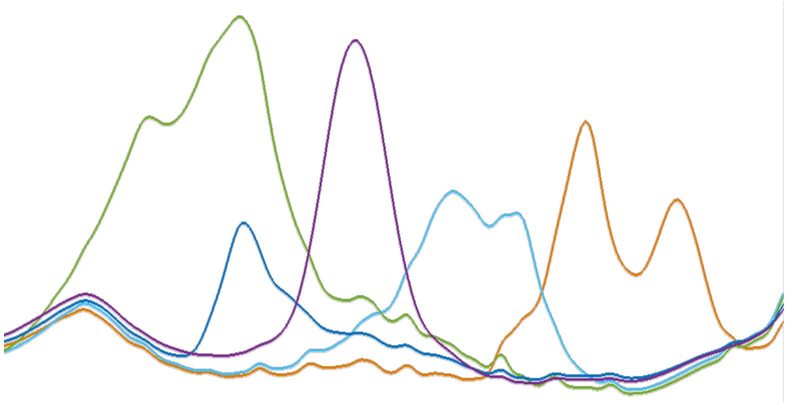
FT-IR OC AND EC: REEVALUATING BIASES AND CALIBRATION UPDATING



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Point Reyes National Park, CA
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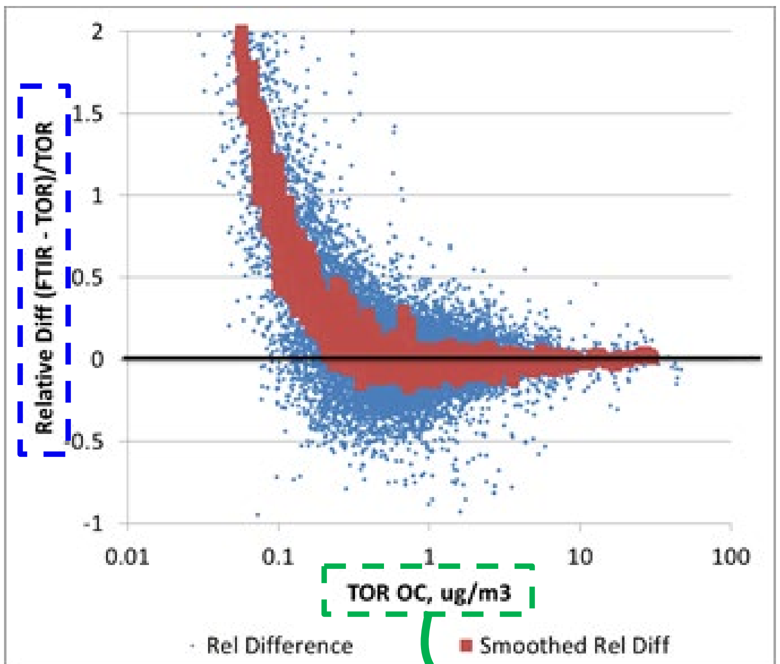
FT-IR Calibration: Outline

- Biases in FT-IR models
  - 2018 IMPROVE Steering Meeting **addressed *FTIR bias***: [Bias]= [FTIR] - [TOR]
  - **Discovery:** Scatter plot of [Bias] vs. [TOR] ***always*** shows a (false) trend.*
    - Trend related to how the ***geometry of how least squares works***
  - ***Real measurement bias*** found on [Bias] vs. [FT-IR] plots (or time series)

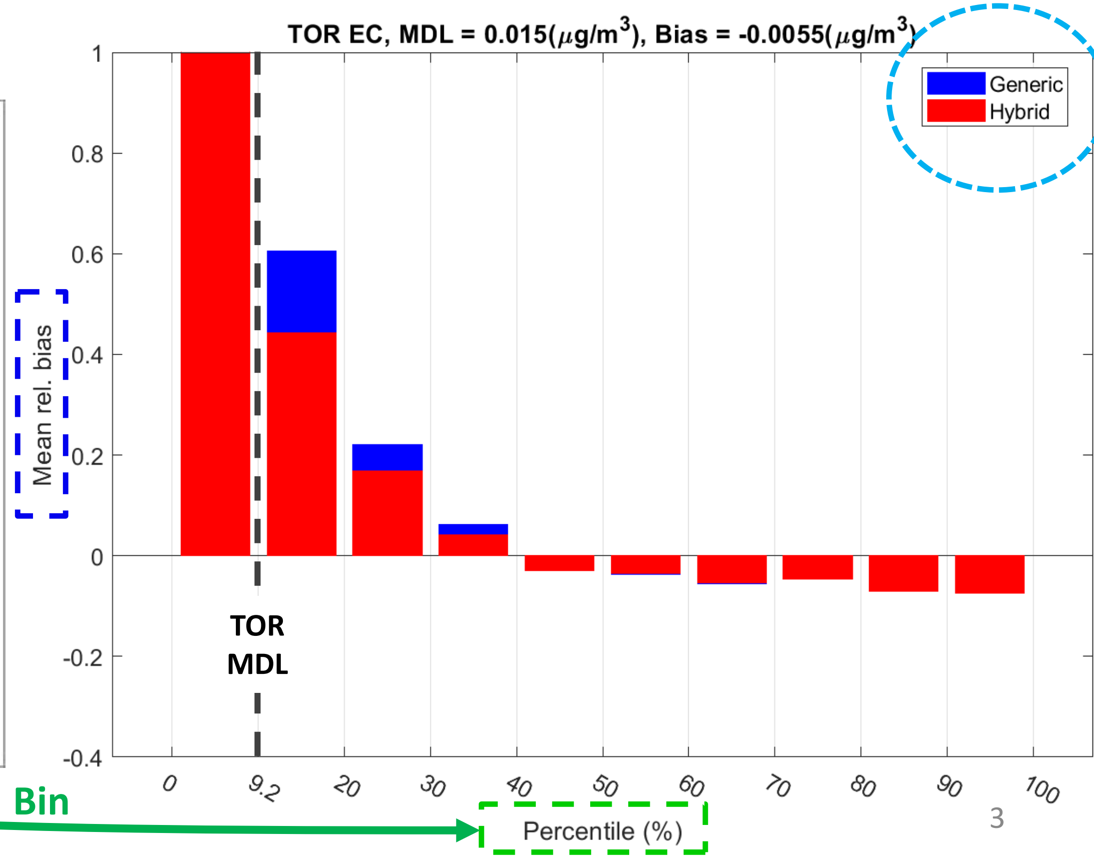
- Recalibration for (routine) OC and EC prediction
  - Propose a moving window method for calibration updating
  - AQRC database synchronization

FT-IR OC and EC "bias plots:" What you may have seen last year…

- <u>**Presented with a problem…**</u>
  - _**[rel. Bias] = [FTIR-TOR]/[TOR]**
- <u>Led us to a diagnostic tool:</u> the **"mean relative bias plots"***
  - **Bin samples using data percentiles**
  - Calculate **mean rel. bias within each bin**
- <u>**One objective for 2018 meeting**:</u> presented ***various ways to (try) to reduce*** "the bias trend"



Figures adopted from "RE: FTIR OC and EC data for 2015" from Bret.Schichtel@colostate.edu

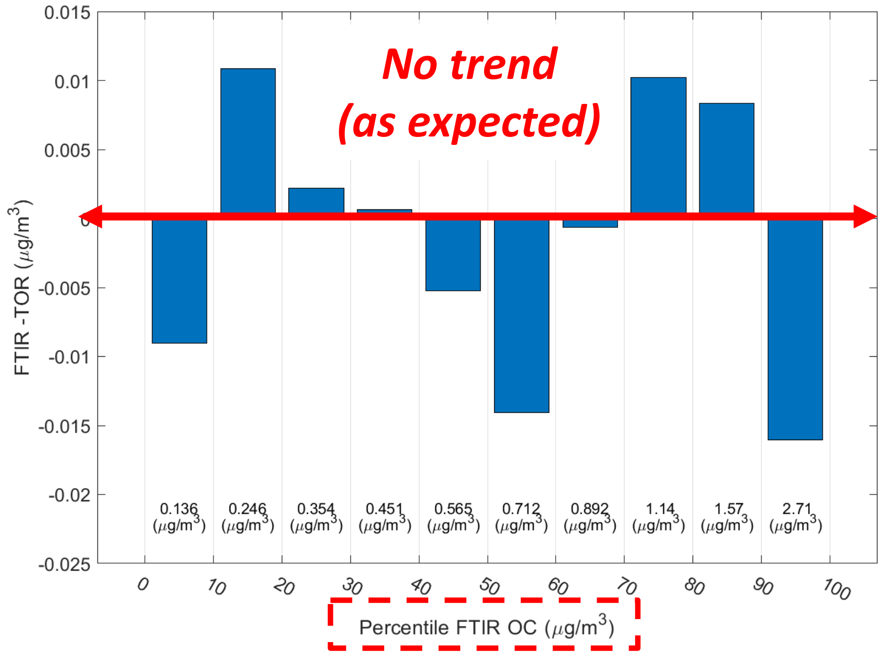


Bin

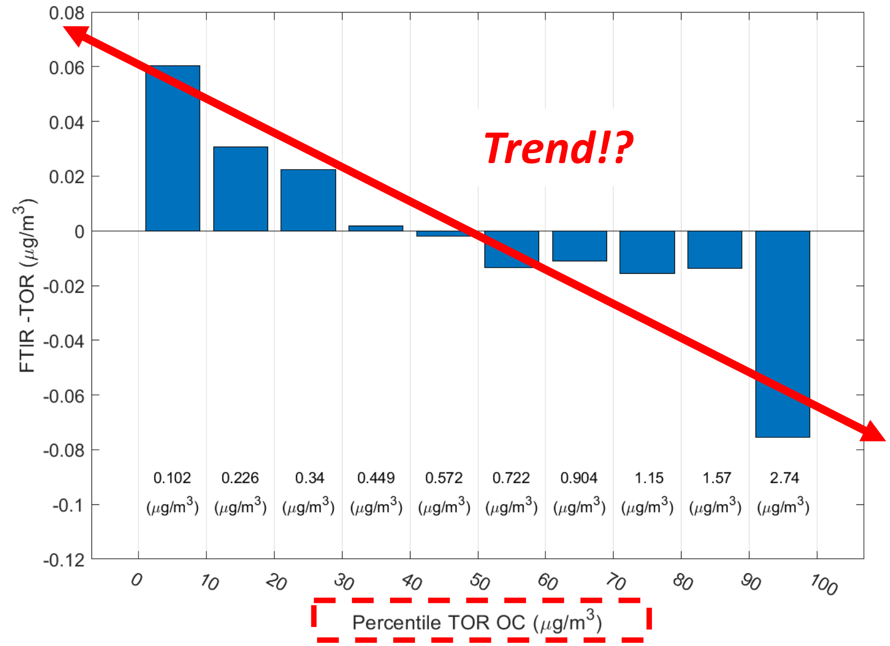
*- Taken directly from Dillner et al. 2018 IMPROVE STEERING presentation

From Reality to Simulations…
Stranger Things with Least Squares

- Simulated simple "**FT-IR OC calibration**"– one X variable , one Y variable (*N*=1,000,000)
  - X=[one IR absorption measurement]
  - Y=[TOR]
  - Y^{hat} =X*b=[FTIR]
  - ***No bias in this simulation!***



Plot bias ***against FTIR***



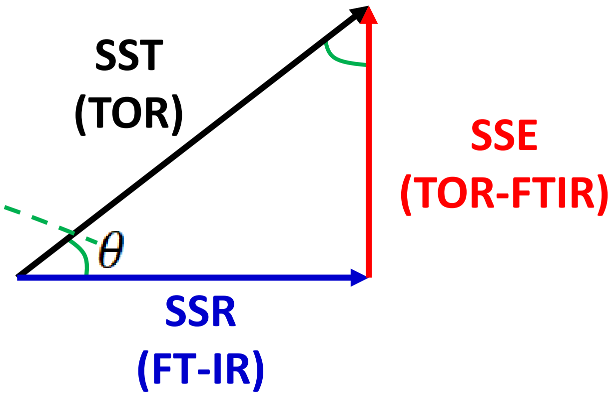
Plot bias ***against TOR***

*- Discussed this at length at CIRA (May 2019)– powerpoint available upon request.

Why does this always happen with least squares?

- **Geometry.**
  - Easiest way to understand: ***sum-of-squares partitioning of Y (TOR)***

$$R_{xy}^2 = \frac{SSR}{SST} = cos^2(\theta)$$



$$\theta = arccos\left(R_{xy}\right)$$

$R_{xy}^2 < 1$ implies trends!

[Sum-of-squares in TOR] = [SS explained by FTIR calibration] + [SS error]

SST = SSR SSE

Attributes:

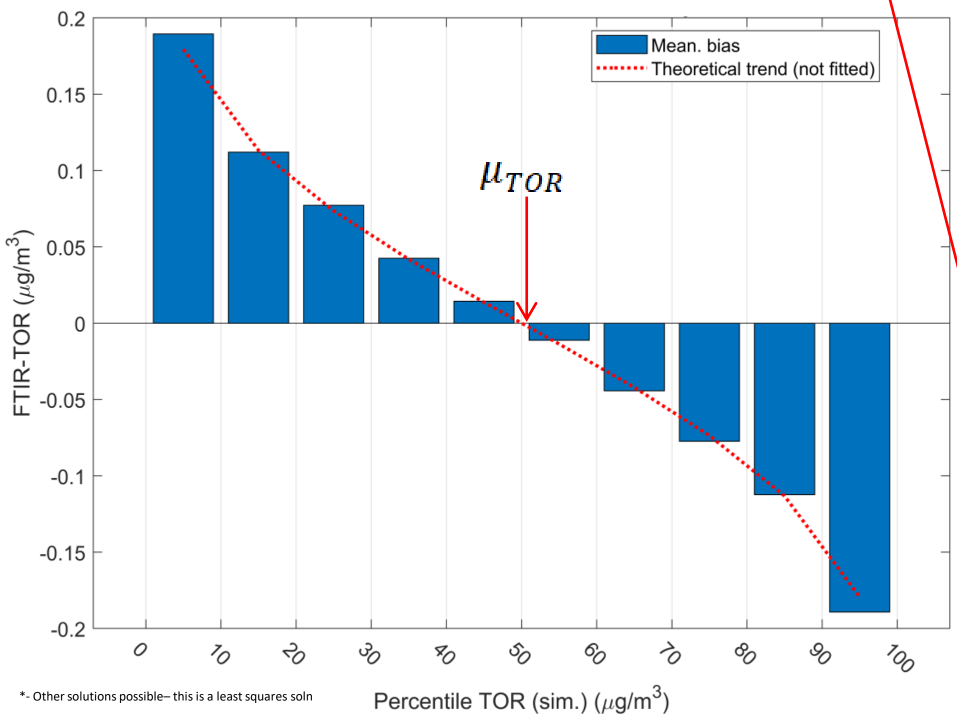
- ***Oblique angles*** imply dependence between sides
- Plotting dependent data (x,y) ***implies trends***→ hence our "bias" problem!
- Final note: **what's the angle θ?**

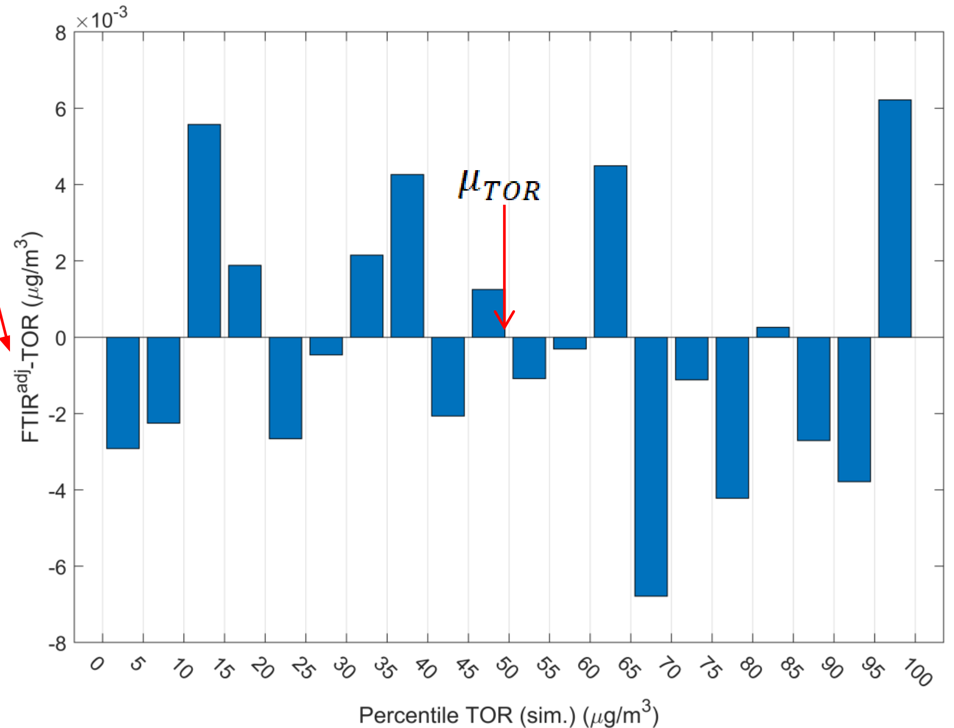
How to address geometry:* Adjustment by Example

- Geometry ***suggests***…* $[FTIR - TOR] = (1 - R_{xy}^2)\mu_{TOR} - (1 - R_{xy}^2)[TOR]$

  Intercept (+) Slope (-)

- **To adjust FTIR predictions to counter trend…**
  - Rearrange and solve for TOR $[TOR]_i = \frac{1}{R_{xy}^2}([FTIR]_i - \mu_{TOR}) + \mu_{TOR}$
  - Rename TOR to ***FTIR^{adj}*** $[FTIR]_i^{adj} = \frac{1}{R_{xy}^2}([FTIR]_i - \mu_{TOR}) + \mu_{TOR}$



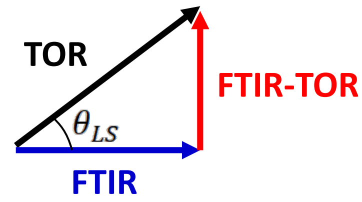


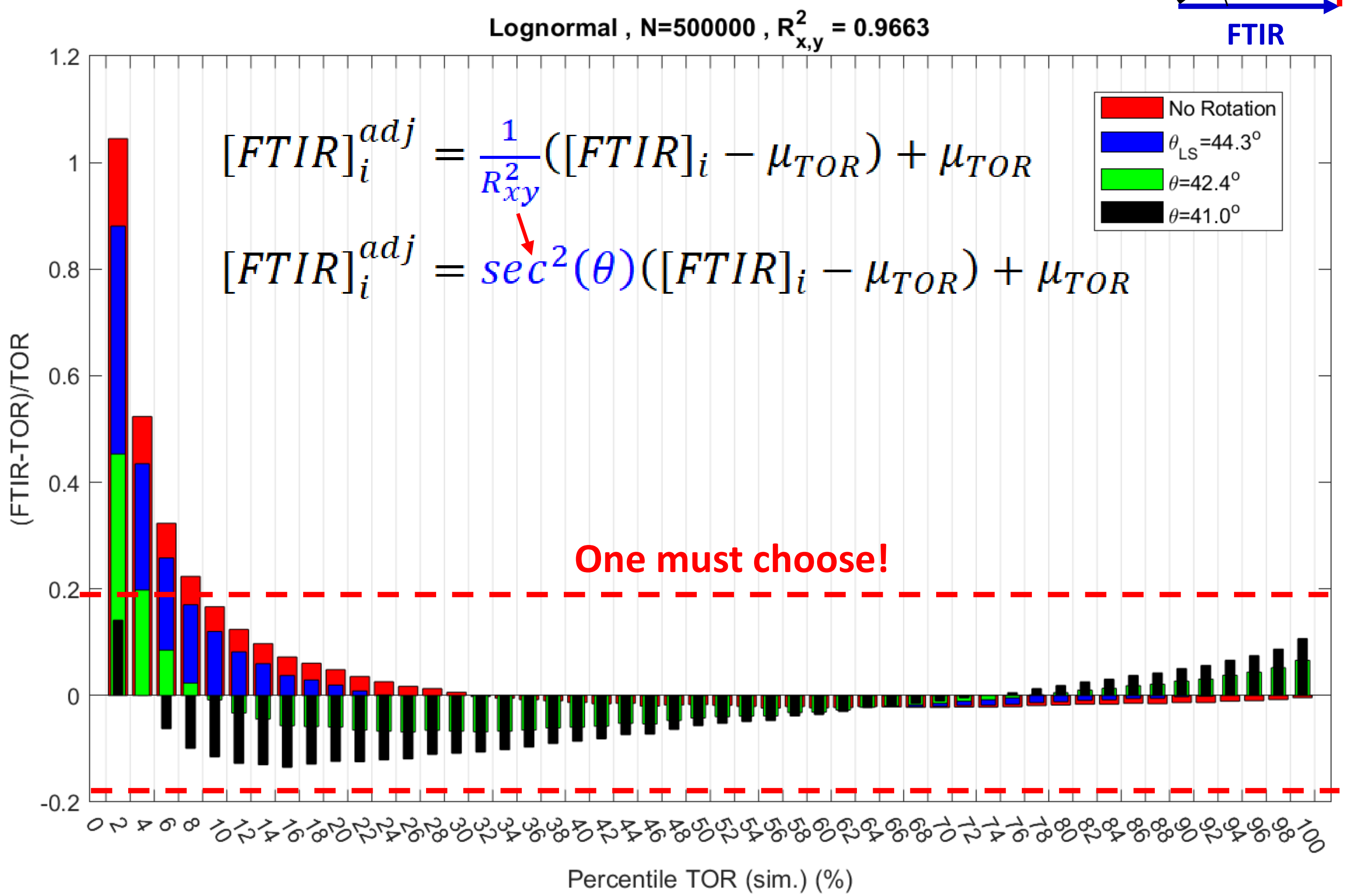
*- Other solutions possible– this is a least squares soln

How to address geometry:*
A General Framing

- If data are ***not normal*** (e.g., lognormal), use ***generic adjustment expression***

1. Calculate θ from the least squares solution → $\theta_{LS} = arccos(R_{xy})$
2. Adjust θ by trial-and-error

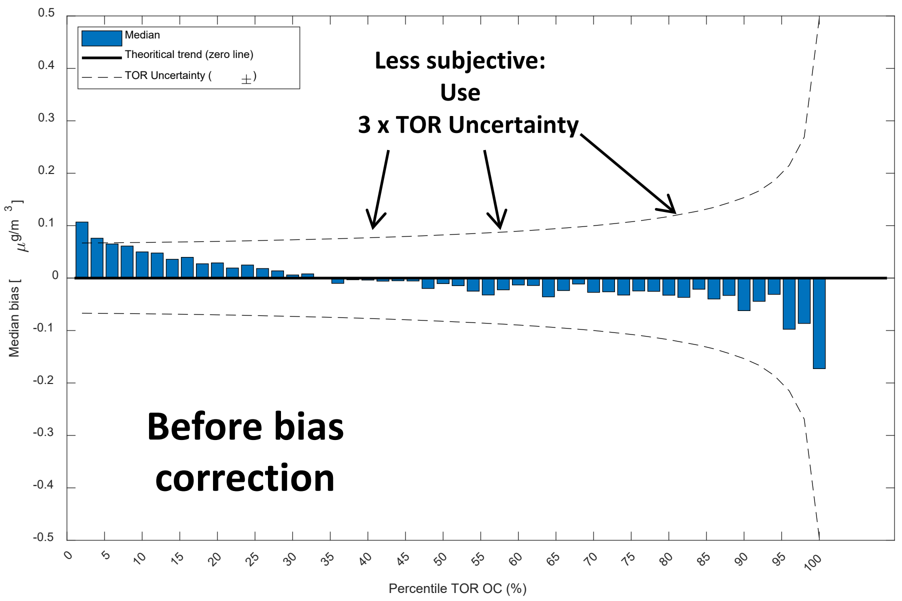


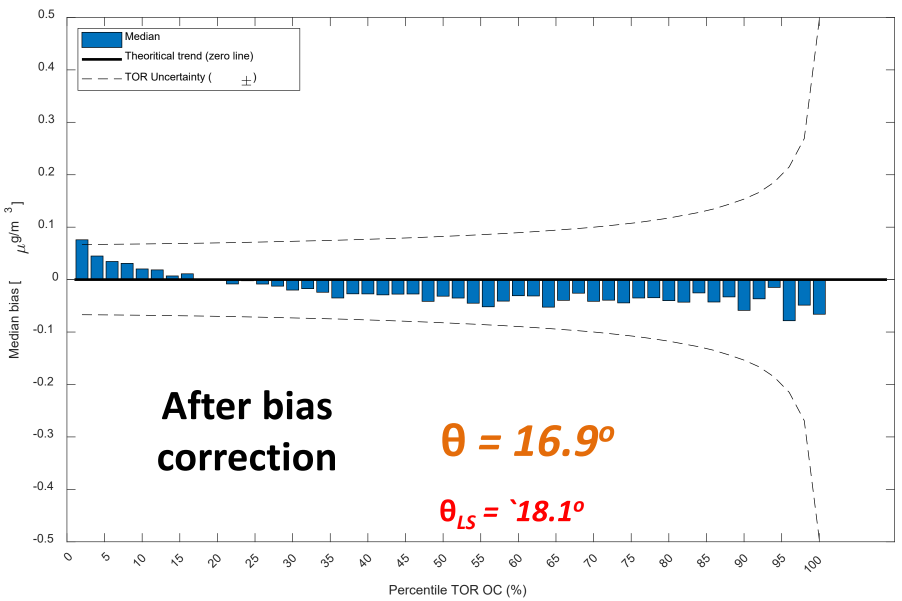


$$[FTIR]_i^{adj} = \frac{1}{R_{xy}^2}([FTIR]_i - \mu_{TOR}) + \mu_{TOR}$$

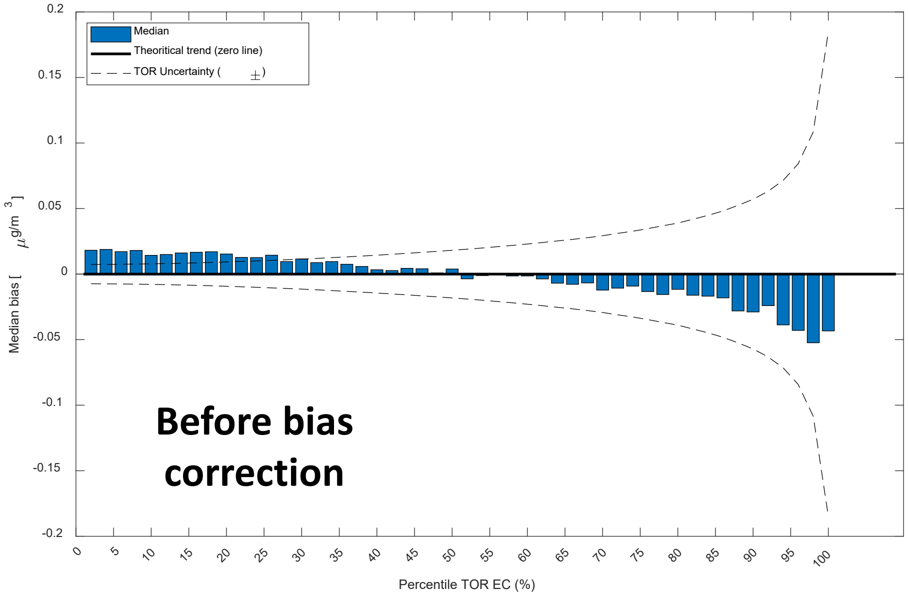
$$[FTIR]_i^{adj} = sec^2(\theta)([FTIR]_i - \mu_{TOR}) + \mu_{TOR}$$

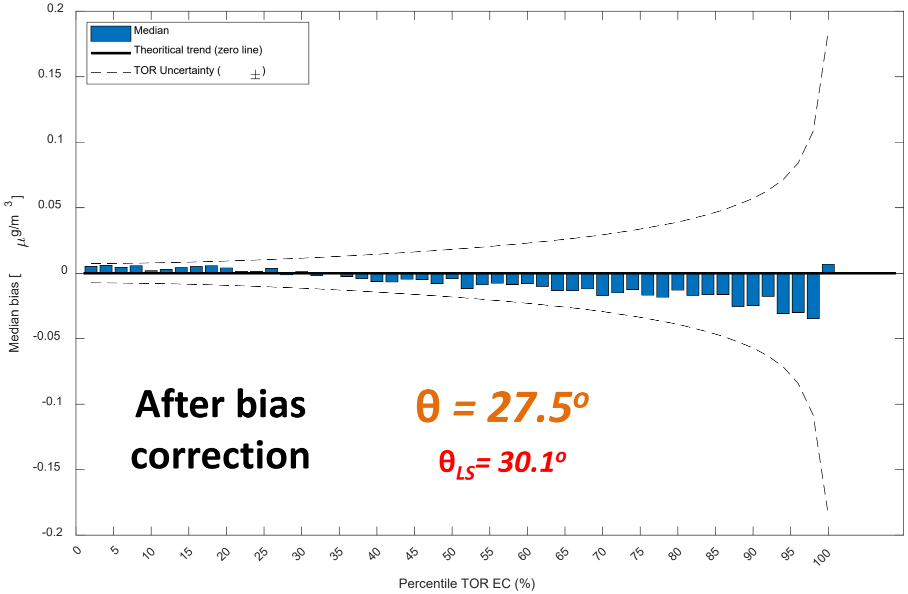
IMPROVE 2015 – Median bias OC



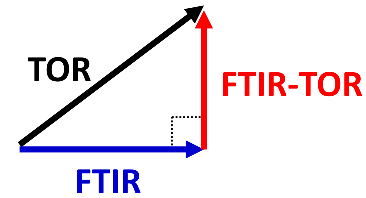


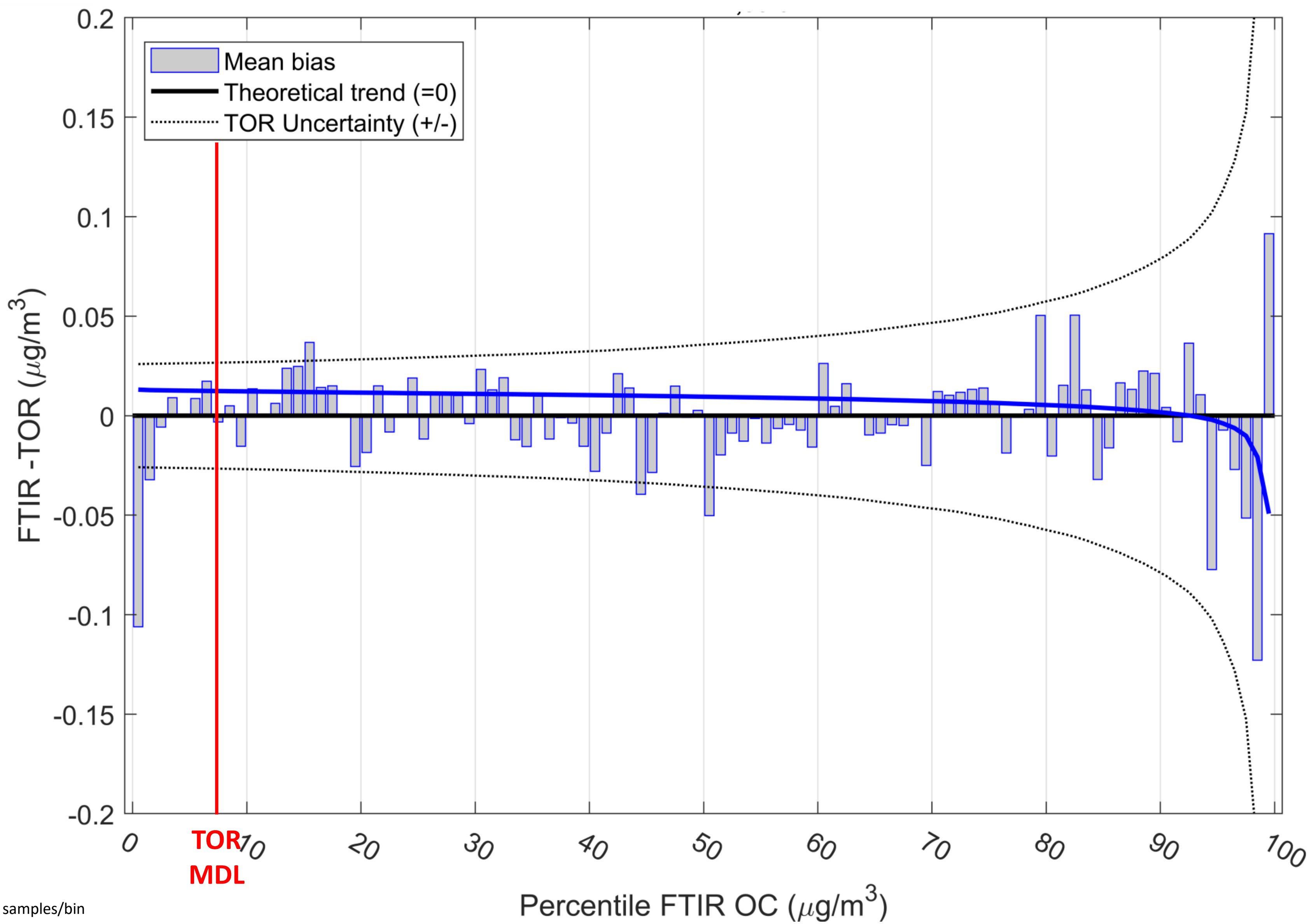
IMPROVE 2015 – Median Bias EC





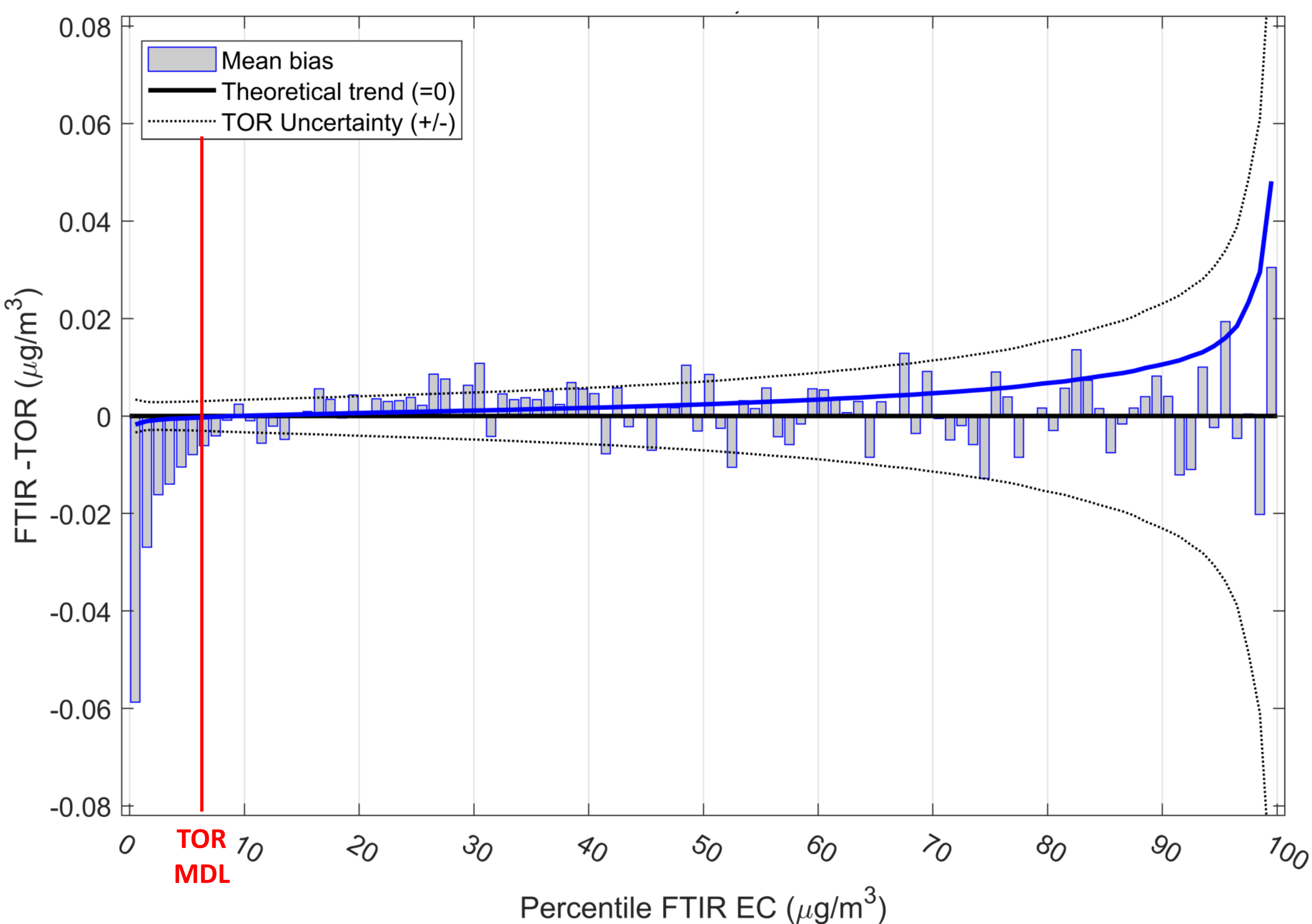
Real Measurement Bias in FTIR OC





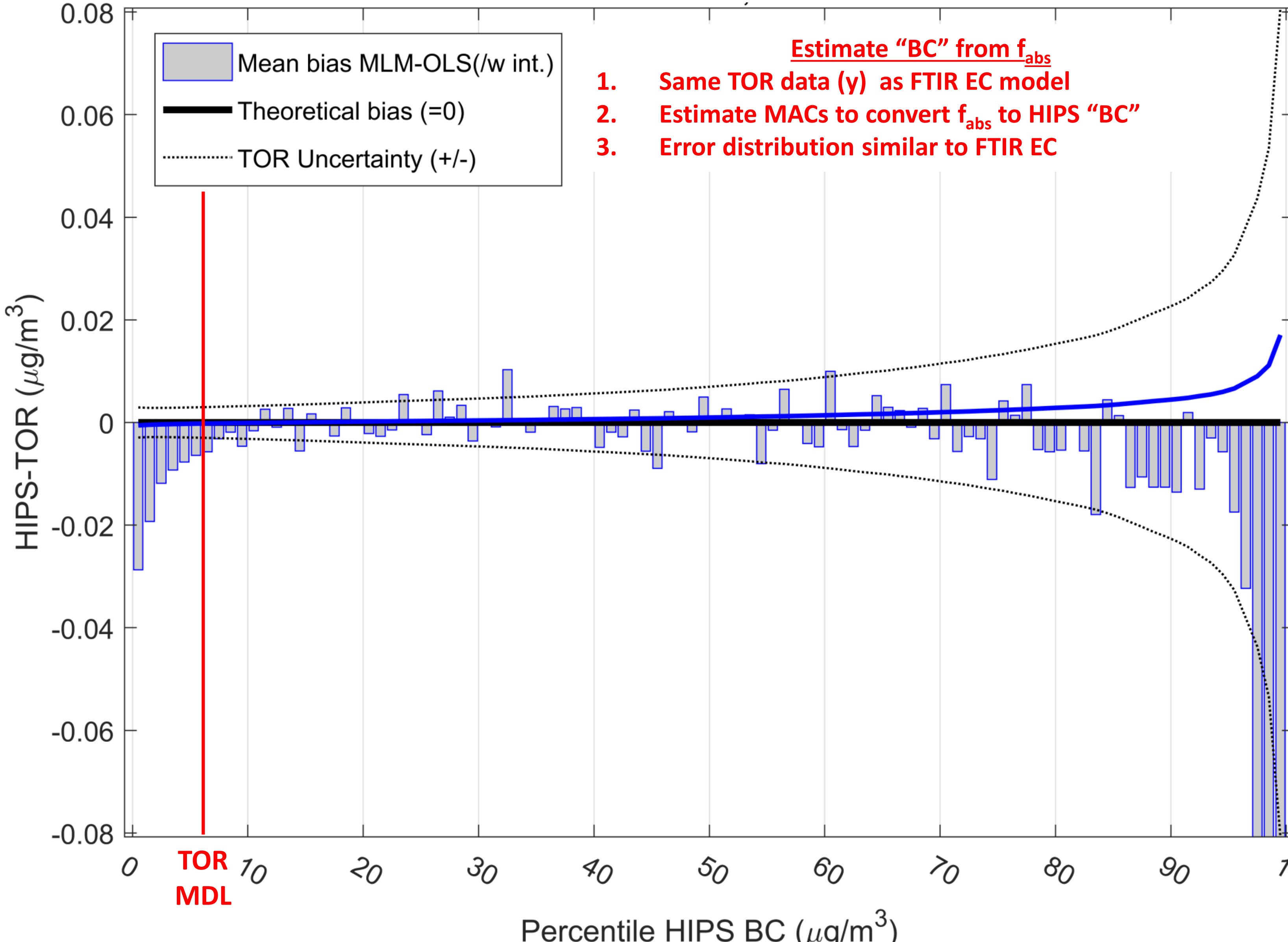
*- N_{bin} = samples/bin

Real Measurement bias in FT-IR EC



Real Measurement biases in HIPS "BC":

A non-FTIR example



Recalibration for Routine OC and EC Prediction An Example

- Say we…
  - Develop an **FT-IR OC calibration** from ***three months*** of IMPROVE 2013 samples
    - **Calibration spans: July 1, 2013 – Sept. 30, 2013**
    - Reminder: "**A calibration**" = a set of coefficients, $\boldsymbol{b}$, that converts IR absorption into mass (OC or EC), i.e.,

$$[OC] = [\boldsymbol{spectrum}] * \boldsymbol{b}$$

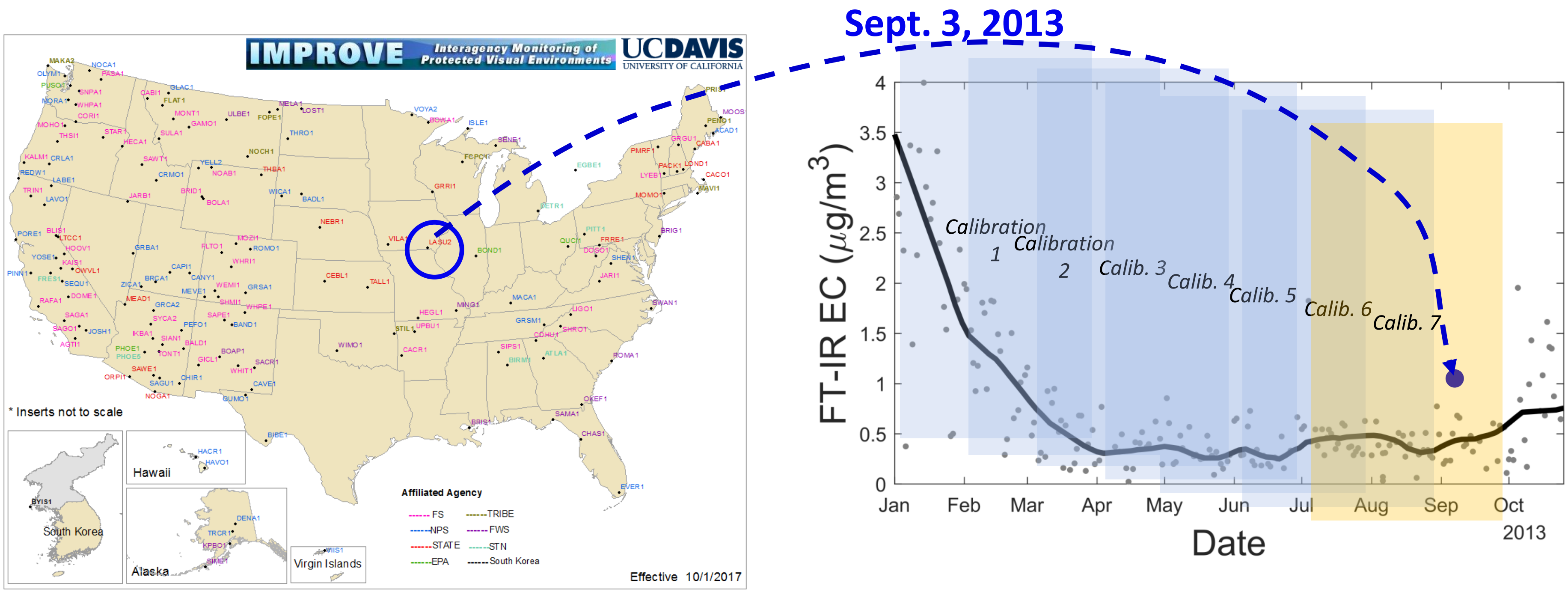
- Q: What's an efficient way to regularly update the calibration to ensure robustness?

- A: Employ an ***"moving window" type calibration***

How it works:
A Three Month Moving Window Example

<u>Potential Benefits</u>

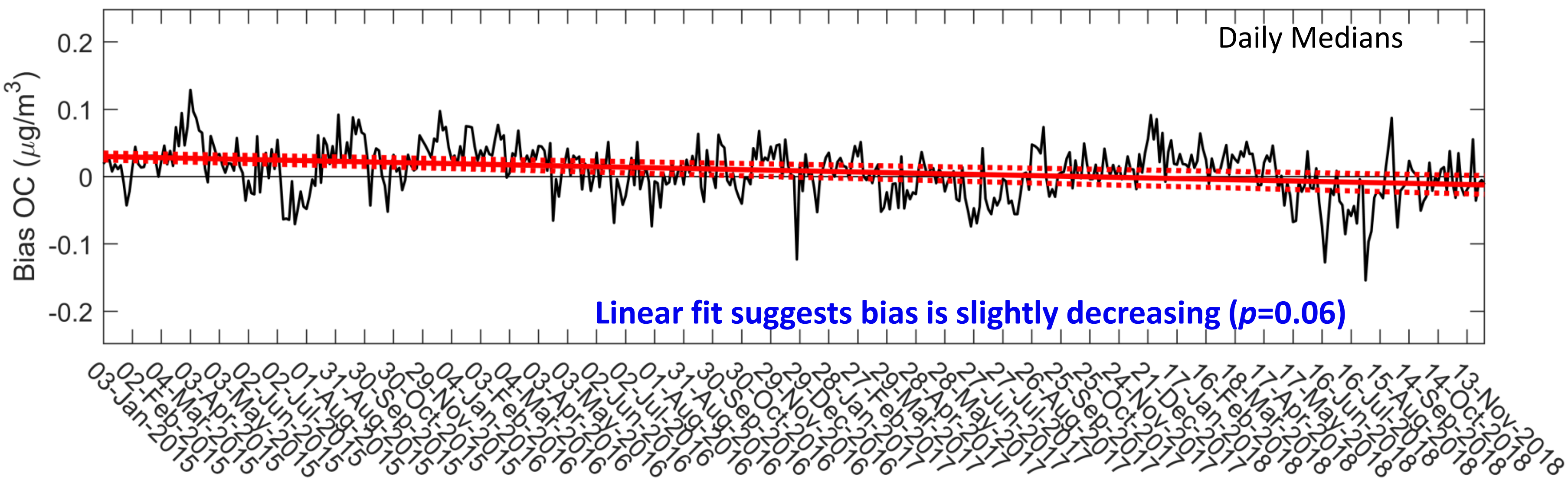
- Tunes the calibration to ***instrument shifts/drifts (in FTIR and TOR instruments)***
- May adapt the calibration to ***seasonality***



Moving Window Performance on **IMPROVE 2015-2018 OC**

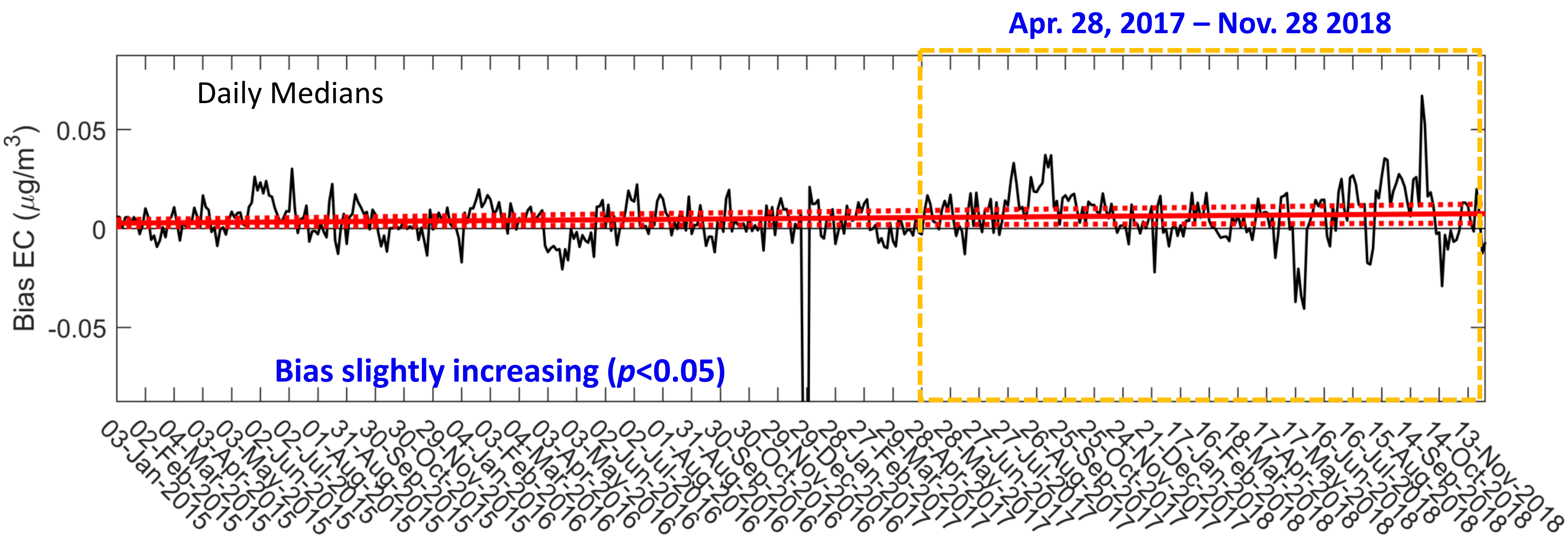
Year	R^2	**Bias (%)**
2015	**0.969**	**3.2**
2016	**0.877**	**2.2**
2017	**0.976**	**-0.2**
2018	**0.980**	**-0.3**

- **Twelve-month moving window** works best
  - Used 14% IMPROVE sites as per Bruno's analysis
  - Window shifts in one month increments
- Performance for four years of data…
  - ***Roughly speaking: FT-IR OC bias appears to improve over time***



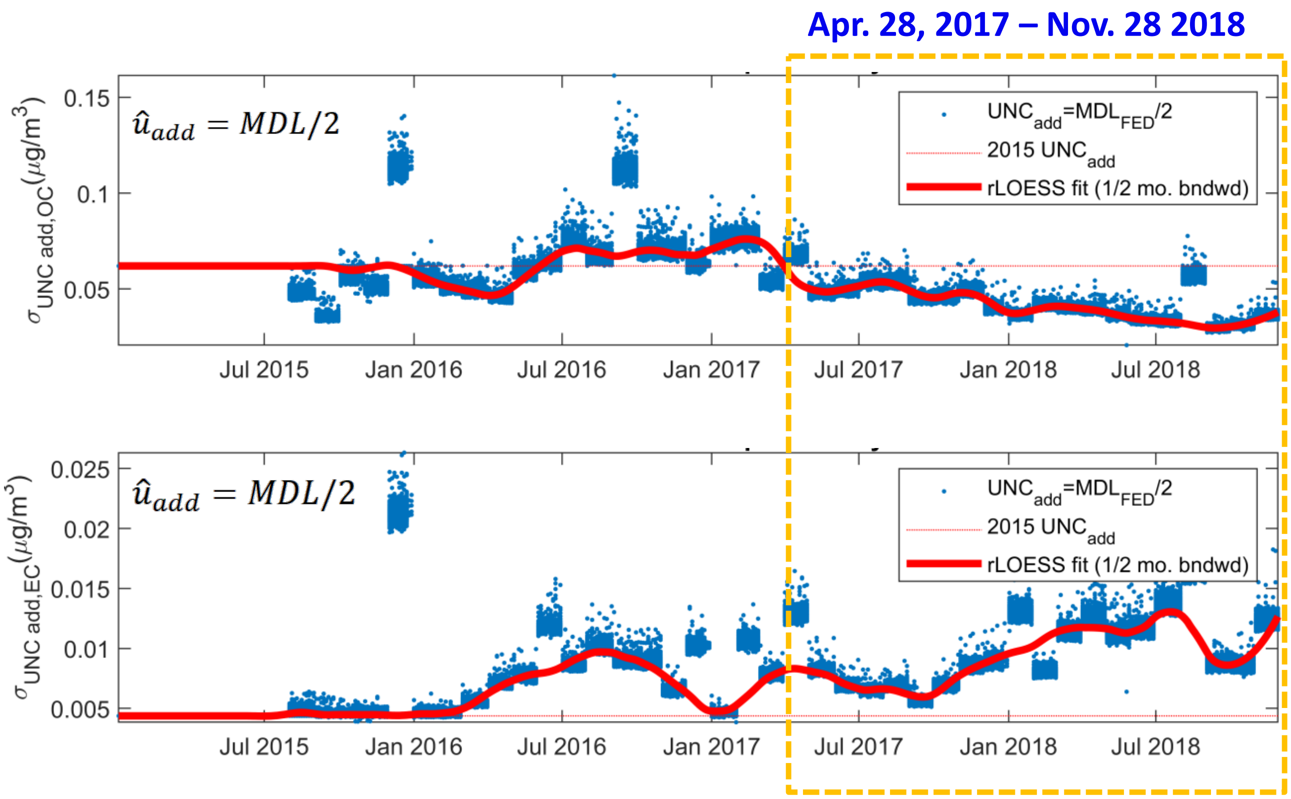
Moving Window Performance
IMPROVE 2015-2018 EC

Year	R^2	Bias (%)
2015	0.879	**5.1**
2016	0.874	**3.6**
2017	0.871	**6.5**
2018	0.807	**5.4**



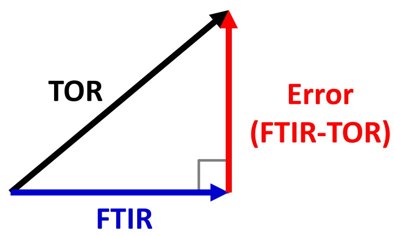
A Question on Drift: Where does it come from?

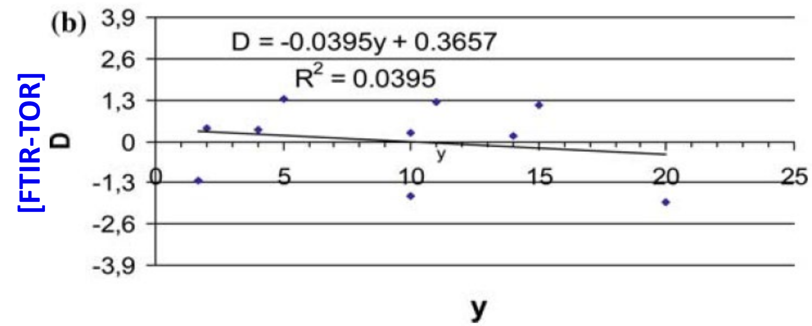
- **Perhaps TOR?**
  - Downloaded MDL data from the FED wizard (August 25, 2019) $\hat{u}_{add} = MDL/2$



Conclusions: Biases

1. Geometry of least squares guarantees
   - A linear trend on [Bias] vs. [TOR] plot
   - **Occasionally revisited in the literature**





Besalú, E., et al., *An overlooked property of plot methods. Journal of Mathematical Chemistry, 2006.* ***39(3): p. 475-484.***

2. May adjust geometric bias on [FT-IR]-[TOR] vs. [TOR] plot
   - Neither revisited nor mentioned in the literature…

3. True measurement biases found on…
   - [FT-IR]-[TOR] vs. [FT-IR] plot
   - [FT-IR]-[TOR] vs. time plot
   - **Use these plots for diagnostic purposes before θ adjustment!**

Practical Conclusions: Routine Calibration Updating

1. Upload(ed) spectra into AQRC database
   - IMPROVE 2017 through present in IMPROVE database
     - 2015 and 2016 to be added within a month
   - All CSN spectra (2017-present) are in CSN database

2. Database: connects collocated TOR data with FTIR spectra
   - For ***14% of IMPROVE sites*** and ***13% of CSN sites*** **that retain TOR**

3. Update calibration: ***moving window, monthly shifts***
   - Determine FTIR OC and EC in all samples ***from all IMPROVE sites***

4. Future work:
   - Assess ability to handle drift in FTIR and TOR measurements
   - Assess impacts of aerosol sources on predictions (and drifts)

Acknowledgements

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Supporting Analysis

S1: Geometry of least squares: More Advanced Presentation material

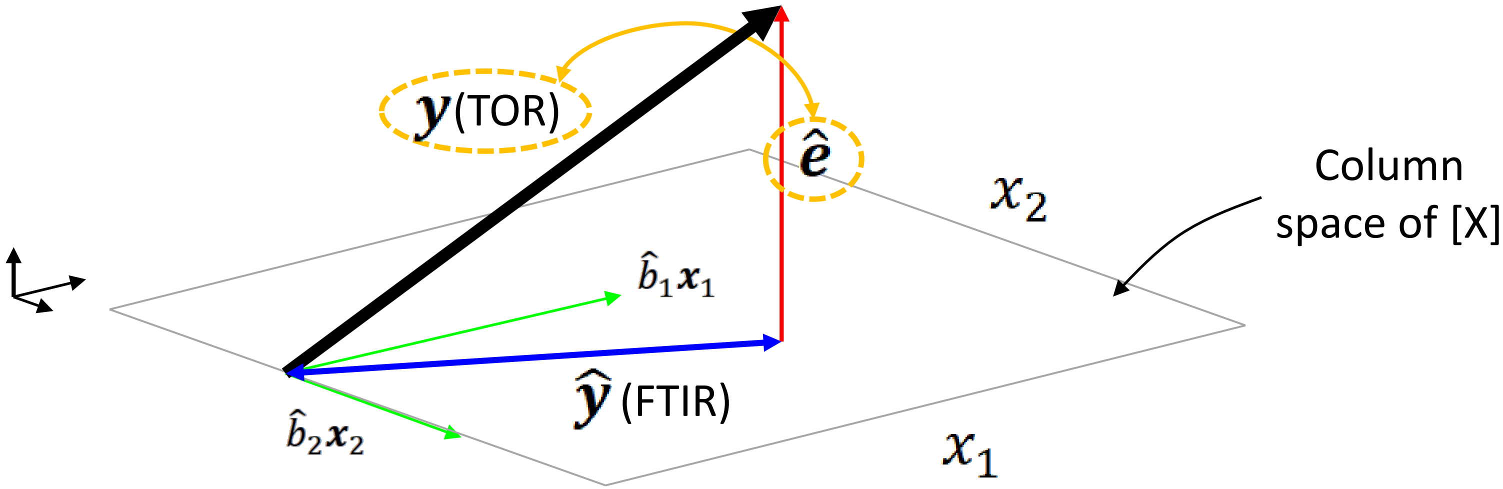
S2: Addl. Moving Window Material, Uncertainty Calculations

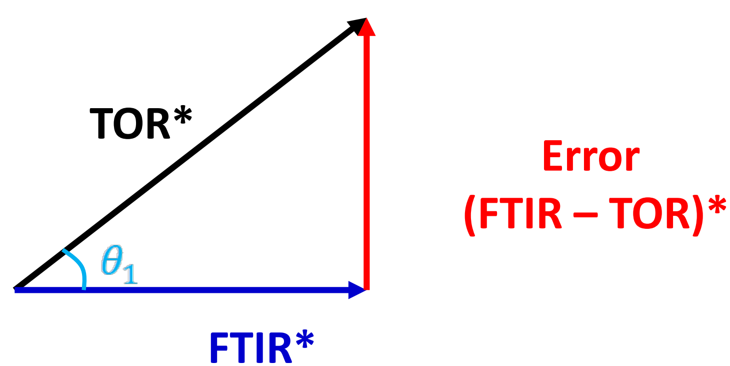
S3: An attenuation model for EC and OP

Section 1: Back to School…
Vector geometry of least squares

$$\boldsymbol{y} = \hat{b}_1 \boldsymbol{x}_1 + \hat{b}_2 \boldsymbol{x}_2 + \hat{\boldsymbol{e}}$$

$$\boldsymbol{y} = \hat{\boldsymbol{y}} + \hat{\boldsymbol{e}}$$

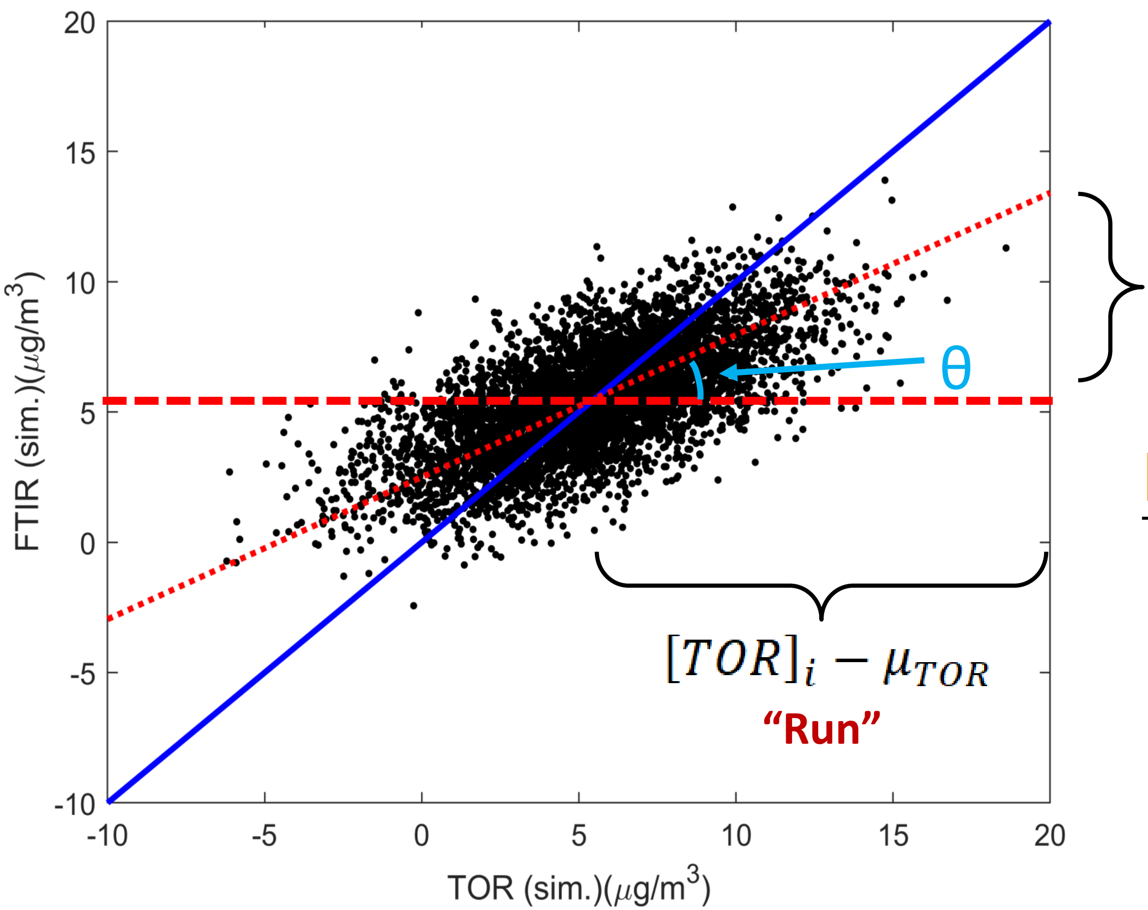




* Vector length = sum-of-squares

S1: An Adjustment Formula
(ATW thinks this is correct)

Trying to ***completely eliminate the bias is a fools errand***…
Nevertheless, it may be addressed.



"Rise"

$[FTIR]_i - \mu_{TOR}$

$$\frac{[FTIR]_i - \mu_{TOR}}{[TOR]_i - \mu_{TOR}} = tan(\theta)$$

<u>Adjustment method</u>

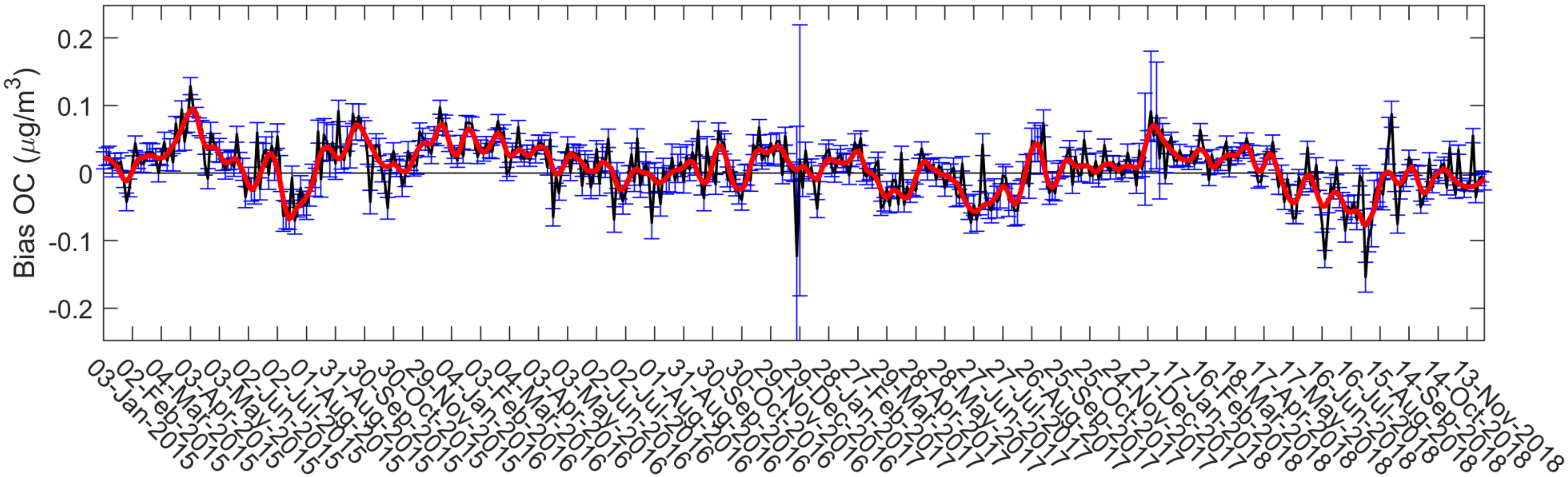
Choose θ by trial and error until plots "look good"*

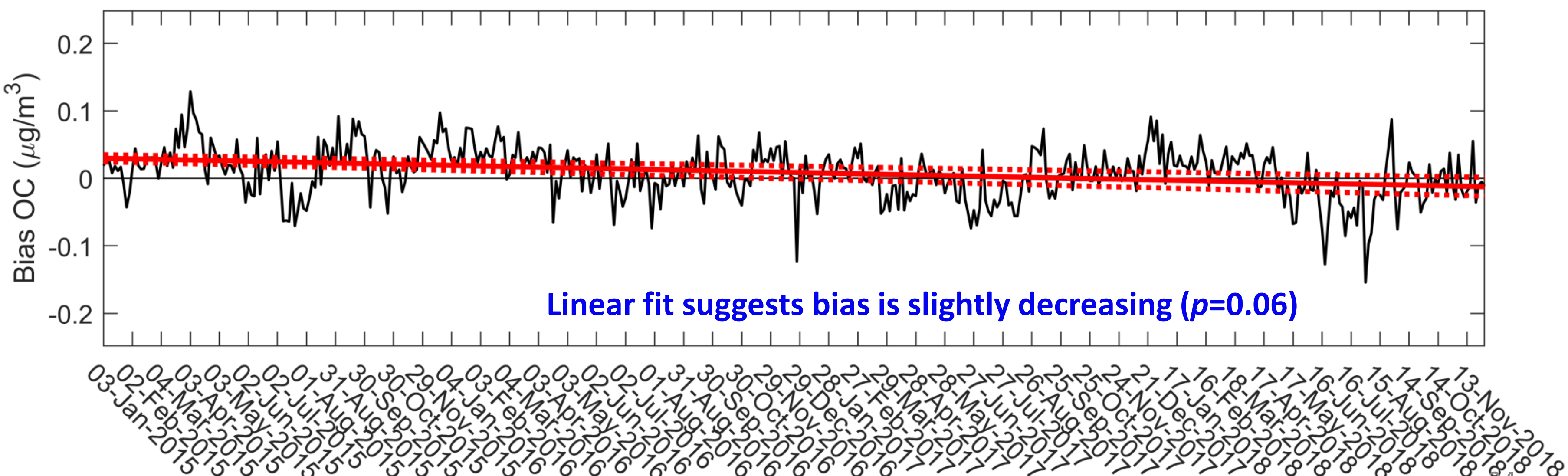
Adjustment equation $$[FTIR]_i^{adj} = [TOR]_i = cot(\theta)([FTIR]_i - \mu_{TOR}) + \mu_{TOR}$$

Note that $\theta = \frac{7\pi}{4}\theta_1 \pm \frac{\pi}{4}$ from triangle slide– as far as I can see

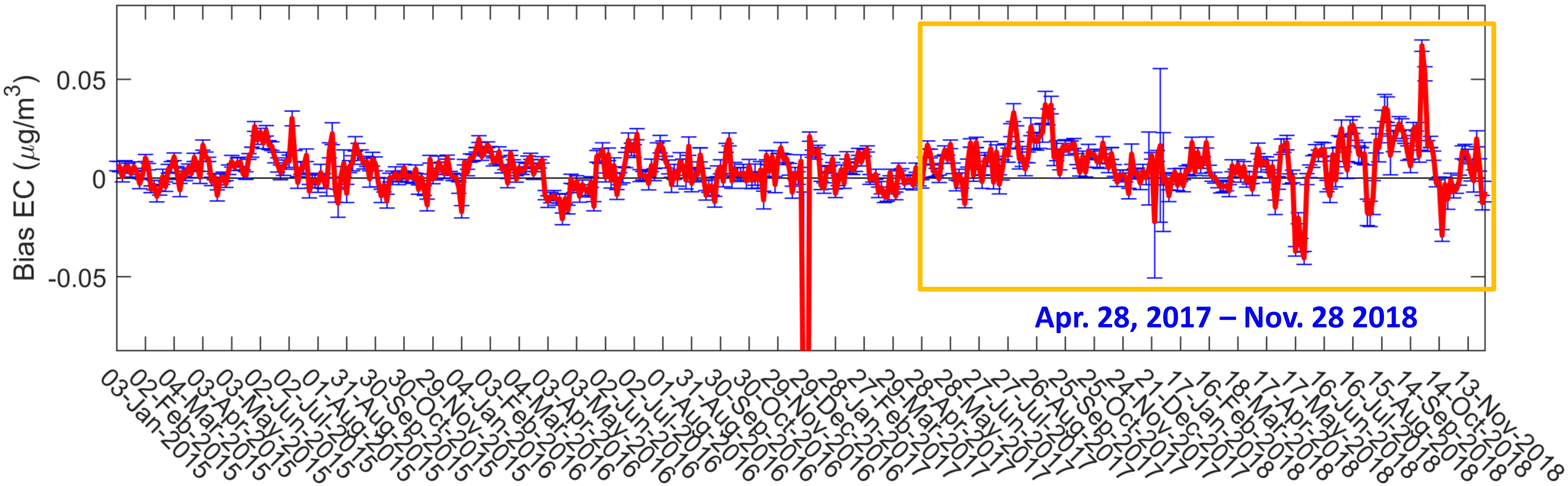
*- There are several solutions that work exactly for normally distributed samples– including a rearrangement of the eqn on the previous slide

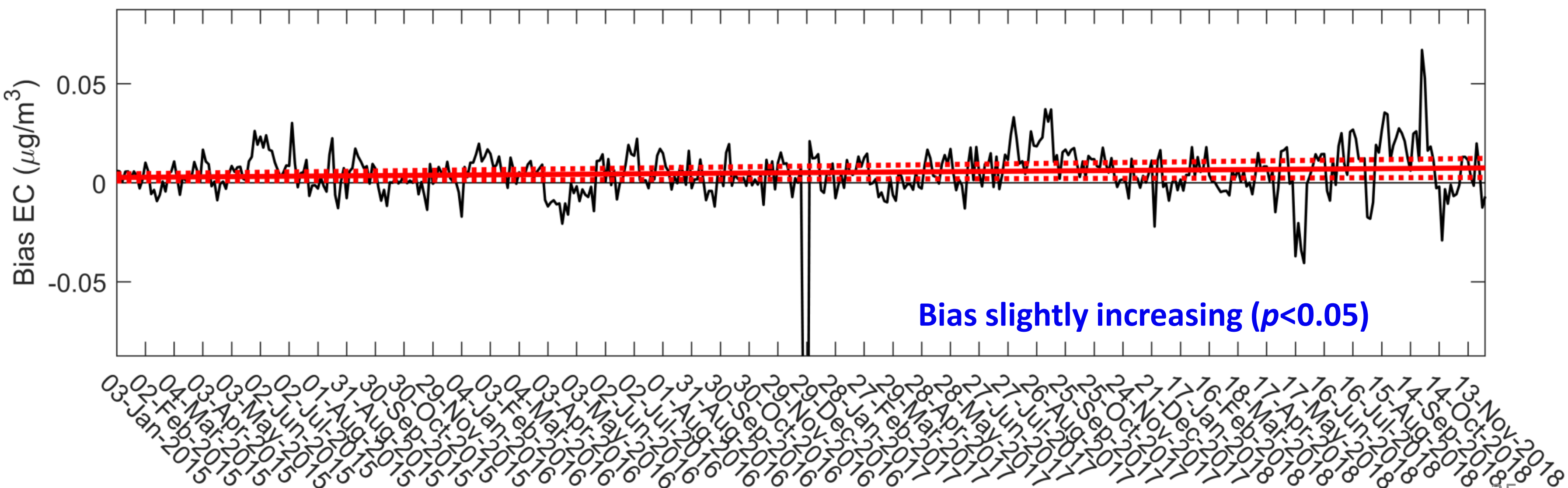
Section 2: Moving Window Results
Temporal OC (real) Bias: Daily Medians





S2 :Temporal EC (real) Bias: Daily Medians

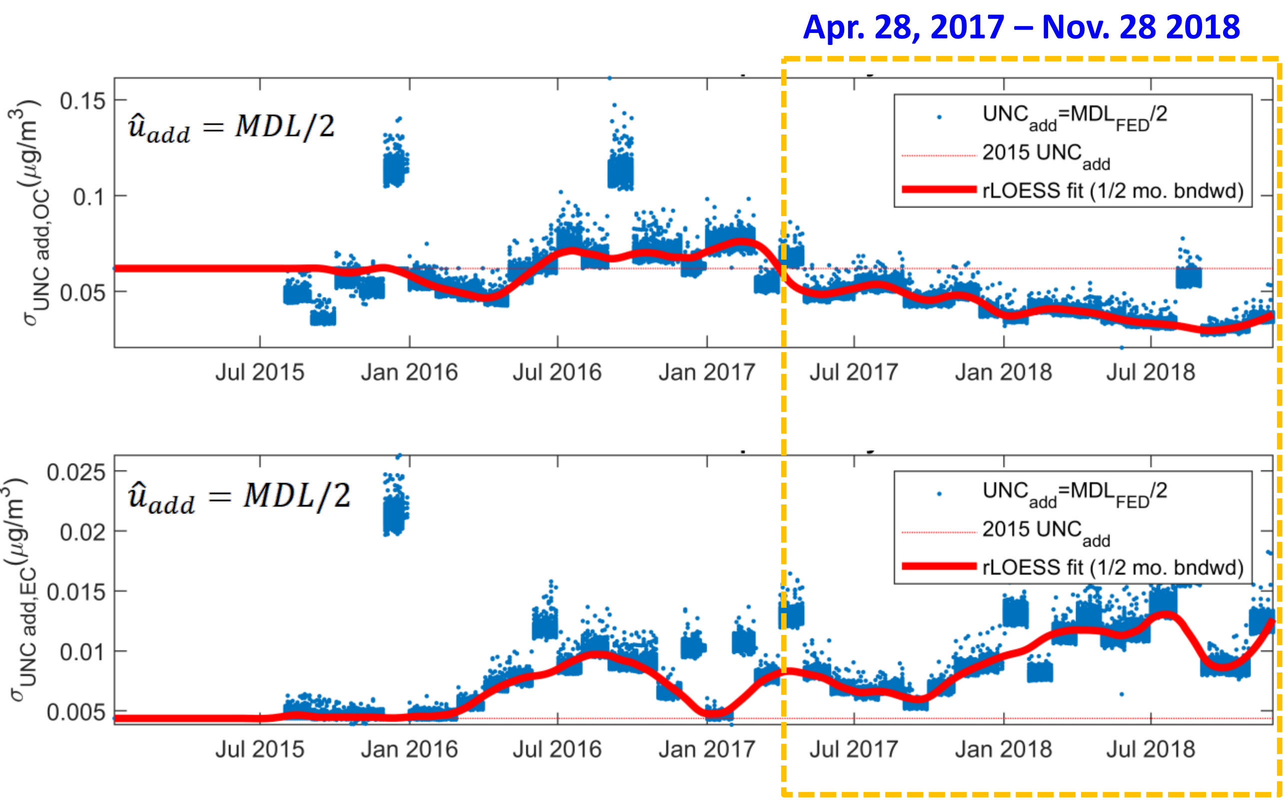




S2: A Question on Drift: Where does it come from?

- **Perhaps TOR?**
  - Downloaded MDL data from the FED wizard (August 25, 2019)

$$\hat{u}_{add} = MDL/2$$



- Notice that OC uncertainty drops and EC uncertainty consequently rises

- **Changes track with real FT-IR OC, EC biases through time**

S2: Models for Measurement Error and Uncertainty (Restated)

Observations:

- Using standard methods to estimate sample uncertainty in TOR, we see that FT-IR OC errors are approximately on the order of TOR OC (field) errors
  - Simply: $$\hat{u}_{ik} = \sqrt{\hat{u}_{k,add}{}^2 + \hat{u}_{k,rel}{}^2 C_{ik}^2}$$
    - $\hat{u}_i =$ uncertainty of sample *i*, species *k (e.g., OC)*
    - $\hat{u}_{k,add} =$ additive uncertainty for species k
    - $\hat{u}_{k,rel} =$ relative/multiplicative uncertainty for species k
    - $C_{ik} =$ mass concentration of sample i, species k

Other details on metric calculations

Additive uncertainty (u_{add}; C_{FB} = field blank conc.)

$$\hat{u}_{k,add} = \frac{P_{95}(C_{i,FB}) - P_{50}(C_{i,FB})}{\Phi^{-1}(1 - \frac{\alpha}{2})} \approx \frac{P_{95}(C_{i,FB}) - P_{50}(C_{i,FB})}{2}$$

Robust standard deviation (normal, α=0.05)

MDL (k=2) is a rearrangement of the expression

$$MDL = 2\hat{u}_{k,add}$$

Relative uncertainty (u_{rel})

$$\hat{u}_{k,rel} = \frac{P_{84}(D_i) - P_{16}(D_i)}{2} \leftarrow D_i = \frac{C_{i1} - C_{i2}/\sqrt{2}}{\bar{C}_i} \leftarrow \bar{C}_i = \frac{C_{i1} + C_{i2}}{2}$$

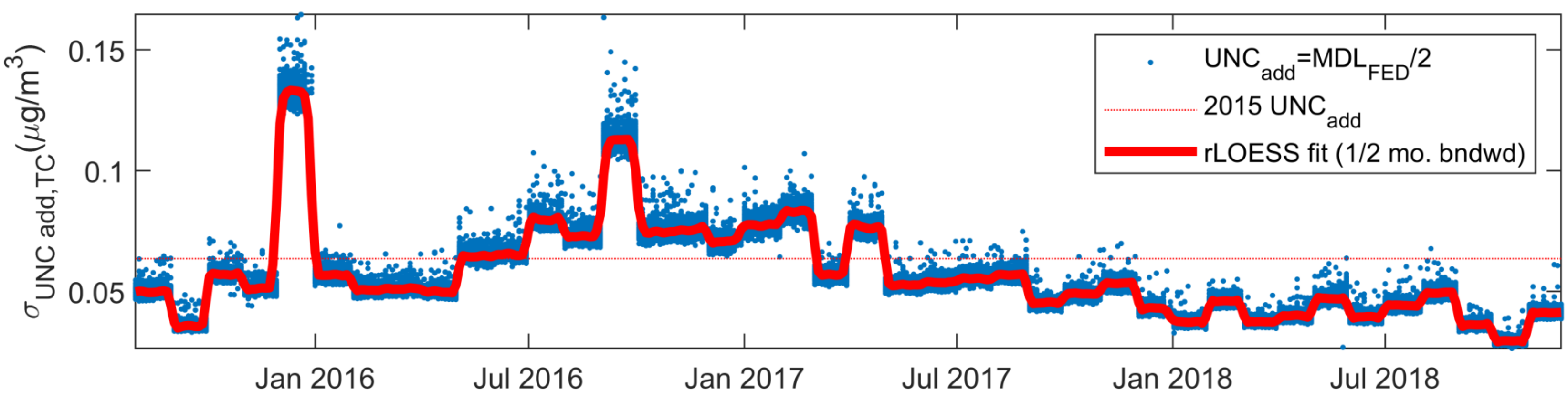
Hyslop, N.P. and W.H. White, *Estimating precision using duplicate measurements. Journal of the Air & Waste Management Association, 2009.* ***59(9): p. 1032-1039.***

Current Approach:
Fed Download, fit, interpolate (round 1)

- According to IMPROVE (DRI) SOPS we can use…
  - Therefore, as we showed on previous slide…

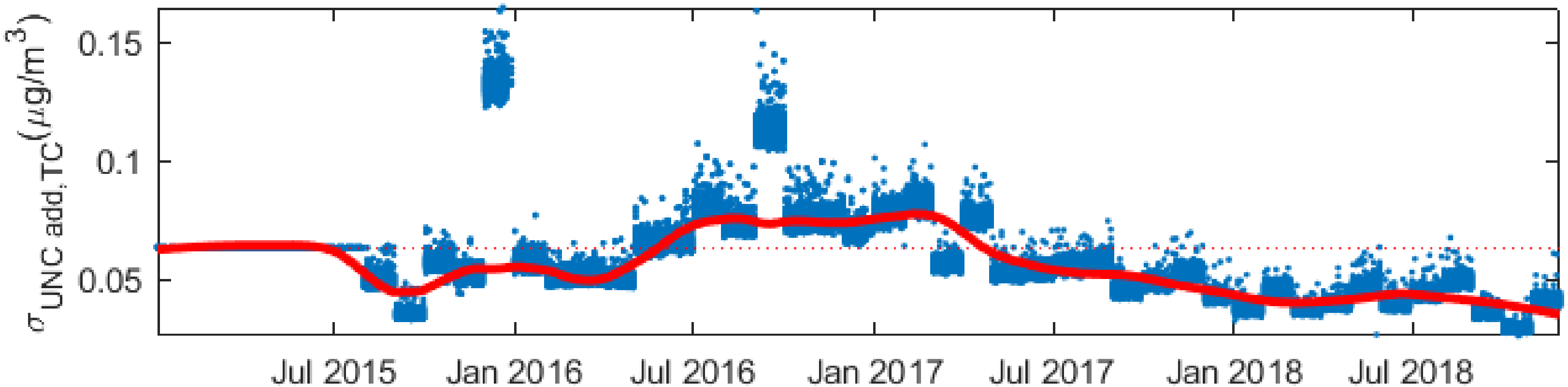
$$\hat{u}_{add} = MDL/2$$

- Since MDLs are not associated with each sample, let's fit a function (smoother) to the time series and then ***find uncertainty for each sample via interpolation***
  - First, used a robust smoother with an ½ month bandwidth to eliminate (false) jumps in uncertainty (red line)
    - Nice piecewise behavior– probably not physically realistic
  - MDLs were not available for OC,EC,TC from Jan.-Aug. 2015→ used a constant value (not shown) from our database over this range (red dashes)



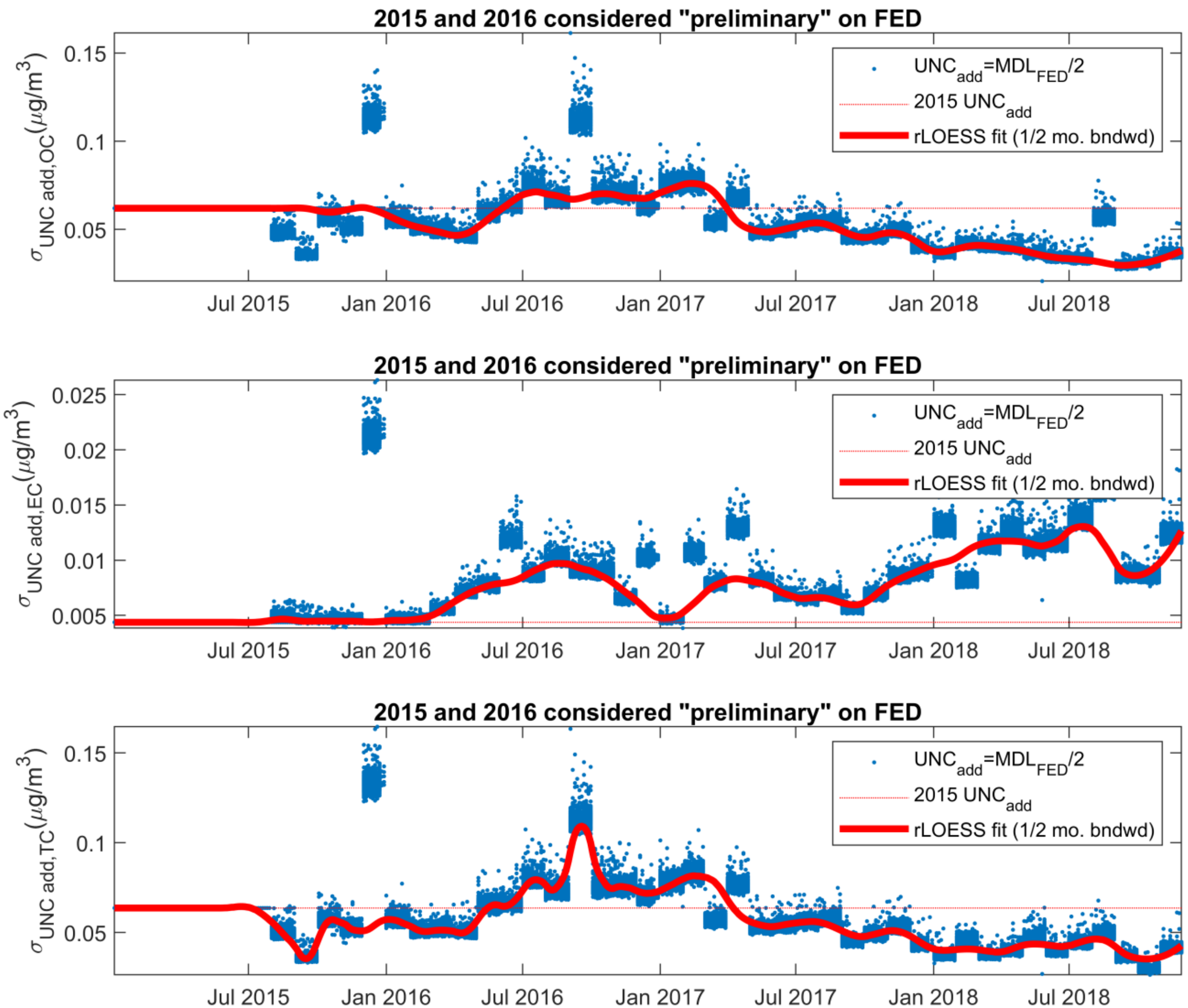
Better approach: 8mo bandwidth

- Certainly appears more reasonable to assume a smoother series
    - ***Downward trend in uncertainty starting ~Jan. 2017***
    - DRI changed FID to IR detector
- But does that seem reasonable?
    - Is this the real life, or is this just fantasy?*



*- F. Mercury et al. 1975

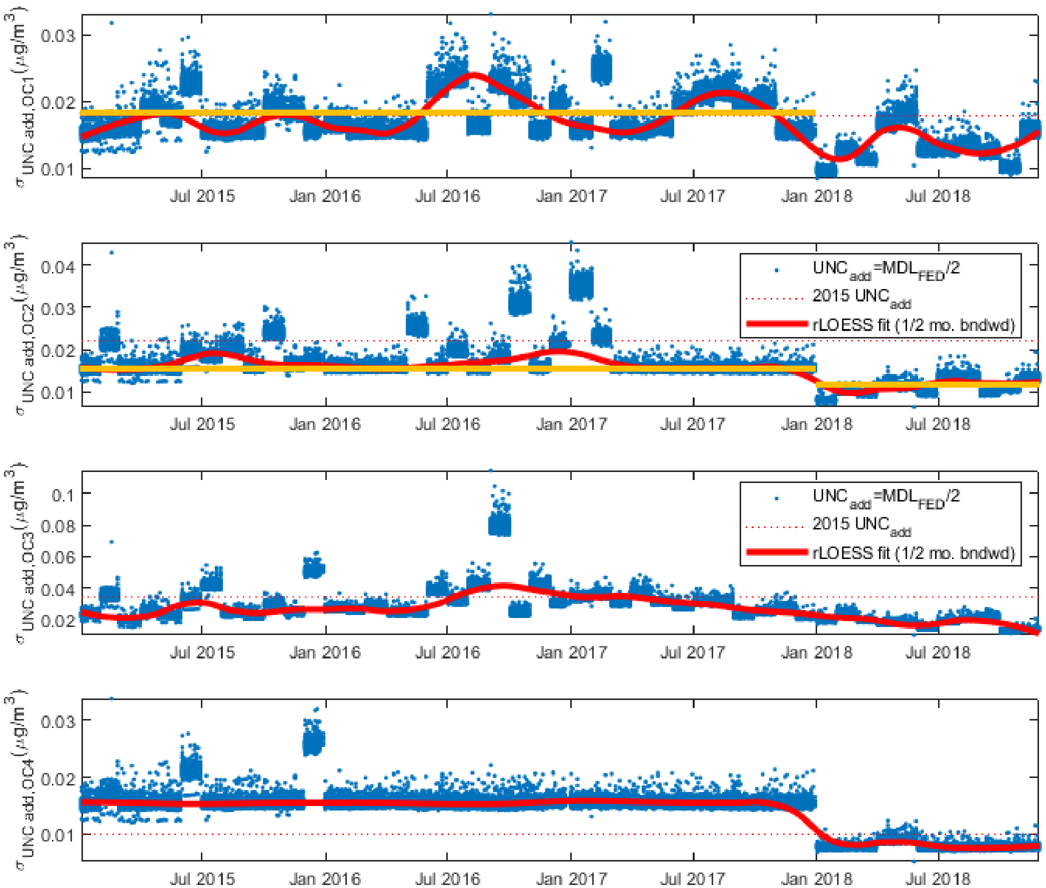
Looking at OC,EC, and TC



- OC additive uncertainty ***decreases***
- EC additive uncertainty correspondingly ***increases***
- Interesting since these uncertainties probably should not be *physically* coupled, perhaps?
- Furthermore, what explains an increase in EC additive error?
- **Review sources of additive error in TOR**

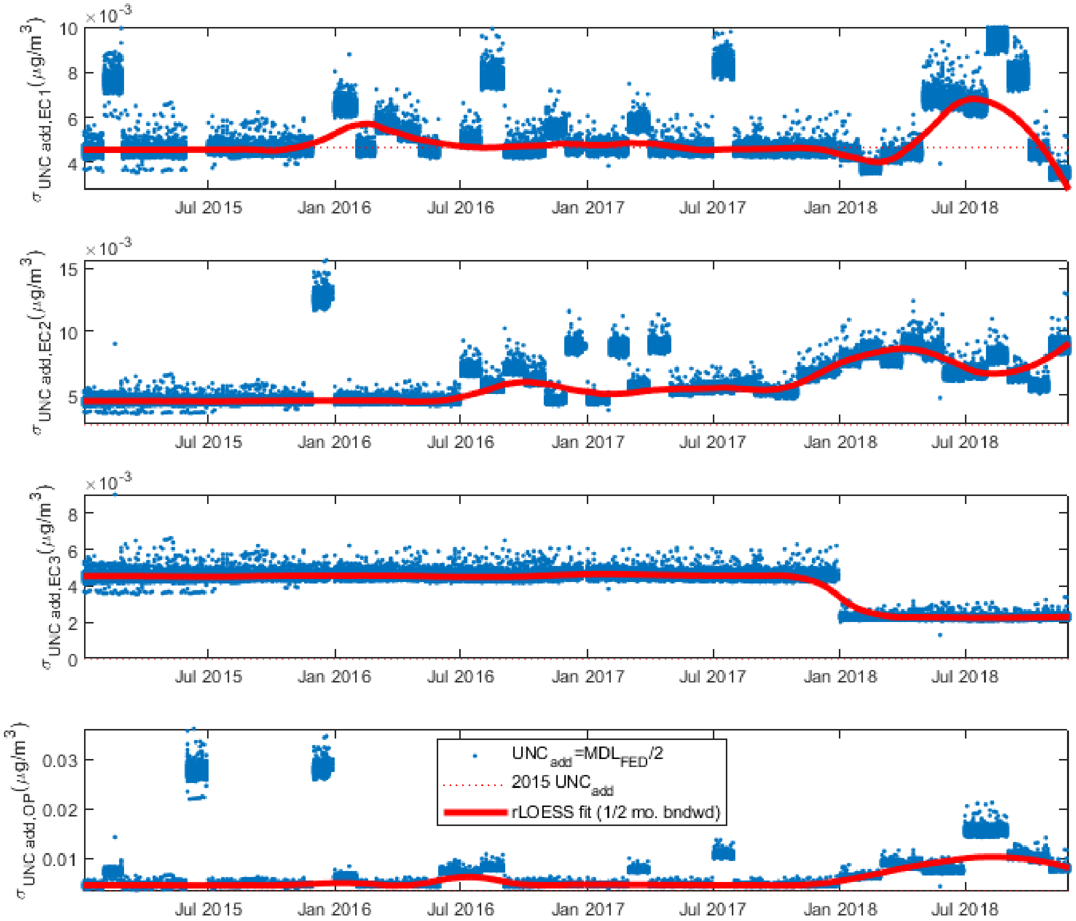
Additive Uncertainty in OC fractions

- Some calculation methodology probably changed in 2018– according to OC4
- Could explain some or all of the downward “trend”



Additive Uncertainty EC Fractions

- Calculation methodology probably changed in 2018– clearest in EC3
  - Could explain some or all of the upward "trend"



Section 3:
A Model for EC and OP Attenuation?

- Chow et al. (2004) presents the following (simple) model of attenuation whereby EC and OP may be determined from He-Ne transmittance– in the TOR oven– according to the following governing equation…

$$[\mathrm{Carbon}]_{\mathrm{after}\ O_2} = [\mathrm{EC}] + [\mathrm{OP}] = \frac{\tau_{\mathrm{attn,EC}}}{E_{\mathrm{a,EC}}} + \frac{\tau_{\mathrm{attn,OP}}}{E_{\mathrm{a,OP}}}$$

$$\tau_{\mathrm{attn,EC}} = -\ln\left(\frac{T_i}{T_f}\right) \qquad \tau_{\mathrm{attn,OP}} = -\ln\left(\frac{T_{\min}}{T_i}\right)$$

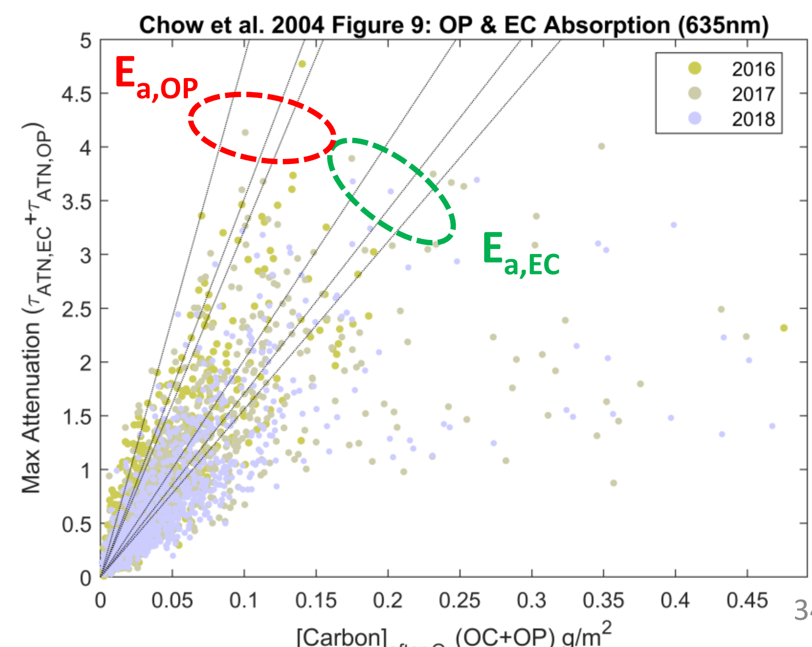
- Perform a linear regression as…

$$\mathbf{y} = [\mathrm{EC}] + [\mathrm{OP}]$$

$$[X] = [\tau_{\mathrm{attn,EC}} \quad \tau_{\mathrm{attn,OP}}]$$

$$\boldsymbol{b} = \left[\frac{1}{E_{\mathrm{a,EC}}} \quad \frac{1}{E_{\mathrm{a,OP}}}\right]$$

"MAC" (m^2/g)

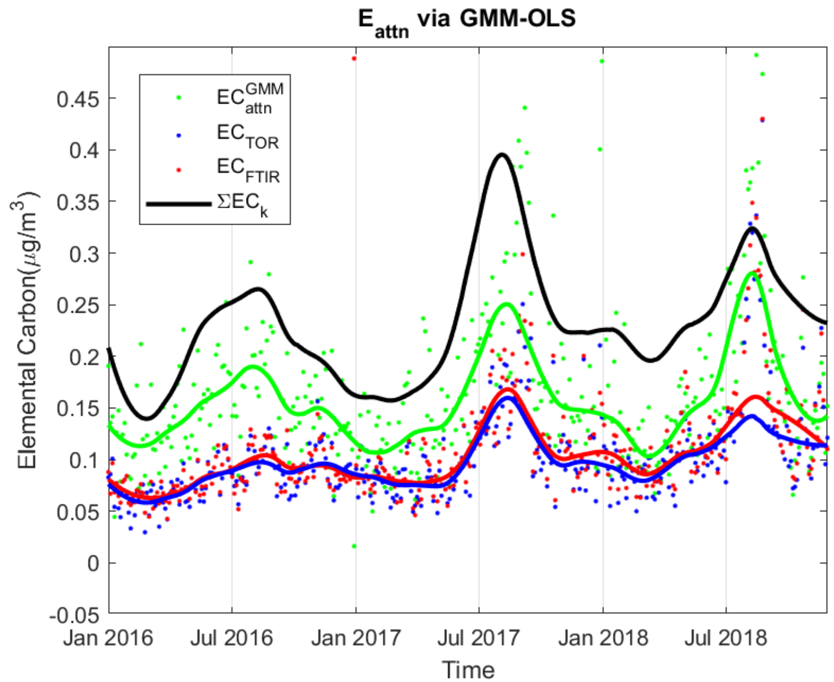


Chow, J.C., et al., *Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols. Environmental Science & Technology, 2004.* ***38(16): p. 4414-4422.***

A Final Question: FT-IR and TOR Stability

- Will ***FT-IR*** affect long-term trends if *substituted* for ***TOR*** relative to *possible* uncertainties in ***OP estimates***?
  - Daily medians plotted

- ***Estimated EC*** using oven laser transmittance (= **EC_{attn}**)*
  - …via methods developed in Chow et al. 2004.
  - Details in Section S3 for Supp. Mat.



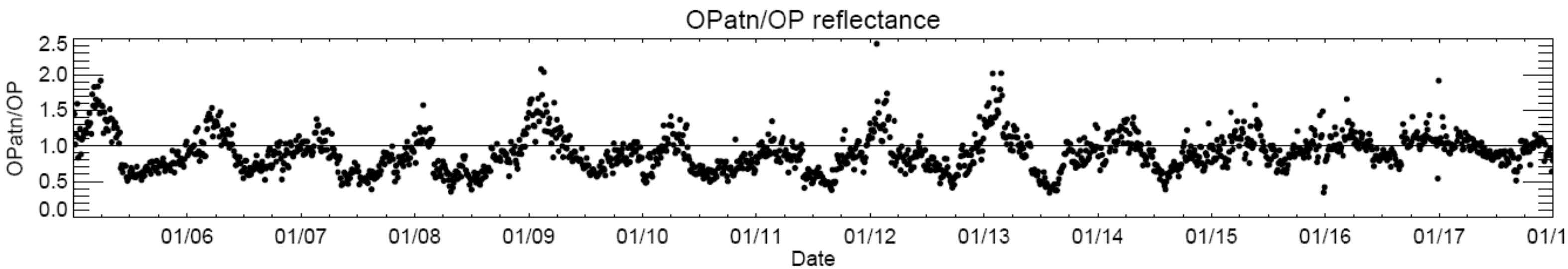
Perhaps FT-IR biases– relative to TOR– are much smaller than differences in measured EC compared to true atmospheric EC?

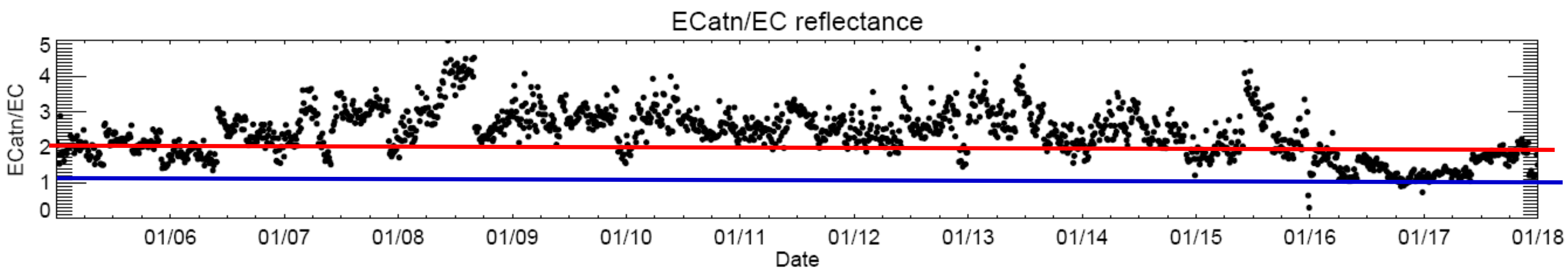
Chow, J.C., et al., *Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols. Environmental Science & Technology, 2004.* ***38(16): p. 4414-4422.***

Thanks Jenny Hand☺

Context II: Daily network median ratios of OP_{atn}/OP and ECatn/EC (from "TOR Optical Analysis", J. Hand, 8/30/19)

$$EC_{attn} = x_1 b_1 = \frac{\tau_{attn,EC}}{E_{a,EC}} \qquad OP_{attn} = x_2 b_2 = \frac{\tau_{attn,OP}}{E_{a,OP}}$$





- Jenny Hand shows…
  - EC is slightly overpredicted in 2016-2018 (~10-100%, perhaps): 1 is ideal on bottom fig
  - Jenny performed OLS regressions by first grouping samples by season and region

Section 3:
Cluster Analysis and then Regression for MACs?

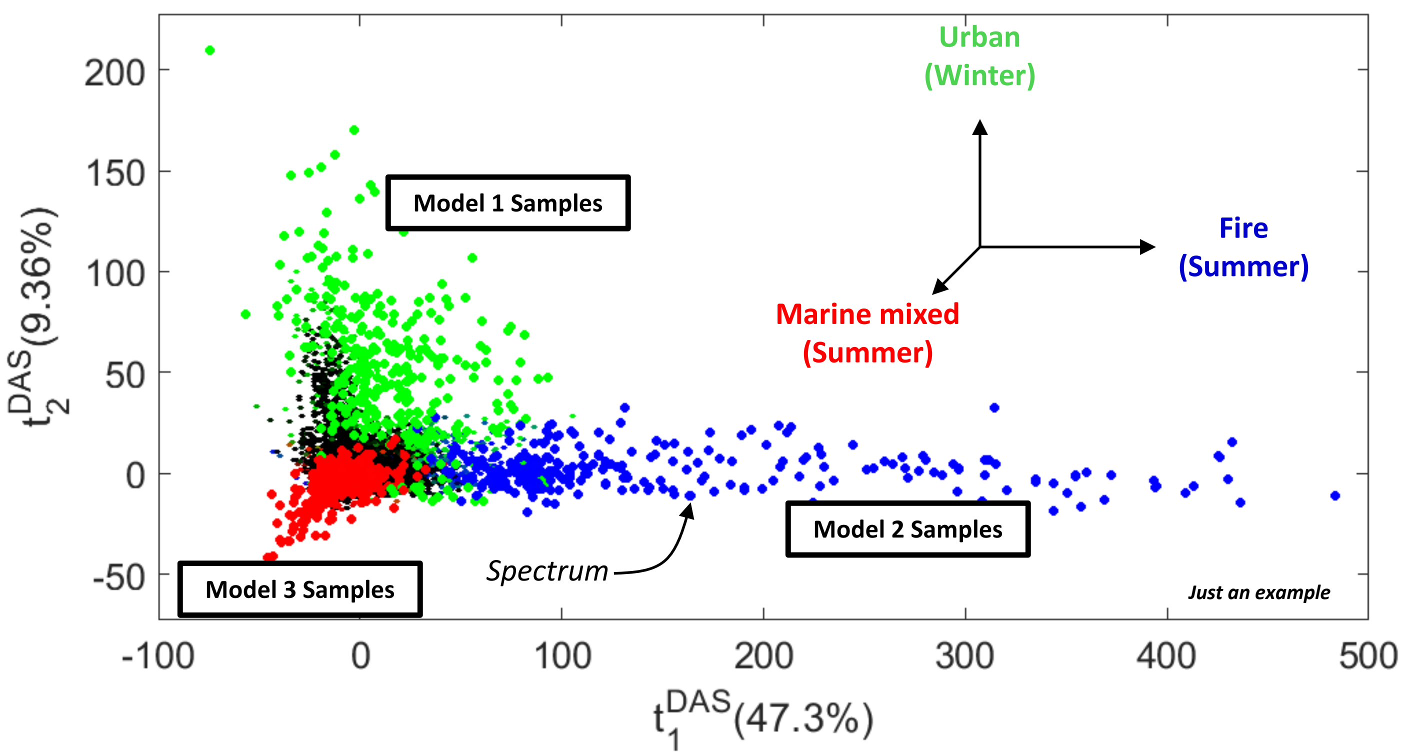
Thoughts:

- Perhaps we can bring something similar to the table with our Gaussian Mixture Model (GMM) cluster analysis

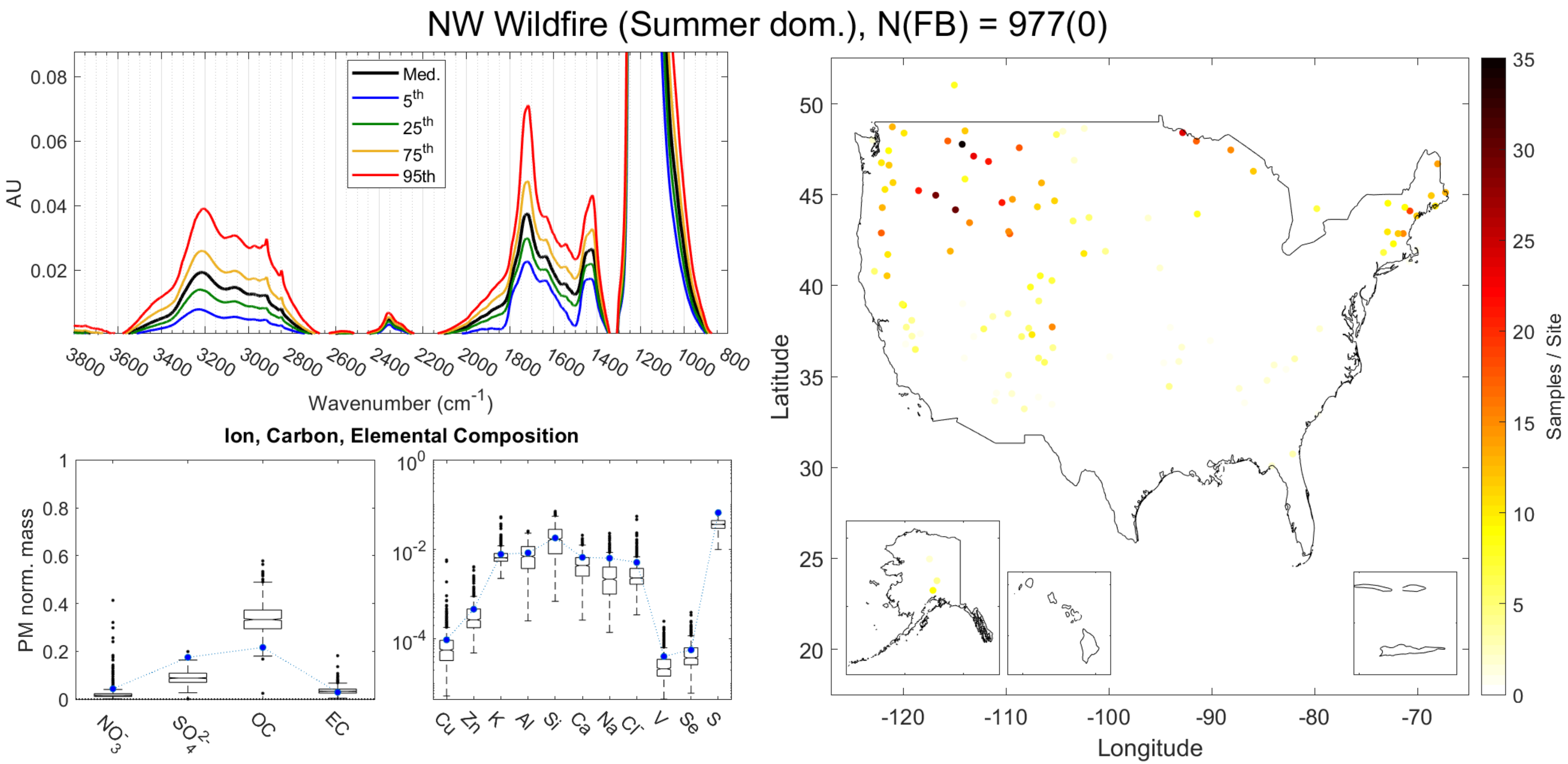
Gaussian Mixture Modeling (GMM): Basically clustering before regression

Big point: use source attribution(ish) information to homogenize EC_{attn}, OP_{attn} regressions

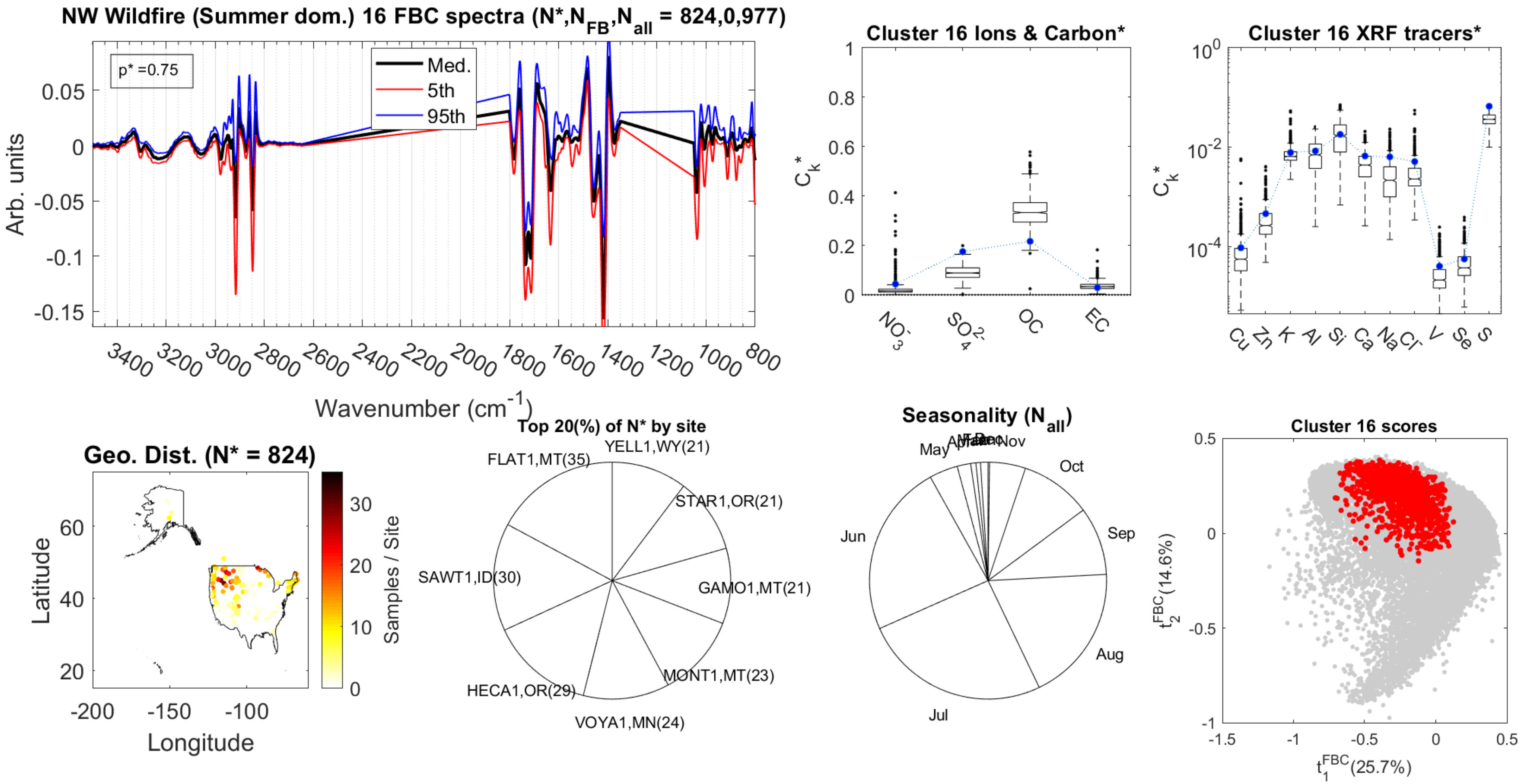
1. GMM already developed from IMPROVE 2015 FT-IR spectra (**21 clusters**)
2. Apply GMM to 2016-2018 spectra→ place samples into clusters
3. Develop a regression for each cluster (**21 models**) using OLS, WLS, IRLS in turn
4. Check out the estimated MACs, time series, etc.



Refresher: A Typical GMM Cluster
Essentially Region + Season Dependence

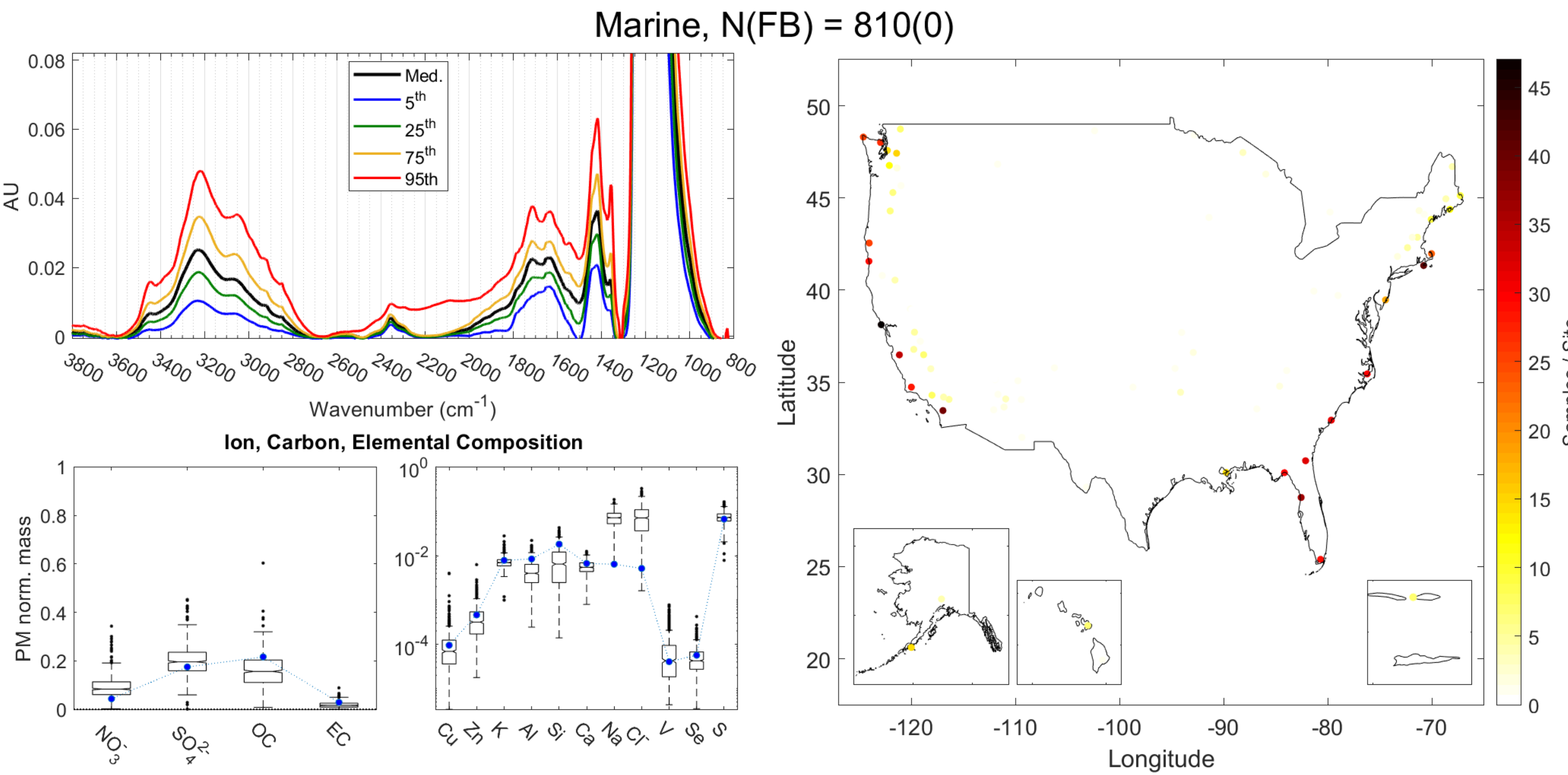


Update 10/10:
More Details about NW Wildfire Cluster

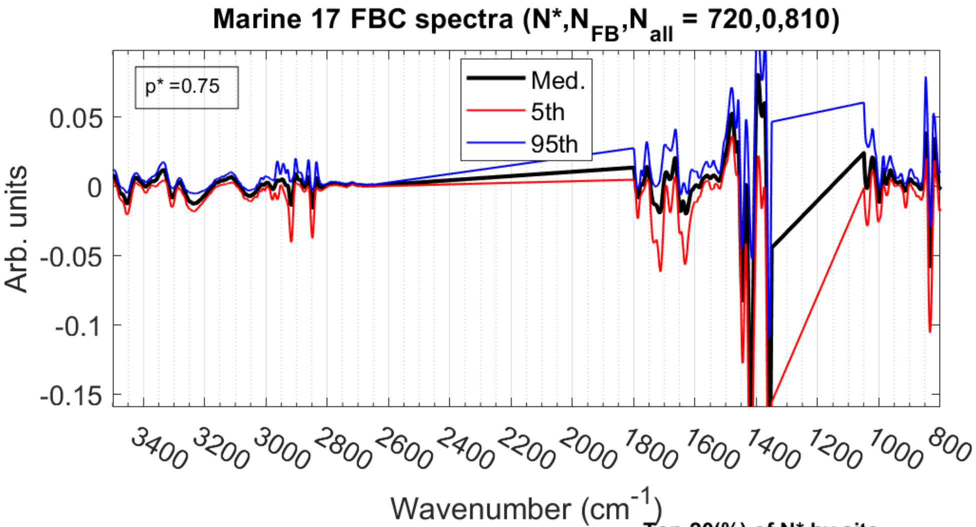


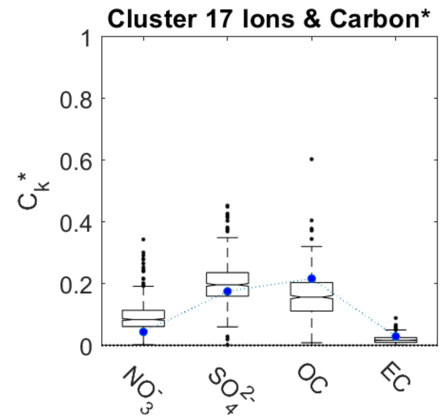
Asterisk *- denotes samples with at least a 75% chance of being in this cluster over any other cluster

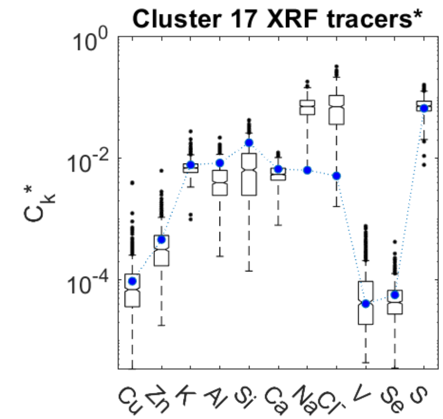
Refresher: Atypical Non-regional/seasonal Cluster

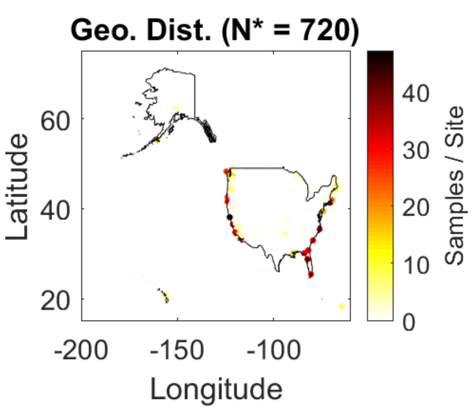


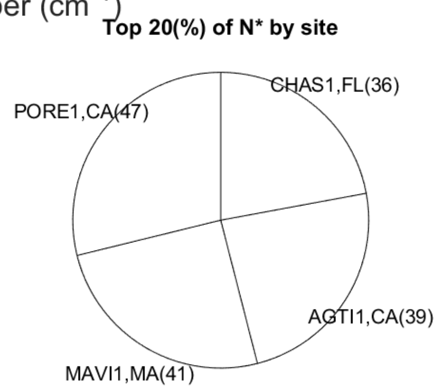
Update 10/10:
More Details about Marine Cluster

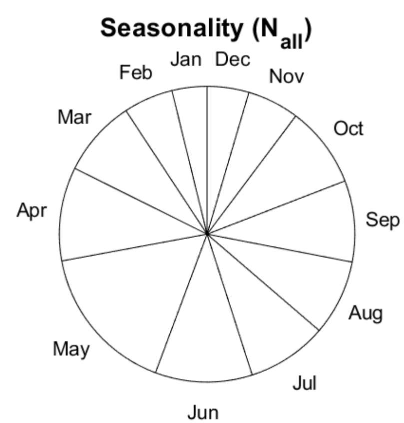


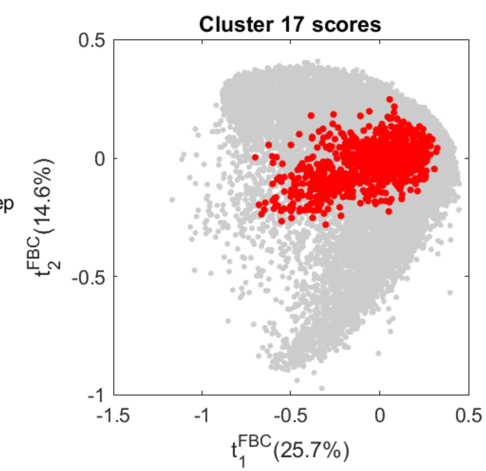








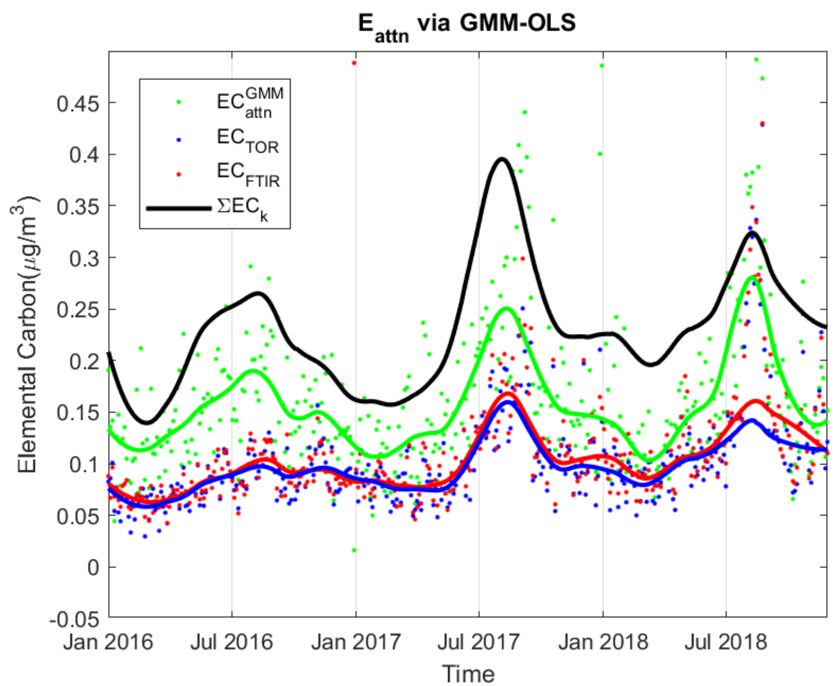




Asterisk *- denotes samples with at least a 75% chance of being in this cluster over any other cluster

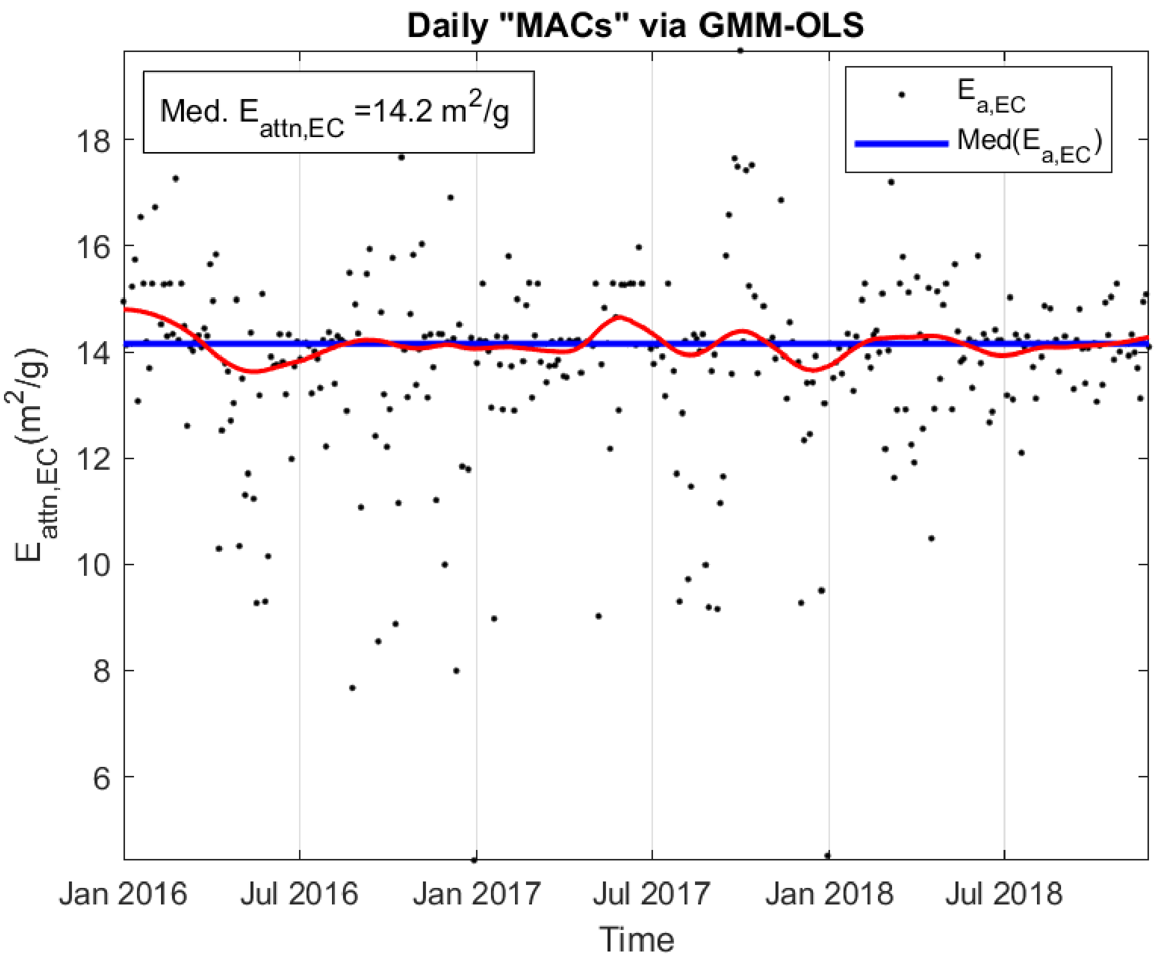
GMM-OLS Regressions

- Does the GMM route matter to trends?
  - Certainly follows general shape of TOR and FTIR OC series more closely
  - Best to do GMM-OLS over OLS (time only)



GMM-OLS: Return of the MACs?

- I could show you 21 “MACs”… one for each cluster
- Instead, **GMMs allows calculation of “MACs” ($E_{a,EC}$) on a per sample basis using a weighted average scheme**



How can you get a “MAC” for each sample from a GMM?

Gist: **Use GMM to *average* the cluster-model MACs to give a MAC for each sample**

First: Predict EC for a sample (*i*) using all *K* cluster models

- Each IMPROVE sample therefore has 21 EC predictions given K=21 clusters calculated
  - Let’s also call Chow’s “$E_{a,EC}$” = “MAC”

$$EC_{attn,(i,k)} = \frac{\tau_{i,EC}}{MAC_k}$$

$$\tau_{attn,EC} = -\ln\left(\frac{T_i}{T_f}\right)$$

Dropped “attn”
Indexed on sample *i*

- Example: EC_{attn} predicted from cluster 1 model for sample *i* is given as…

$$EC_{attn,(i,1)} = \frac{\tau_{i,EC}}{MAC_1}$$

For cluster 10 model…

$$EC_{attn,(i,10)} = \frac{\tau_{i,EC}}{MAC_{10}}$$

And so on…

How to get a “MAC” for each sample

Second:

- Find (posterior) probabilities, ***p(k)***, of belong to cluster
- Use to calculated ***a weighted average of EC predictions***

$$EC_{attn,i} = p_1 \frac{\tau_{i,EC}}{MAC_1} + \cdots + p_{21} \frac{\tau_{i,EC}}{MAC_{21}}$$

$$EC_{attn,i} = \sum_{k=1}^{21} p_k \frac{\tau_{i,EC}}{MAC_k}$$

Comments:

1. What’s nice about probabilities: they live between 0 and 1
2. Formula makes intuitive sense: the “closer” a sample is to a cluster, the higher the likelihood (*p(k)*) it has the mass attenuation associated with that cluster
3. Alternatively, if a sample is close to several clusters it’s MAC may be a sort of “simple average” of those MACs
   - Causal point: the clusters themselves should make sense from a chem. phys. standpoint for the model to be more than an exercise in linear algebra. ☺

How to get a "MAC" for each sample

<u>Third:</u> Separate *k* and *i* terms and reduce to find sample specific MAC (MAC_i)

Starting with…

$$EC_{attn,i} = \sum_{k=1}^{21} p_k \frac{\tau_{i,EC}}{MAC_k}$$

Pull tau from the sum…

$$EC_{attn,i} = \tau_{i,EC} \sum_{k=1}^{K} p_k \frac{1}{MAC_k}$$

Let the following be the MAC for sample *i*

$$(MAC_i)^{-1} = \sum_{k=1}^{K} \frac{p_k}{MAC_k}$$

Sample MAC is therefore…

$$MAC_i = \left(\sum_{k=1}^{K} \frac{p_k}{MAC_k} \right)^{-1}$$