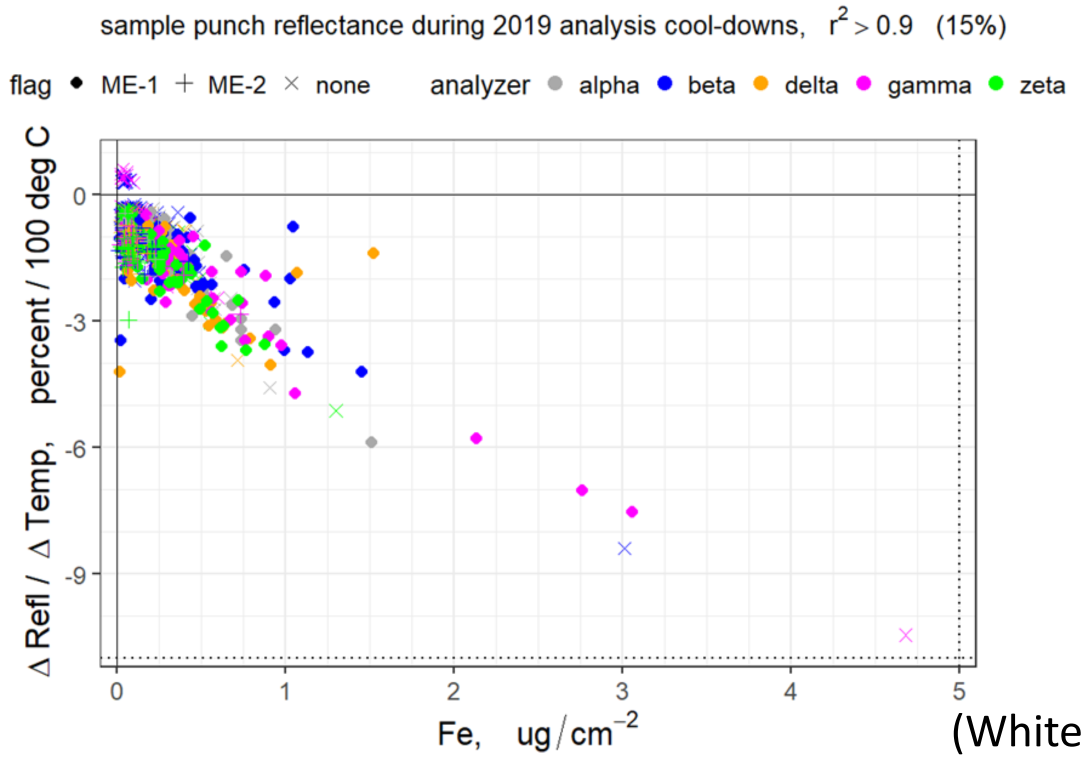
- Chow et al,. 2004, found TOR-LAC was independent of temp, but TOT was not

Limitations and Issues with TOA

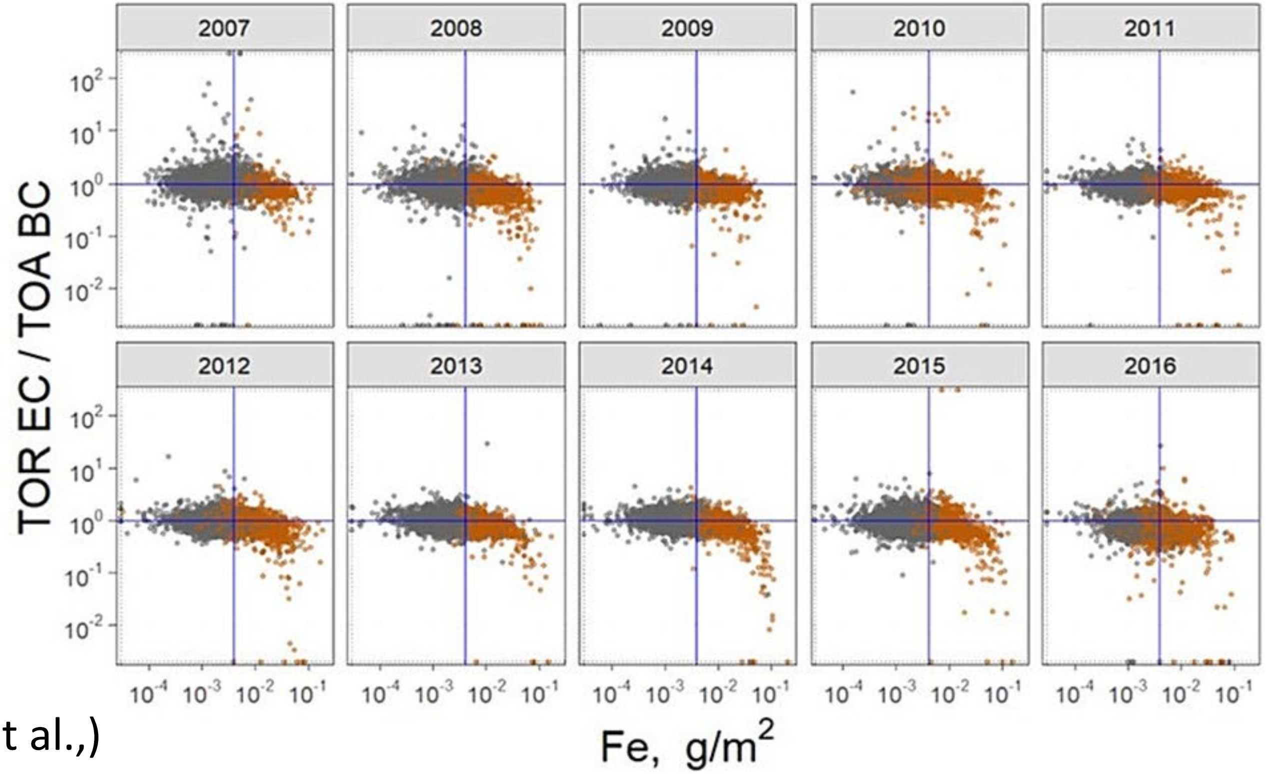
- Calibration
  - TOA instruments can’t be fundamentally calibrated for OC and LAC
    - No objective definition to distinguish between the two components exists (e.g. Baumgardner et al., 2012)
    - OC/LAC split is operationally defined and varies by method
    - Can’t directly monitor for analytical drift in OC/LAC split

  - Analyzers can be calibrated for Total carbon (TC)
    - TC is generally reproducible across analyzers, instrument types, laboratories (e.g. Schmidt et al., 2001; Chow et al., 2004)

Dependence of OC/LAC split on PM Composition



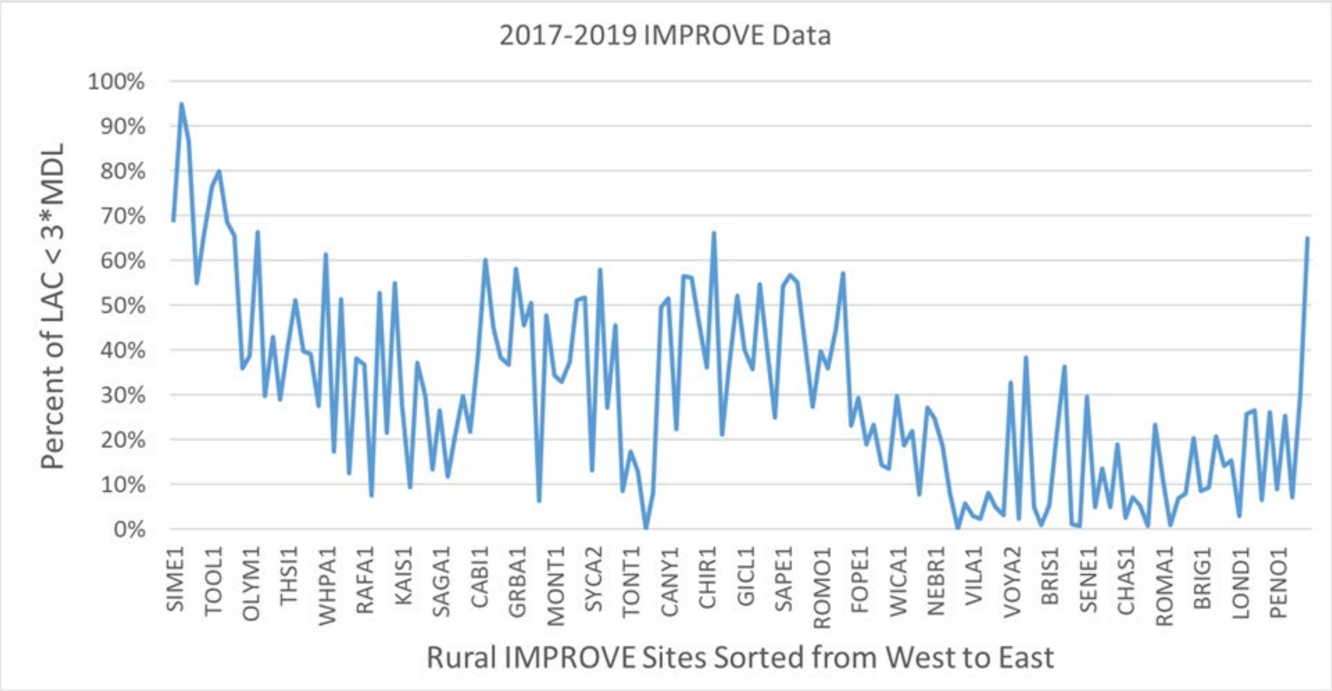
(White et al.,)

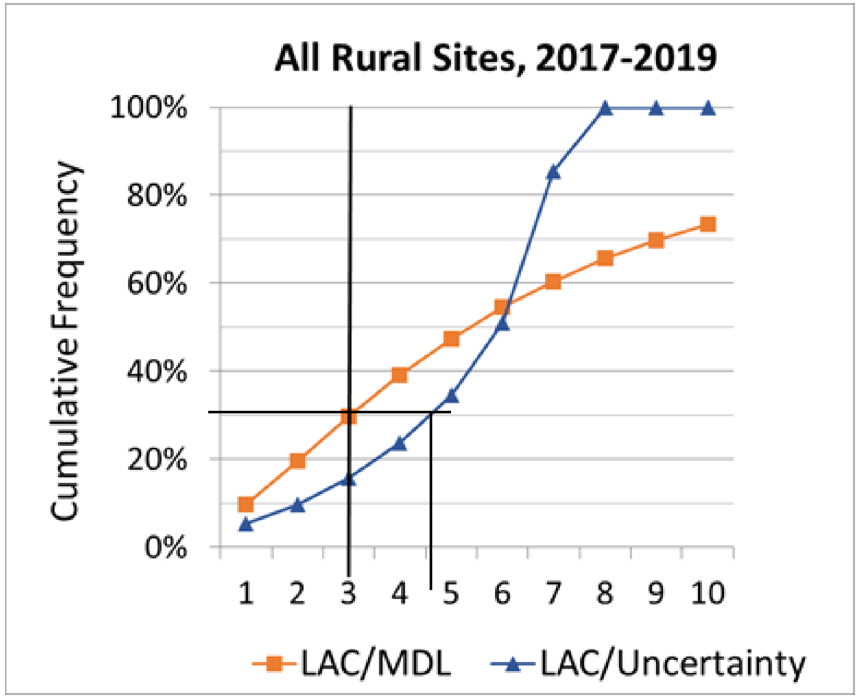


- Some iron oxides get darker when heated
- TOR increases OP and decreases LAC to compensate for the increased reflectance

- LAC is underestimated at high Fe.
  - As iron concentrations increase the LAC to black carbon ratio decreases
  - BC derived from TOA transmittance an uninfluenced by soil absorption

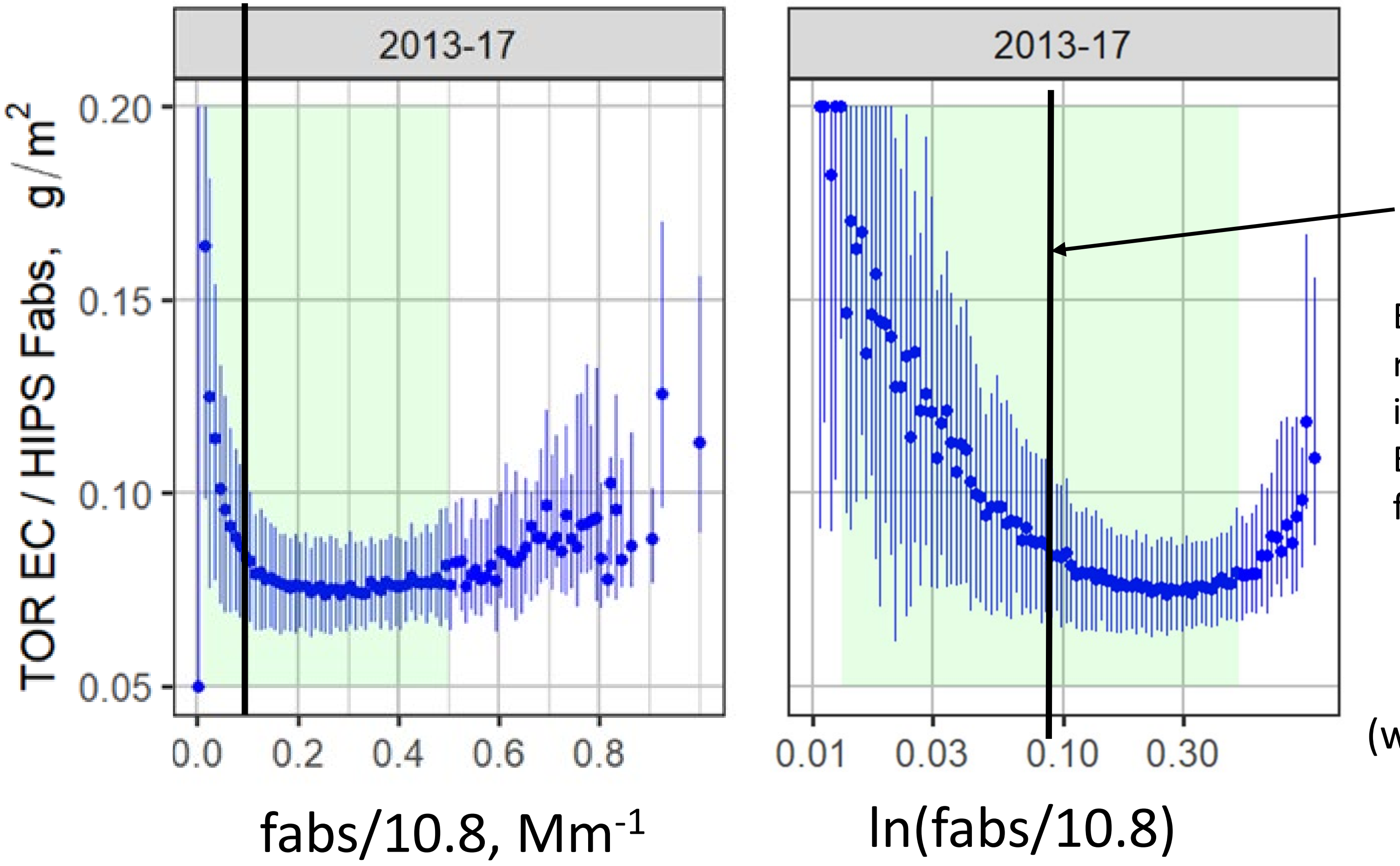
LAC Signal to Noise Ratio





- In Alaska and Hawaii more than 80% of the data are below the LQL and in the west 20% of sites have 50% of values below the LQL.
- 30% of all data were below the LQL, but most have values > 2*uncertainty.

*lower quantifiable limit (LQL) = 3*MDL where the MDL is derived from field blanks.



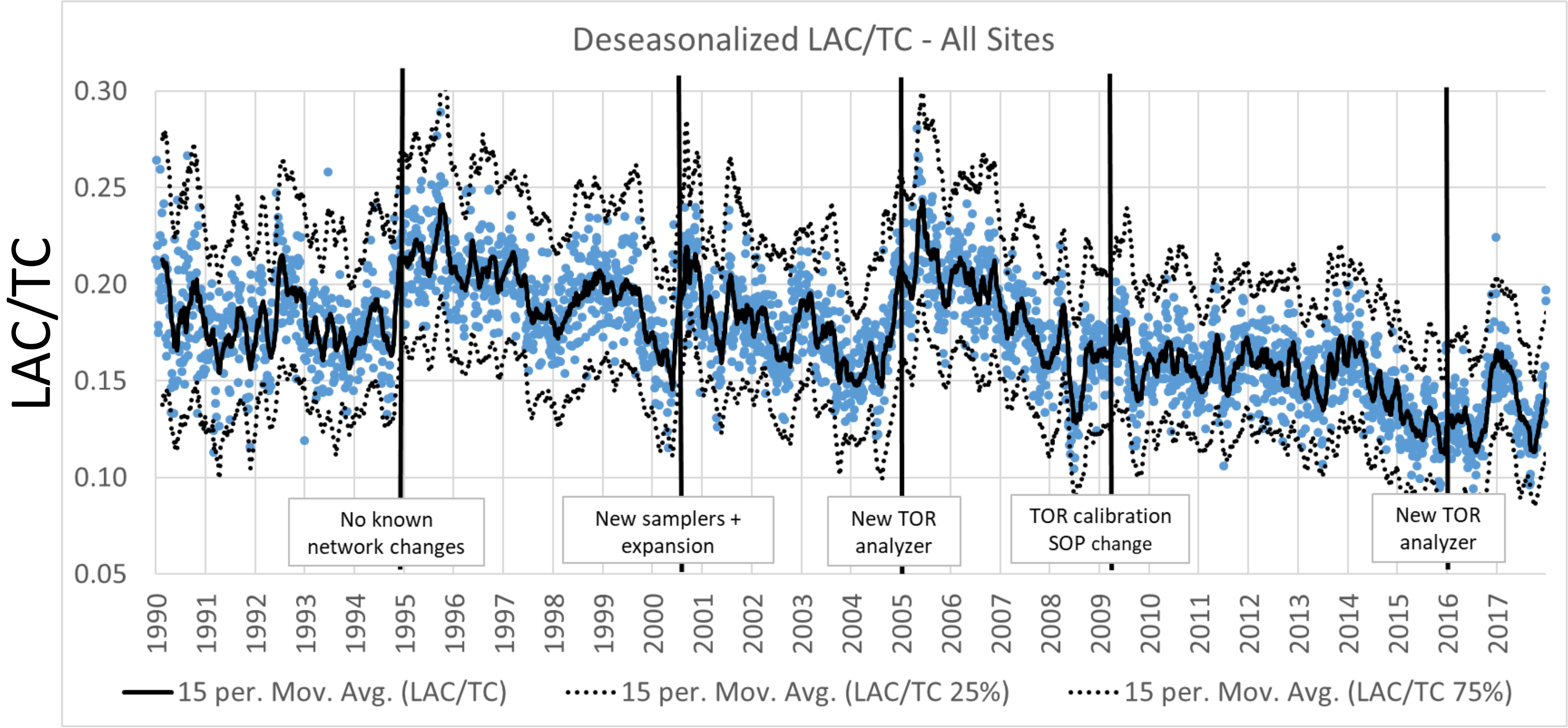
~LQL = 3* MDL

Each point and vertical bar represent the median and inter-quartile range of all EC/Fabs ratios within ~0.001 fabs.

(white 2020);

- As fabs goes to 0 so should LAC and the LAC/fabs should be relatively constant
- Low concentrations of LAC appears to be biased high (OC slip into LAC fraction)
  - fabs is calibrated to 0 and should be unbiased
- The increase in LAC/fabs at high fabs is at least partly due to HIPS filter loading artifact

Do these issues impact trends?



- There are discontinuities and interesting trends in LAC fractions some of which are coincident with network/analyzer changes and trends in TOR-Reflectance (Hand)

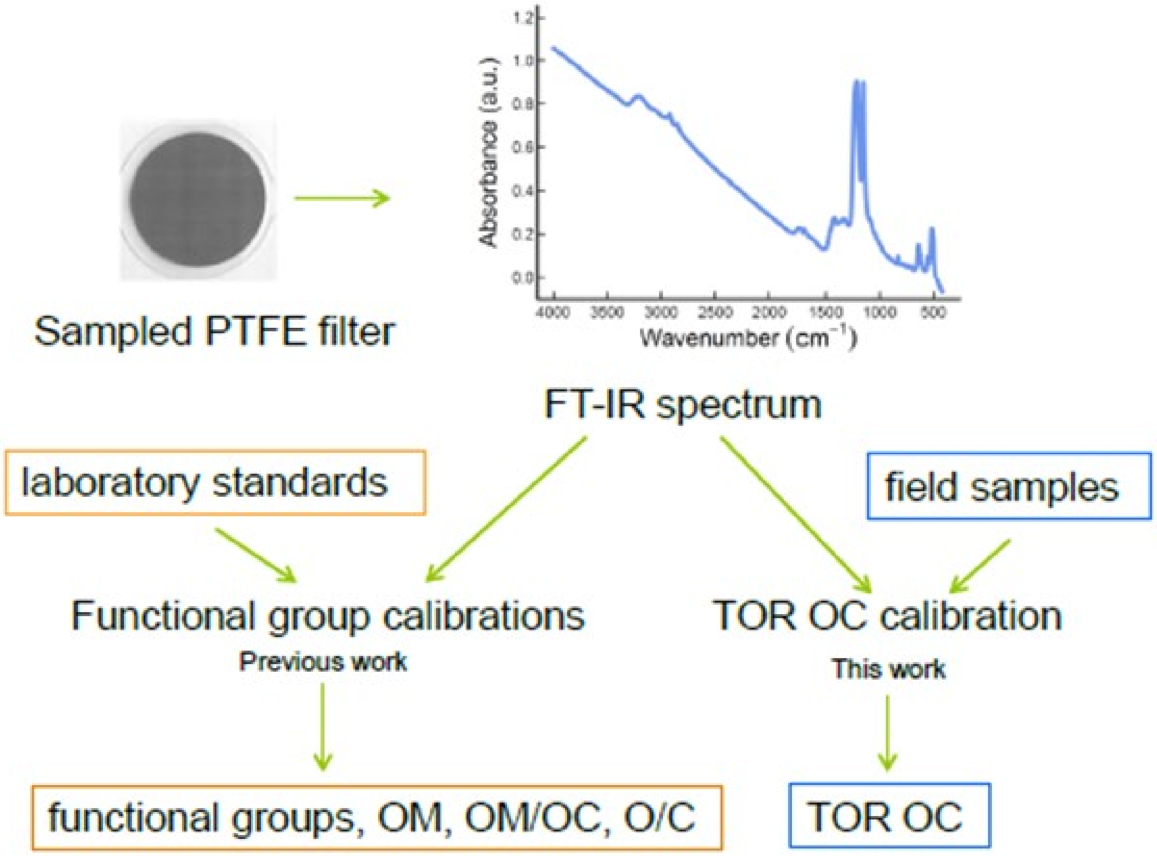
Pros

- TOR has successfully been implemented in IMPROVE for >30 yrs
  - Used in spatial and temporal trends
  - Source apportionment
  - Atmospheric chemistry assessments
  - Epidemiological assessments
- TOA analyses used in CSN and international PM networks
- LAC is highly correlated with ambient absorption
- TC and likely OC are unbiased in most samples

Cons

- TOR instrument is not fundamentally calibrated for OC and LAC
  - evidence of instrument drift in LAC
  - OC-LAC influenced by PM composition
- OC-LAC split
  - operationally defined
  - instrument dependent
- poor signal to noise
  - low concentrations are potentially biased high
- TOR is a relatively expensive analysis

FTIR: Fourier transform infrared spectroscopy



- Calibrate to standards
  - Standards are not representative of complex atmospheric aerosols
  - Provides estimates of organic mass (OM) and OM/OC ratio
  - Generally underestimates OM by up to 30%
- Empirically calibrate to TOR OC and LAC
  - Does not require standards
  - Maintain ~20% of TOR network
  - Multiple calibration models needed, e.g. smoke, non-smoke, urban

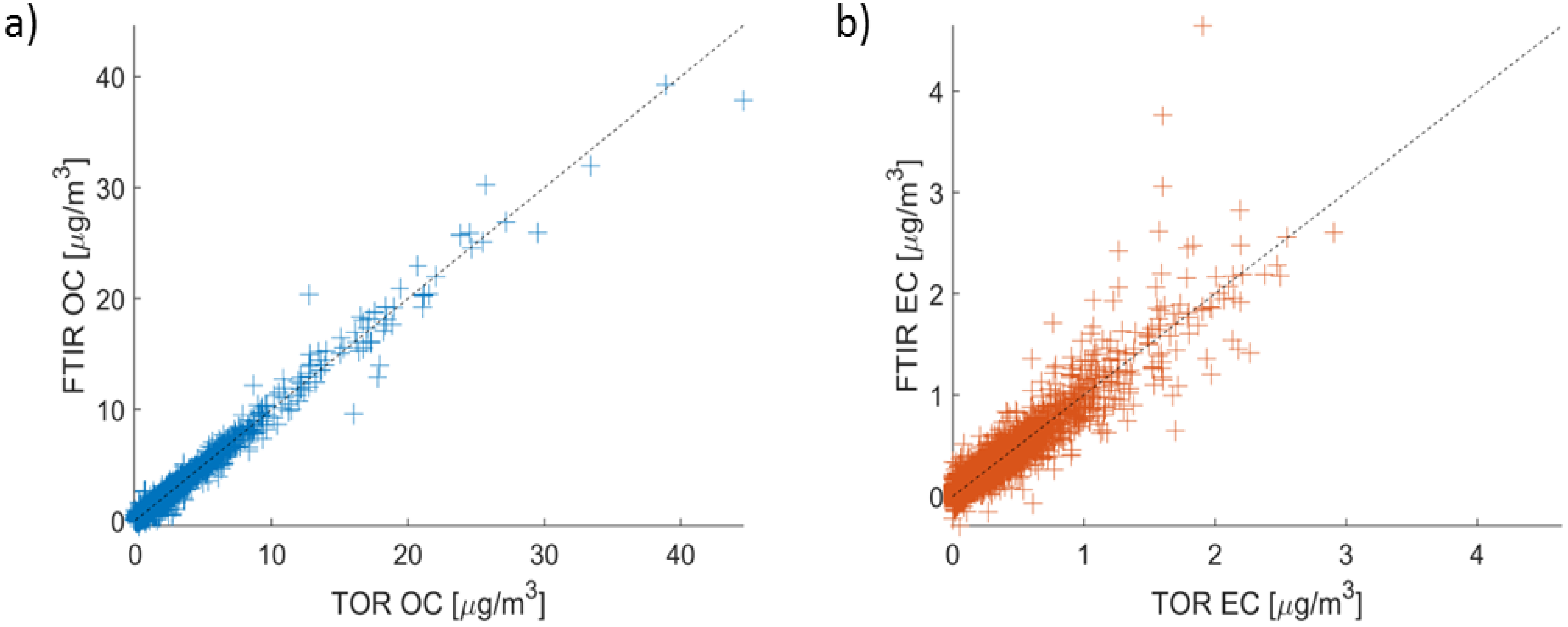
Data Driven Calibration

- Develop calibration models using TOR data measured at ~20% of network sites with errors on the order of those measured by TOR. The method is based the model:

$$m_{c,i} = \sum_j b_j A_{i,j} + e_i$$

  - $m_{c,i}$ are the TOR OC or LAC data for sample i; $A_{i,j}$ is the absorbance for sample i at wavelength j
  - b_j is the calibration coefficient for wavelength j; e_i - error
- PLS regression is used to invert equation for bj which are applied to FTIR spectra to estimate OC and LAC
- Calibration dataset needs to span the concentrations and composition found in the network
  - Multiple calibration models are needed, since smoke and near roadway impacted samples have high error with the general calibration model

FTIR vs TOR OC and LAC



- FTIR OC and LAC (EC) predicted concentrations achieved using the Global calibration model.
- Predicted concentrations from both calibration and test samples from 2015 (n = 19,609) (Debus et al., 2020)

	R^2	Bias [µg/m³]	Bias [%]	Error [µg/m³]	Error [%]	MDL [µg/m³]	< MDL [%]	Precision [µg/m³]
OC	0.979	0.01	1.7	0.08	12.5	0.06	0.4	0.08[a]
LAC	0.882	0.00	3.8	0.02	27.1	0.03	12.9	0.02[a]

Pros

- FTIR OC-LAC Shown to be equivalent to TOR OC and LAC
  - Generally within TOR data errors
- Maintains the TOR OC and LAC data record into the future
- Requires continued TOR monitoring at a subset of sites (both a benefit and drawback)
- Potentially useful information on organic mass, composition, origin and aging.
- More cost effective than TOR

Cons

- Not fundamentally calibrated
  - There is no single calibration model and need separate models for smoke and non smoke and potentially near roadway impacted samples
  - Complicates the addition of new sites with unique carbonaceous aerosols
  - Low LAC concentrations are biased high which exacerbates the TOR bias
- Calibrated to TOR OC and LAC data, thus, has all of the same disadvantages of the operationally defined TOR data

Derive OC and LAC from TC and Filter Absorption (fabs)

- TC measured using a thermal method (calibratable stable, and protocol independent)
  - Simple temperature ramp in an oxidative atmosphere
- Filter absorption (fabs) measured using IMPROVE hybrid integrating plate and sphere (HIPS) method

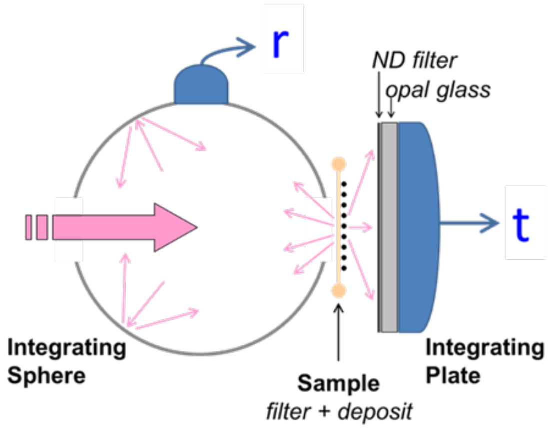
$LAC_{op} = (f_{abs} – Fe * \alpha_{Fe}) / \alpha_{fBC'}$

$OC_{TC} = TC – LAC_{op}$

If measured TC = TOR (OC + LAC), comparibilty is dependent on $LAC_{op} = LAC_{TOR}$

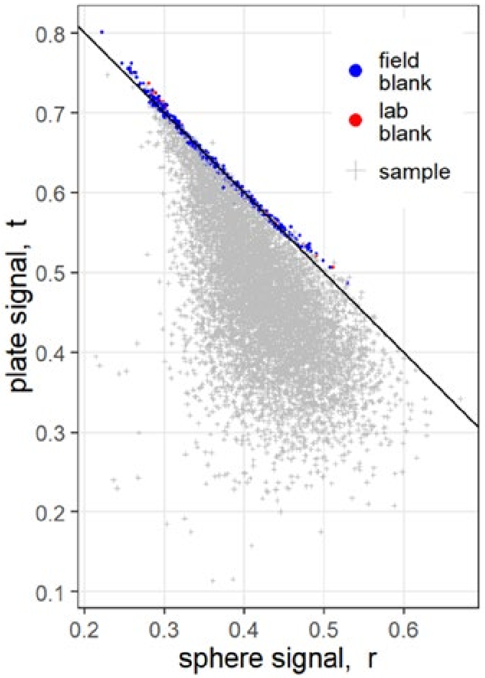
- $\alpha_{fBC'}$, α_{Fe} - Calibration or best fit coefficients related to mass absorption efficiency (MAE) and measurement artifacts
- LAC_{op} can be made to be comparable to TOR-LAC in the recent past, but cannot account for future changes in the true LAC and ambient absorption relationship

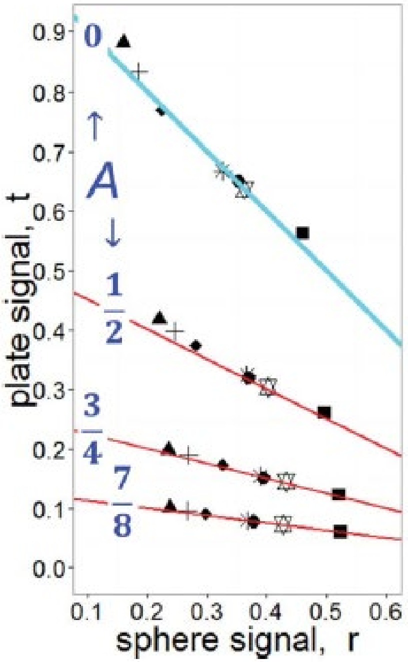
Hybrid Integrating Plate and Sphere (HIPS) to Measure Filter Absorption (fabs)



Illumination: He-Ne laser at 633 nm

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



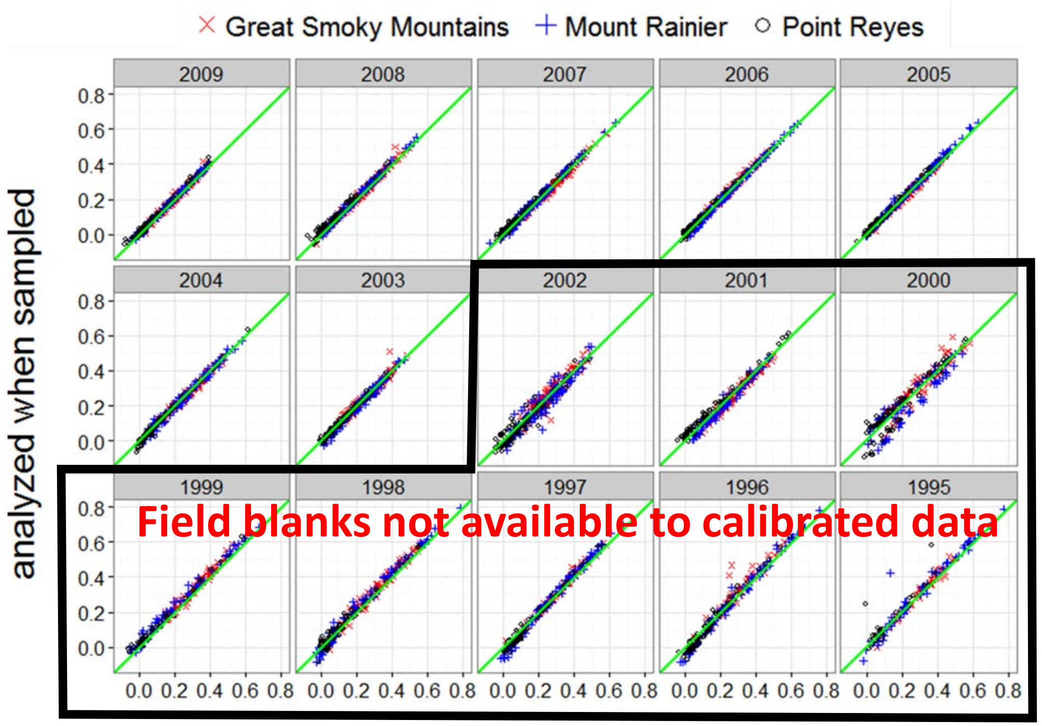


- Filter blanks with layers of absorbing gel overlaid.
- Linear response with increasing absorbance
- Doesn't account for all filter effects

f/v is deposit area / volume of air sampled ~ 93 km sample length

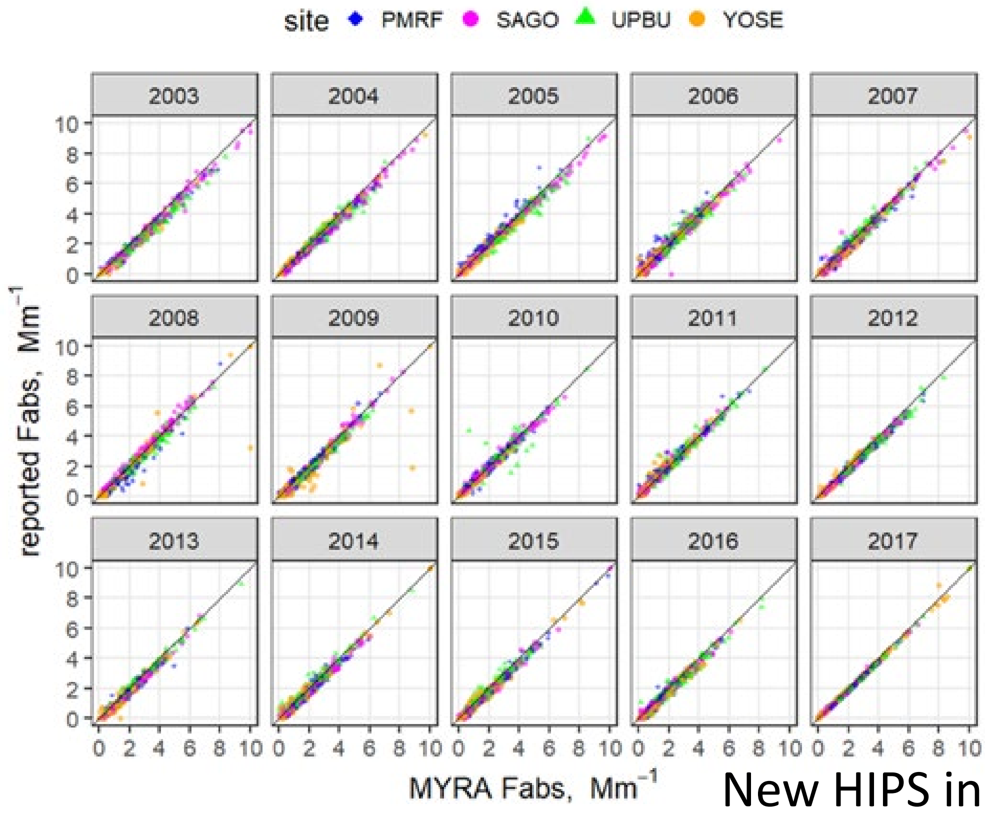
- fabs has been measured in IMPROVE since 1994, properly calibrated since 2003
- White et al., calibrated the system to “zero” using field blanks, but not to standards
- fabs should be more closely related to ambient absorption than LAC, on going study in Reno

HIPS Long Term Reproducibility



Field blanks not available to calibrated data

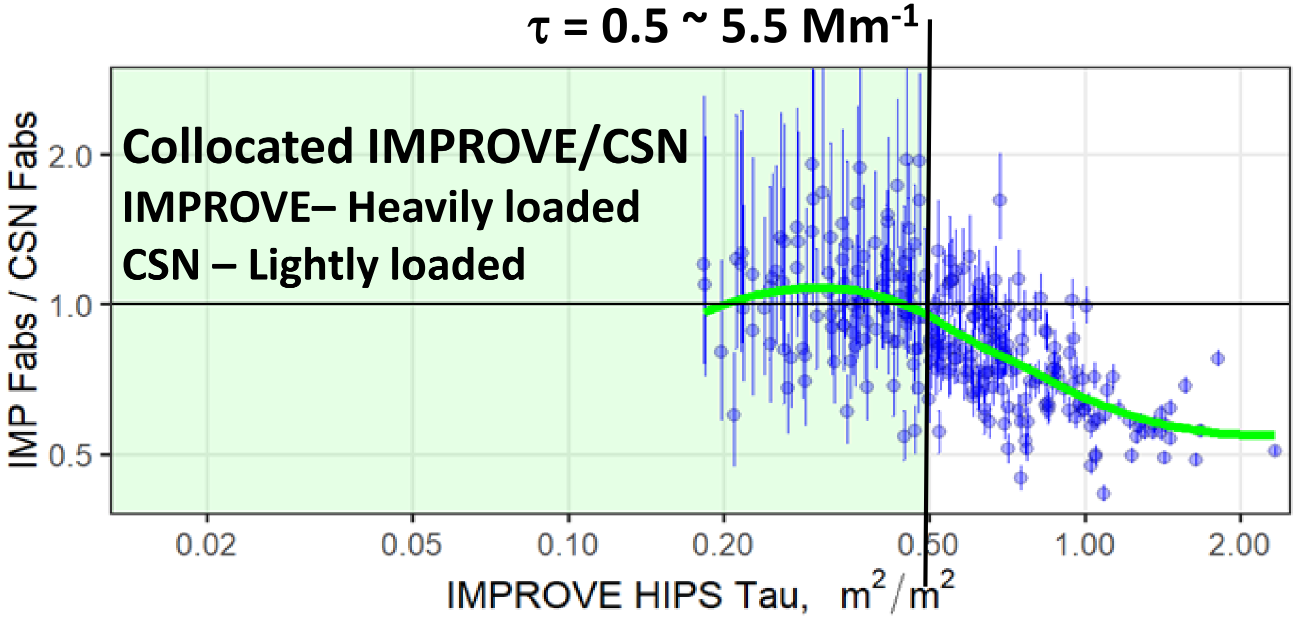
Original HIPS



New HIPS instrument

- HIPS is reproducible over a 15 year time span and independent of the instrument used
- No instrument drift - No long term trends in (original – reanalysis) differences
- Good precision – Sample absorbing properties remained consistent over 15 years
- Fabs from new system is systematically 5% lower than from the old

HIPS Issues: Filter Loading Artifacts



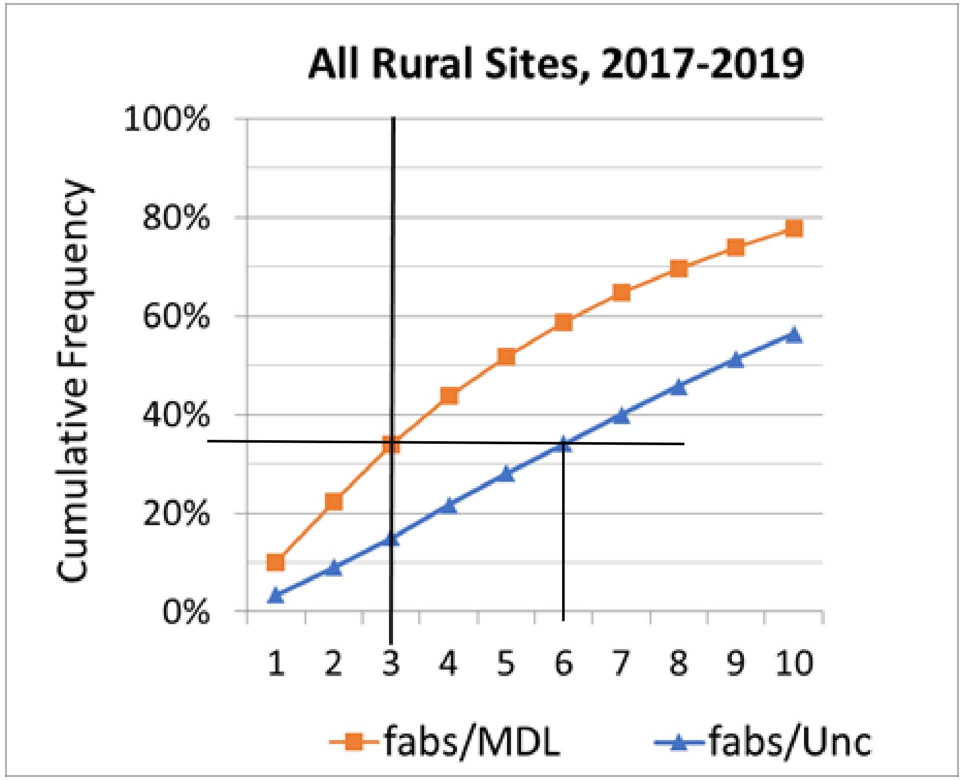
$\sim$Fabs/10.8 Mm^{-1}

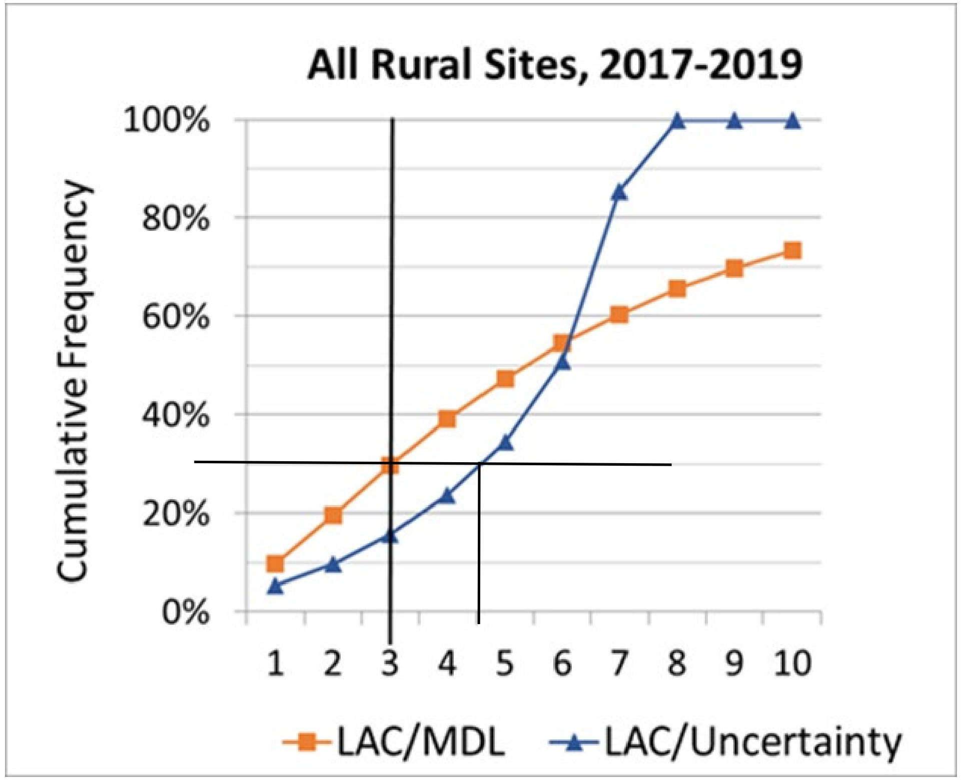
Nonurban IMPROVE data

Period	Samples	Tau ≤ 1/2	Tau ≤ 1/3
2003 – 2017	193,070	94.5%	82.7%
2003 – 2007	58,531	92.2%	77.1%
2008 – 2012	68,438	94.6%	82.7%
2013 – 2017	66,101	96.5%	87.7%

- IMPROVE filter loading is ~order of magnitude higher than CSN
- fabs < 5.5 Mm^{-1}, IMP/CSN fabs ~ 1, fabs < 5.5 Mm-1
- fabs > 5.5 Mm^{-1}, IMP/CSN fabs < 1, and IMPROVE fabs is ~30% low at fabs ~ 11 Mm^{-1}
- About 5% of fabs values at non urban sites have fabs > 5.5 Mm^{-1}

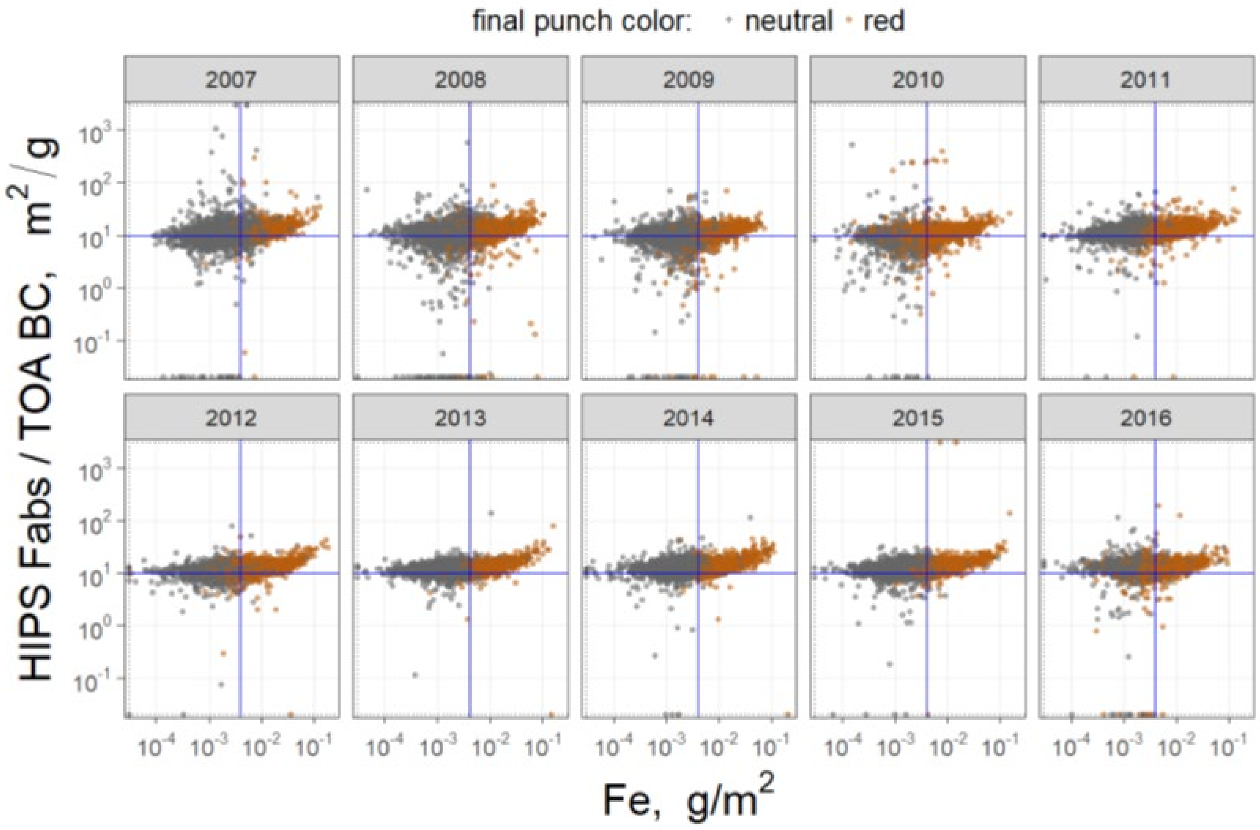
Issues: Signal to Noise





- Similar fraction of fabs values below the LQL as LAC, but uncertainty is lower and low values are unbiased

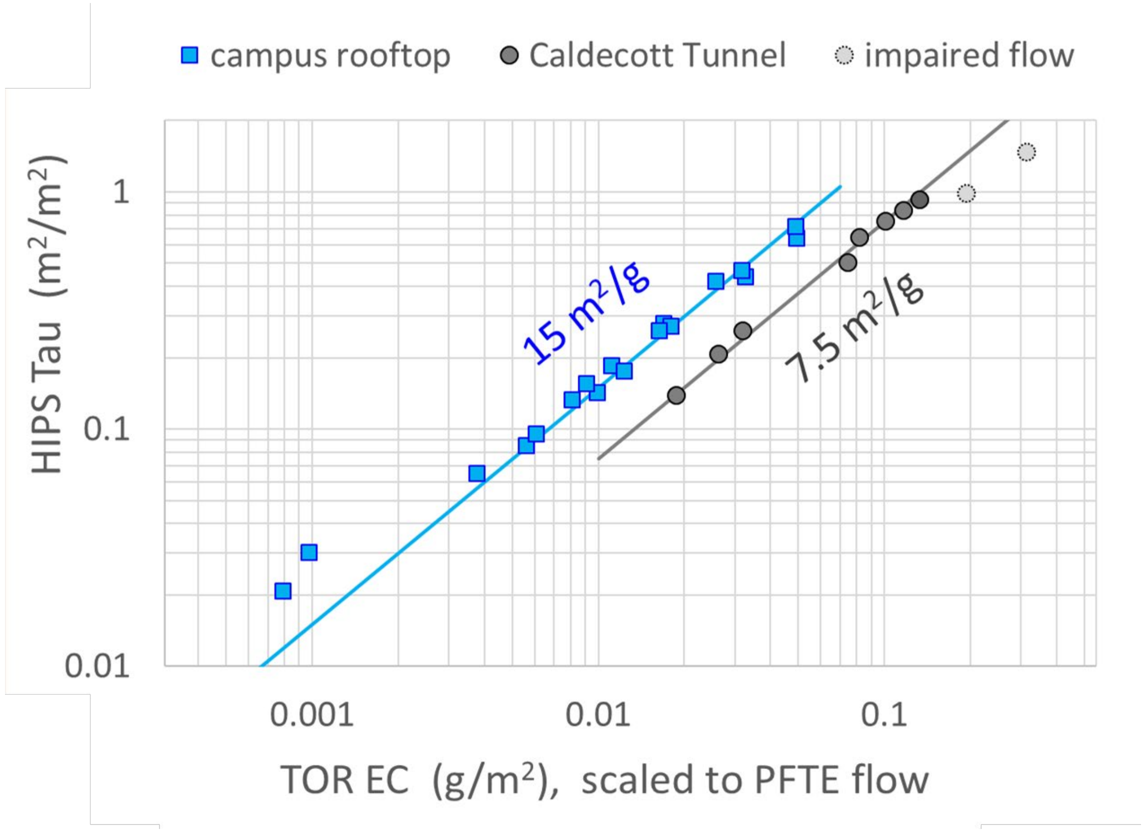
Issues – Absorption by Soil



- TOA BC is derived from the IMPROVE TOA laser transmittance data and is not influenced by soil absorption
- As Fe concentrations increase and filters take on an orange/red color the fabs/BC ratio increases. Indicative of absorption by soil
- Lab estimated soil Fe MAE at 633 nm is ~ 1 m^2/g compared to 10-15 m^2/g for LAC

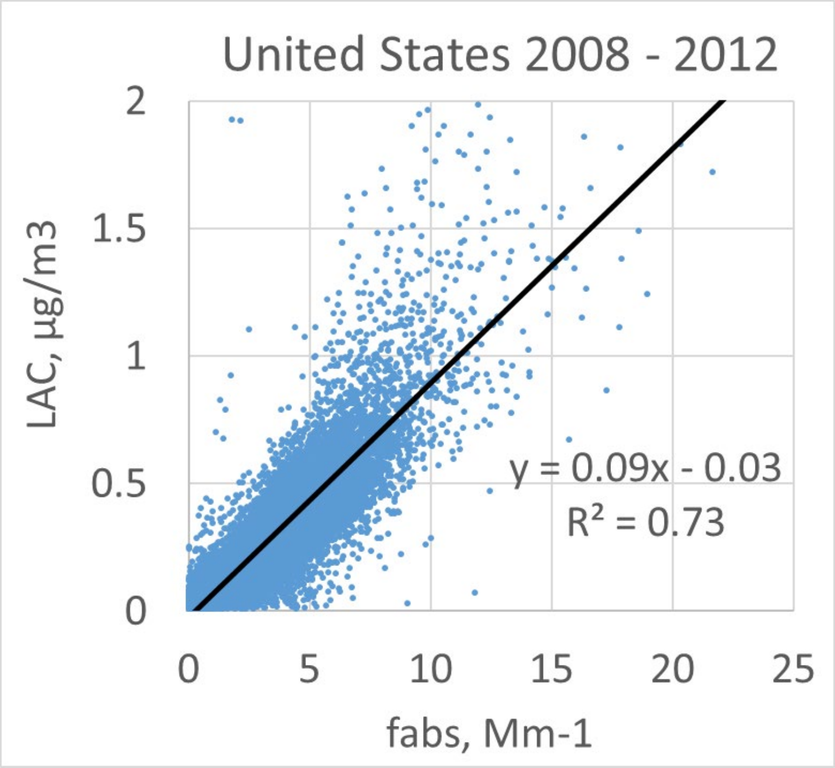
- Contributions from soil complicate estimating LAC from fabs data.
- Soil's different absorption angstrom coefficient from BC complicates estimating absorption at different wavelengths.

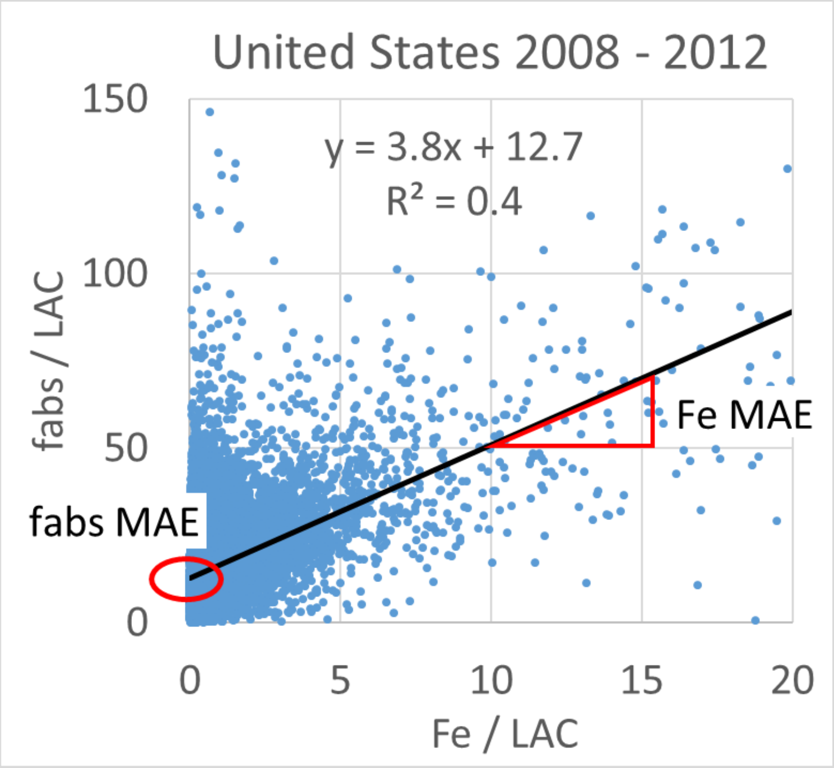
Issues: Variable PM Mass Absorption Efficiency



- Aerosols have different absorption efficiencies depending on source and age
- Fresh mobile sources have an MAE of 7.5 m^2/g compared to 15 m^2/g for mixed and aged aerosol measured on UCDavis rooftop
- Brown carbon from biomass burning and secondary organic reactions have lower MAEs than black carbon
- We can’t account for the variable PM MAEs and any fabs to LAC conversion will be for a typical aerosol. This could introduce differences in fabs and LAC long term trends

Relating fabs to LAC (Recall Bill's presentation)

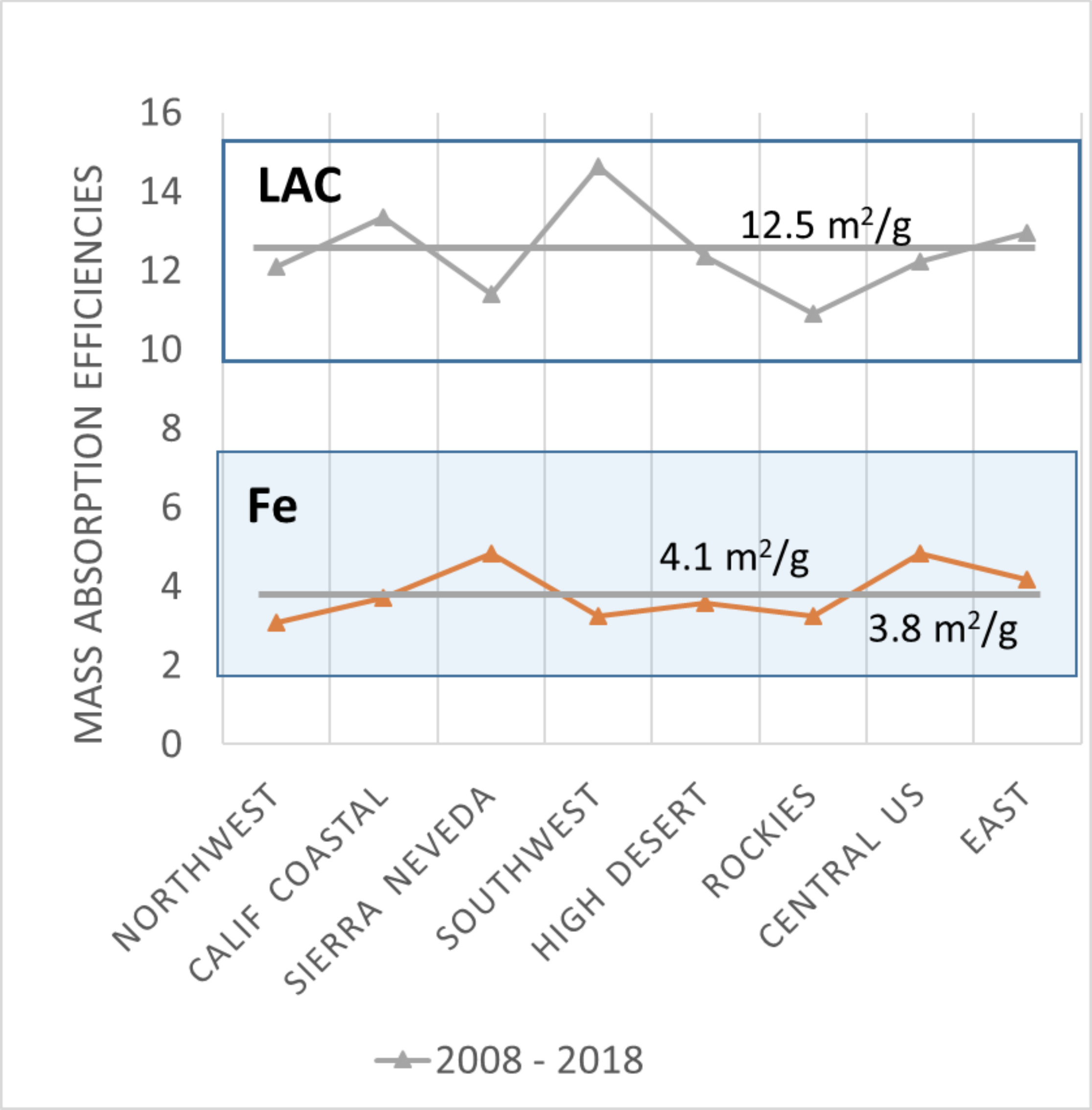




- fabs is highly correlated with LAC. It is also correlated with iron (Fe).
- Iron oxides found in soils can absorb at λ=633 nm.
- Iron oxides can also impact TOR-LAC causing premature volatilization of LAC and changing color during heating.

$$LAC_{fabs} = \frac{(fabs\ - Fe * MAE_{Fe})}{MAE_{LAC}};\ \mathrm{OC} = \mathrm{TC}\ - LAC_{fabs}$$

Mass Absorption Efficiency (MAE)

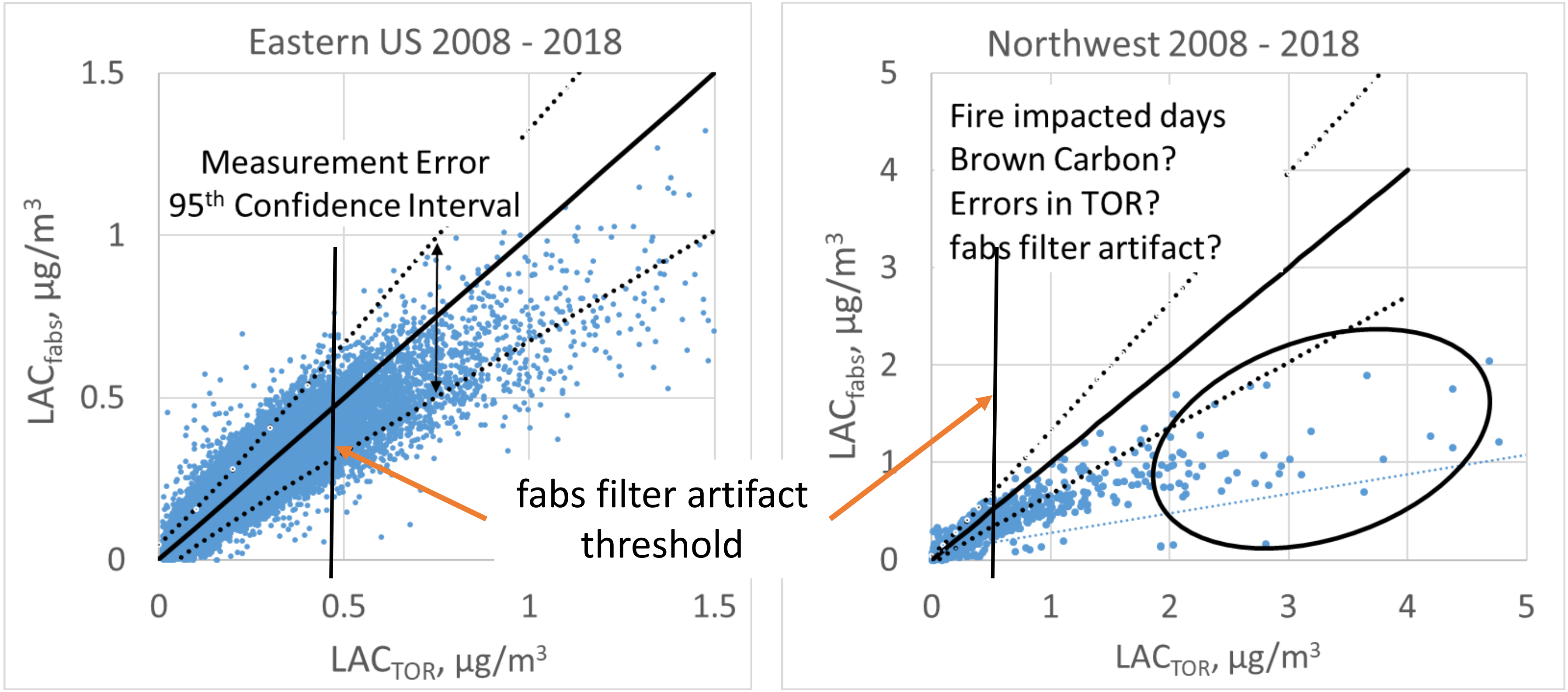


- LAC and Fe MAE's have little spatial variability
- LAC MAE's change across the carbon epochs (Fe MAE less so)
- Little seasonality in LAC and Fe mass absorption efficiencies (not shown)

Linear Regression used to estimate MAE's

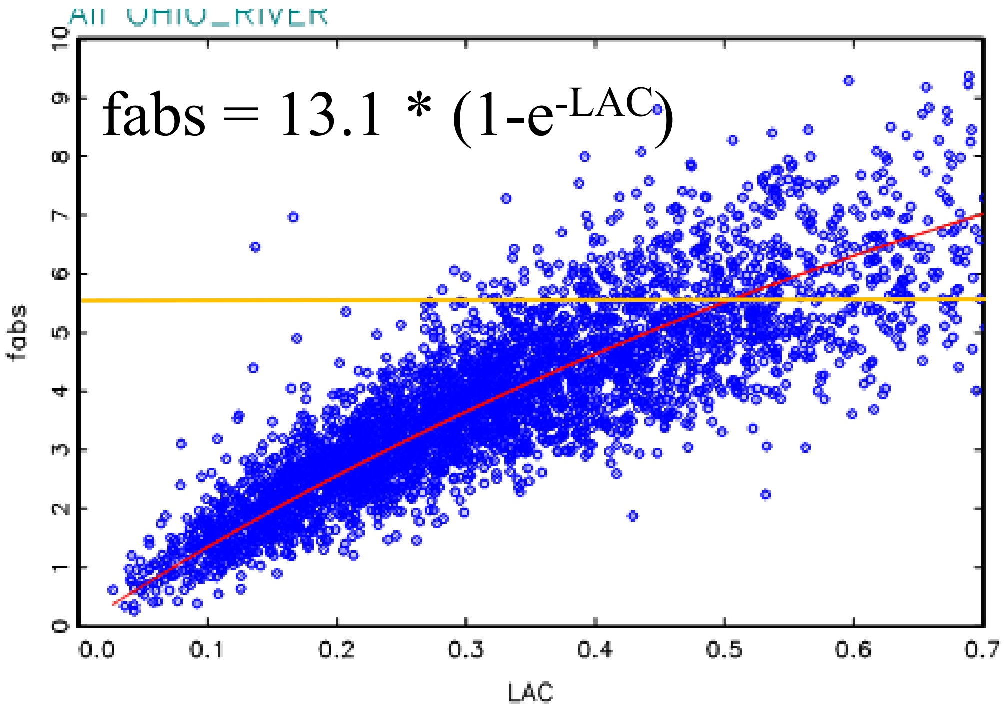
$$LAC_{fabs} = \frac{(fabs\ - Fe * MAE_{Fe})}{MAE_{LAC}}$$

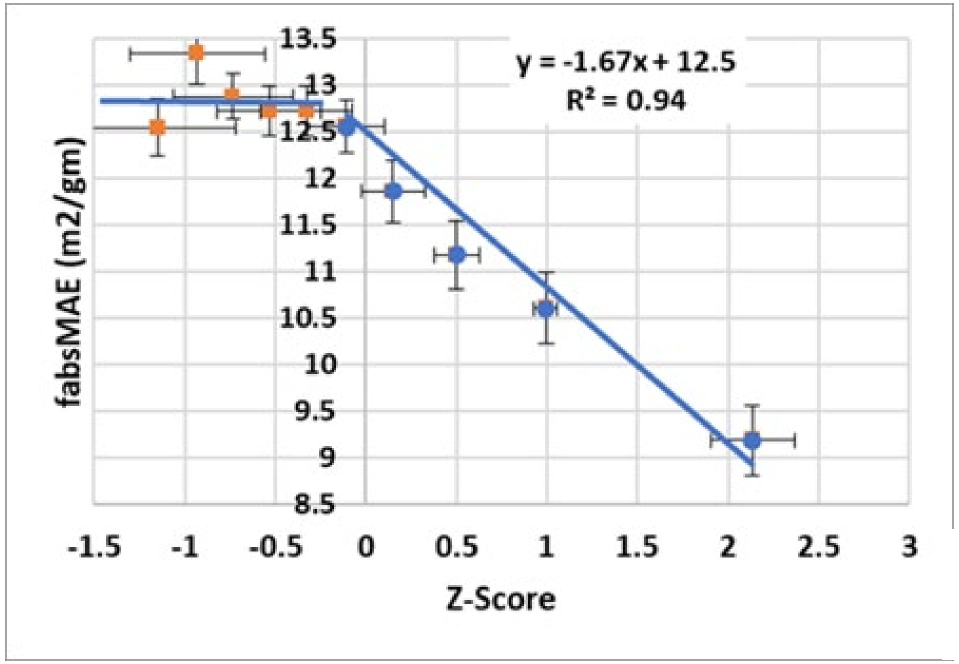
LAC_{TOR} vs LAC_{fabs}



- fabs reproduces LAC well in U.S. Most of the variance is explained by measurement error
- $LAC_{fabs} < LAC_{TOR}$ at higher concentrations (> 0.6 µg/m³)
  - Evidence of fabs filter artifact? Smoke impacted days have lower MAEs?

Nonlinear fabs vs LAC models

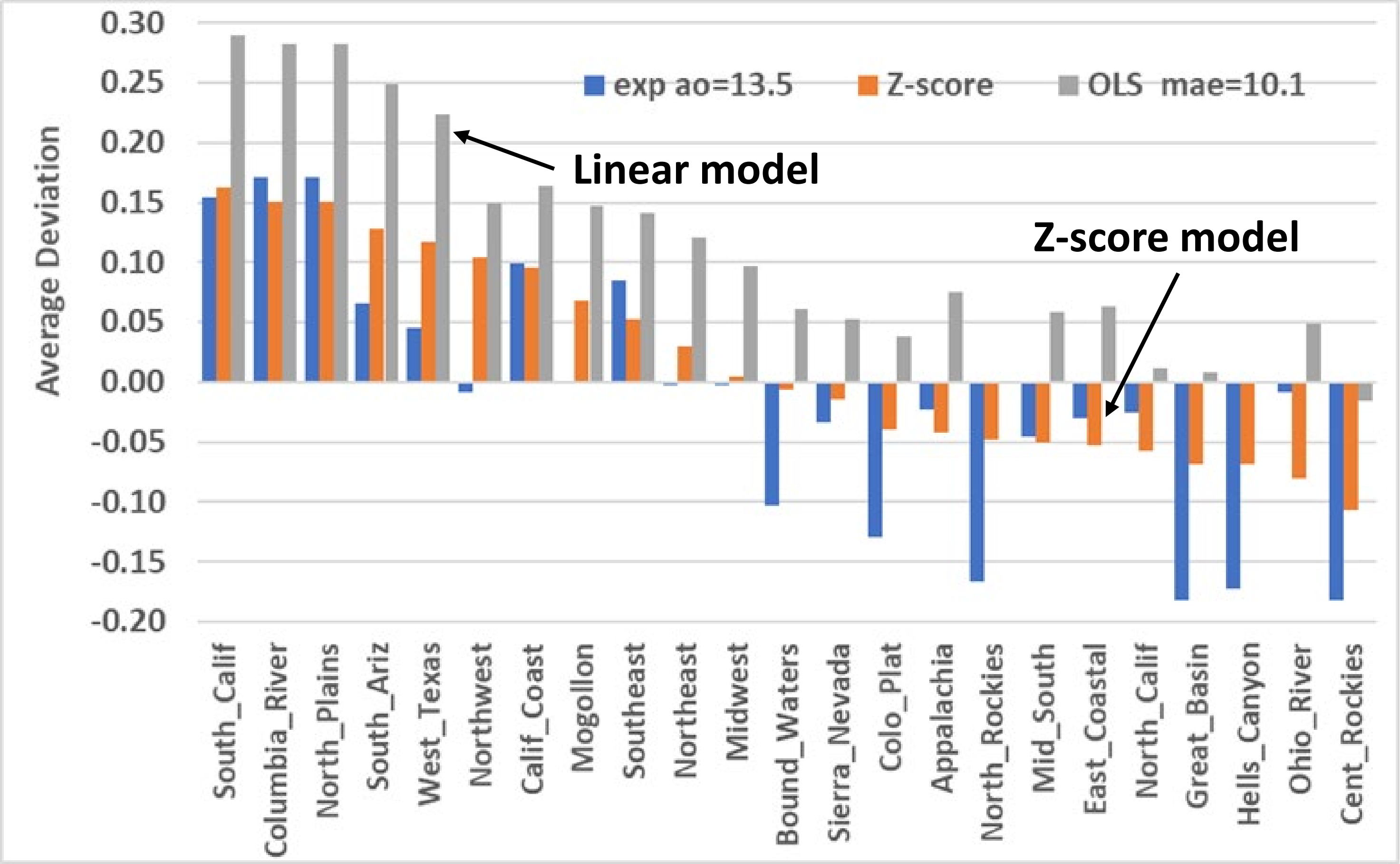




$$z = \frac{1}{N}\sum_{1}^{N}\frac{x_i-\bar{x}}{\sigma}$$

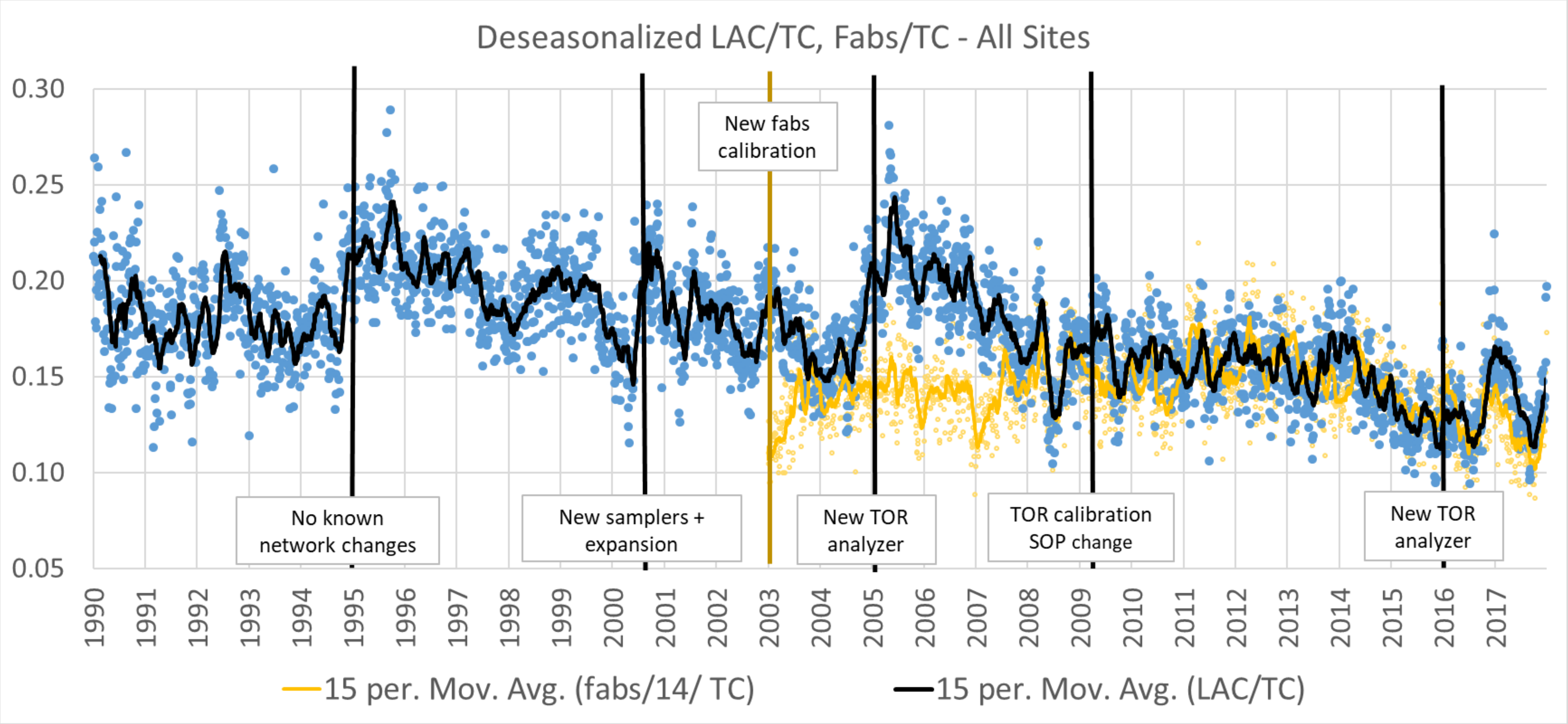
- As shown by Bill the data can be better fit by an:
  - Exponential relationship between fabs and LAC
  - Inverse hockey stick z-score model that assumes that the nonlinear relationship is relative to values in a region as opposed to absolute values
- The nonlinear fabs to LAC relationship is not fully explained by filter loading artifact

$\mathrm{LAC}_{\mathrm{fabs}}$ vs $\mathrm{LAC}_{\mathrm{TOR}}$



- The model with the best performance depends on the region.
- On average the z-score model has the smallest bias

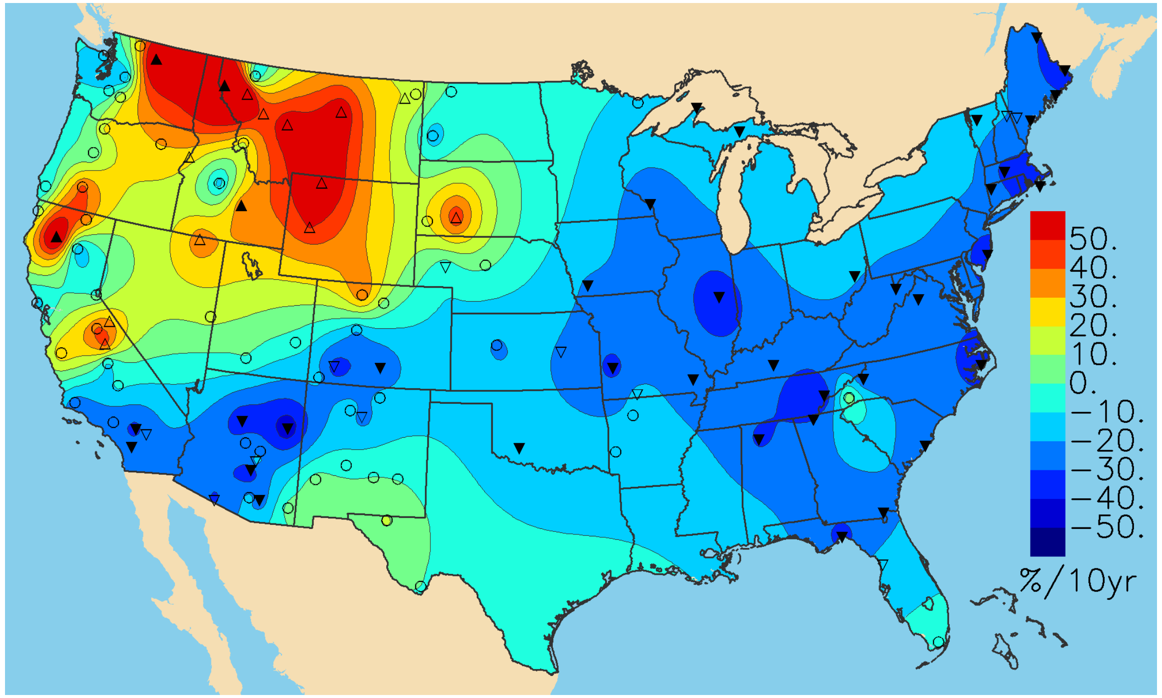
LAC vs fabs trends



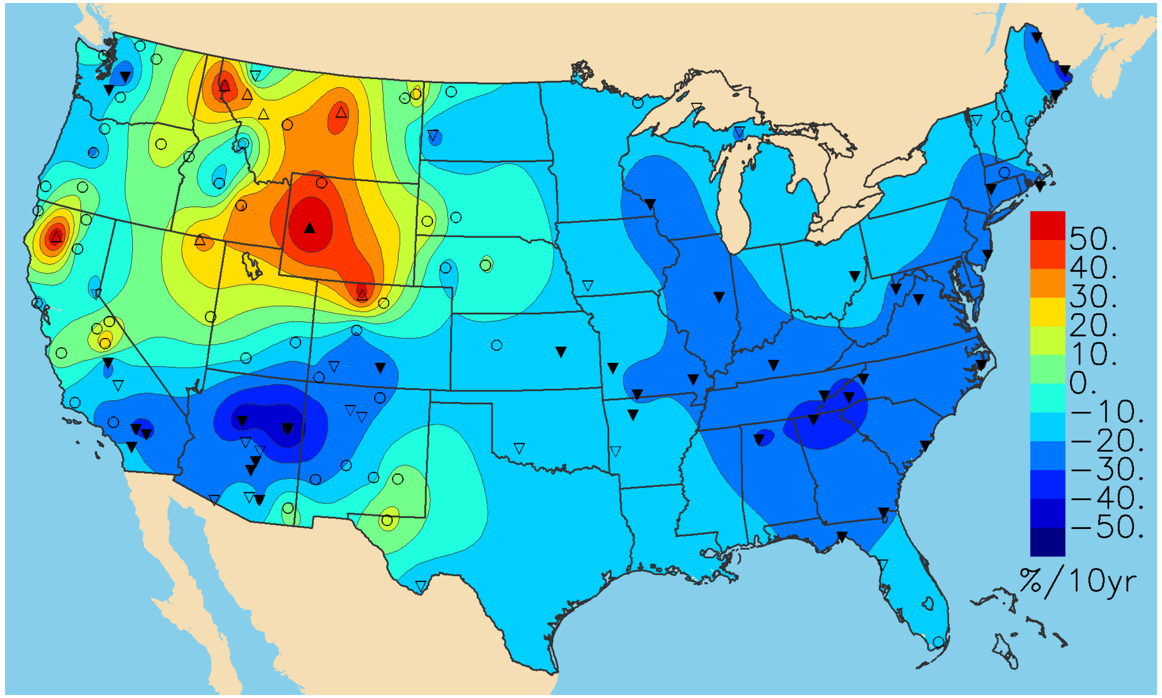
- Filter absorption (fabs) measured by HIPS is thought to be highly related to LAC
  - Provided LAC MAEs have not changed, the trends in fabs/TC should mimic LAC/TC trends
- Fabs/12/TC trends differ from LAC/TC from 2003 – 2008, but are similar post 2008

Trends, 2008-2018

LAC$_{fabs}$



LAC$_{TOR}$



Impacts Alternative OC-LAC measurements on RHR trends

- OC typically accounts for more than 90% of the TC and light extinction and errors in LAC estimated from fabs will have small effect on total light extinction
- LAC + OC are constrained by the measured TC
  - OC bsp ~ 4 g/m^2 * 1.8 * OC = 7.2 * OC
  - EC bap = 10 g/m^2 * EC
- Miss apportionment of LAC introduces a 30% error in the miss apportioned fraction, which is generally a small fraction of scattering
- See Scott's presentation on effects of alternative carbon measurements on RHR trends.

TC and HIPS Measurements System

Pros

- Total Carbon
    - Instruments can potentially be calibrated
    - Reproducible and not operationally or instrument dependent
    - Good precision, Cost effective
- HIPS - fabs
    - Calibrated to 0
    - Shown to be linear with increasing absorptance
    - Reproducible and not operationally or instrument dependent
    - Good precision and unbiased at low concentrations
    - Inexpensive analysis on Teflon filter

Cons

- Total Carbon
    - Contains contributions from both OC and LAC
    - Requires a separate sampling module and quartz filter
    - Low information content
- HIPS - fabs
    - 33% of IMPROVE fabs is below LQL = 3* MDL
    - Filter loading artifact causing low bias
        - affects < 5% of IMPROVE samples
        - Not an issue for CSN samples
    - Contributions of absorption from iron oxides
    - LAC mass absorption efficiencies are dependent on composition and aging of aerosols

Estimates of OC and LAC from TC and fabs

Pros

- TC and fabs have been demonstrated to be a stable and reproducible measurements and not subject to instrument drift.
    - Trends are reflective of changes in the concentrations and properties of aerosols
- OC generally accounts for the majority of TC and errors in LAC derived from fabs will have small effect on OC.
- Light scattering and absorption derived from TC and fabs will have small affect on RHR trends

Cons

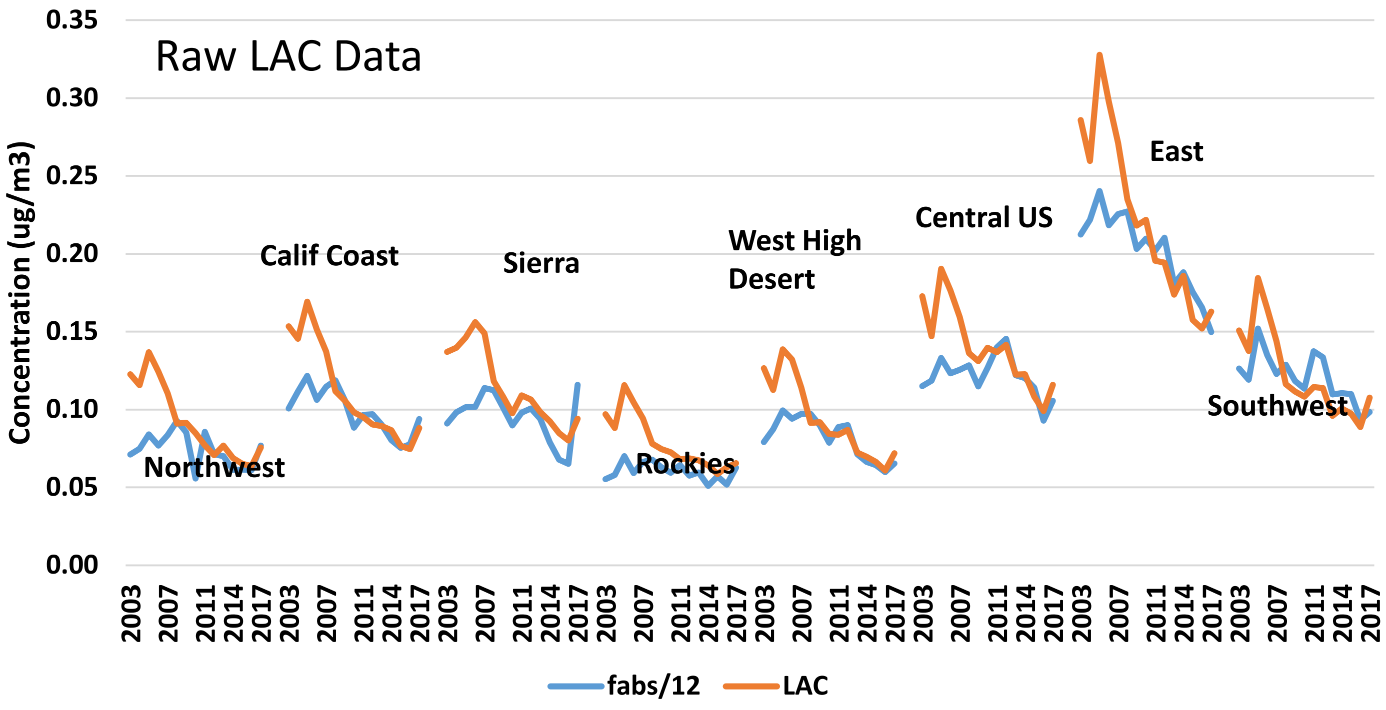
- The cause of the nonlinear fabs – LAC relationship is not known
    - Caused by fabs filter loading artifact?
    - Caused by changing aerosol absorption properties with concentrations?
- LAC derived from fabs is a surrogate for ambient LAC
    - Without additional information, LAC_{fabs} can't fully account for the spatial and temporal variability of LAC composition and optical properties

Carbonaceous Aerosol Measurements

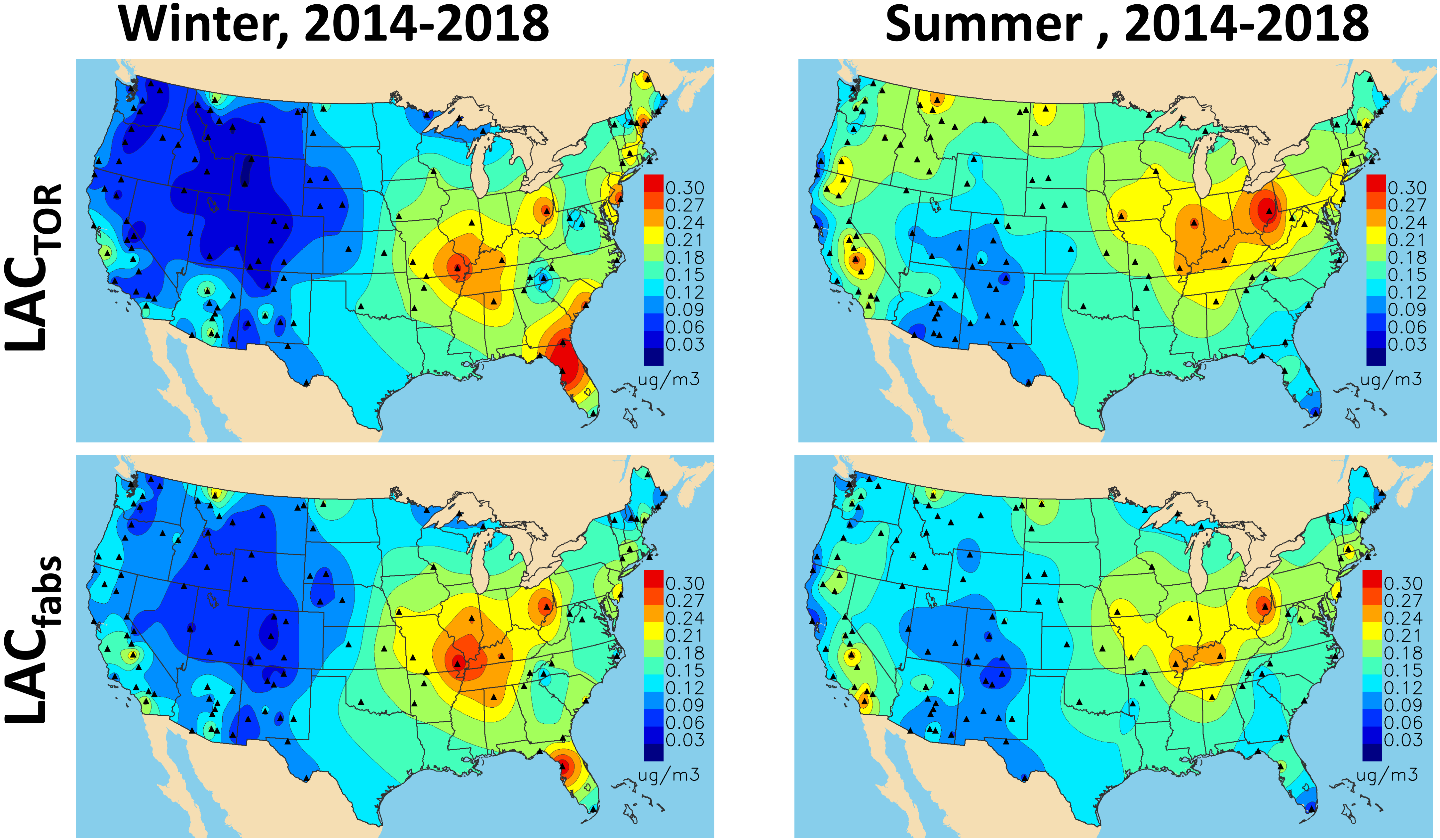
	TOR			FTIR				HIPS
	TC	OC	LAC	TC	OC	LAC	TC	(fAbs)
Instrumental / Method Universality	N			Y			Y	Y
Calibration (Bias) (Reference Material)	Y	N	N	N	N	N	Y	Y-N
Stable meas. (Trends)	Y	Y	N		Y	N	Y	Y
High Precision	Y	Y	N		Y	N	Y	Y
Measure at relevant low concentrations	Y	Y	N (biased)		Y	N (biased)	Y	N (not biased)
Cost (H, M, L)	H	H	H	M	M	M	M	L
Comparable to TOR data	Y	Y	Y		Y	Y	Y	maybe
Fundamental/ Species Specific	Y	N	N	N	N	N	Y	N
Multi Carbon Species	Y			Y			N	N

Discussion

LAC vs fabs Trends



- LAC and fabs have different trends from 2003-2008 but similar trends from 2008-2017
- Malm et al., 2019 suggests the LAC from 2003-2008 is overestimated



Winter, 2014-2018

Summer , 2014-2018

LAC_{TOR}

LAC_{fabs}

LAC_{TOR} - concentrations from the TOR analysis. LAC_{fabs} - estimated from fabs data using MAE_{LAC} = 12.5 and MAE_{Fe} = 4