IMPROVE Carbonaceous Aerosol Data: LAC underestimation TC-fabs

Recall Bill's 2018 discussion

- Heuristic argument that TOR LAC (EC) is significantly underestimated by ~ 30%

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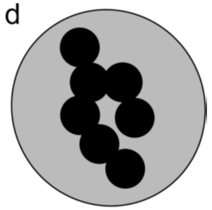
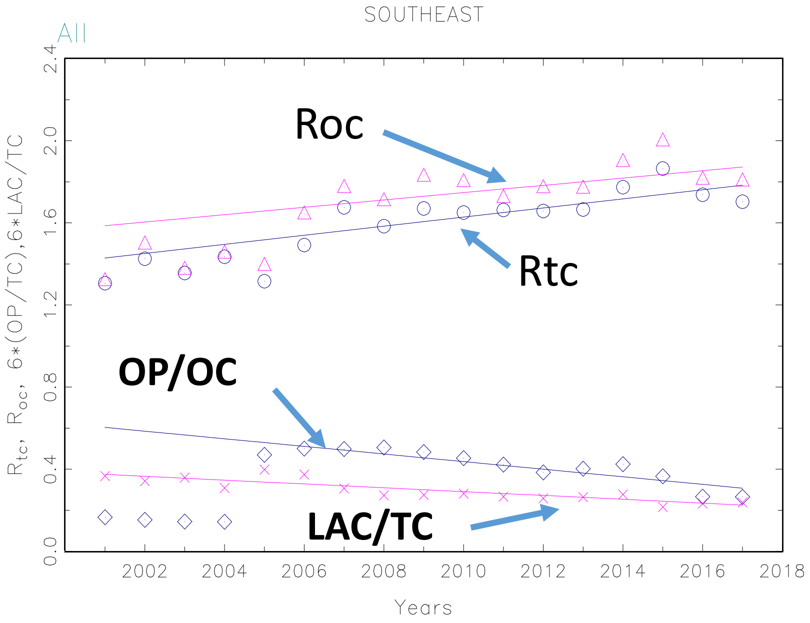
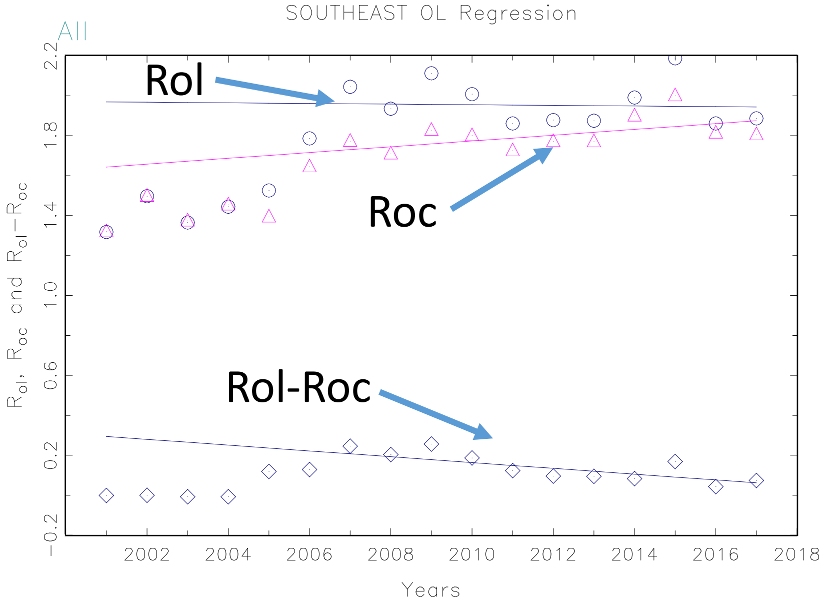




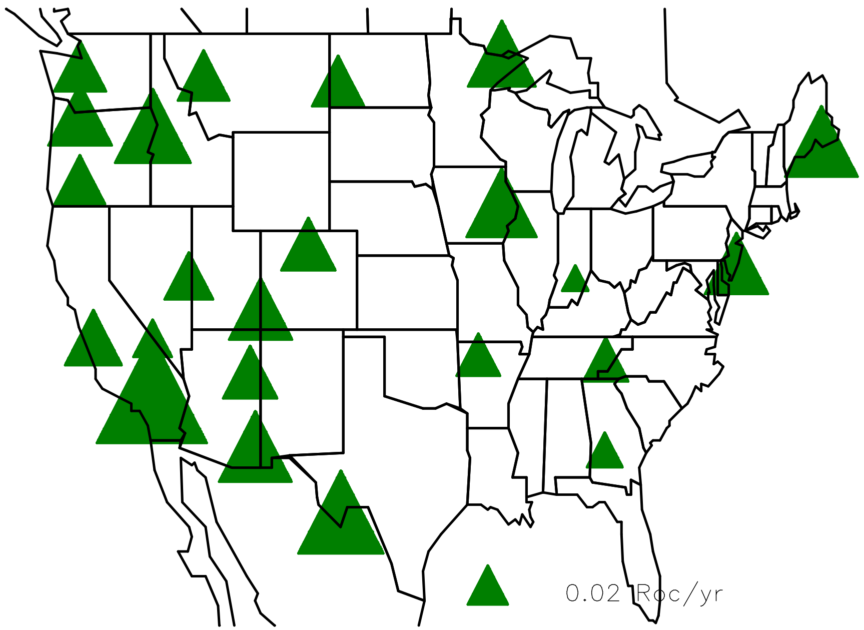


- Roc and Rtc found through regression analyses
- A decrease in the LAC / TC ratio should result in an increase in R_{TC} since $R_{LAC} \approx 1$

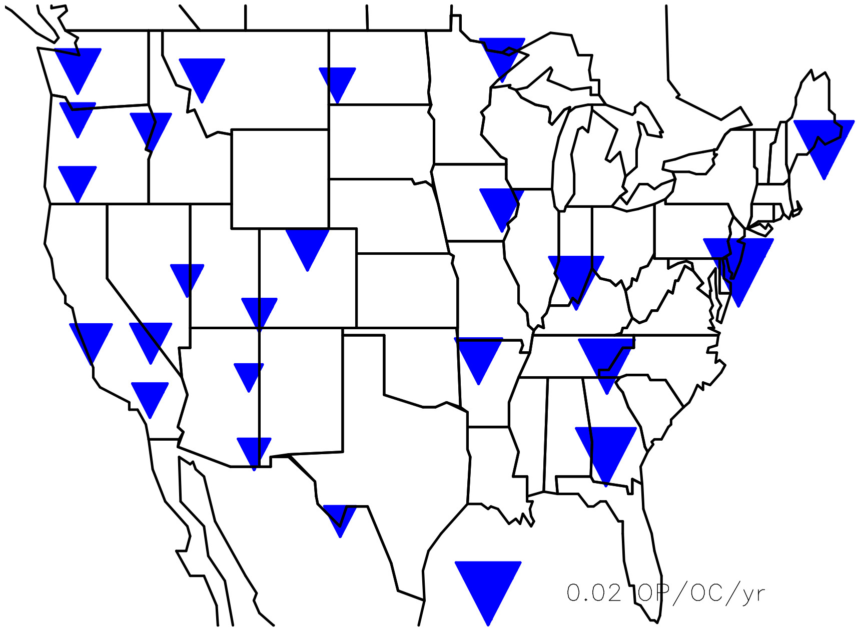
- As LAC/TC decreases R_{TC} increases over time.
- But same trends are observed for R_{OC} and OP/OC **suggesting either OP is a mixture of stuff with lower R or OP has a LAC component.**

- OL=OC-OP is referred to as "low temp carbon".
- $FM=a_1SO_4+a_2NO_3+a_3OL+a_4(SS+LAC+OP+dust)$
- $a_3=R_{ol}$ is approximately constant over 2006-2017
- Difference between R_{ol} and R_{oc} decreases over time consistent with a decrease in LAC fraction of OP.
- R_{oc} is approaching value of R_{ol} implying organic fraction of OP has similar molecular mass as OL.

Rate of Increase in R_{oc}/yr 2008-2017



Trend in OP/OC Ratio 2008-2017



GREEN is positive or increase and BLUE is negative or decrease

- R_{oc} is increasing across entire United States.
- And OP/OC is decreasing across entire U.S with the highest rate of decrease in the Eastern U.S.
- If OP contains low R carbon and LAC is underestimated a decrease in OP/OC is consistent with R_{oc} increasing.

Estimating the fraction of OP that is OC

OC = OL + OP + LAC

OMC = R_{oc}*OC = R_{oc}(OL+OP)

OMC = R_{ol}(OL + f*OP)

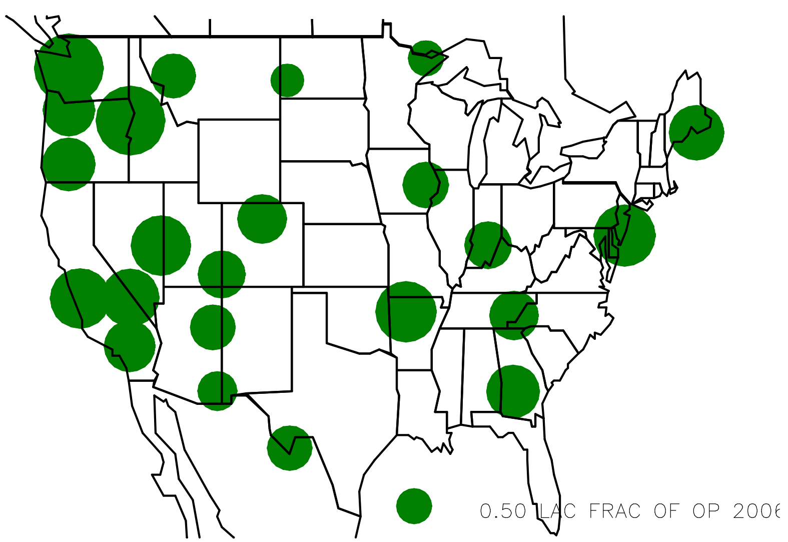
Where f is the fraction of OP that is OC and (1-f)OP is fraction of OP that is low R carbon (LAC?).

Therefore **R_{oc}*(OL+OP)= R_{ol}*(OL+f*OP)** and solving for f yields

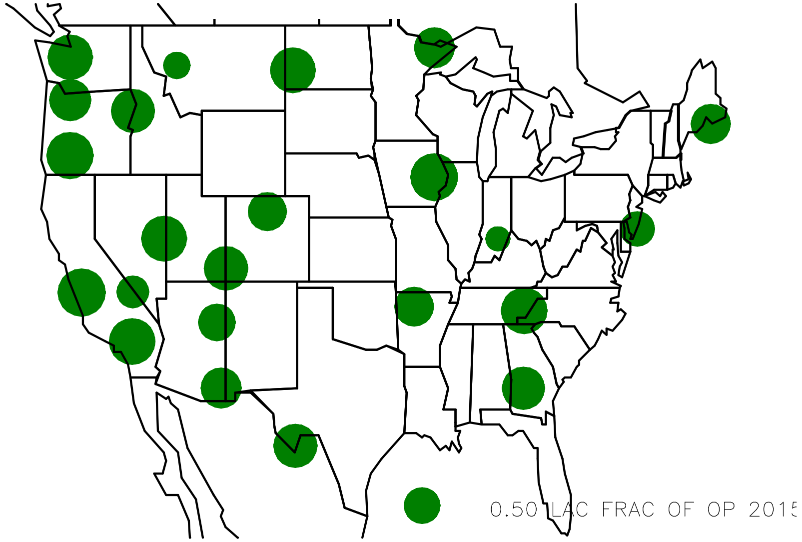
$$f = \frac{OL(R_{oc} - R_{ol}) + OP(R_{oc})}{OP(R_{ol})}$$

Fraction of OP that is LAC

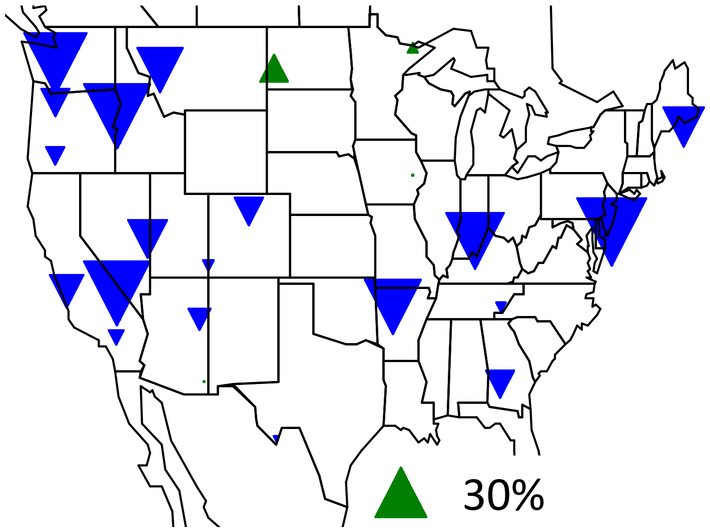
Year 2008-2009



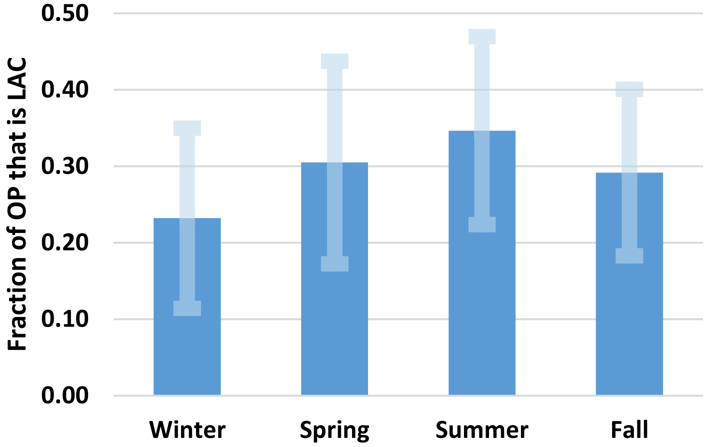
Year 2016-2017



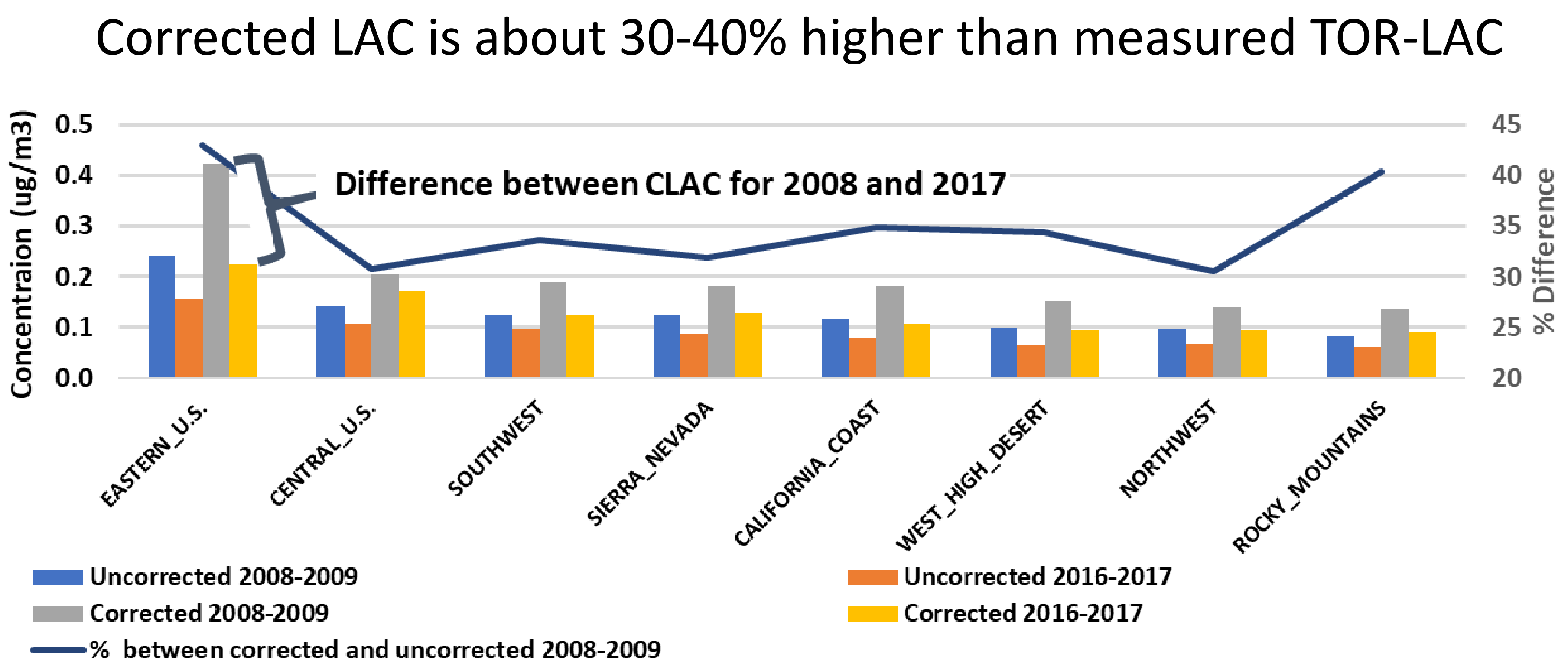
The fraction of OP that is LAC has gone down from 2008 to 2017.



Seasonal dependence of average 2008-2017 fraction of OP that is LAC

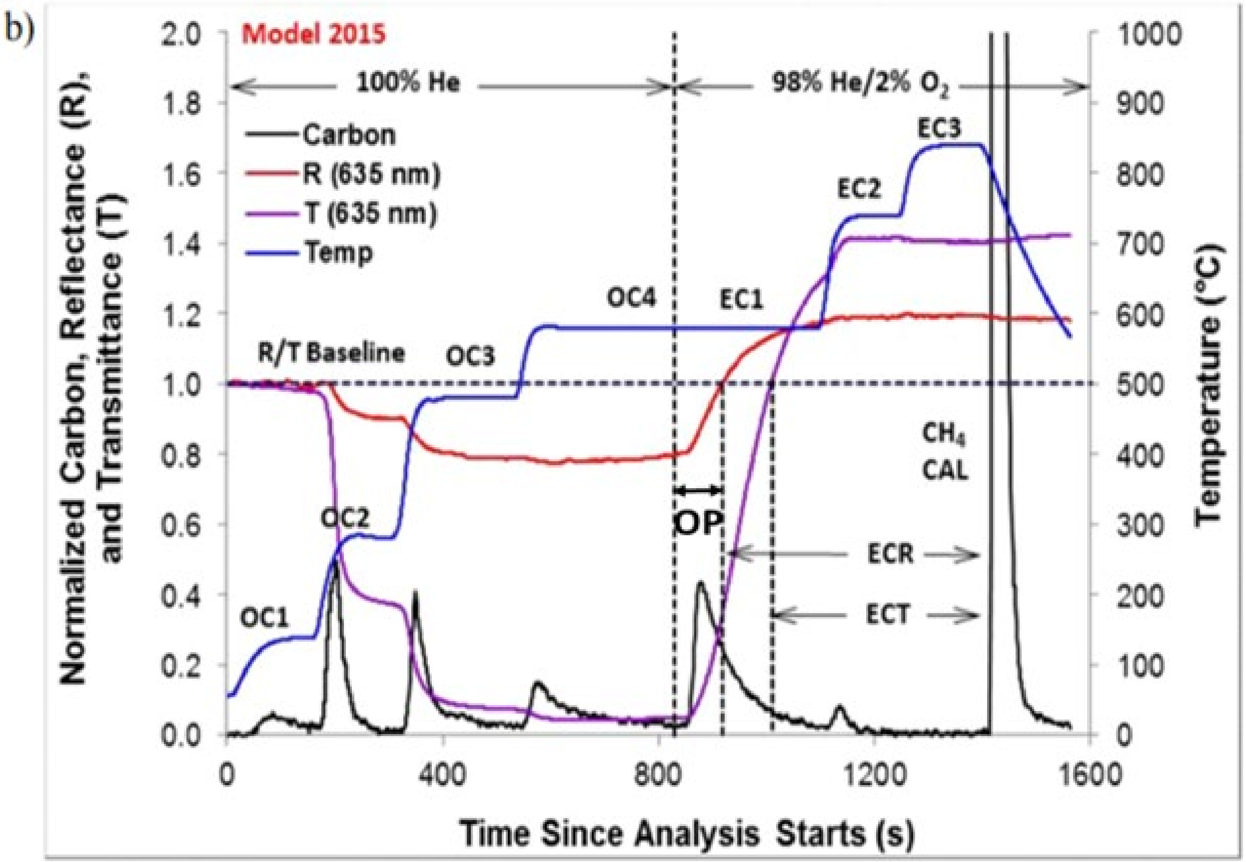


TOR-LAC Compared to Corrected LAC



The average measured or uncorrected LAC as well as the corrected LAC, CLAC, concentrations are shown for 2008-2009 and 2016-2017 for each of the eight regions. The blue line represents the % difference between corrected and uncorrected 2008-2009 CLAC concentrations.

Thermal Optical Analysis



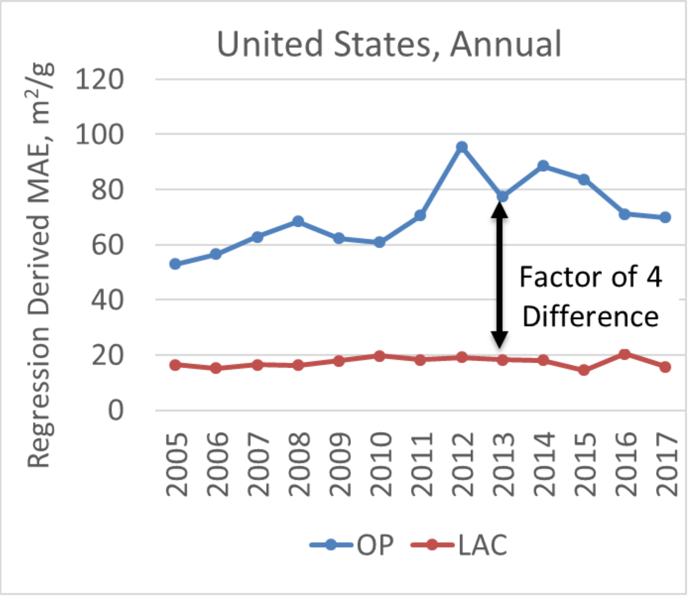
- Inherent assumptions (because we can't calibrate for OC/LAC)
  - All non absorbing-pryolized OC volatilizes prior LAC (no OC slip)
  - All OP volatilizes prior to LAC **or** OP and LAC have the same MAE
  - LAC and other aerosol optical properties remain constant during heating
  - The laser signal accounts for all changes in sample absorption
  - Note: negative OP can account for premature volatilization of LAC, e.g. brown carbon or oxidized LAC during heating

Limitations and Issues with TOA

- Early/late volatilization of OC and LAC during analysis
  - Organic carbon may be retained after the He atmosphere and could bias OC/LAC split particularly for low temperature protocols (Boparai et al., 2008)
    - Levoglucosan doped tunnel samples produced significant OC slip for TOT-550 (Subramanian et al., 2006)
    - Any bias is likely sample composition dependent
  - Significant fractions of LAC and OP have been shown in laboratory experiments to evolve in the He atmosphere. (Yu et al., 2002; Subramanian et al., 2006; Boparai et al., 2008)
    - Depends on peak temperature, composition (previous slide)
    - This is seen in IMPROVE thermograms where the reflectance/transmittance increase in He atmosphere (early split) (Chow et al., 2004)
    - **Implications:**
      - **OP does not necessarily volatilize before LAC**
      - **The OC-LAC split depends on the similarity and stability of the optical properties of native and char LAC**

Limitations and Issues with TOA

- Mass absorption efficiency (*k*) of OP >> EC
  - Regression Analysis on IMPROVE data
    - Chow04
      - *k*ec ~ 20 m2/g   *k*op ~50 m2/g
    - Hand current work
      - *k*ec ~ 15 m2/g   *k*op ~70 m2/g
  - From lab generated/manipulated samples
    - Subramania06
      - *k*ec ~ 22.9 ± 5.4 m2/g   *K*op ~ 35.2 ± 12.7 m2/g
    - Boparai08
      - *k*ec ~ 6 + filter transmittance dependence (later slide)
      - *K*op ~ 46.2 ± 4.4 m2/g
  - Note, *k*ec and *k*op will vary and depend on the aerosol composition, measuring wavelength, and other parameters



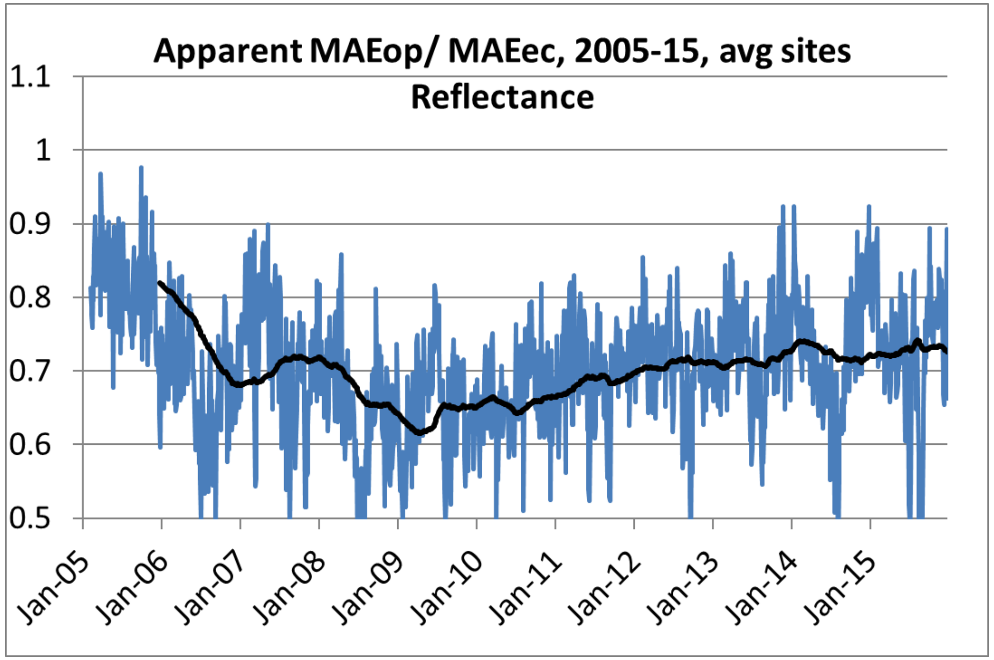
LAC and OP MAE derived by OLS regression of OP+LAC against transmittance (Chow04)

$$[\text{carbon}]_{\text{after O}_2} = [\text{EC}] + [\text{POC}] = \frac{\tau_{\text{ATN,EC}}}{E_{\text{a,EC}}} + \frac{\tau_{\text{ATN,POC}}}{E_{\text{a,POC}}} \quad (5)$$

The regression results suggest trend in OP MAE which would cause a trend in the OC/LAC split

Ratios of Apparent Mass Absorption Efficiencies

- $MAE_{OP} / MAE_{LAC} = \tau_{ATN,\ OP} / \tau_{ATN,\ LAC} * LAC/OP$ $\tau_{ATN,\ LAC} = \ln(R_{fnl} / R_{init})$; $\tau_{ATN,\ op} = \ln(R_{init}/R_{min})$



- Apparent MAE of LAC fraction is ~1.5 times larger than OP fraction
  - Carbon with lower MAE (i.e. LAC) is preferentially volatilized before high MAE carbon (i.e. OP)
- Apparent $MAE_{OP} < 3* MAE_{LAC}$ suggesting an underestimation in LAC
- The potential LAC underestimation has a long-term trend

Does TOR Underestimate Light Absorbing Carbon?

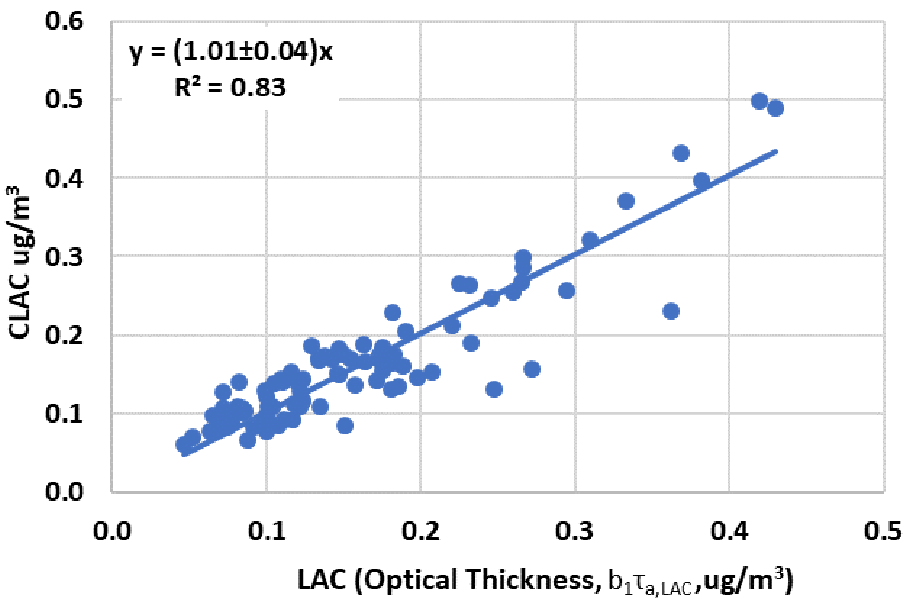
- Appears that OP-MAE should be greater than LAC-MAE
- However, apparent MAE of OP is smaller than apparent MAE of LAC measured with reflectance
- Suggests that IMPROVE TOR LAC is underestimated and OP overestimated
- Supports the Malm et al., analysis. Can this be shown using the TOR optical data?

LAC and OC Optical Apportionment

- Chow et al., 2004: $$[\text{carbon}]_{\text{after } O_2} = [\text{EC}] + [\text{POC}] = \frac{\tau_{\text{ATN,EC}}}{E_{\text{a,EC}}} + \frac{\tau_{\text{ATN,POC}}}{E_{\text{a,POC}}} \quad (5)$$
  - Where
    - [LAC] and [OP] are the measured areal mass concentrations (μg/cm^2)
    - $\tau_{a,LAC}$ and $\tau_{a,OP}$ are the attenuation of light due to [LAC] and [OP], derived from initial, minimum and final transmittance measurements.
    - MAE_{LAC_o} and MAE_{OP_o} are unknown mass absorption efficiencies of LAC and OP
  - Assumptions
    - MAE_{LAC_o}, MAE_{OP_o}, $\tau_{a,LAC}$, and $\tau_{a,OP}$ are relatively constant across filter samples
      - Aerosol optical properties are relatively constant
      - Filter affects are relatively constant across
      - Minimum and maximum transmittance are detectible and no early OC/EC split
  - MAE_{LAC_o} and MAE_{OP_o} can then be derived from OLS regression analysis
  - Corrected LAC and OC can then be estimated from derived MAEs and measured τs

LAC and OP - Optical Apportionment (Correction)

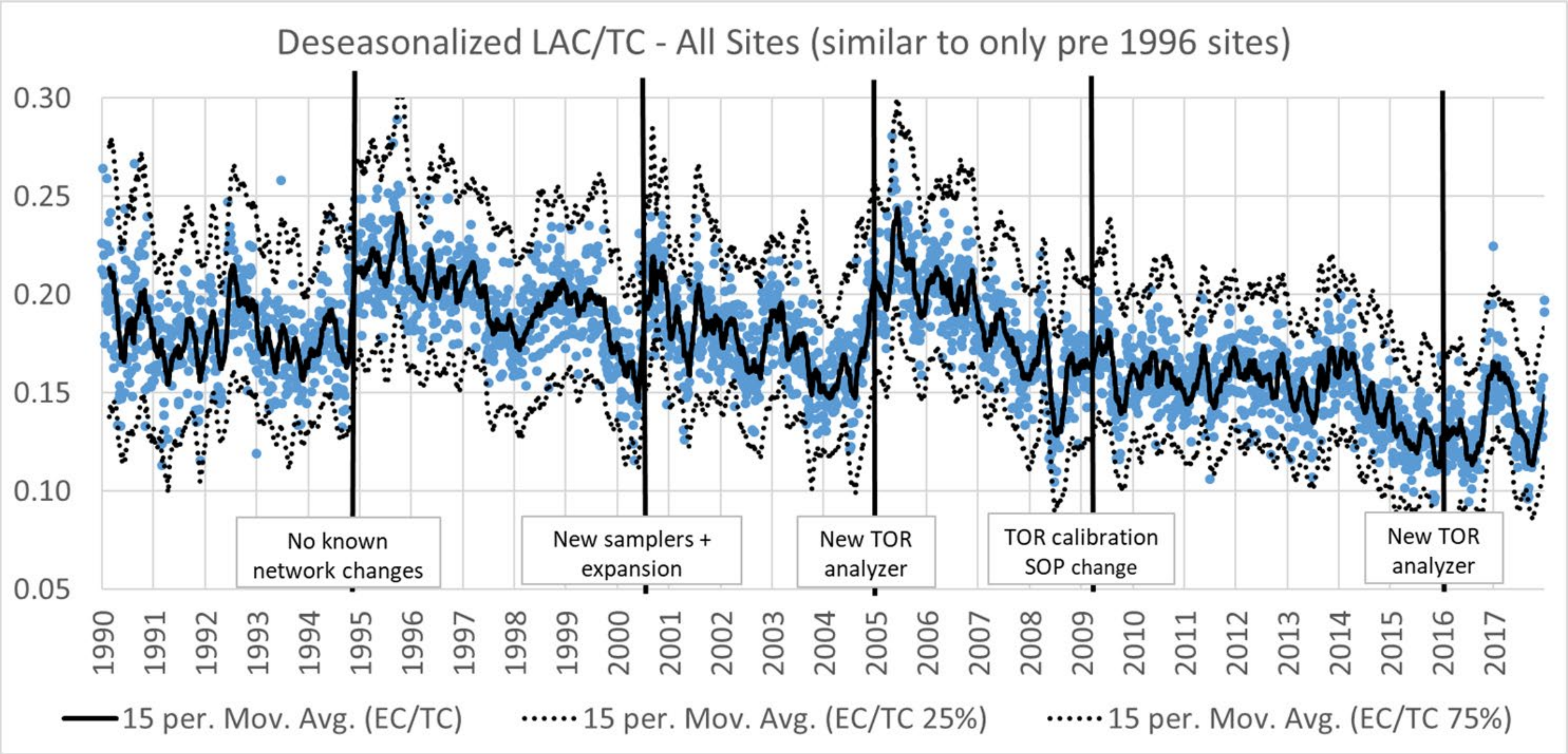
Malm et al. 2019



Chow et al. 2004 $$[LAC] = \frac{\tau_{a,LAC}}{MAE_{LAC_o}} * \frac{A}{V}$$

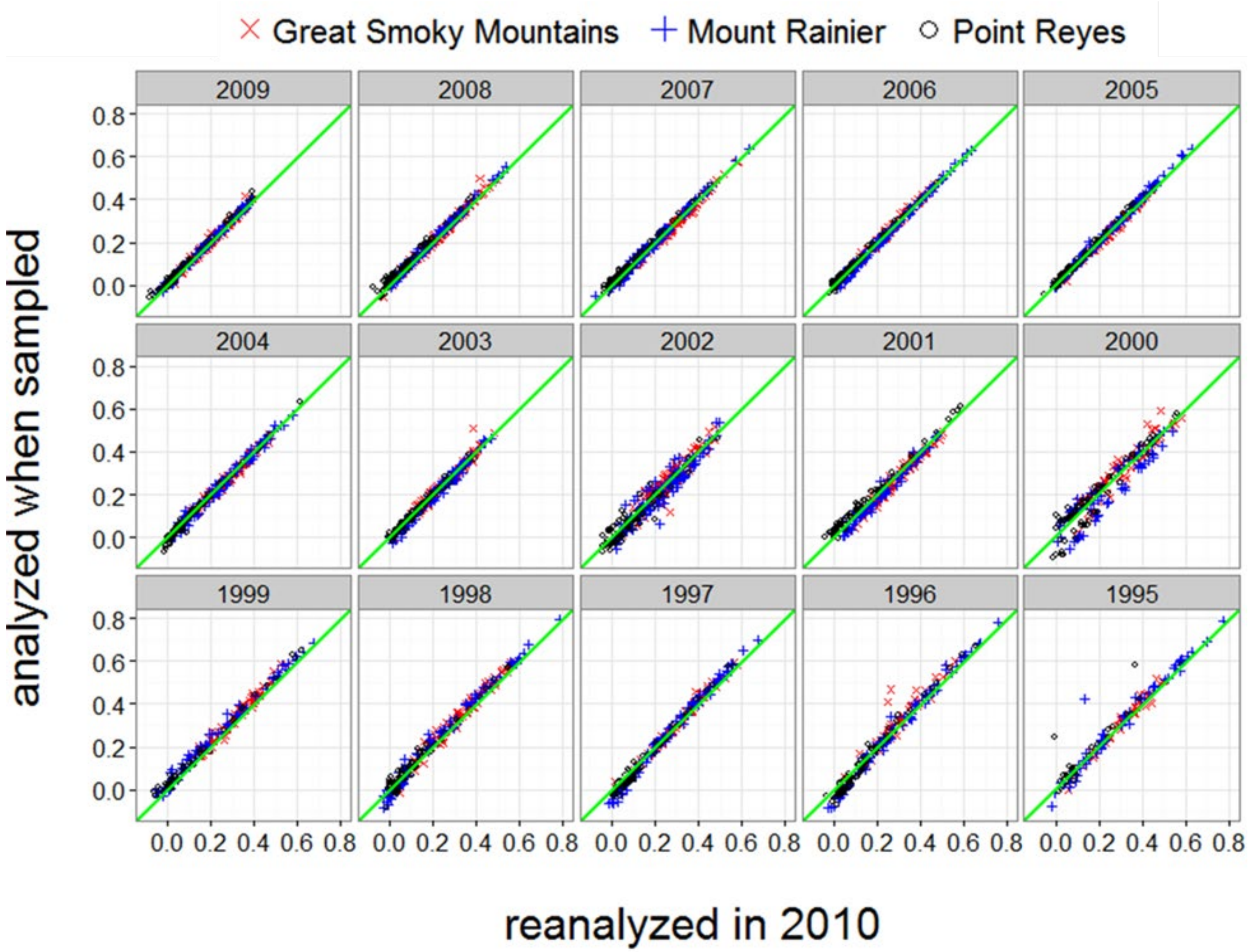
- Conducted regression for each year and one of eight regions of data
- The optical corrected LAC has very good agreement with the corrected LAC with a regression slope near 1
- Further suggests that reported LAC concentrations obtained using TOR is an underestimate of true concentrations by ~30% on average.

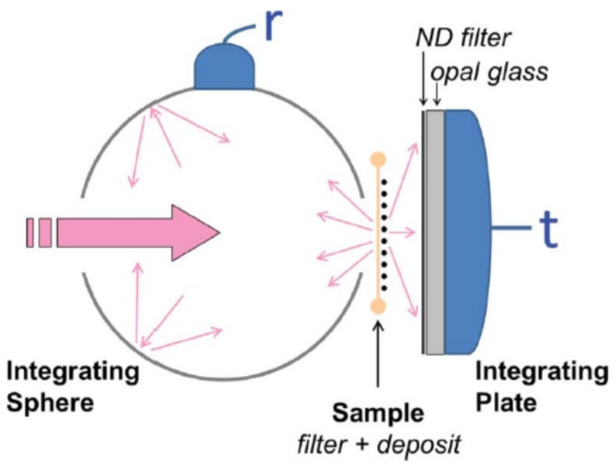
LAC Trends



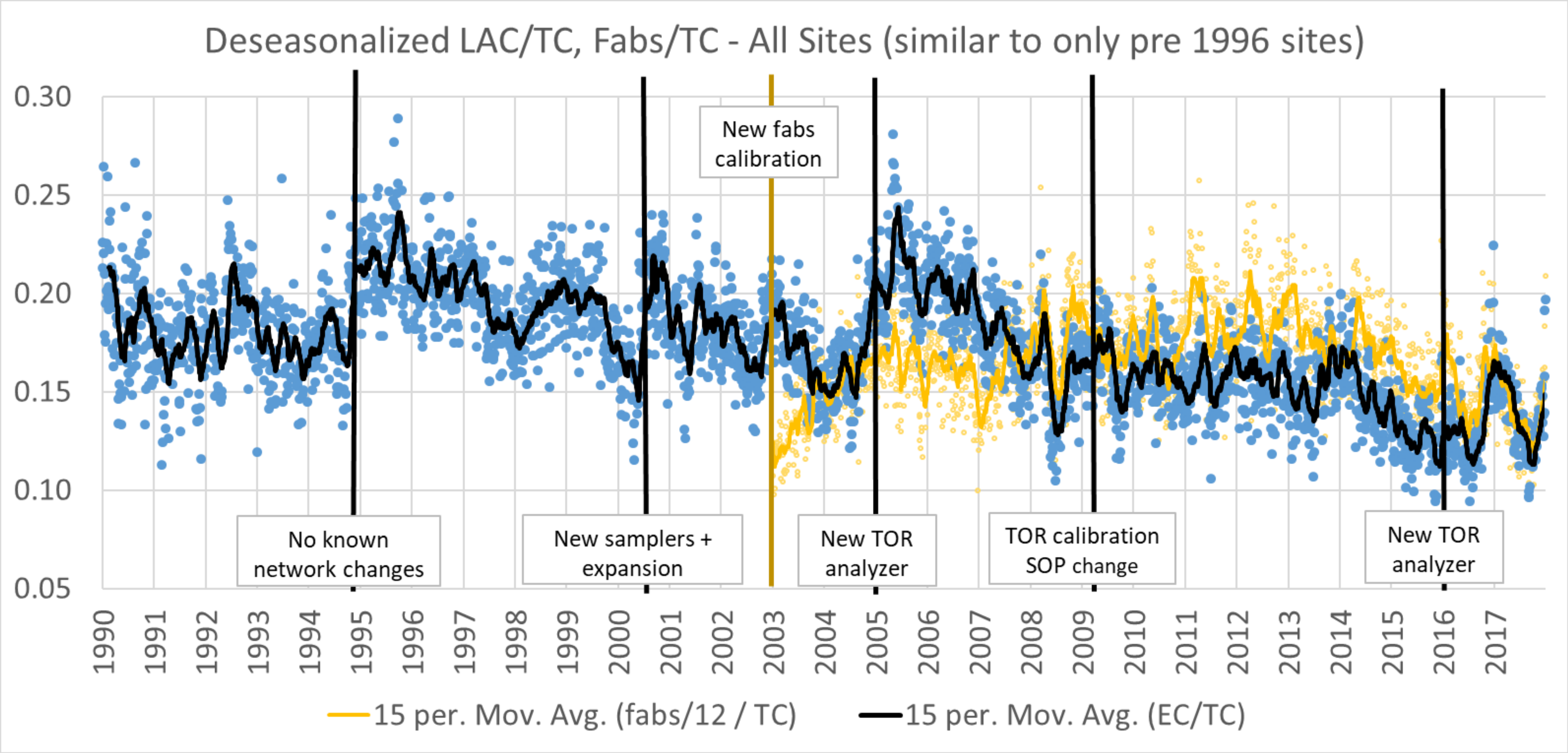
- There are discontinuities and interesting trends in LAC fractions some of which are coincident with network/analyzer changes and trends in TOR-Reflectance (Jenny)
- Are these changes in carbonaceous aerosols and/or potential analytical issues?

Filter absorption HIPS



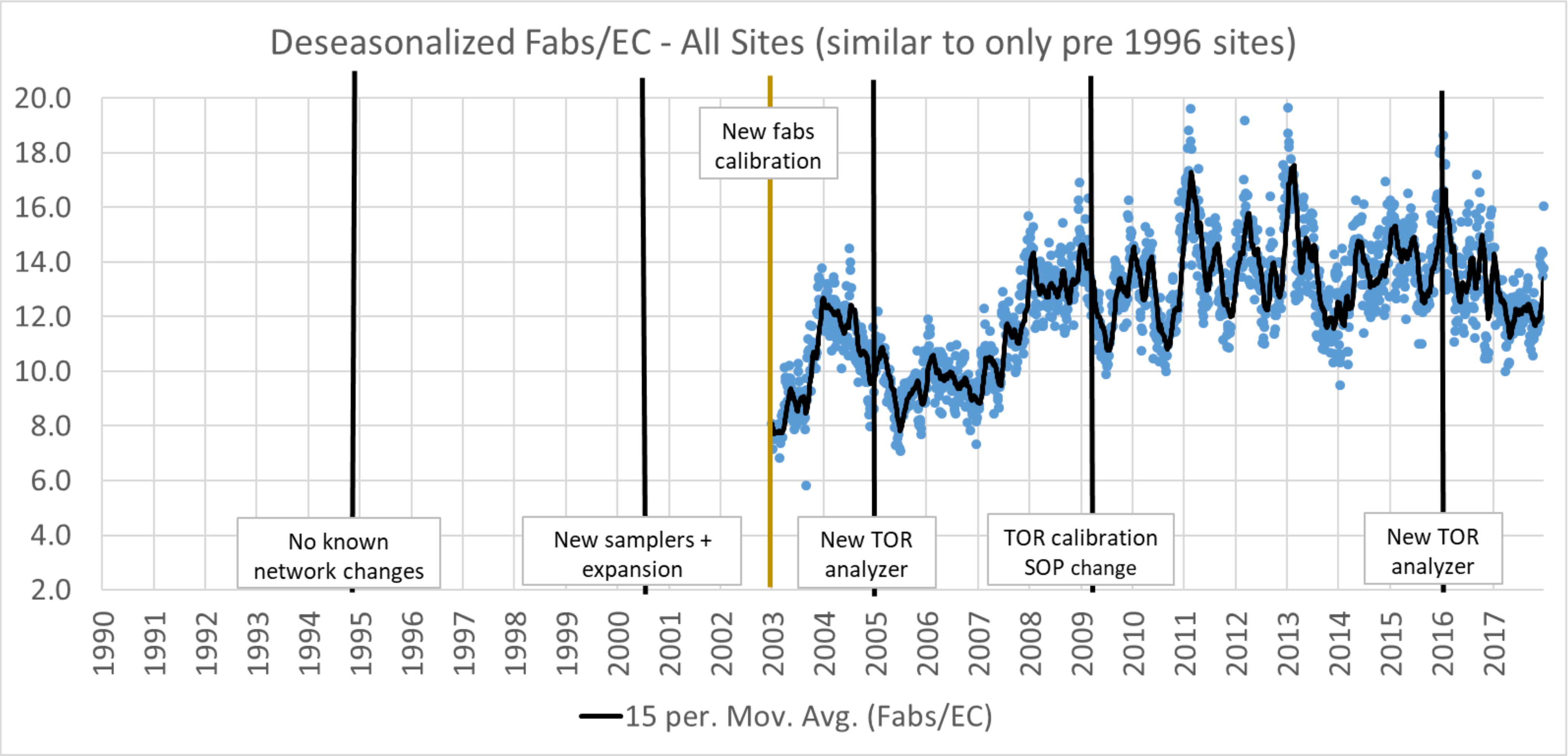


- HIPS has proven to be reproducible over a 15 year time span.
- A recent reanalysis has again demonstrated the reproducibility and precision of the HIPS measurement (White et al., 2019, AGU)

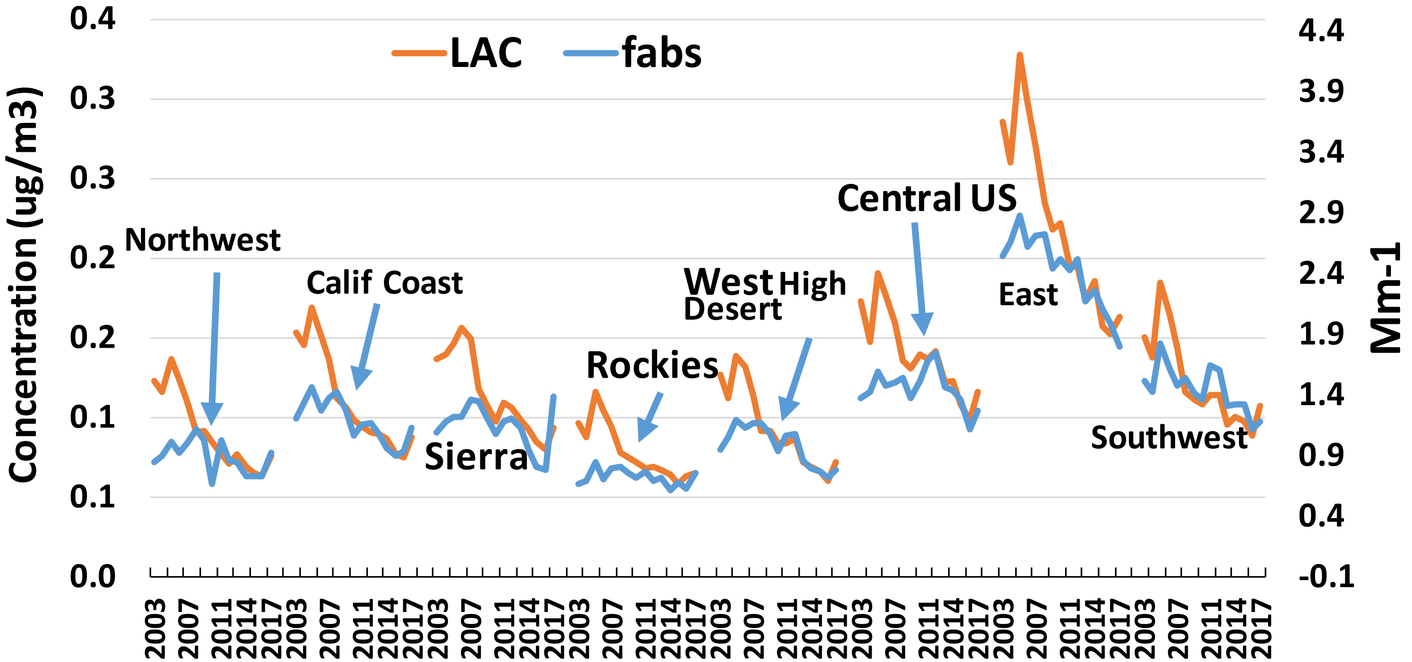


- Filter absorption (fabs) measured by HIPS is thought to be highly related to LAC
    - Provided LAC MAEs have not changed, the trends in fabs/TC should mimic LAC/TC trends
- Fabs/12/TC trends differ from LAC/TC from 2003 – 2008, but are similar post 2008

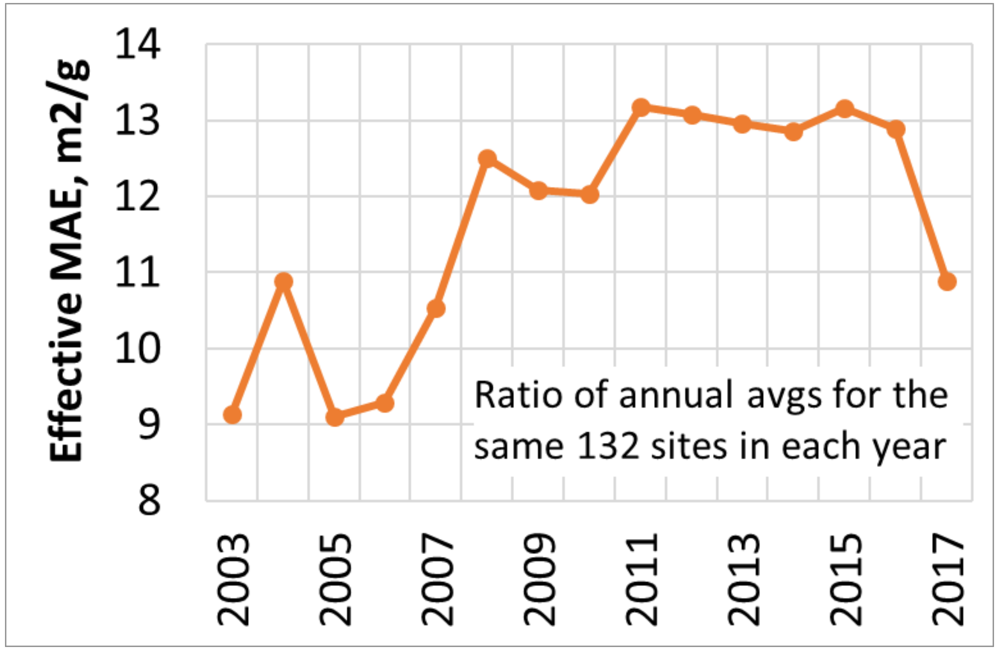
Changes in Effective LAC Mass Absorption Efficiencies (m2/g)



TOR-LAC vs Fabs



Either the LAC MAE had a decreasing trend from 2003-2008 or the LAC and/or f_{abs} are anomalous.



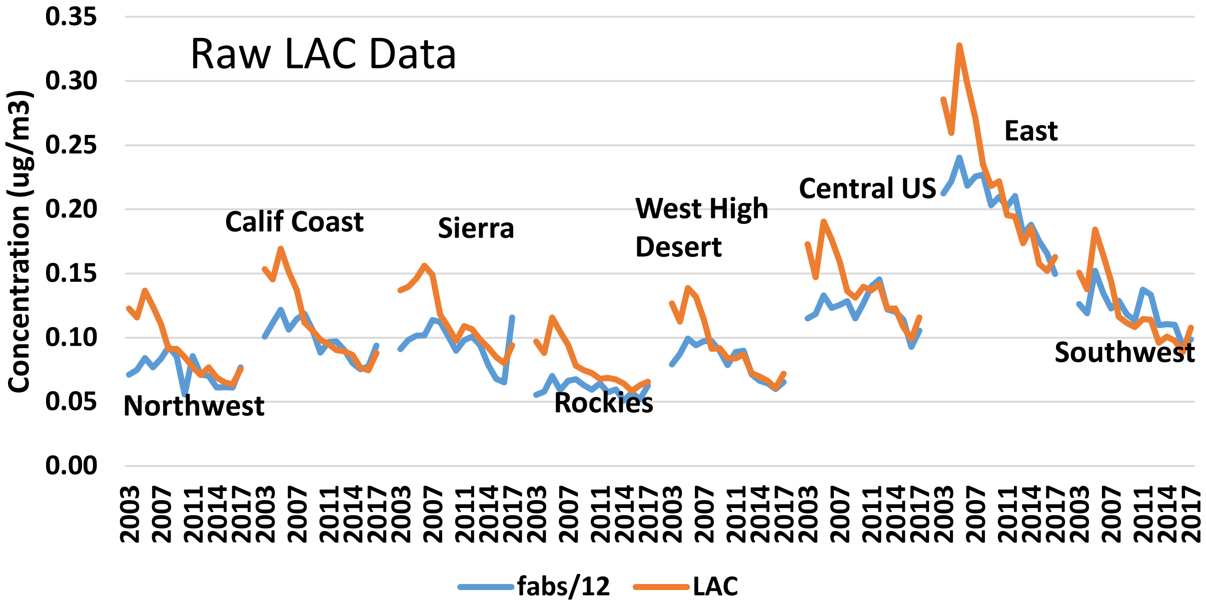
Averaging over years 2008-2017

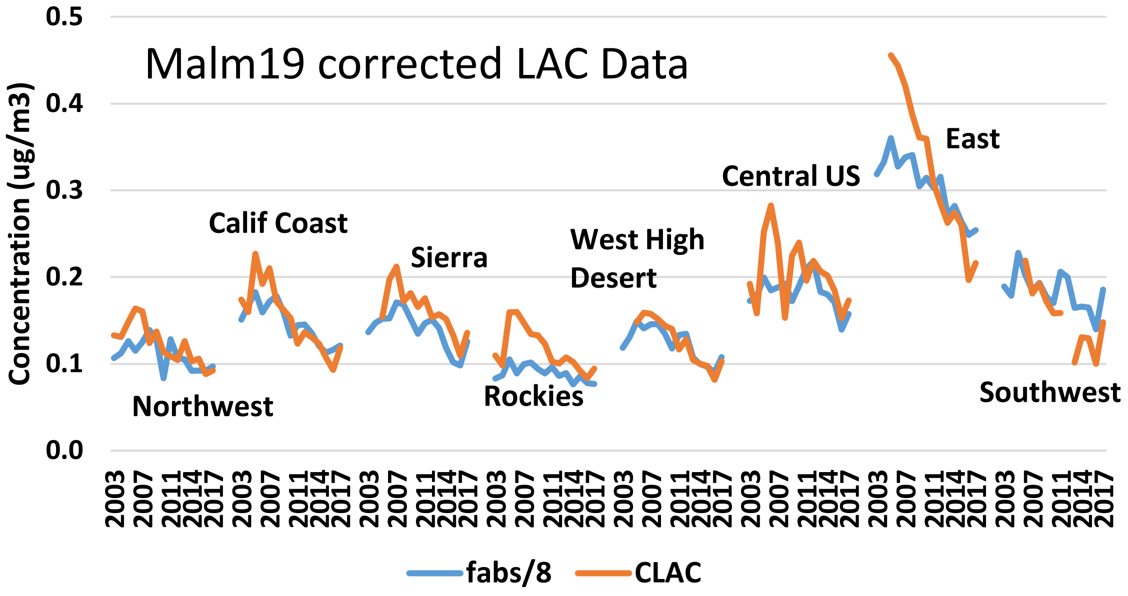
- FMAE=fabs/LAC≈ 12.0 m^2/g
- CMAE=fabs/CLAC ≈ 8.0 m^2/g
- MAE=0.75*fabs/CLAC ≈ 6.0 m^2/g

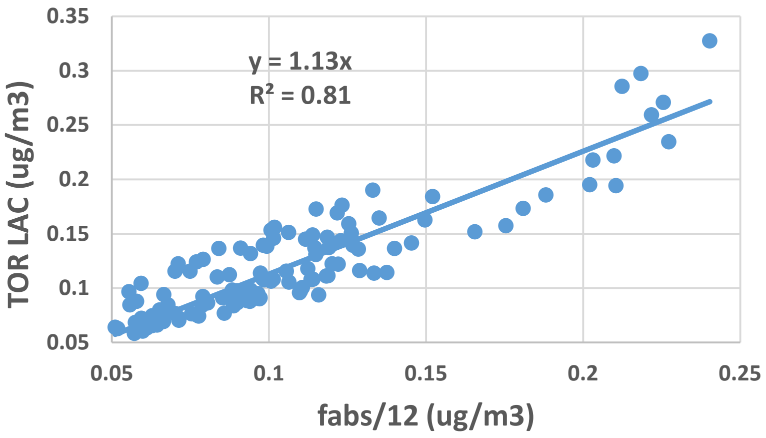
Average over years 2005-2007

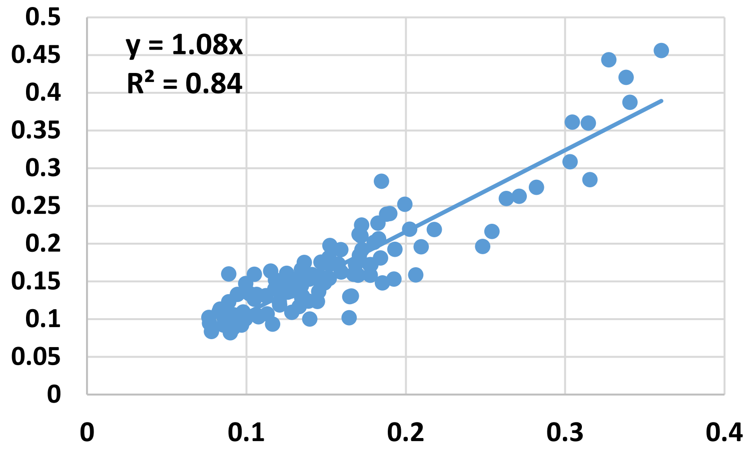
- FMAE=fabs/LAC ≈ 12.0 m^2/g

Impact of LAC corrections on Trends









- The corrected LAC generally reduced the 2003-2008 differences in the LAC and fabs trends
- Suggest that LAC MAEs may have been relatively constant since 2003

Can TC and f_{abs} be used in place of OC and EC and what about trends?

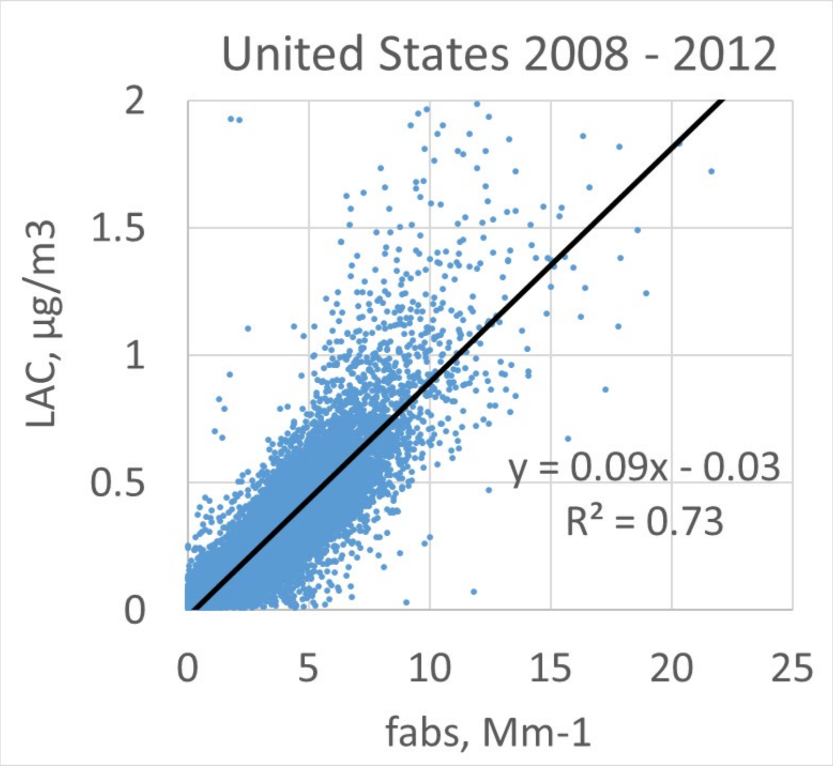
"new" TC = "old" TC = (OC + EC)

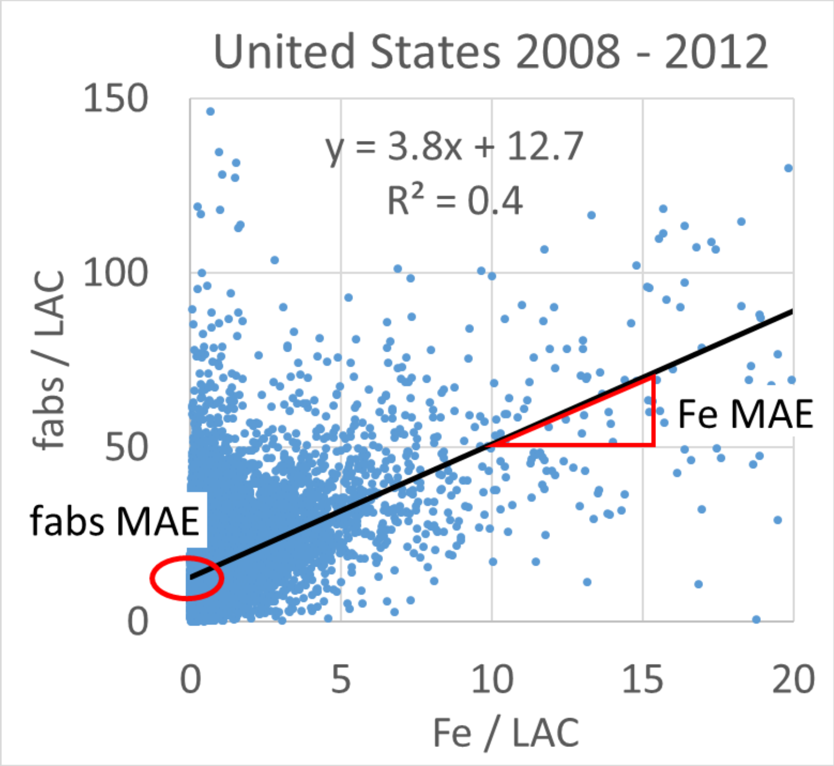
$OC_{TC} = TC – LAC_{op}$

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

- $\alpha_{fBC'}$, α_{Fe} - Calibration or best fit coefficients related to mass absorption efficiency (MAE)
  - f_{abs} is not necessarily atmospheric absorption

Relating fabs to LAC

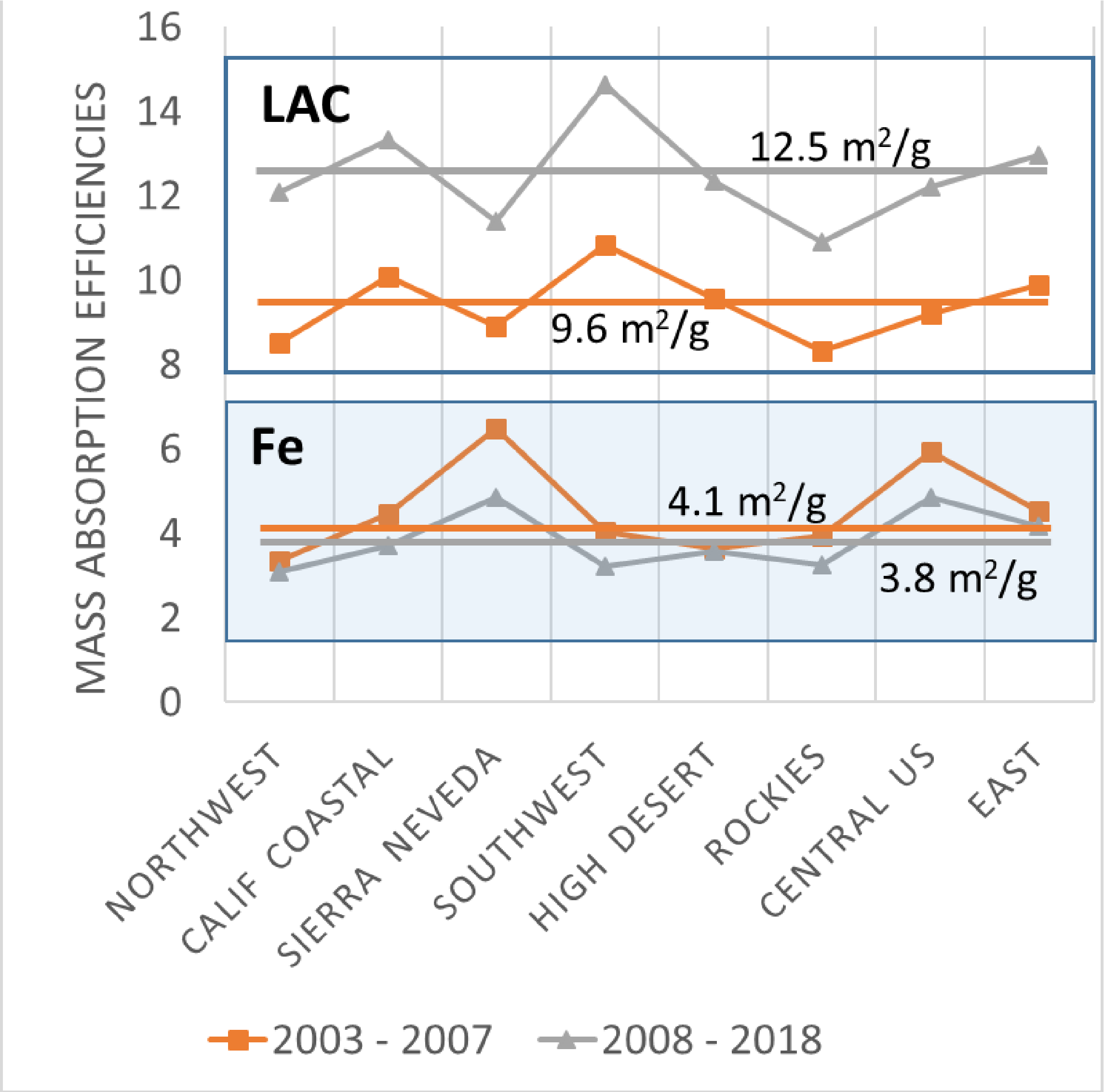




- fabs is highly correlated with LAC. It is also correlated with iron (Fe).
- Iron oxides found in soils can absorb at λ=633 nm.
- Iron oxides can also impact TOR-LAC causing premature volatilization of LAC and changing color during heating.

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

Mass Absorption Efficiency (MAE)

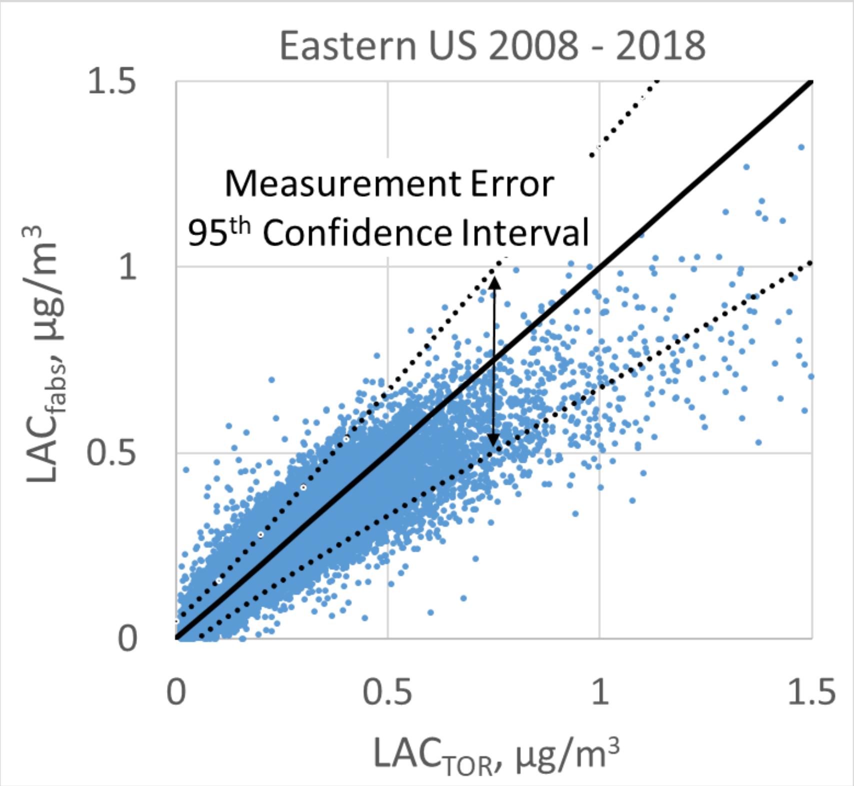


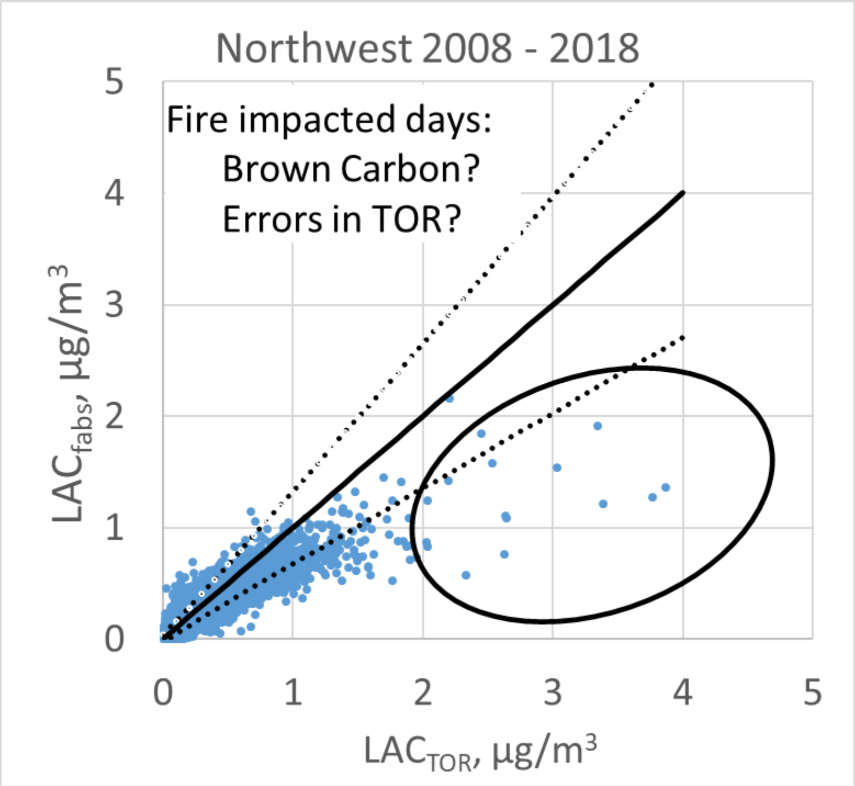
- LAC and Fe MAE's have little spatial variability
- LAC MAE's change across the carbon epochs (Fe MAE less so)
- Little seasonality in LAC and Fe mass absorption efficiencies (not shown)

Linear Regression used to estimate MAE's

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

LAC_{TOR} vs LAC_{fabs}



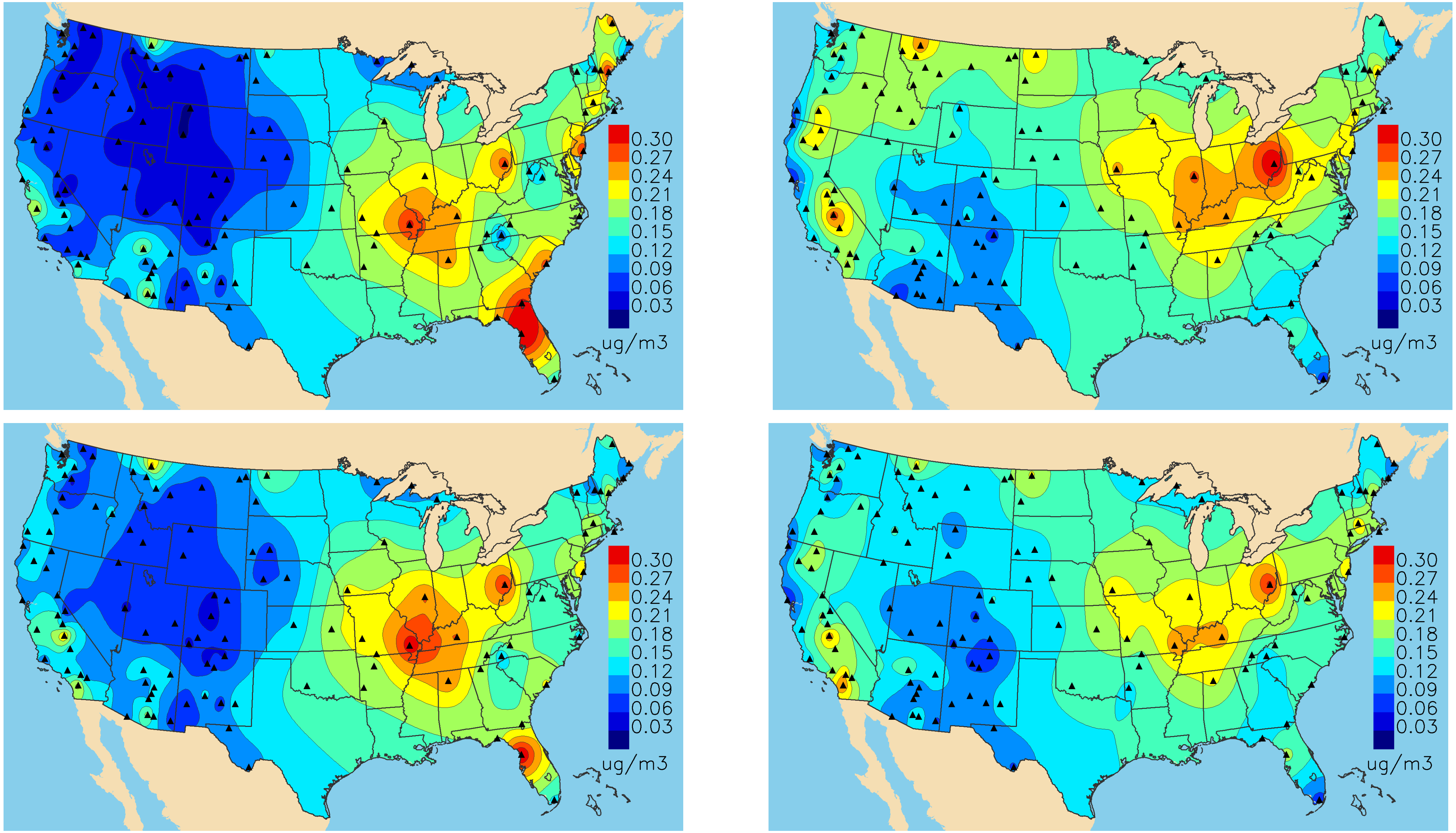


- fabs reproduces LAC well throughout the U.S. with most of the variance explained by the measurement error.
- $LAC_{fabs} < LAC_{TOR}$ at higher concentrations (> 0.75 µg/m^3)
  - HIPS or TOR issue?

Winter, 2014-2018 **Summer , 2014-2018**

LAC_{TOR}

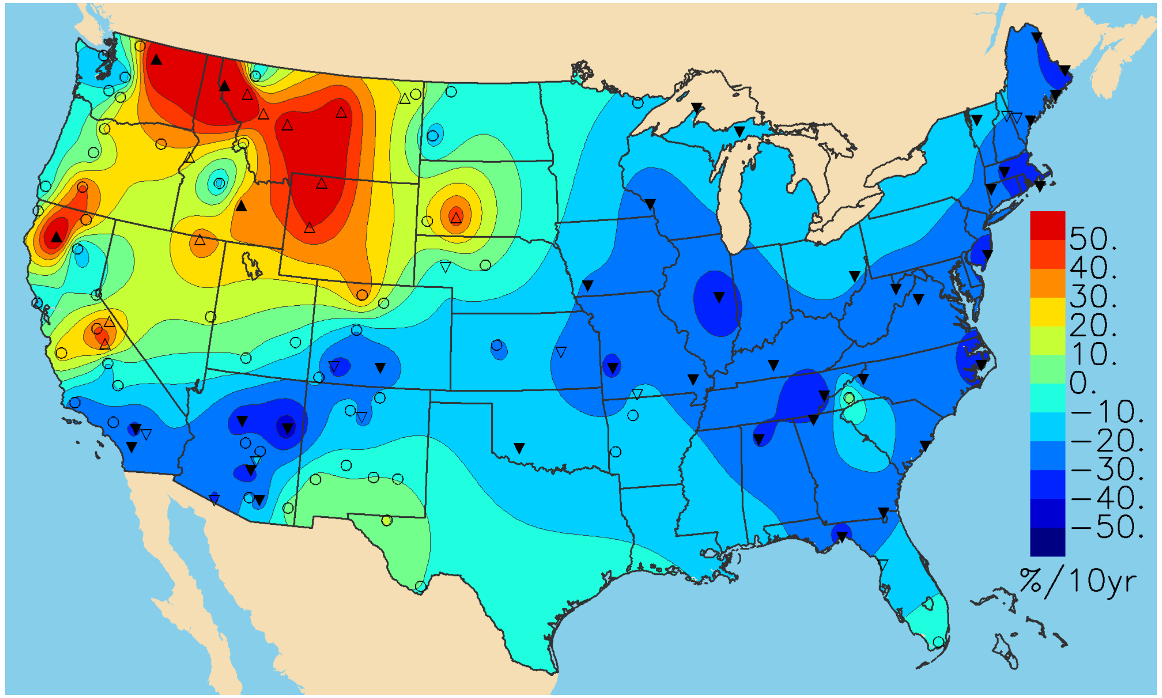
LAC_{fabs}



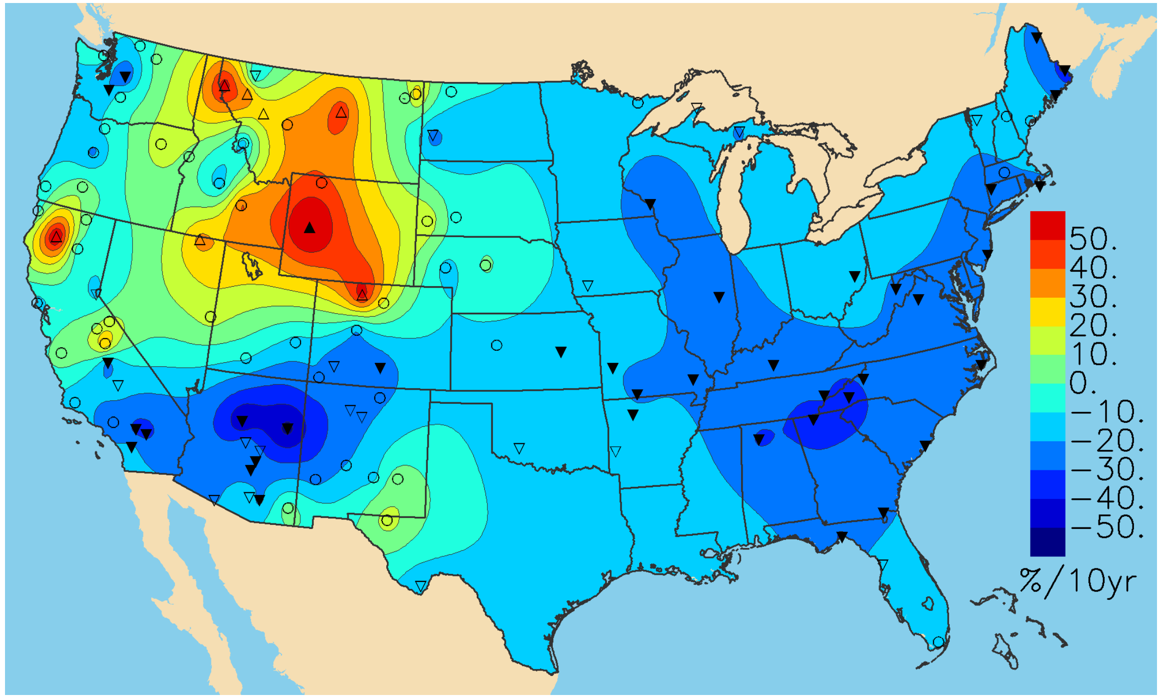
LAC_{TOR} - concentrations from the TOR analysis. LAC_{fabs} - estimated from fabs data using MAE_{LAC} = 12.5 and MAE_{Fe} = 4

Trends, 2008-2018

LAC_{fabs}



LAC_{TOR}



Discussion

- TC and fabs are being explored as alternatives to TOR OC and LAC measurements. These analysis methods are stable, accurate and cost effective. Together TC and fabs are relatable to TOR OC and LAC and the emissions causing the measured values.
- IMPROVE data are used to track long term trends of reconstructed haze. Substitution of TOR OC / LAC by TC and fabs causes little to no changes on the haze metrics (not shown).
- Important issues remain including
    - What are the implications for non haze assessments including health, PM2.5, modeling, radiative forcing assessments?
    - What is the cause of the poor comparison between TOR-LAC and fabs prior to 2008? Is this due to changing aerosol optical properties or analytical issues?
    - TOR-LAC may significantly underestimate ambient LAC and be biased by changing aerosol composition, e.g. fires and soil. Should fabs be used to reproduce TOR-LAC or an estimate of ambient “black carbon”?

- end

Outline

- Motivation for scrutinizing OC/LAC data and trends
- Review of potential limitations and issues in TOR data
  - No applicable traceable OC and LAC calibration standards
  - Dependence of OC/LAC split on operational protocols
  - Differencing optical properties of OP and LAC TOR fractions
- Evidence for underestimation of LAC
  - Apparent OP and LAC MAE's
  - Statistical analyses
- Long term trends in LAC and fabs
- Past Retrospective analyses
  - Reproducibility of fabs
  - Reproducibility of TOR OC/LAC fractions
- Potential retrospective quartz filter study
  - Stability of LAC/OC trends
  - Stability of fabs trends
  - Variability in aerosol mass absorption efficiencies

Limitations and Issues with TOA

- Calibration
  - Traceable standard for calibrating total carbon exist, e.g. sucrose
    - TC is generally reproducible across analyzers, instrument types, laboratories (e.g. Schmid et al., 2001; Chow et al., 2004)
    - Standards such as sucrose do not account for the complex mixtures of organic and light absorbing compounds in ambient aerosols
      - Carbon found on some IMPROVE/CSN filter punches post analysis
  - No current traceable standards to calibrate TOA-OC and TOA-LAC against.
    - No objective definition to distinguish between the two components exists (e.g. Baumgardner et al., 2012)
    - OC/LAC split is operationally defined and dependent on the temperature ramp protocols and optical correction method as well as sample constituents.
      - Different TOA analyzer can produce different OC/LAC splits
      - Can’t directly insure no analytical drift in OC/LAC split
        - E.g due to changing aerosol compositions over time

OC/LAC Dependence on TOA Temperature and Optical Protocols

Subramanian et al., 2006

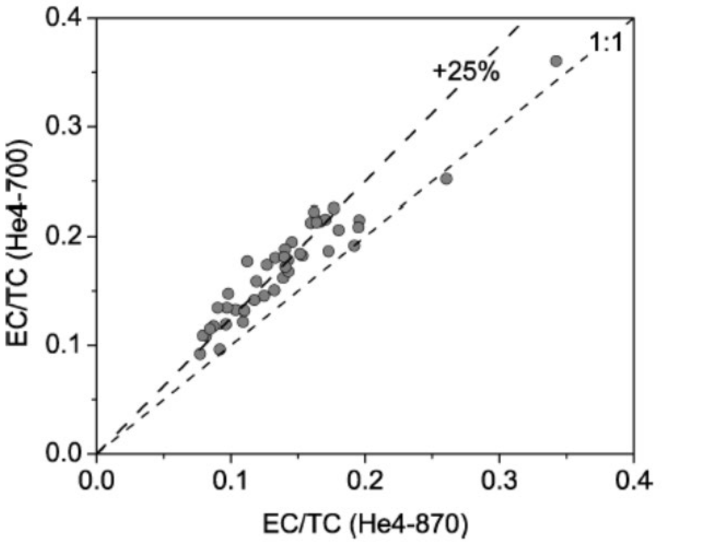


FIG. 3. Scatter plot of the EC (as a fraction of TC) measured by the He4-870 and He4-700 temperature protocols for parallel punches taken from 43 different ambient samples including 24-hour denuded samples and undenuded samples with sampling durations of 8, 24, 48, or 96 hours. The He4-700 protocol gives 25 ± 13% (average ± standard deviation) higher EC/TC ratios than the He4-870 protocol. The maximum EC loading for these samples is 8.4 μg-C/cm^2 (measured by the He4-700 protocol).

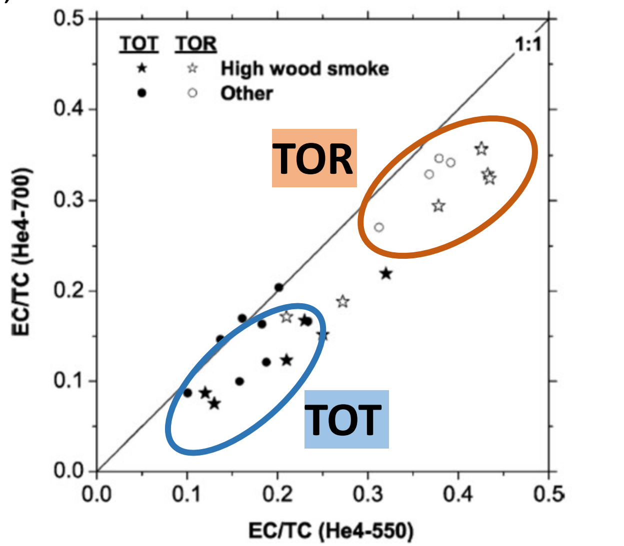


FIG. 13. Scatter plot of EC (as a fraction of TC) measured with He4-550 and He4-700 protocols for paired punches from high wood smoke and other ambient samples. The He4-550 protocol typically measures more EC than the He4-700 protocol, except for the three ambient samples close to the 1:1 line. Results are shown for OC/EC splits defined using transmission (TOT) and reflectance (TOR). TOR EC is not available for some of the samples included in the TOT inter-comparison, including the three TOT samples that show good agreement between the two temperature protocols.

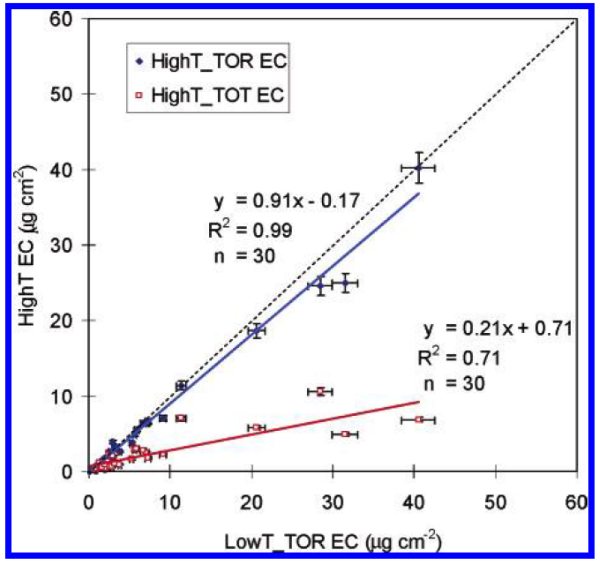


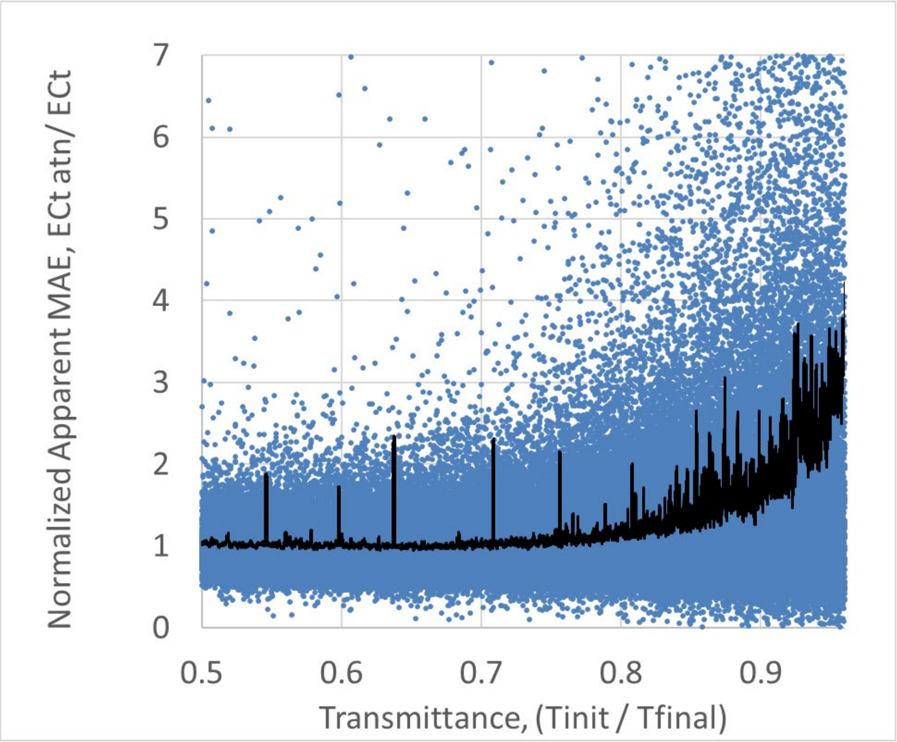
FIGURE 6. TOR-corrected EC from the LowT protocol and both TOR and TOT-corrected EC from the HighT protocol for the IMPROVE network samples. The IMPROVE comparison includes 30 samples from 16 IMPROVE network sites (SAGU1, SIPS1, STAR1, UPBU1, WHIT1, SEN1, ACAD1, MELA1, MOMO1, PUSO1, HECA1, REDW1, WASH1, GUMO1, SEQU1, and YOSE1) that represent a variety of carbon source contributions (fires, secondary organic aerosol, vehicle exhaust, carbonates). (The dashed line indicates the 1:1 correspondence.)

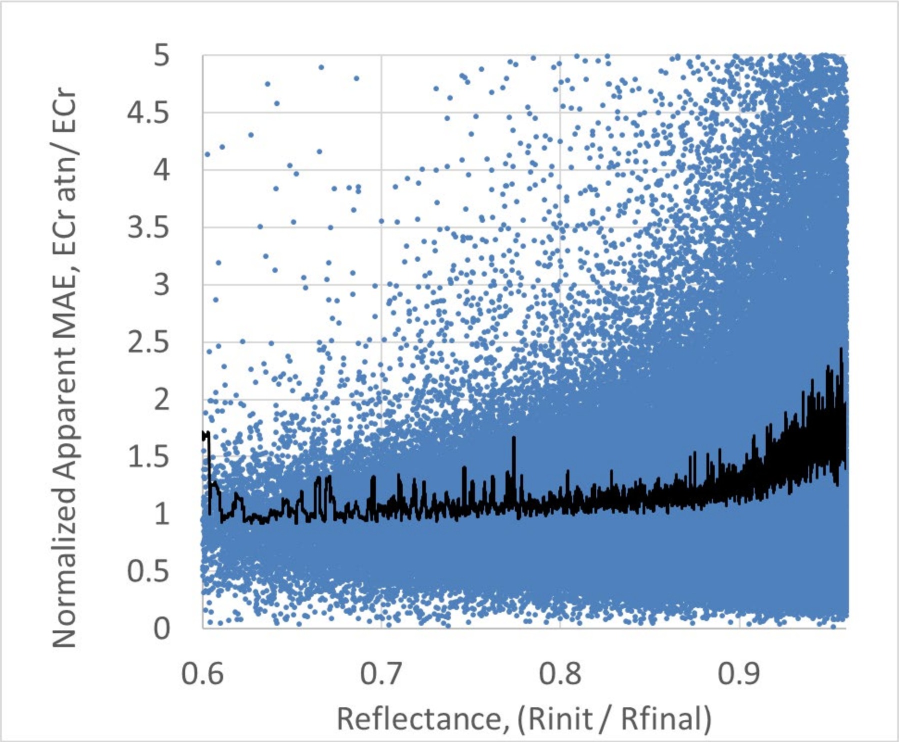
- TOT-EC decreases w/ temp
- Subra suggest less OC slip
- Do higher temps increase the LAC MAE?

- TOR-EC is generally higher than TOT-EC
- TOR-EC high temp is generally lower than low Temp

- Chow et al,. 2004, found TOR-EC was independent of temp, but TOT was not
- Why different study results?

Dependence of Apparent MAE on Fabs



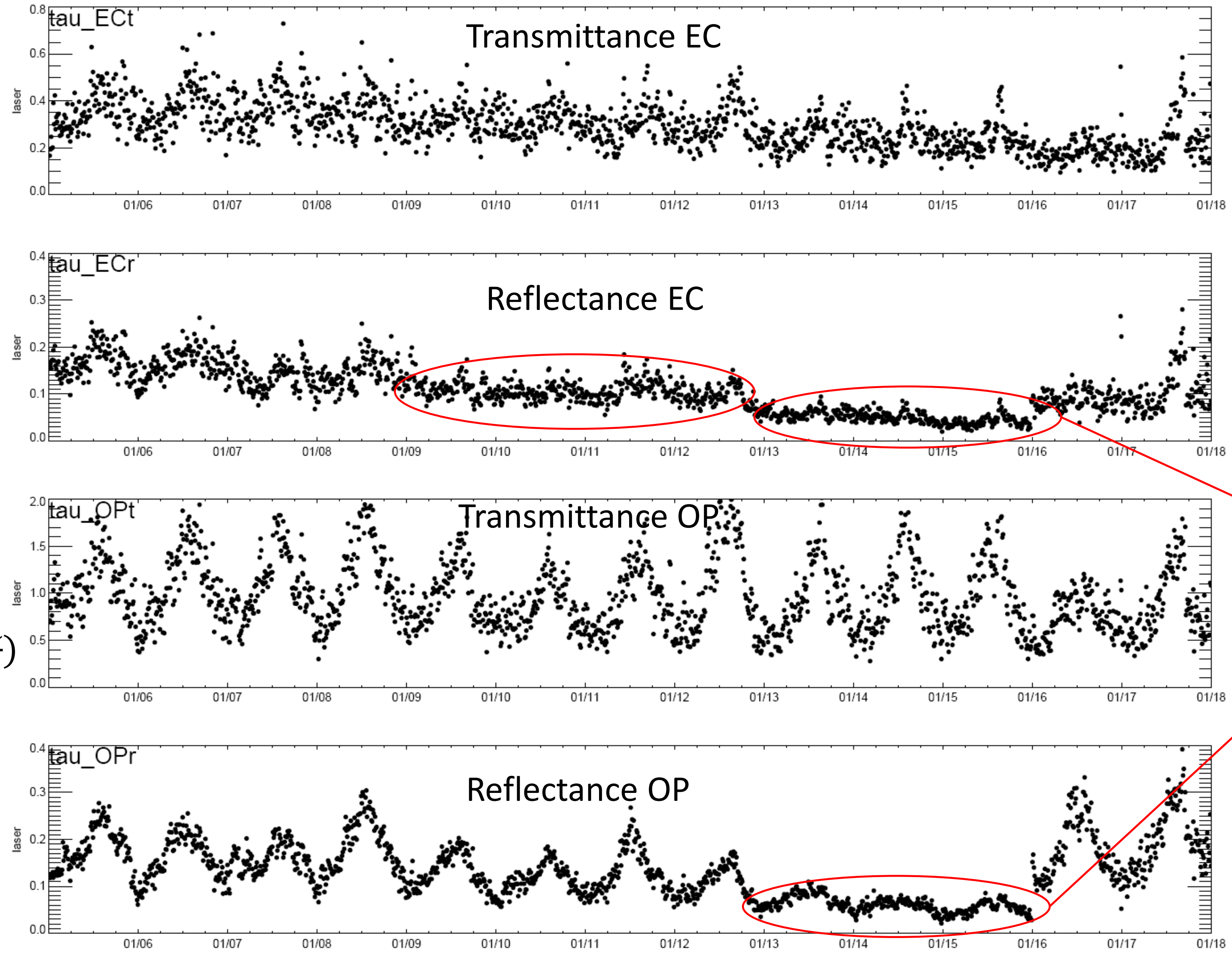


- MAE’s tend to increase with decreasing absorbing aerosol
- If OP and LAC have the same MAE, the EC apparent MAE could be larger
- OC/EC split may depend on filter mass loading and trends in mass loading result in trend in OC/EC split bias

Daily network median attenuation

$$\tau(EC) = -\ln\left(\frac{Initial}{Final}\right)$$

$$\tau(OP) = -\ln\left(\frac{Minimum}{Initial}\right)$$



Flattening and loss of seasonality

Jenny has a number of slides investigating these changes

TOR Retrospective Analyses

Retrospective analysis of IMPROVE Carbonaceous Aerosol Measurements

- Are the current LAC and fabs trends real? Did the MAEs change from 2003-2008?
- HIPS analyzer is calibrated or registered to clean filters and not particulate light absorbing standards.
  - Instrument could drift with time increasing error or introducing biases and false trends.
  - The excellent reproduction of fabs measurement in 15 year retrospective analysis of GRSM, MORA, and PORA data suggest that the instrument is precise and reproducible and absorbing aerosol is preserved on filters stored in hostile environments.
- The issues/limitation of the TOA analyzers and inability to calibrate OC and EC fractions to standards suggest that instrument drifts could occur biases LAC trends
  - Retrospective analysis of quartz filters to evaluate validity of trends has not been done
  - Loss of carbonaceous material during storage is a potential issue, but the positive results from the HIPS retrospective analyses suggest that the LAC fraction should be retained during cold storage

Potential retrospective analysis to understand divergent LAC and fabs Trends

- Three potential outcomes in a TOR retrospective analysis
  - Reanalysis reproduces the original LAC concentrations and trends. Implications:
    - TOR is a valid long-term analysis for tracking trends in LAC
    - TOR LAC/OC could still be biased
  - Reanalysis does not match original LAC, but does match fabs data. Implications:
    - TOR LAC is not strictly be suitable for long-term trend analysis
    - Fabs is a valid surrogate for tracking changes in LAC and presumably its emissions
    - The mass absorption efficiencies have not change over the time period of analysis
    - Trends in apparent OP and LAC MAE's do not affect OC/LAC split
  - Reanalysis does not match original LAC nor the fabs data. Implications:
    - TOR LAC may not strictly be suitable for long-term trend analysis
    - The mass absorption efficiencies may have changed over the time period of analysis
    - Trends in fabs are not linearly related to LAC concentrations and emissions.
    - Particulate LAC may not be stable in cold storage and results are inconclusive.

Past TOR Retrospective Analyses

Re-analysis of IMPROVE carbon samples

Follow-up to January 2008 IMPROVE – CSN Carbon PM Monitoring Workshop

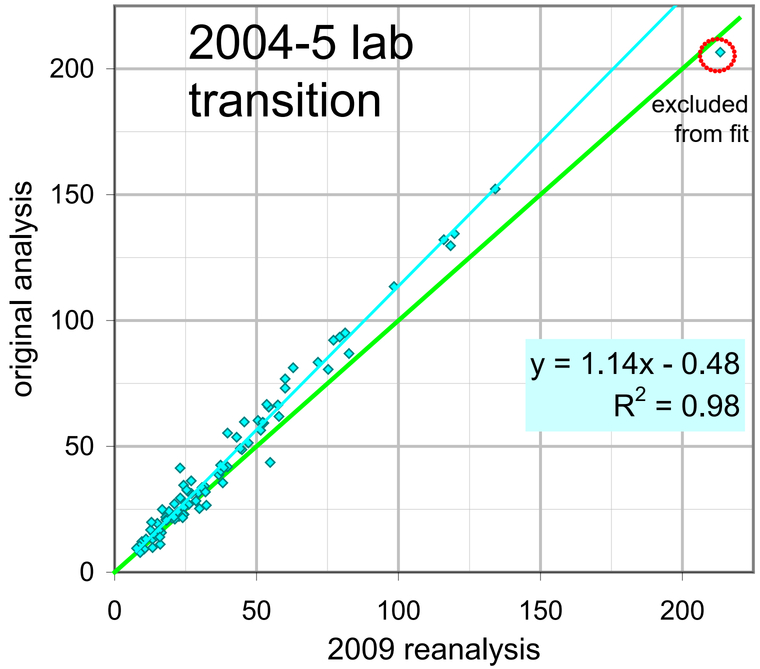
WHW, 2/4/10 – data from Dana Trimble, 9/30/09

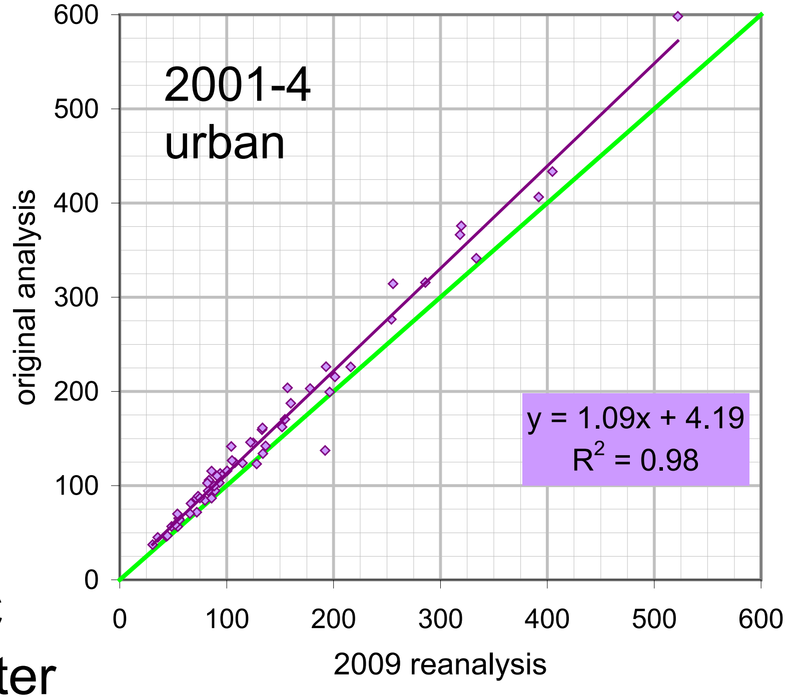
The homework assignments:

Transition to the new analyzer: Reanalyze a total of 96 filters as an initial exploration. Draw 12 filters from each of the following 8 months: 11/03, 12/03, 1/04, 2/04, 11/04, 12/04, 1/05, 2/05. Within each month, draw 4 filters each from the top, middle, and bottom thirds of that month's (previously measured) TC loadings.

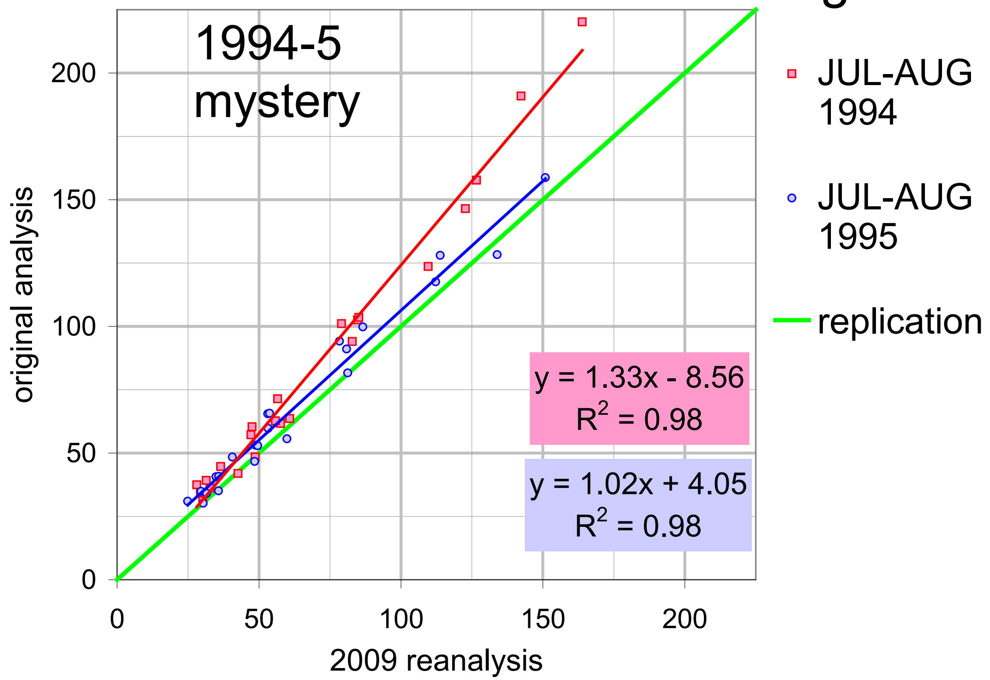
The unexplained empirical shift in late 1994: Reanalyze a total of 48 filters as an initial exploration. Draw 12 each from the following 4 months: 6/94, 7/94, 6/95, 7/95. Within each month, draw 4 filters each from the top, middle, and bottom thirds of that month's (previously measured) TC loadings.

Pre-2005 measurements collocated with CSN: Reanalyze a total of 72 filters (~10% of all available) as an initial exploration. These should be selected from all collocated monitoring sites and distributed more or less uniformly throughout the pre-2005 period with about 1/3 each from the top, middle and bottom thirds for each site.



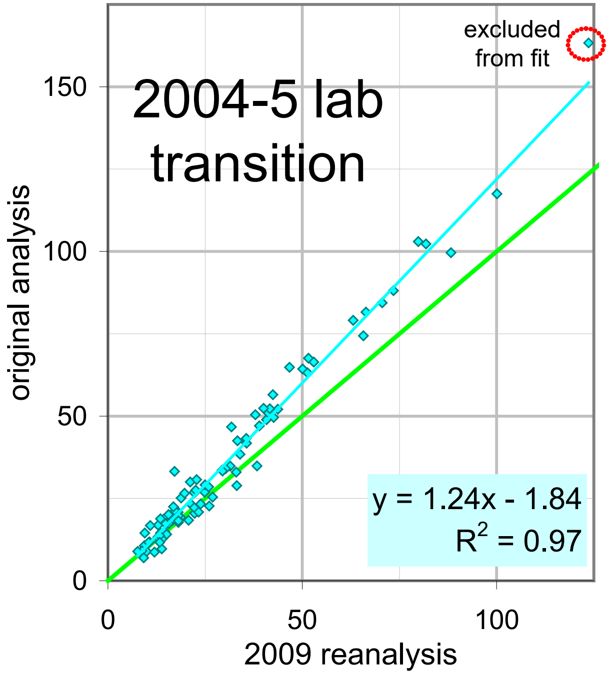


TC ug/filter

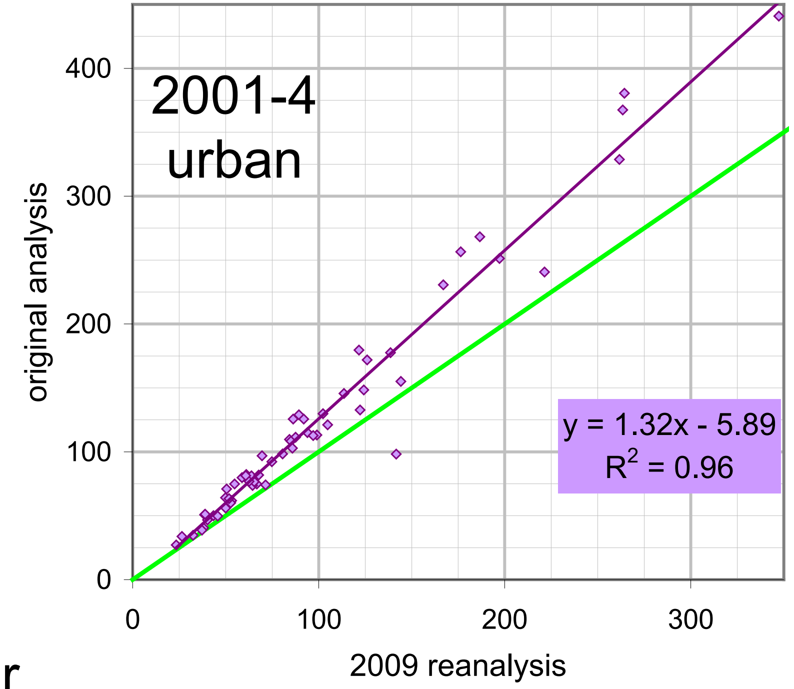


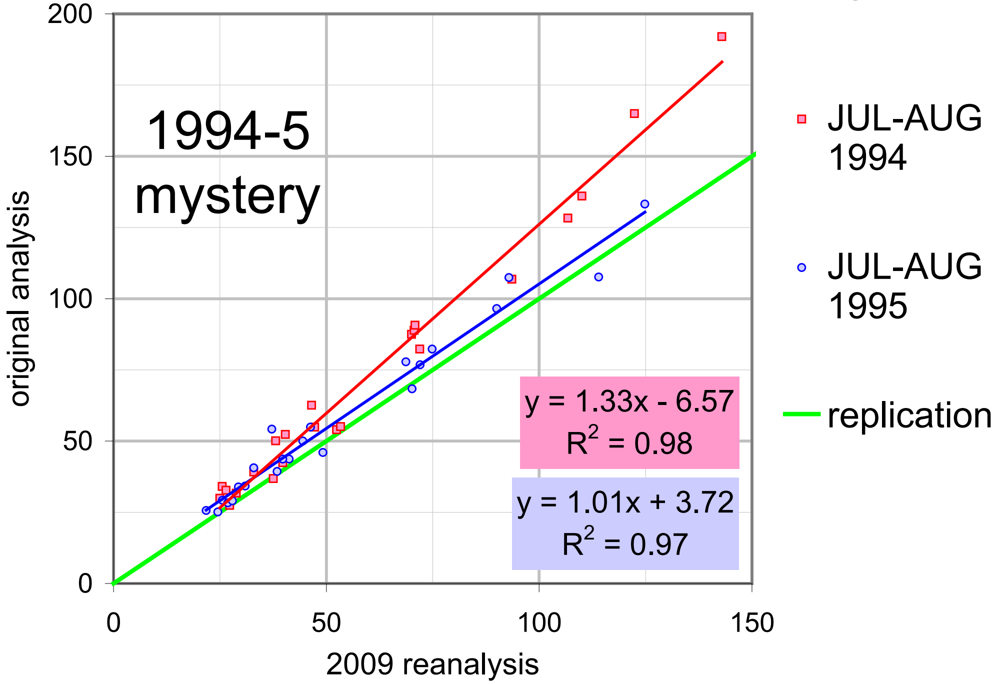
For $TC_{original}$ > 50 ug/filter (> ~1.5 ug/m^3 ~ $34xMDL_{DRI}$), reanalysis almost always gave lower TC values.

← Curiously, this apparent loss was considerably greater from samples collected ***15*** rather than ***14*** years earlier.



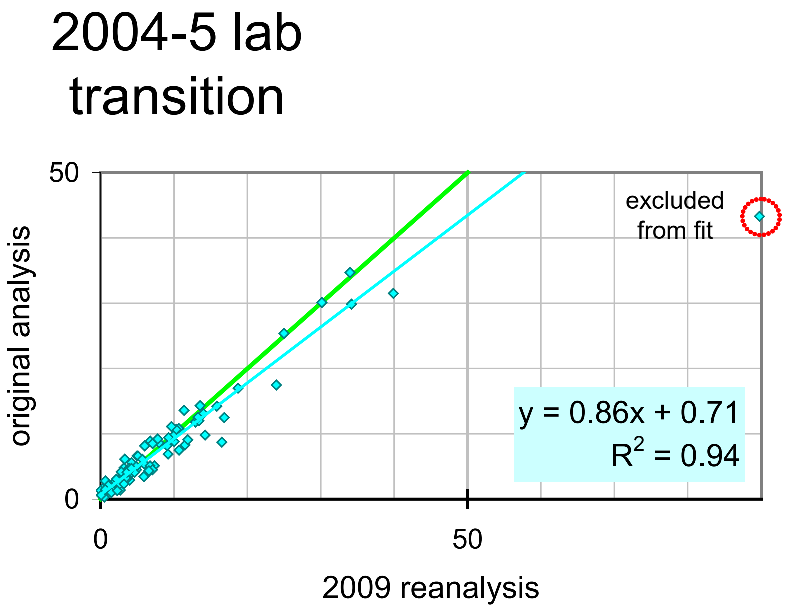
OC ug/filter

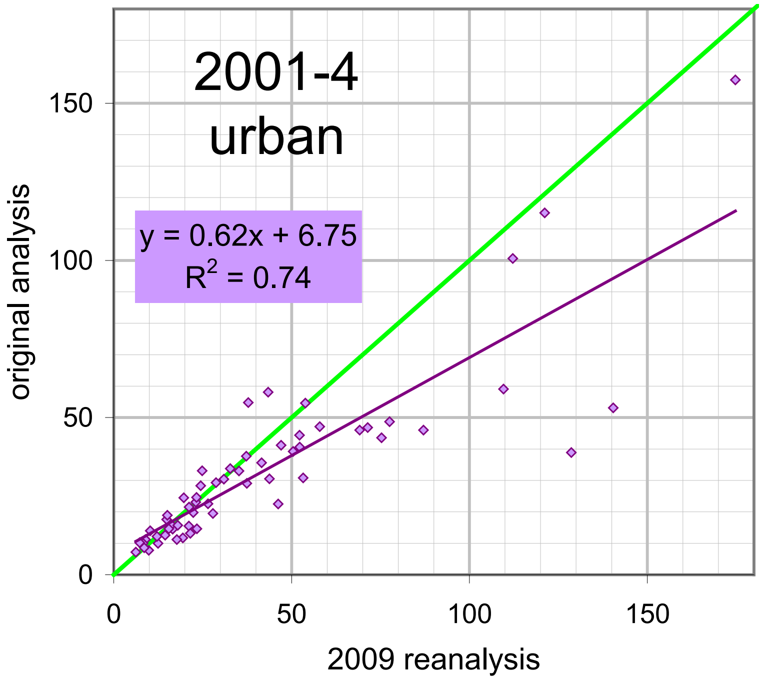


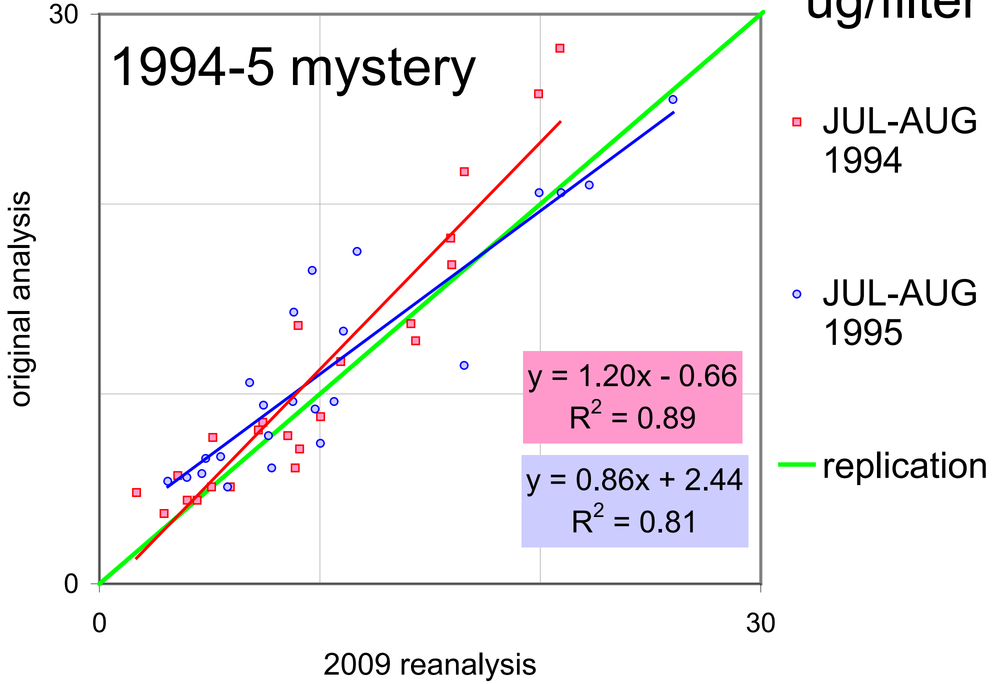


Samples collected before and after 2000 show different changes in their EC – OC splits. For the younger samples, the TC decrease reflects a larger decrease in OC, often offset by an *increase* in EC. →

EC ug/filter







← For the older samples, reanalysis more often gave lower values for EC as well as OC.

Summary: geometric-mean difference, original – 2009 reanalysis, by epoch or group

	geomean(original/2009) -1		
	OC	**EC**	**TC**
JUL-AUG 1994	**19%**	**8%**	**16%**
95% confidence, original/2009	*(1.152 - 1.239)*	*(0.963 - 1.202)*	*(1.125 - 1.199)*
JUL-AUG 1995	**10%**	**13%**	**9%**
95% confidence, original/2009	*(1.054 - 1.14)*	*(1.007 - 1.26)*	*(1.056 - 1.136)*
NOV '03 - FEB '04	**18%**	**-3%**	**14%**
95% confidence, original/2009	*(1.132 - 1.227)*	*(0.882 - 1.063)*	*(1.097 - 1.184)*
NOV '04 - FEB '05	**14%**	**-3%**	**10%**
95% confidence, original/2009	*(1.085 - 1.206)*	*(0.887 - 1.069)*	*(1.05 - 1.156)*
2001-4 URBAN	**23%**	**-15%**	**13%**
95% confidence, original/2009	*(1.192 - 1.27)*	*(0.785 - 0.927)*	*(1.1 - 1.158)*

- ***If*** these differences are viewed as uncertainties in the original data, then we need to see changes over time of ~ 20% before we can confidently report a change in the atmosphere, particularly for EC.
- Alternatively, are the samples stable under refrigeration?

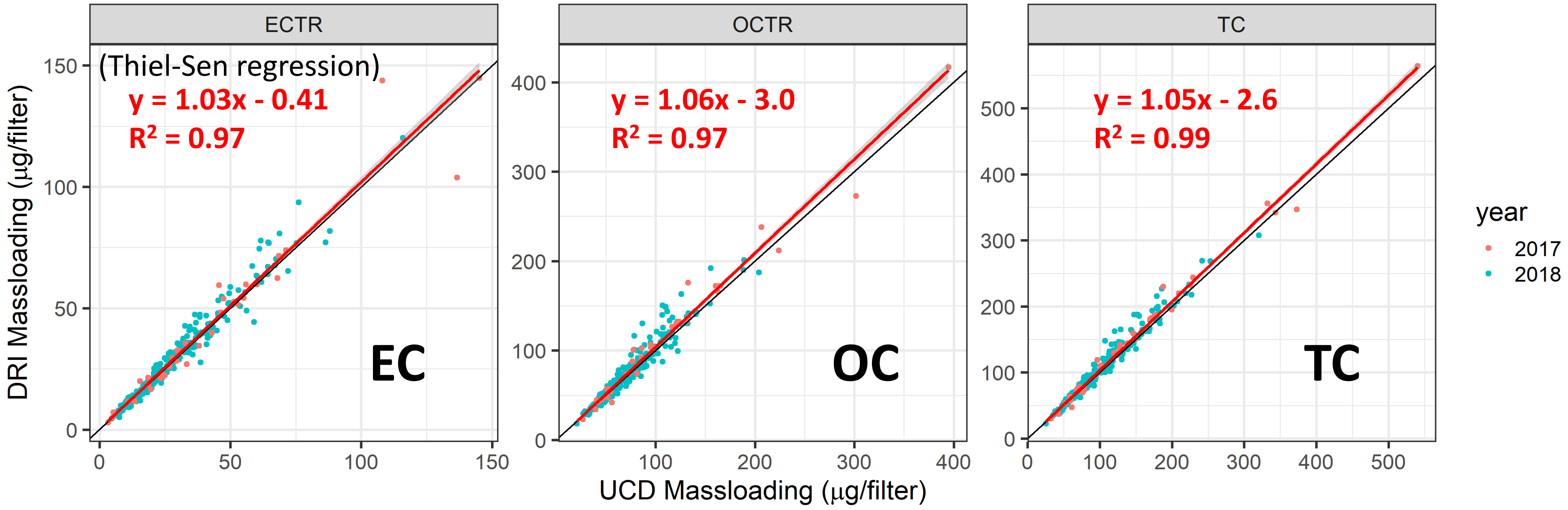
UCD Retrospective TOR Analyses compared to DRI

1. 2007 archived CSN samples (n=273):
   - DRI analyzed in 2008 with *Model 2001* analyzers
   - UCD analyzed in 2017-2018 with Sunset analyzers

3. CSN network samples (n= 3314):
   - DRI analyzed in 2017 - 2018 with *Model 2015* analyzers
   - UCD analyzed in 2017 with Sunset analyzers

Following slides are from Hyslop et al., presentation at the National Ambient Air Monitoring Conference, 2018 Portland, OR

DRI/UCD Comparison: 2007 Archived CSN samples (n = 273)



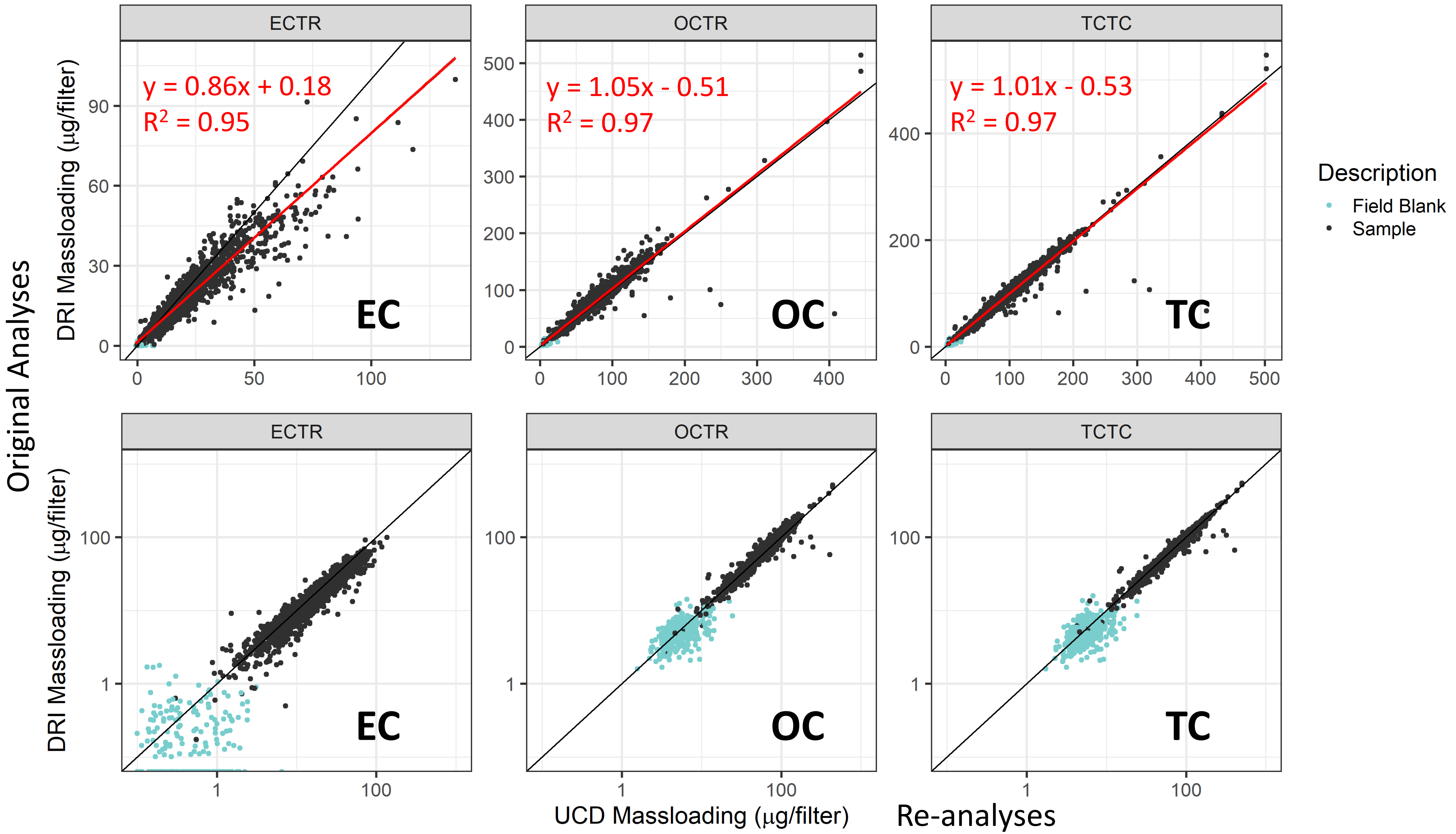
- UCD lab analyzed 273 archived CSN samples from 2007 in summer 2017 and spring 2018
- UCD and DRI results show excellent agreement
- Good sample stability even after 10-11 years of storage.

- When did DRI analyze the 2007 CSN filters?

DRI/UCD Comparison: CSN Network Samples (n = 3314)

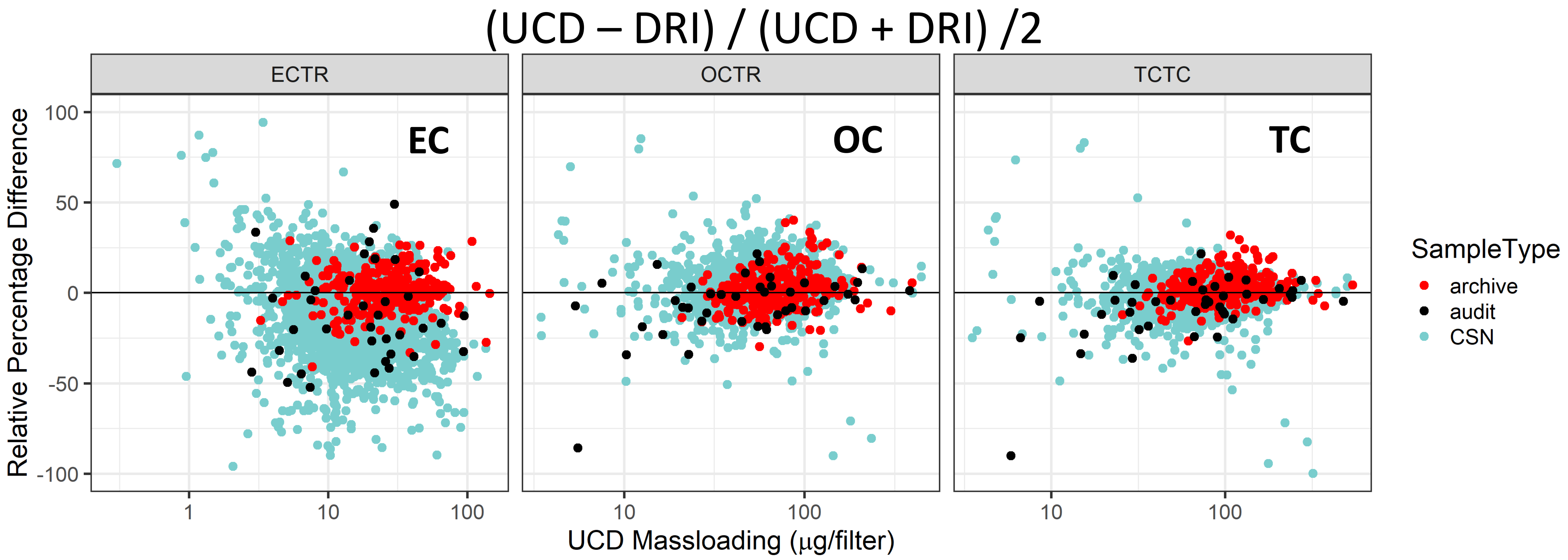
Linear Scale

Log Scale



Re-analyses

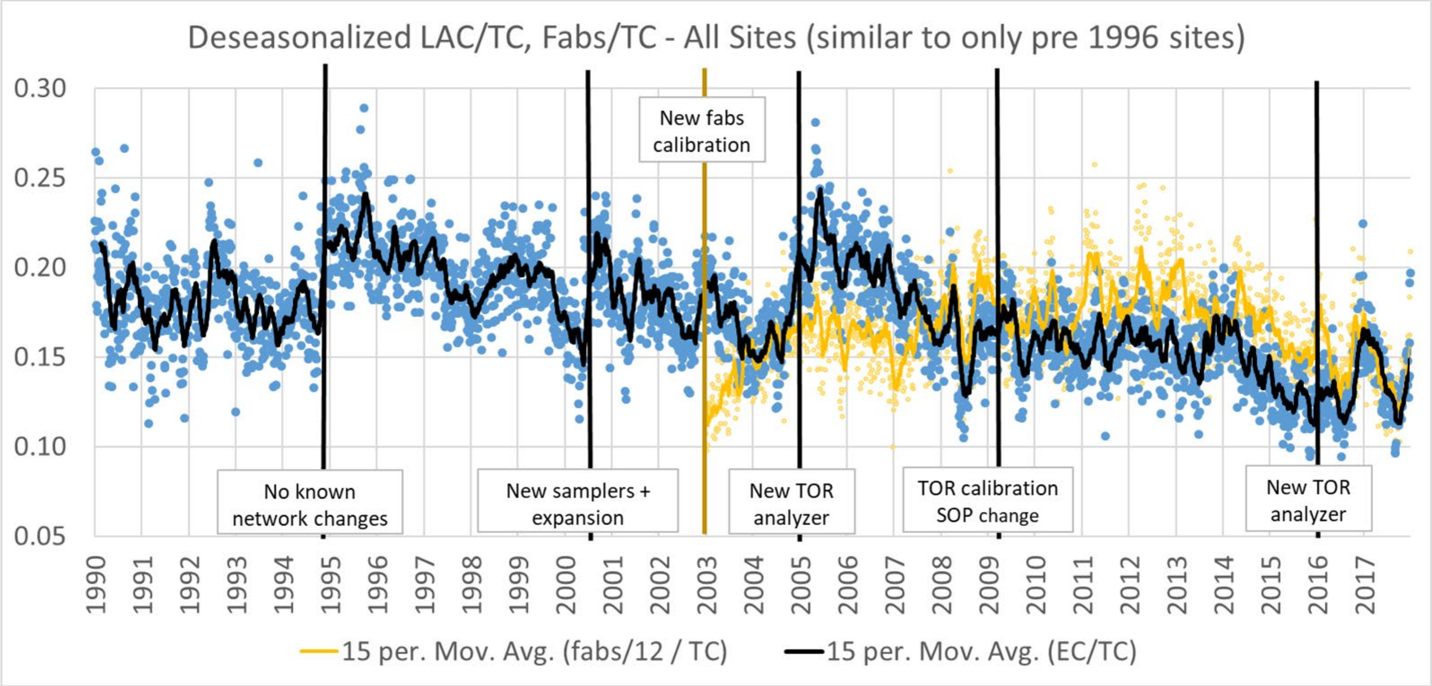
DRI/UCD Comparison: All Sample Types

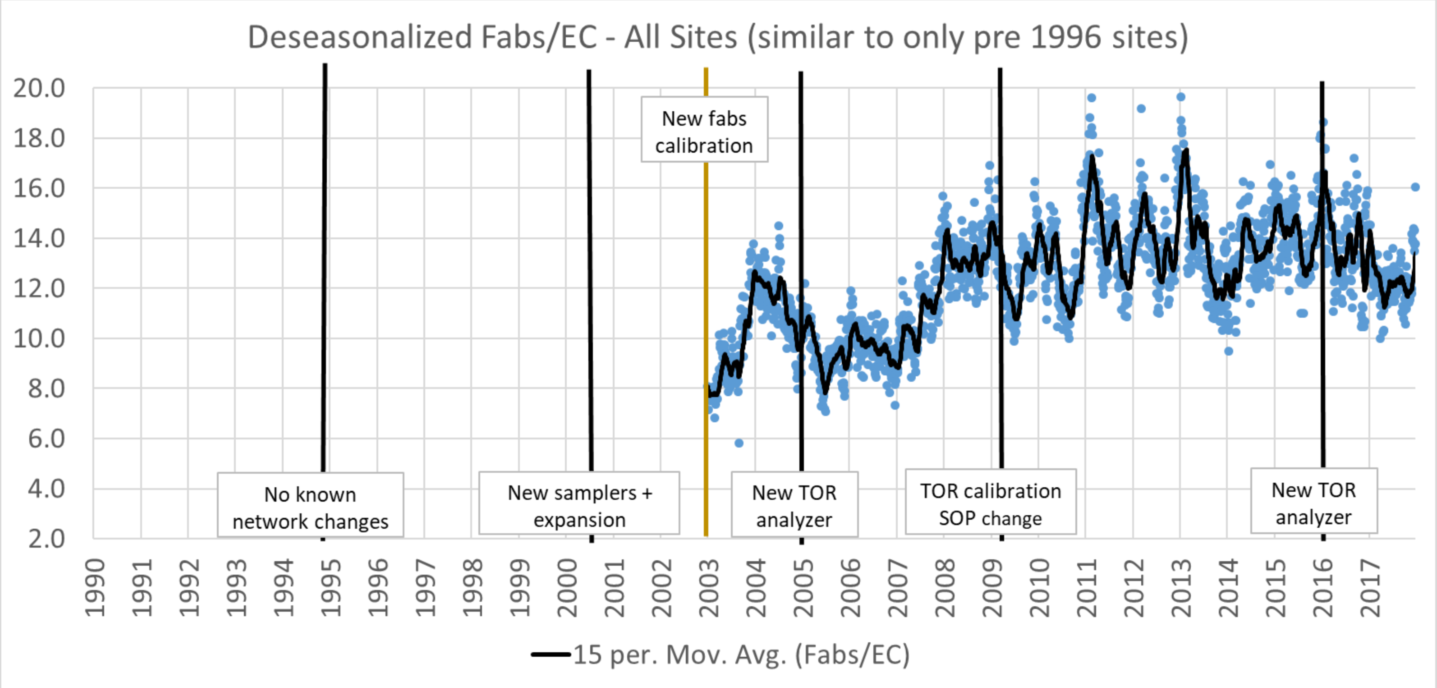


- CSN archive filters analyses using DRI analyzer model 2001, other samples used 2015 analyzer
- In CSN samples, no difference in TC, but UCD EC is lower and OC higher than DRI – potential instrument dependent

Possible TOR retrospective analysis

- Which filters should be reanalyzed to understand:
  - TOR-LAC stability
  - Changing mass absorption efficiencies and fabs stability
  - Filter storage effects
- Suggest:
  - 2003-06 - differing LAC and fabs trends
  - 2011-13 – similar LAC and fabs trends with different MAE's compared to 2003-06
  - 2016-2017 – Used the new analyzer and shorter storage period
  - Reanalyze the median sample in each sample day, i.e. reproduce figure





TOR Uncertainty – Replicates Analyses

White ~2009 – TOR Reanalysis proposal from 2008 carbon workshop

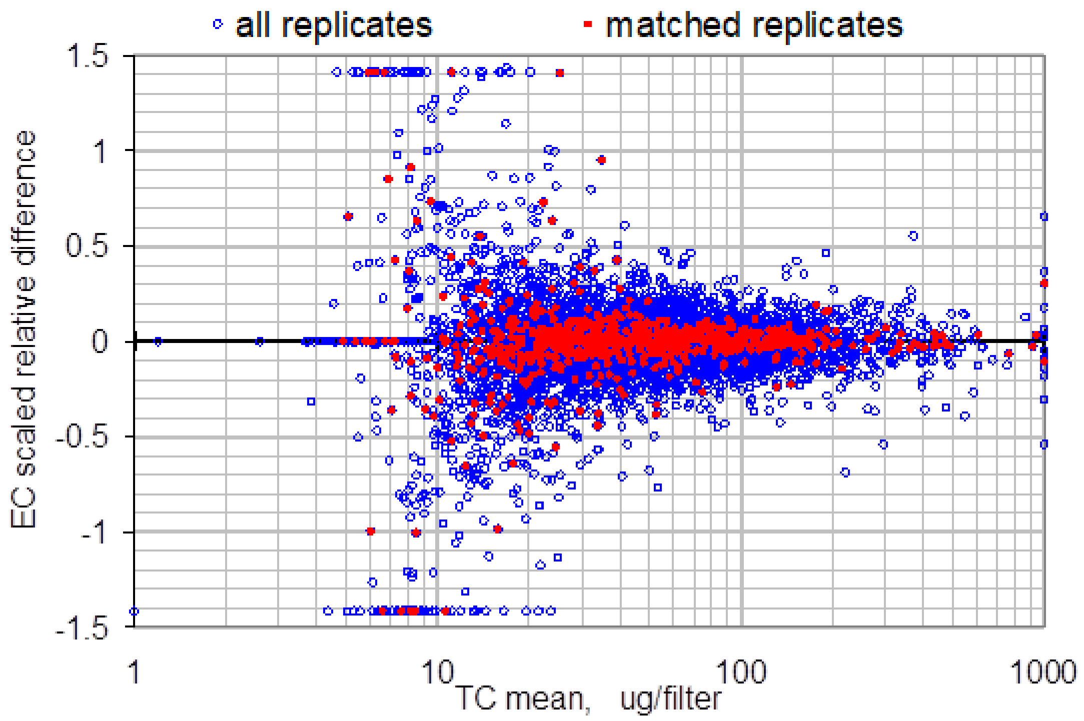


Figure 4. EC results from 5103 routine replicate analyses with current instrumentation and protocol, through April 2007. The scaled relative difference of the replicate and original analyses,

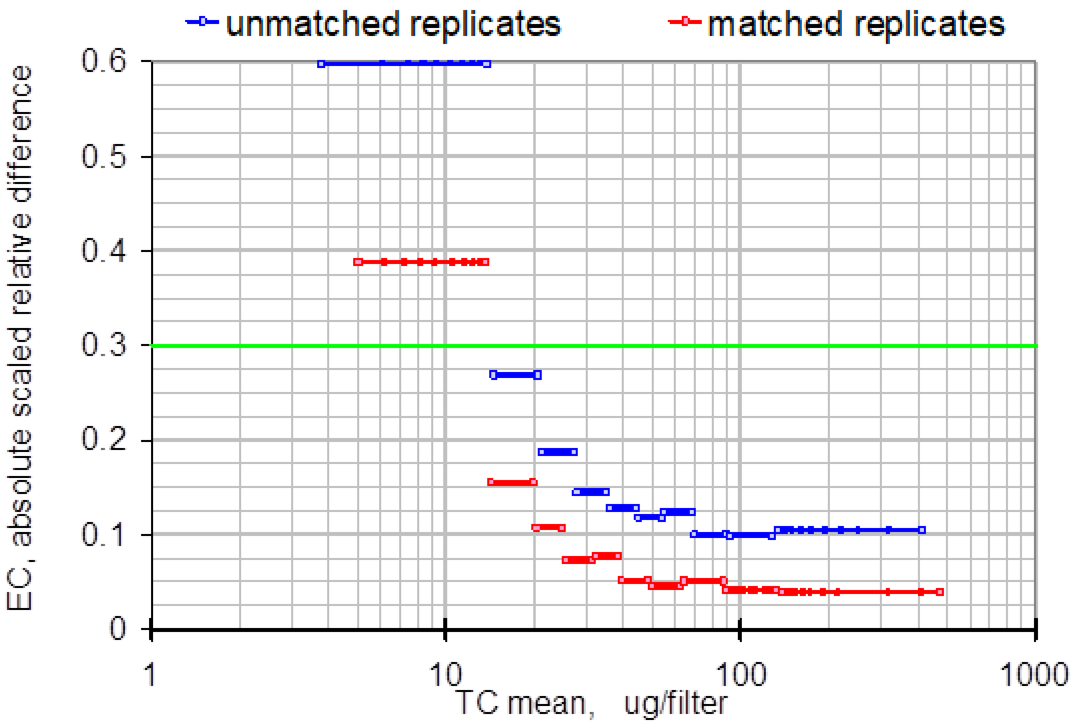


Figure 5. Absolute values of the scaled relative differences from replicate analyses, with horizontal bars representing bounds that encompass two-thirds of the observations in each TC decile.

Errors in the reanalysis are minimized if limited to filter with > 1 micro-g/m3 TC and use the same analyzer on all filter. Should this be done in any TOR reanalysis project?

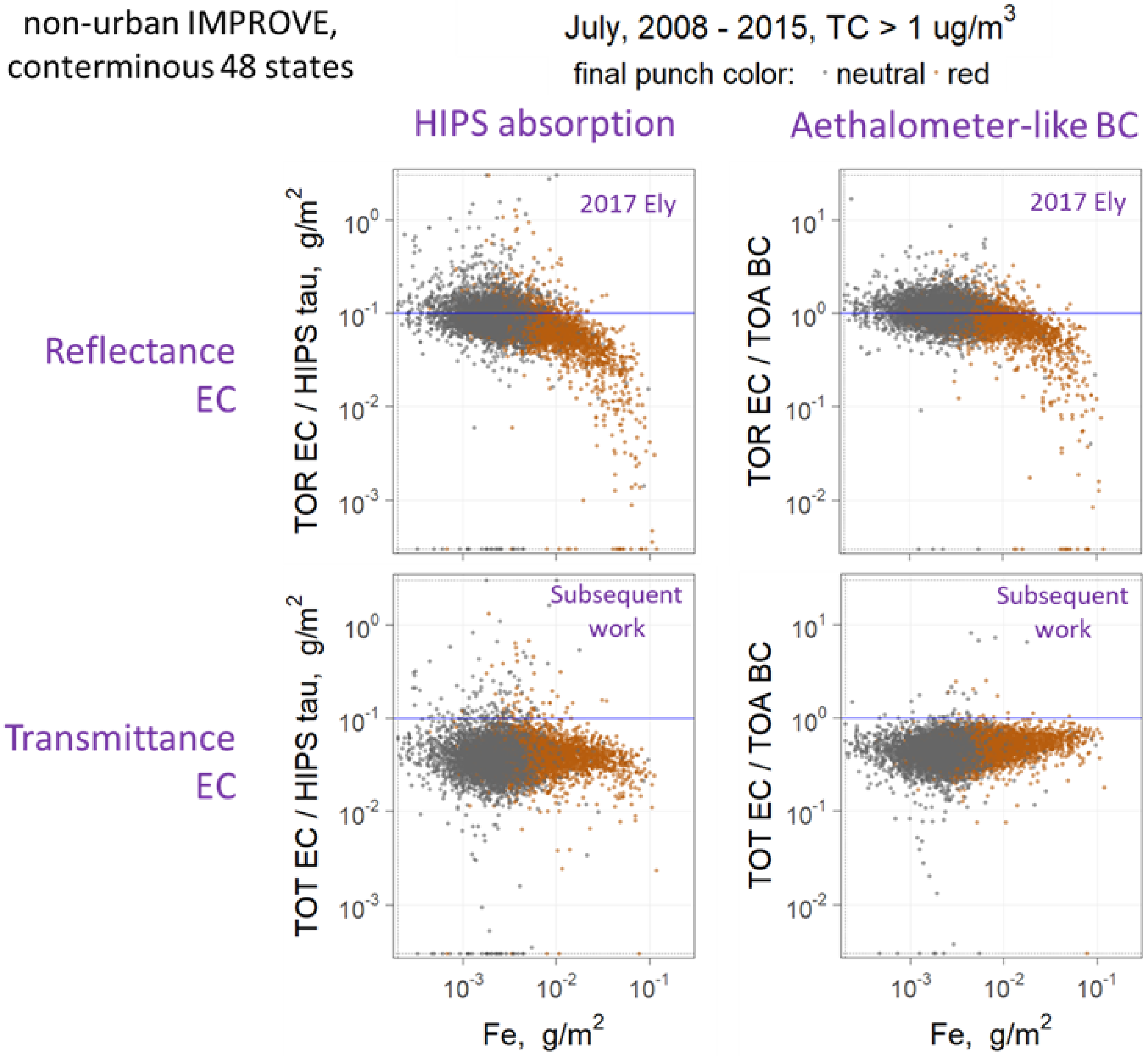
end

Remove OC/LAC Split Dependence on Filter composition

One example:

Apparent loss of LAC in samples w/ high Fe

- Metal oxides and other compounds could catalyze the loss of LAC in He atm (Chow et al., 2001, Fung et al., 2002)
  - A negative OP should correct for this loss
- Fe oxides turn red during heating increasing the reflectance which is compensated for by increased loss of LAC



An optical artifact associated with mineral iron may help to explain the deficits observed in reflectance-corrected, thermally evolved (TOR) EC relative to optically derived LAC in the presence of elevated iron loadings.

It is interesting to note that transmittance-corrected, thermally evolved (TOT) EC does not show the same deficit. The difference may reflect the differing penetration depths of solid mineral particles and semi-volatile pyrolyzable carbon in the quartz-fiber filter.

White et al., 2018

Does LAC Become more absorbing w/ Heating?

- Maybe
- Potential evidence is that OP and LAC apparent MAE increases with increased temperature in He atmosphere
  - can't rule out loss of OP/LAC in He atm, or decreasing OC slip with temperature
- If true, LAC would be underestimated and OP/LAC would volatilize in OC4 fraction

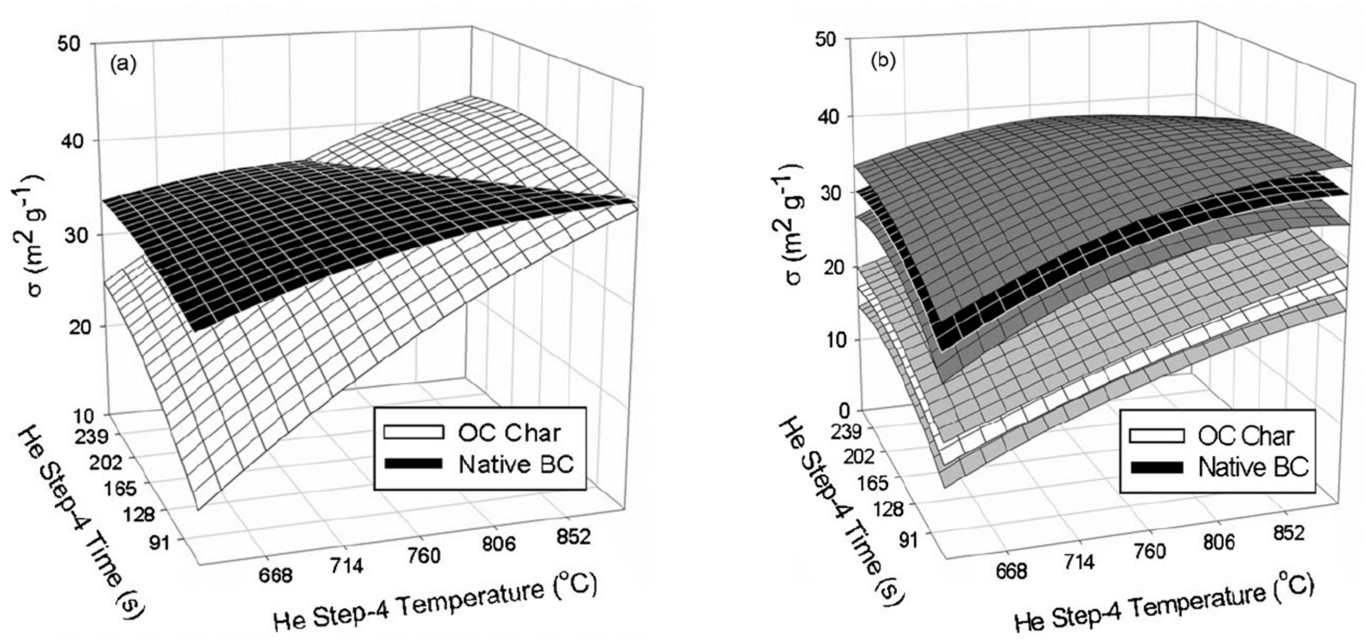


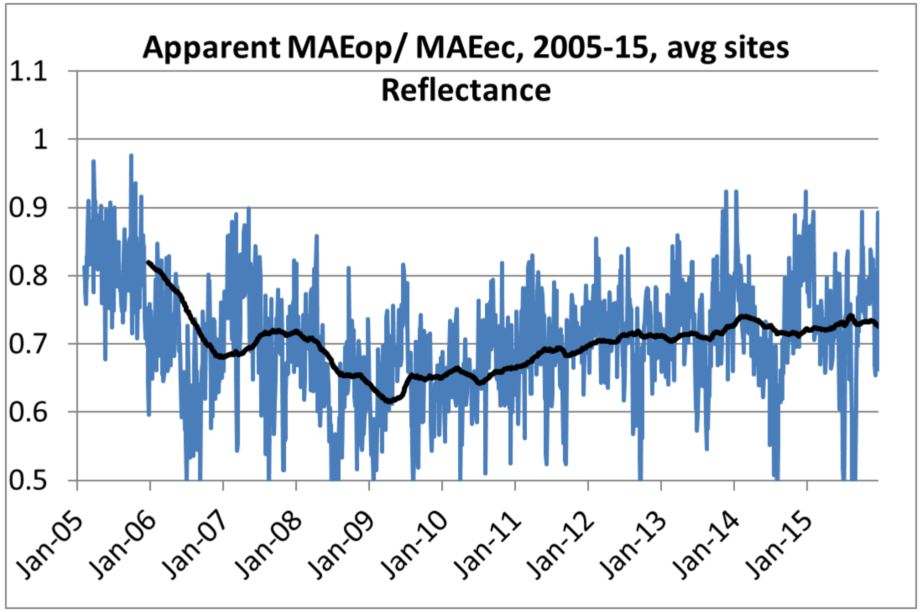
Fig. 10. Overlay of the σ_{BC} and σ_{Char} surfaces for the level-1 sample (a) and level-2 sample (b) from Seattle. OC Char is pyrolyzed OC. Surfaces for the level-2 sample are bracketed by gray-shaded 95% confidence interval surfaces. Confidence intervals for the level-1 sample (omitted for clarity) are comparable to those for the level-2 sample.

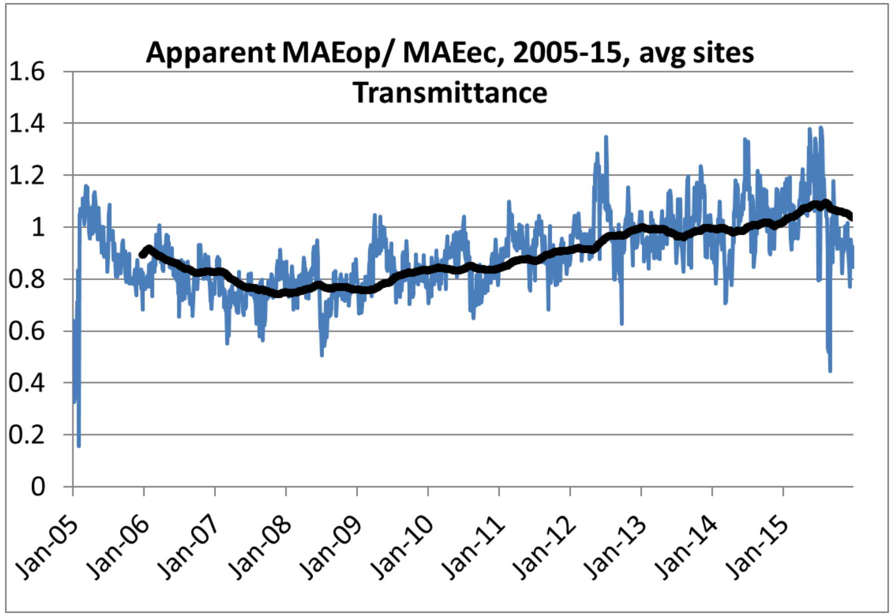
Conny et al., 2009

Ratios of Apparent Mass Absorption Efficiencies

- $MAE_{OP} / MAE_{LAC} = \tau_{ATN, OP} / \tau_{ATN, LAC} * LAC/OP$

$\tau_{ATN, LAC} = \ln(R_{fnl} / R_{init}); \tau_{ATN, op} = \ln(R_{init}/R_{min})$



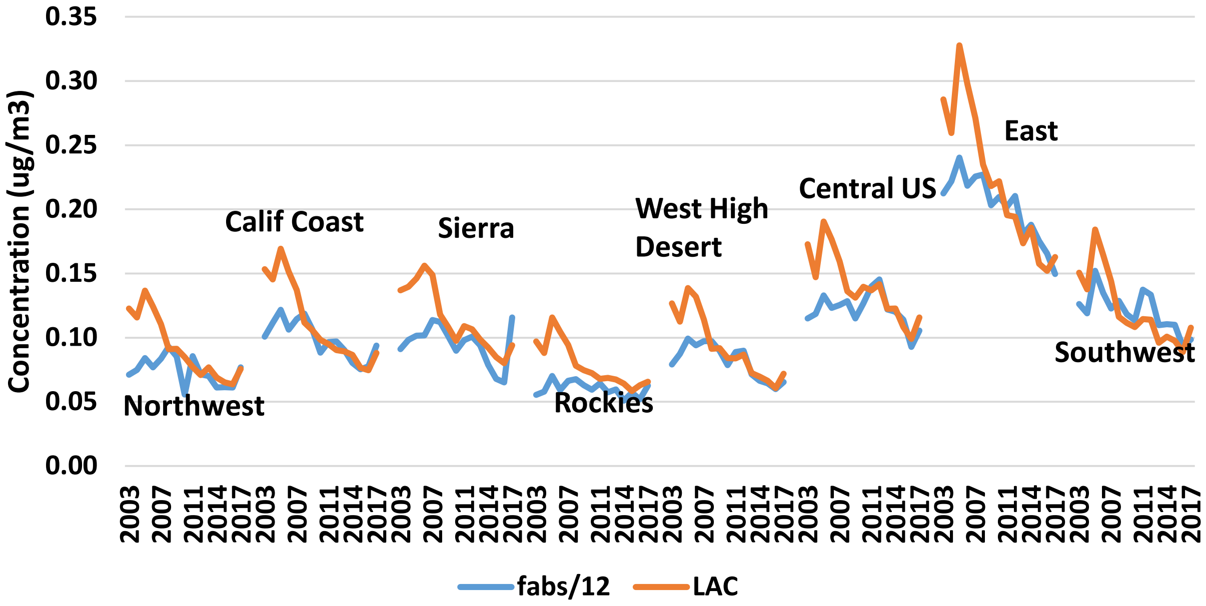


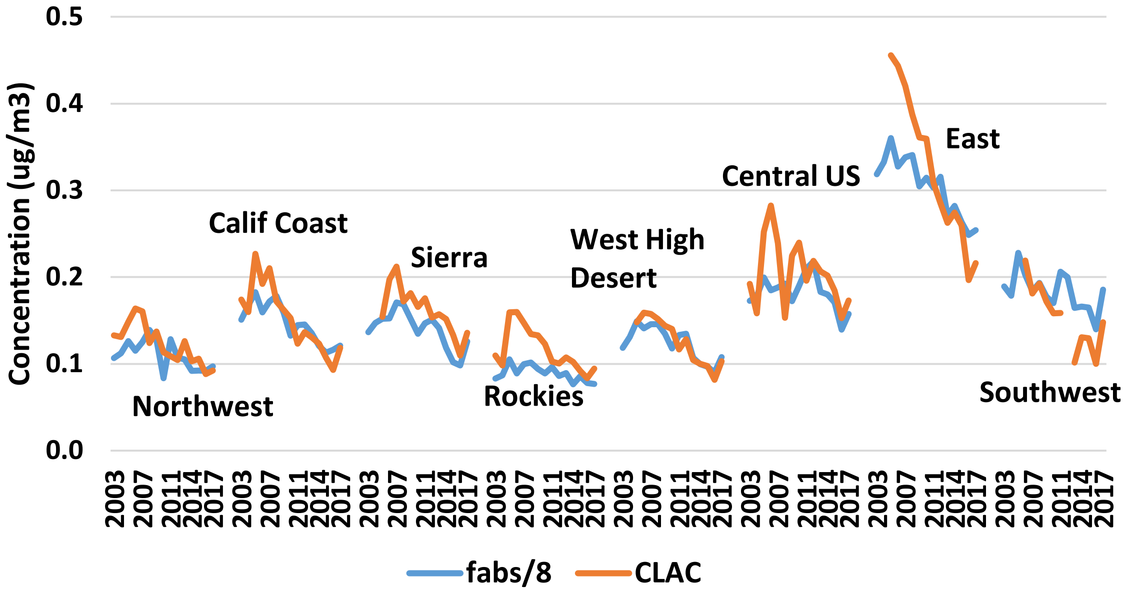
- Apparent MAE of <u>LAC</u> fraction is ~1.5 times larger than OP fraction
  - OP mass ~ 1.5 * LAC mass, $\tau_{ATN, op}$ ~ 1.1 * $\tau_{ATN, LAC}$
  - Carbon with lower MAE (i.e. LAC) is preferentially volatilized before high MAE carbon (i.e. OP)

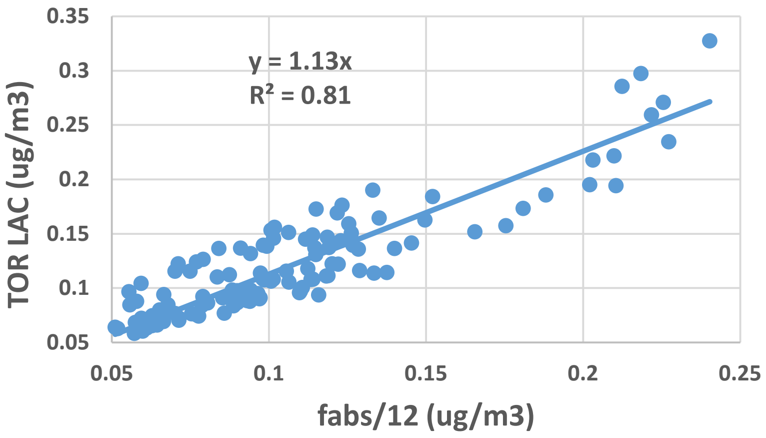
- Apparent MAE of <u>OP</u> is ~1.5 times larger than LAC fraction
  - OP mass ~ 2 * LAC mass, $\tau_{ATN, op}$ ~ 3 * $\tau_{ATN, LAC}$

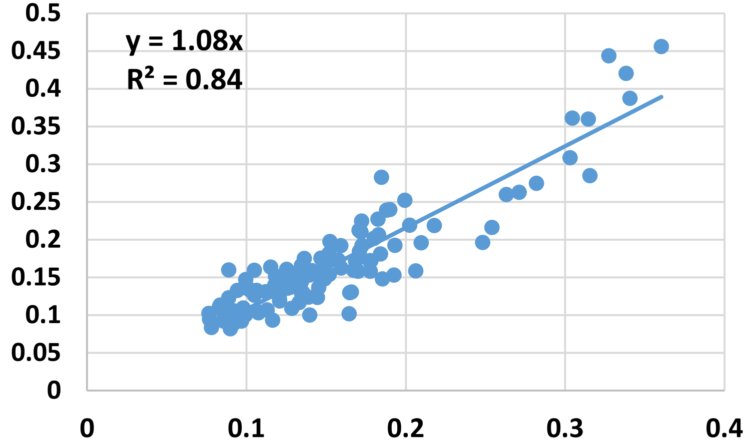
- In both cases apparent $MAE_{OP} < 3* MAE_{LAC}$ suggesting an underestimation in LAC

Impact of LAC corrections on Trends









- The corrected LAC generally reduced the 2003-2008 differences in the LAC and fabs trends
- Suggest that LAC MAEs may have been relatively constant since 2003