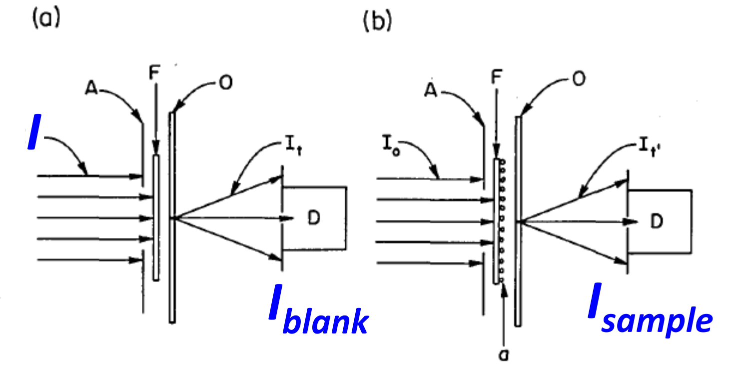
The dance of carbon, iron, and light absorption

1: pas de deux

Independent measurements of filter light absorption

The ur-measurement of absorption:
pre- & post-sampling transmissometry

$$\tau_{abs} = ln\left({}^{I_{blank}}\!/_{I_{sample}}\right)$$



Scattering by the filter itself generally dominates overall attenuation, placing a premium on accurate determination of the blank transmittance. But a program of IMPROVE's scale needs to minimize separate blank measurements.

Fig. 1. The experimental arrangement used in the opal glass method. (a) Filter without aerosol. (b) Filter with aerosol.

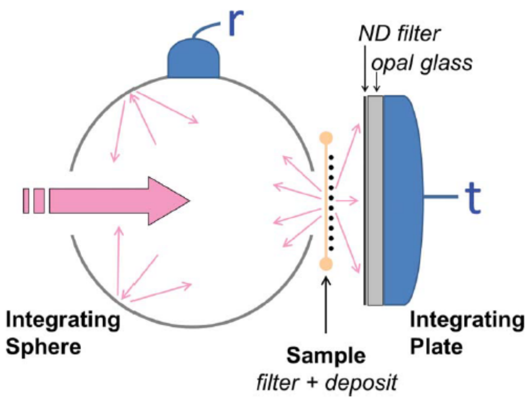
Lin, Baker, and Charlson
June 1973 / Vol. 12, No. 6 / APPLIED OPTICS 1357

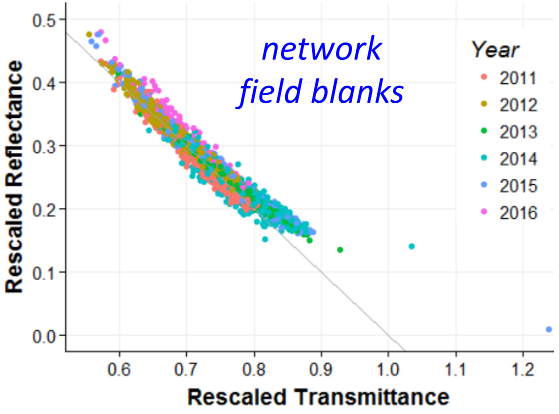
HIPS Fabs

light: He-Ne laser, λ = 632.8 nm
filter: PTFE from module A (optically thin)
lab: UCD
blank: from reflectance of unexposed
back side of sample filter

$$I_{blank} = I \times (1 - r)$$

$$Fabs = ln\left(\frac{I_{blank}}{I_{sample}}\right) = ln\left(\frac{1-r}{t}\right).$$





TOA BC

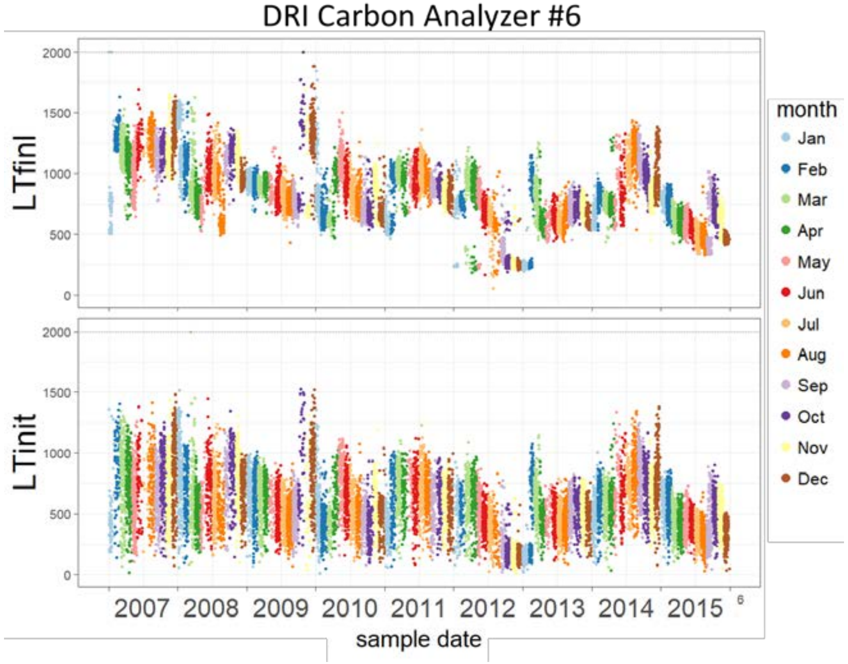
light: He-Ne laser, λ = 632.8 nm
filter: quartz from module C
(optically thick)
lab: DRI
blank: sample filter following IMPROVE_A heating and combustion

$$MAC \times BC = ln\left(\frac{I_{blank}}{I_{sample}}\right),$$

$$BC = ln\left(\frac{LT_{final}}{LT_{initial}}\right)/MAC,$$

$$MAC \equiv 23\,m^2/g$$

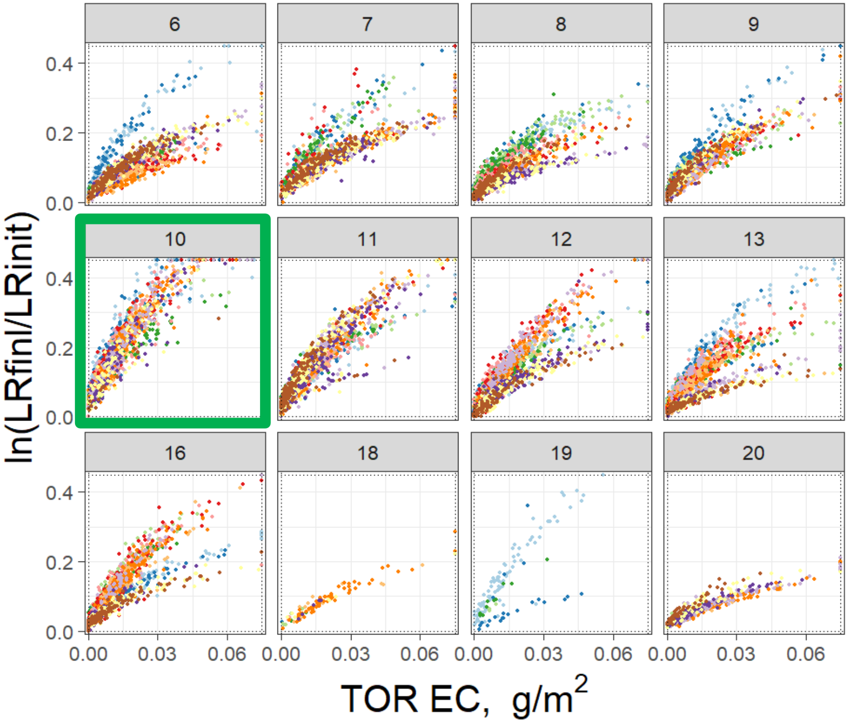
from Aethalometer conventions,
that MAC ~ λ^{-1} and = 16.6 m^2/g at λ = 880 nm.



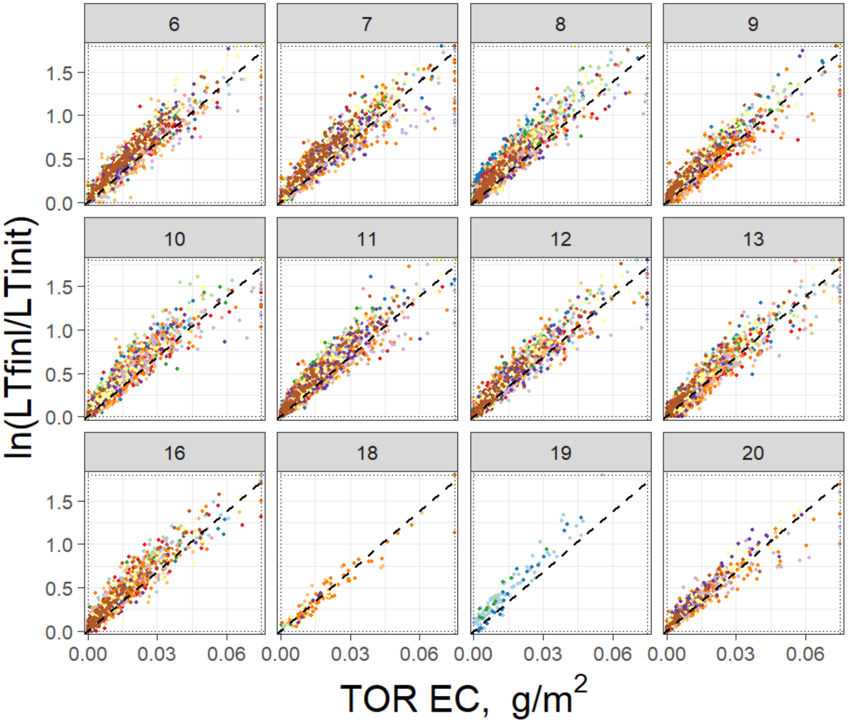
carbon
analyzer (ca)

sample year 2012

DRI laser reflectance

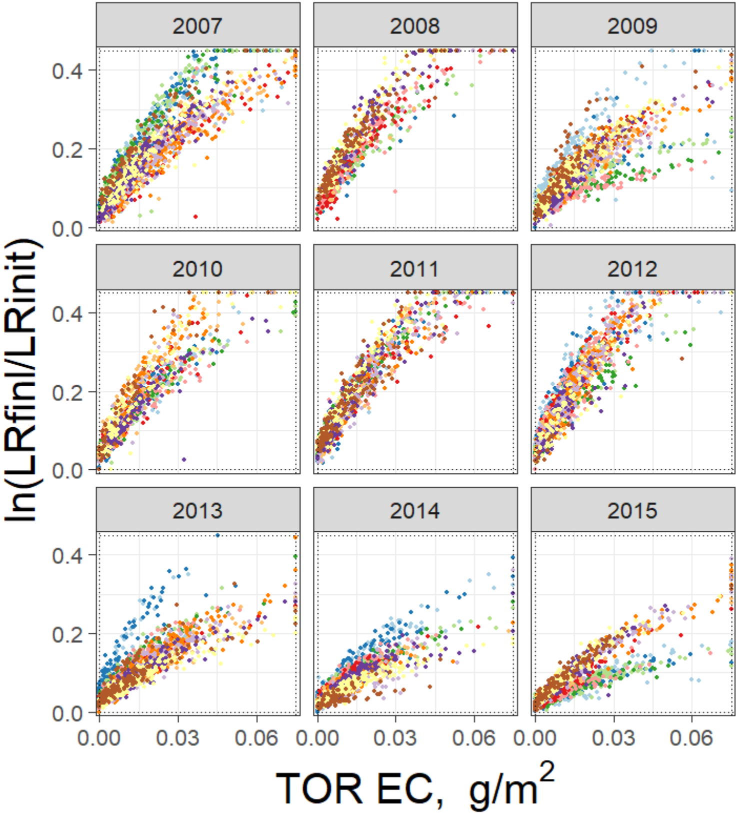


DRI laser transmittance

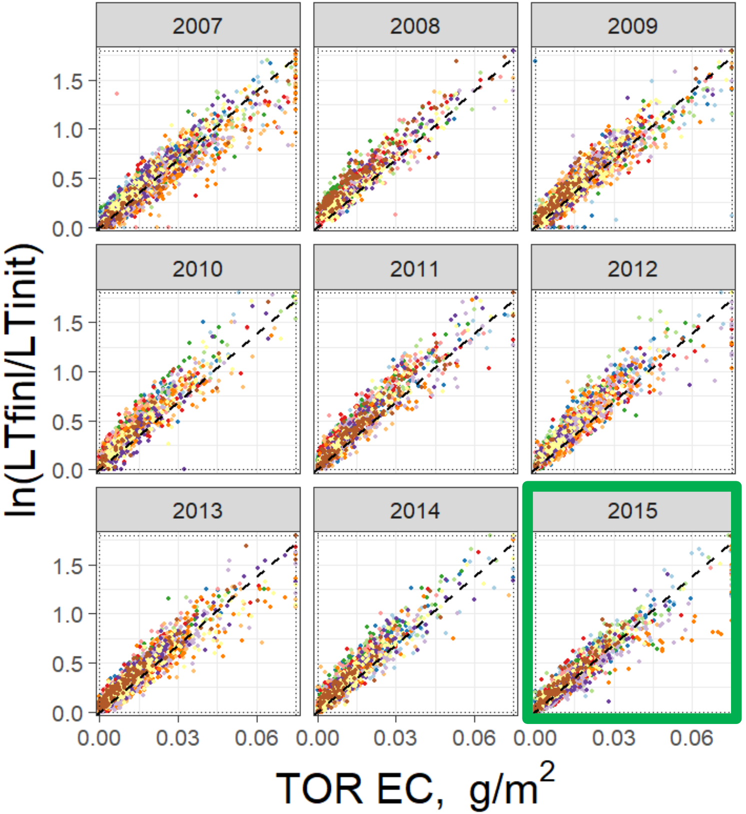


DRI Carbon Analyzer #10

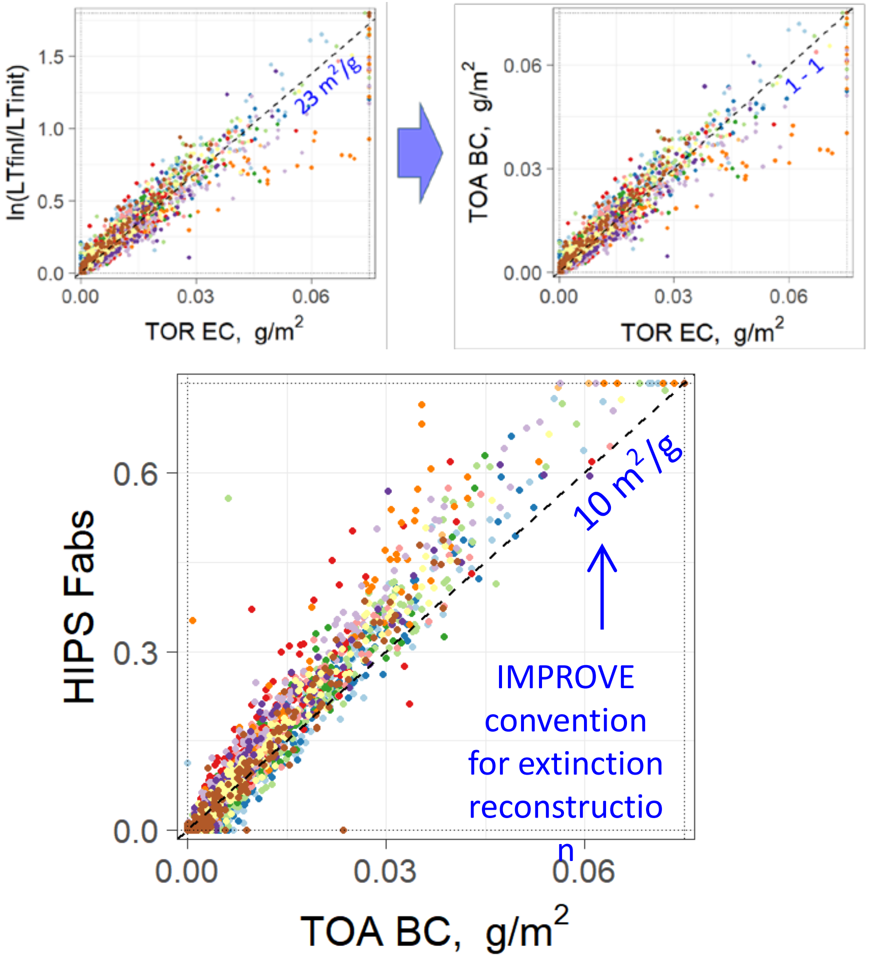
DRI laser reflectance



DRI laser transmittance



ca #10 in 2015



IMPROVE convention for extinction reconstruction

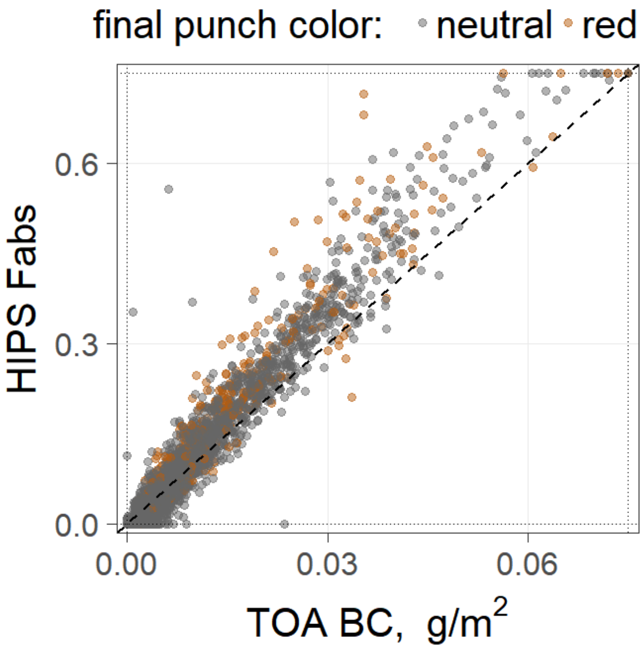
BC and Fabs refer to the same He-Ne laser wavelength, but differ in characterizing the optical baseline. HIPS Fabs captures total absorption from *all* collected PM. TOA BC is determined by the absorption lost during heating and combustion, and is expected to include *only* light-absorbing carbon, the aggregate of black and any brown carbon.

By comparing our two optical measurements we can hope to gain insight into absorption by mineral dust, which should contribute only to Fabs and *not* to BC.

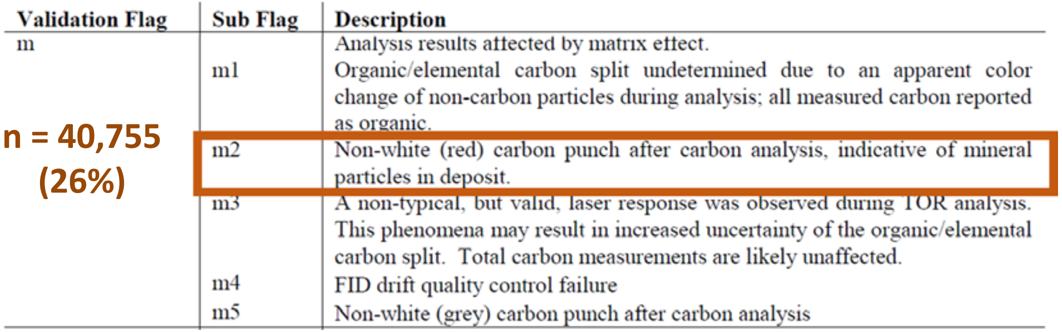
Consider **all 157,767** valid unmasked samples from non-urban sites in the 48 conterminous states during 2007 - 2016. Classical OLS regression yields

$$Fabs = -0.009 + 10.8BC + 3.2Fe, \qquad \boldsymbol{r^2 = 0.908}$$

Can we 'see' this contribution graphically?

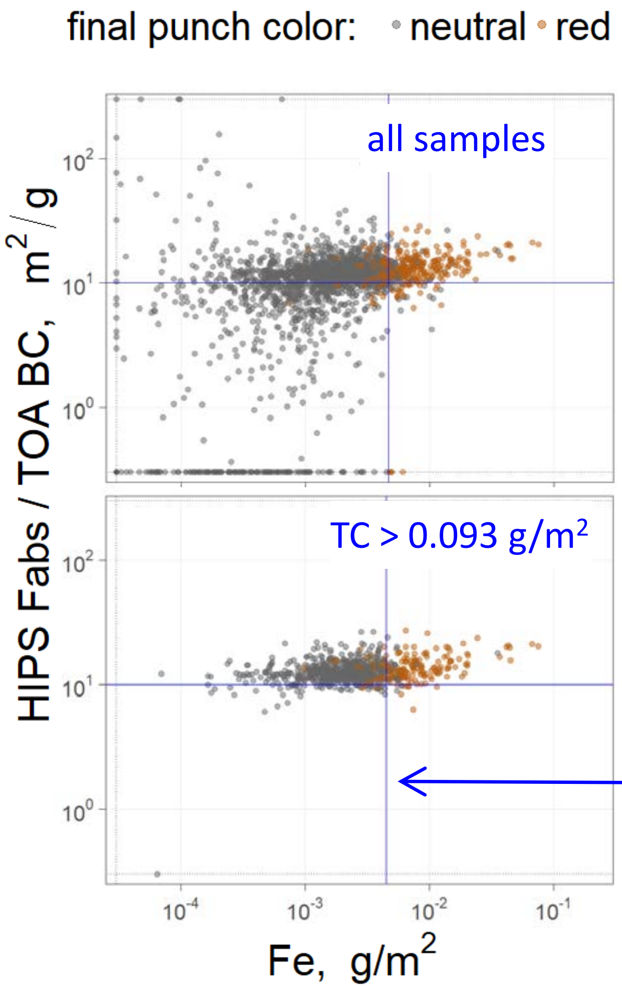


DRI analytical flags give a binary indication of dust levels.



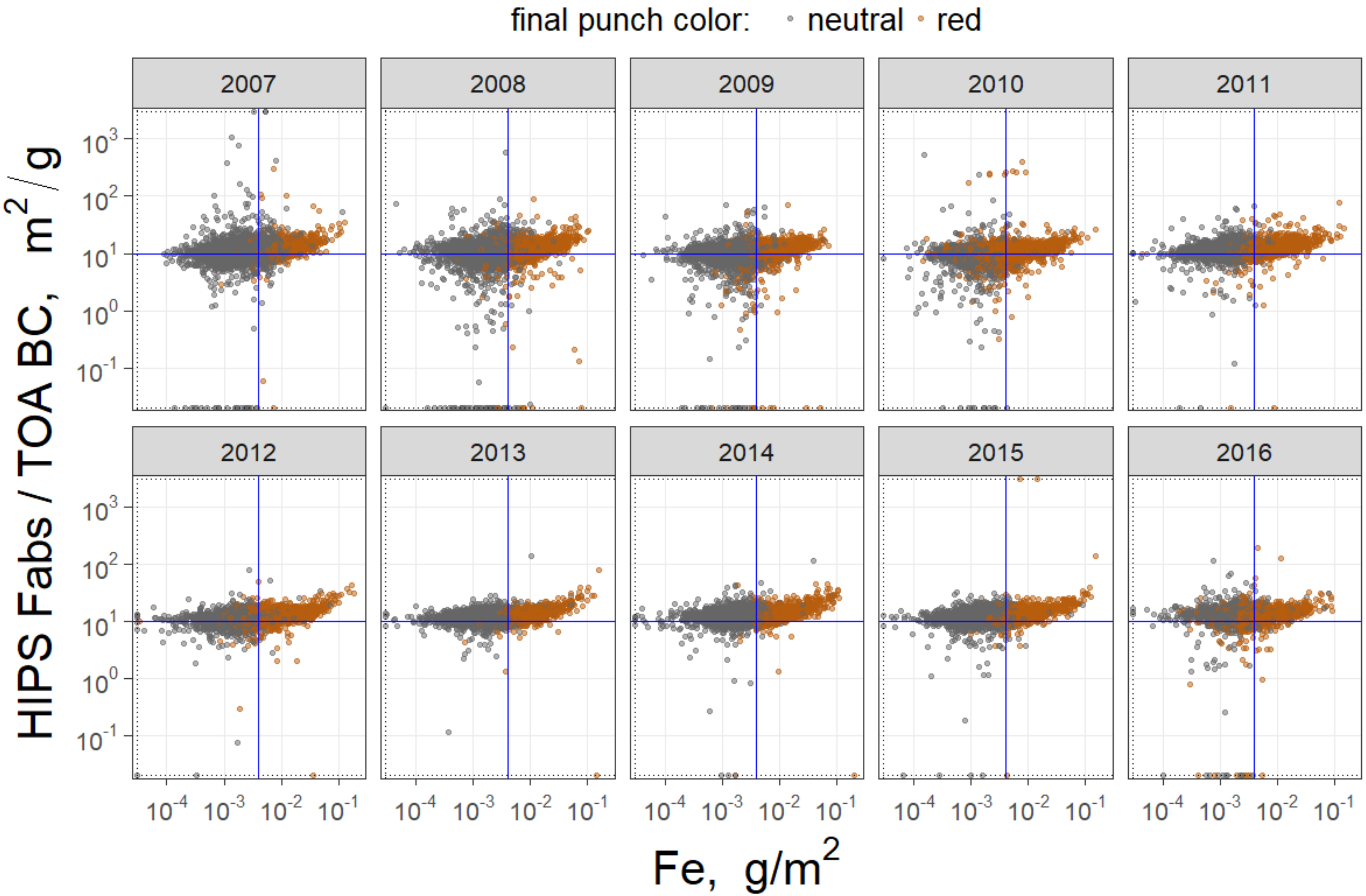
Validation Flag	Sub Flag	Description
m		Analysis results affected by matrix effect.
	m1	Organic/elemental carbon split undetermined due to an apparent color change of non-carbon particles during analysis; all measured carbon reported as organic.
	m2	Non-white (red) carbon punch after carbon analysis, indicative of mineral particles in deposit.
	m3	A non-typical, but valid, laser response was observed during TOR analysis. This phenomena may result in increased uncertainty of the organic/elemental carbon split. Total carbon measurements are likely unaffected.
	m4	FID drift quality control failure
	m5	Non-white (grey) carbon punch after carbon analysis

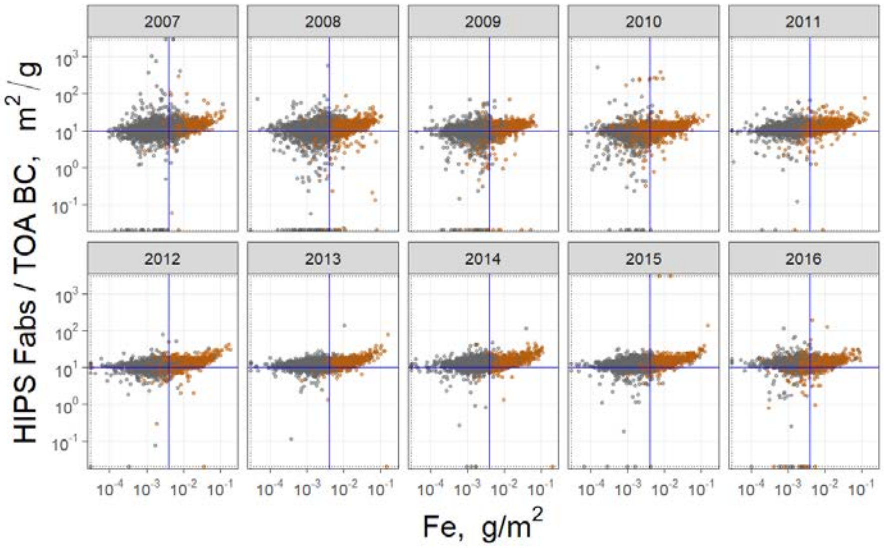
n = 40,755 (26%)



The Fe loading is a continuous metric that offers more information than the punch flags. To limit the visual impact of measurement noise, the scatterplots in following slides will exclude TC loadings under 0.093 g/m^2 (= 9.3 ug/cm^2). At target sample volumes this mass loading represents an ambient concentration of 1 ug/m^3, roughly the 60th percentile reported by the network for TC.

Fe loading corresponding to % red punches


final punch color:
● neutral
● red
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
HIPS Fabs / TOA BC, m^2/g
10^3
10^2
10^1
10^0
10^{-1}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
Fe, g/m^2



So … we ***can*** ‘see’ the contribution of Fe to non-BC absorption! It is a minor fraction that is consistent throughout the decade.

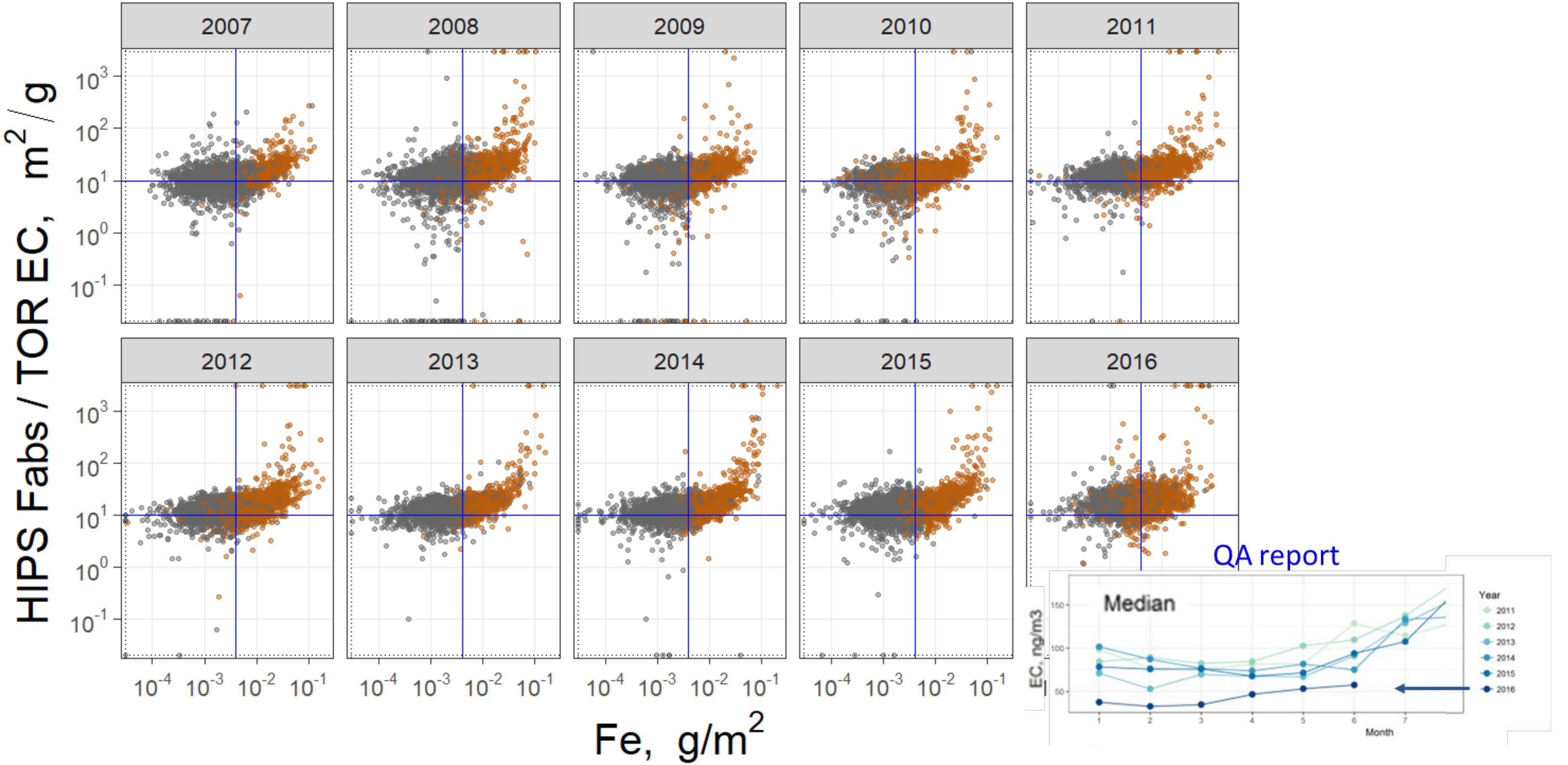
The regression coefficients, applied to grand averages (n = 157,757), account for 105% of observed Fabs and attribute 4% of that total to Fe-bearing minerals.

2:

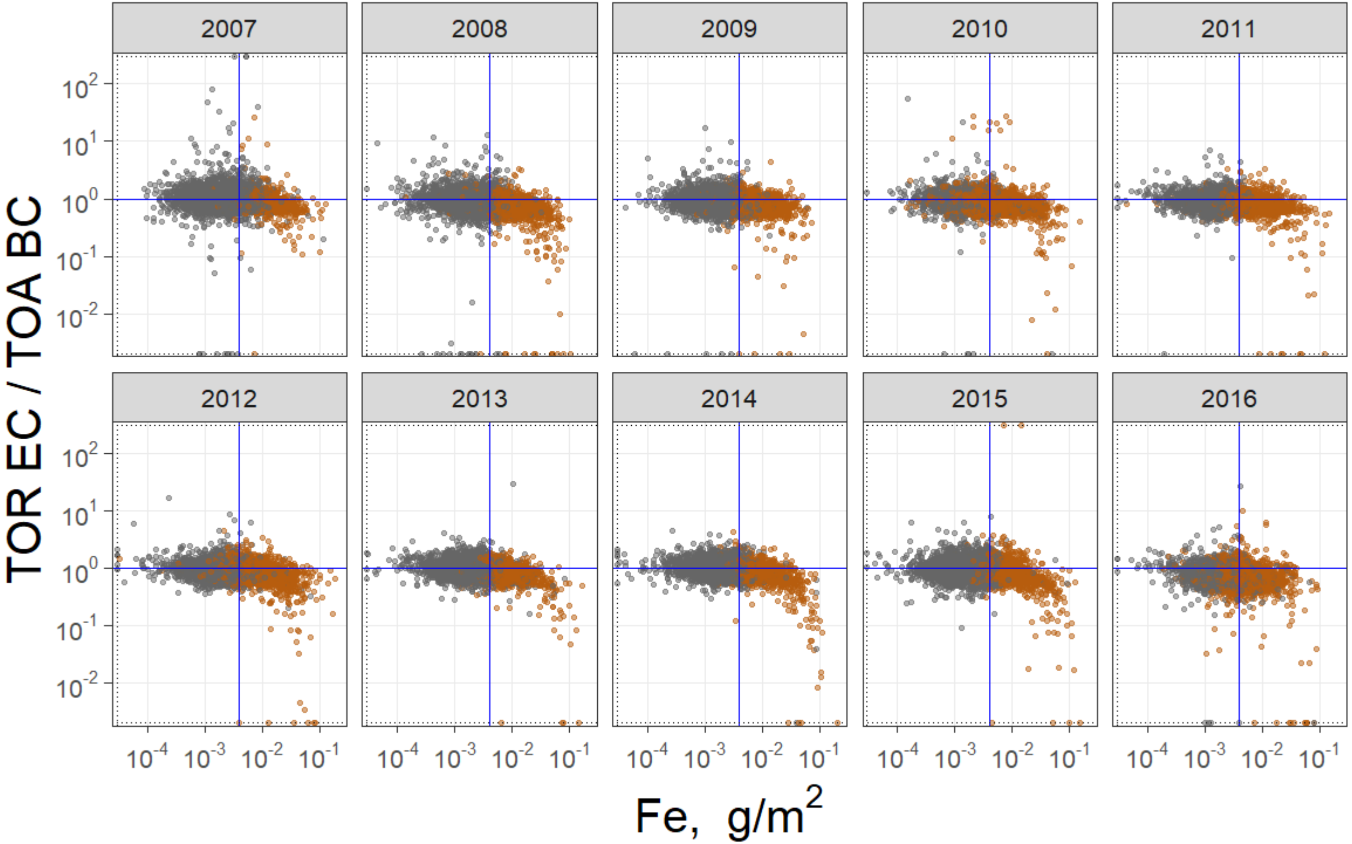
Evidence of Fe interference in the TOR EC determination

Substituting EC for BC degrades the OLS relationship, and strengthens the relative importance of Fe.

$$Fabs = 0.040 + 8.5EC + 5.2Fe,\ \boldsymbol{r^2} = \mathbf{0.788}$$

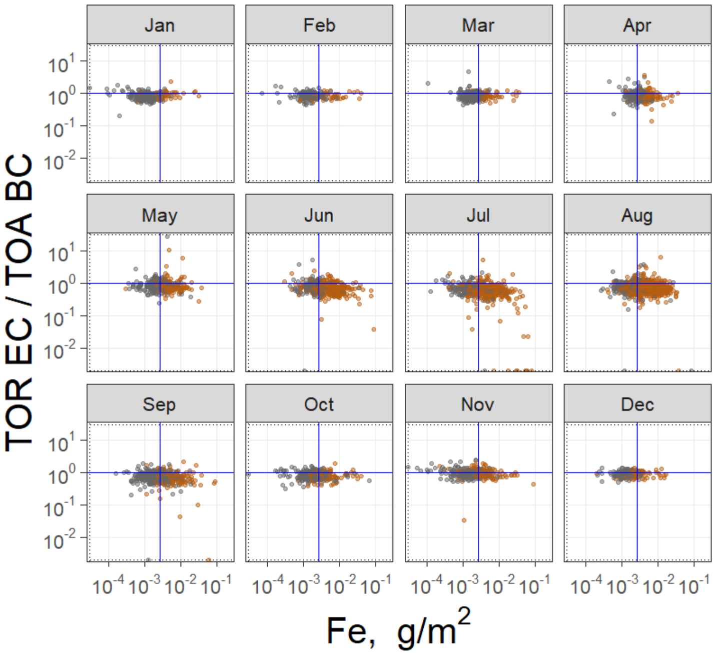


That is because some of the BC that is removed from the quartz filter during heating and combustion is not reported as TOR EC. Because the EC goes missing only in the presence of Fe, regression attributes that BC absorption to the presence of Fe.

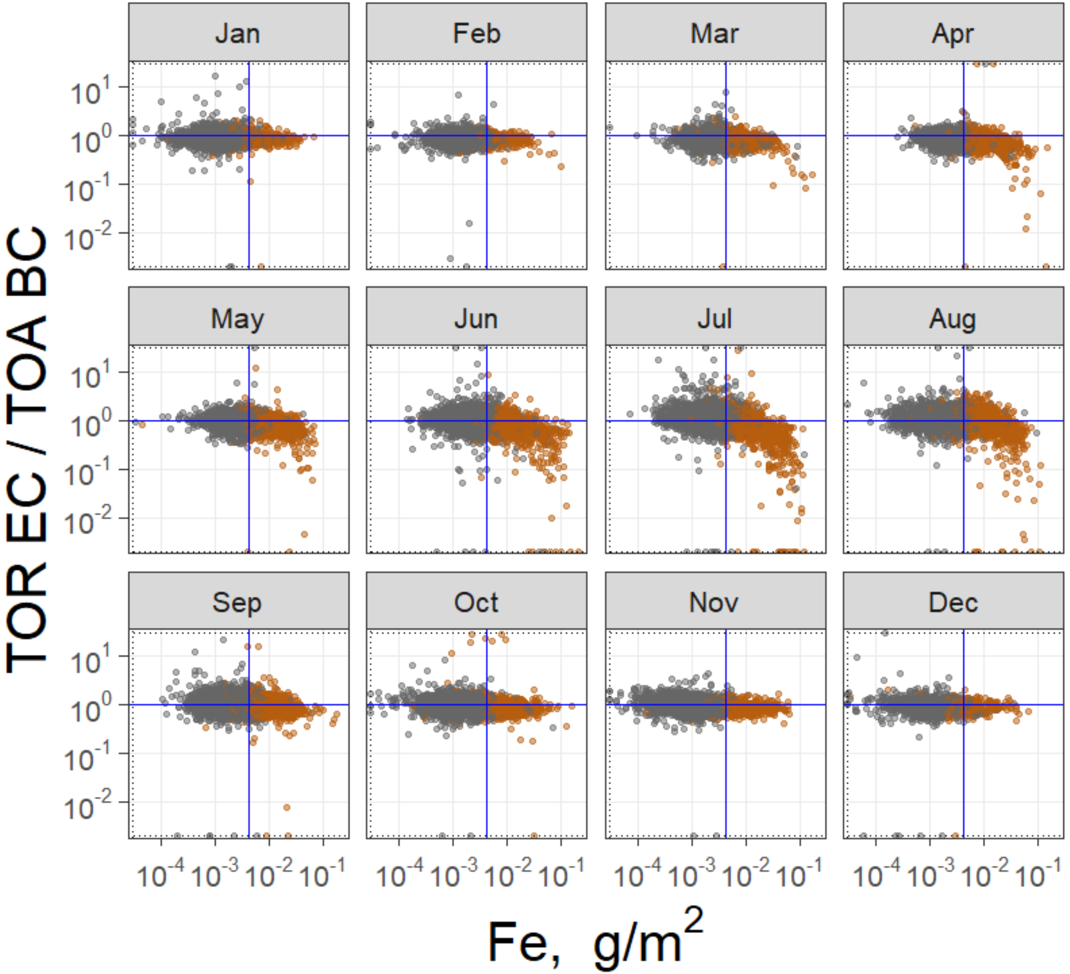


This ‘accounting gap’ is strongly concentrated in the summer. The months from September through February show little dependence on Fe.

2016



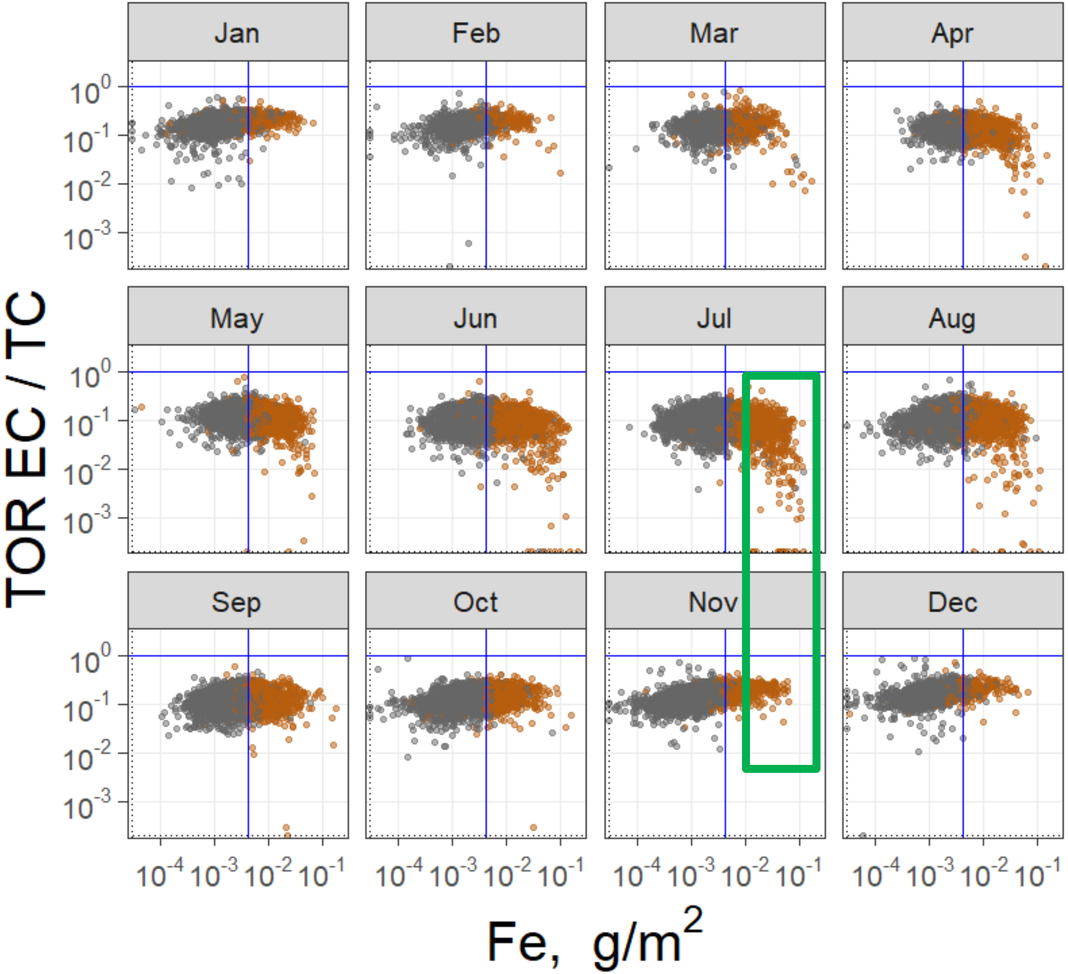
2007 – 2015



The seasonal interaction of Fe with the EC/TC split can also be seen without reference to either of our absorption measurements.

Similarly Fe-rich samples from July and November show quite different ranges of TOR splits, for example. And this difference is observed only in the presence of Fe.

2007 – 2015

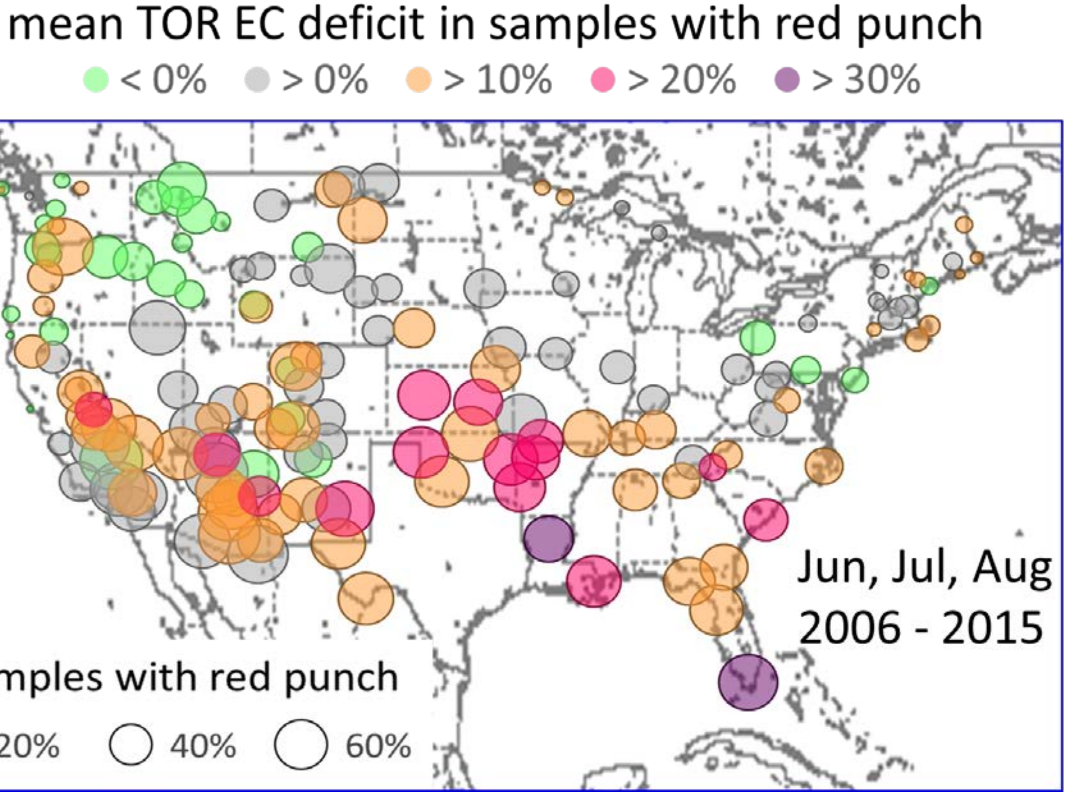


We can get an indication of iron's "average interference" in the TOR EC determination from the shift in EC/BC ratios observed in samples flagged for red final punches.

We assume a site's mean loading of "native EC" ($\overline{EC_{native}}$) to be proportional to its mean observed BC ($\overline{BC_{obs}}$), in the ratio $\overline{EC_{obs}}/\overline{BC_{obs}}$ observed in samples not flagged for red punches. Applying this expectation to the <u>summer</u> months yields the deficits

$$\frac{\overline{EC_{native}}-\overline{EC_{obs}}}{\overline{EC_{native}}}$$

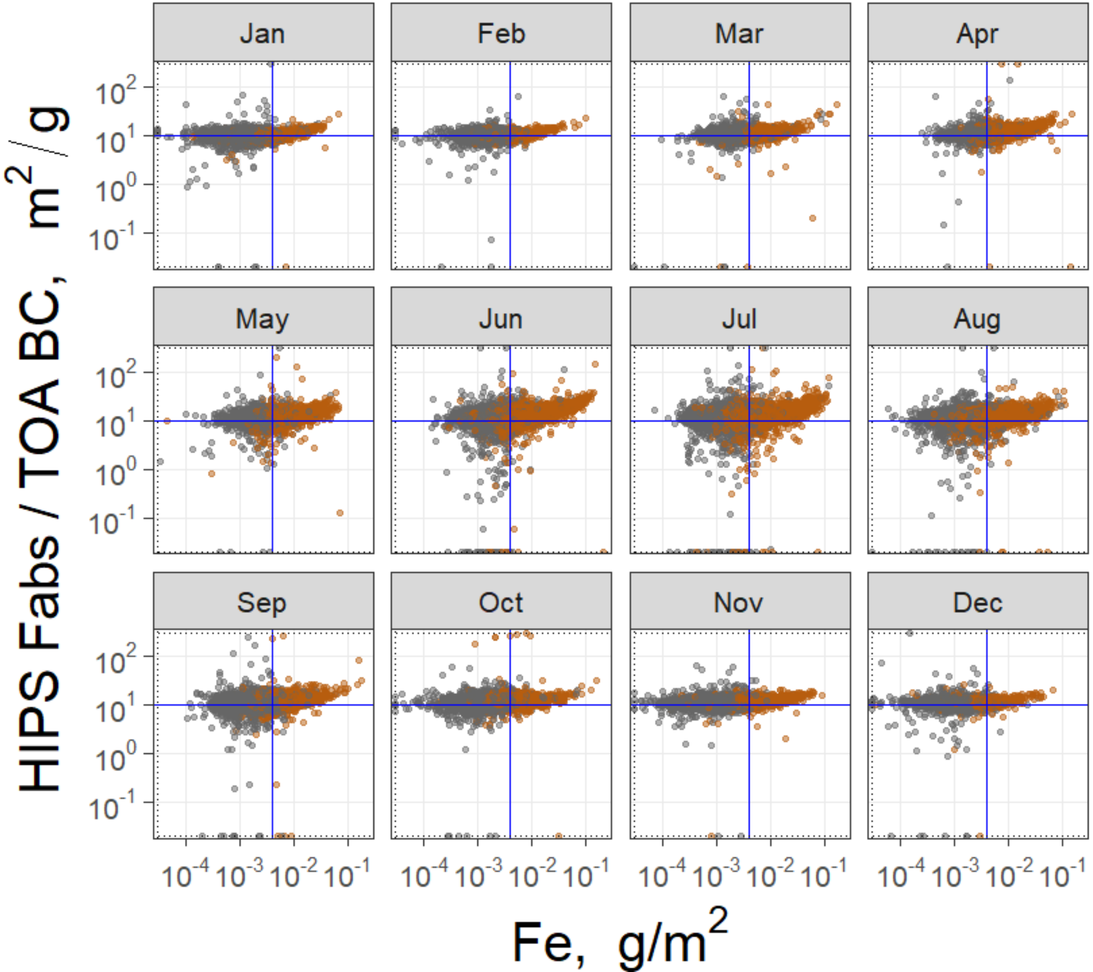
shown here for samples with red punches.



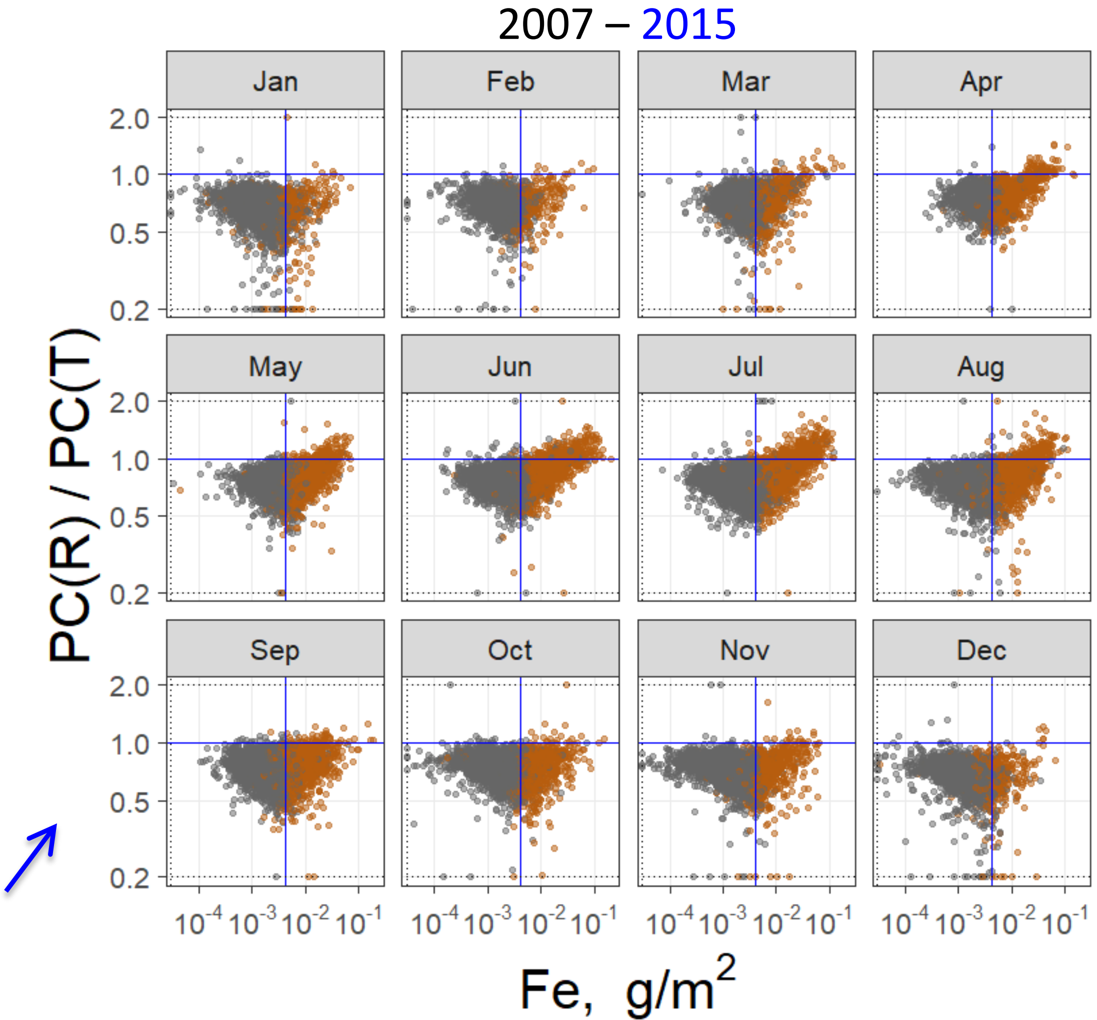
The form of the relationship among Fabs, BC, and Fe is fairly consistent throughout the year, as was already implied by the fit of the overall regression.

Interestingly, the relationship's noise peaks in summer. This is when TOR EC most diverges from TOA BC, but the scatter is not obviously associated with Fe content. It may instead reflect the seasonality of sulfates and other non-absorbing species, whose light-scattering interferes with the Fabs and BC measurements.

2007 – 2016



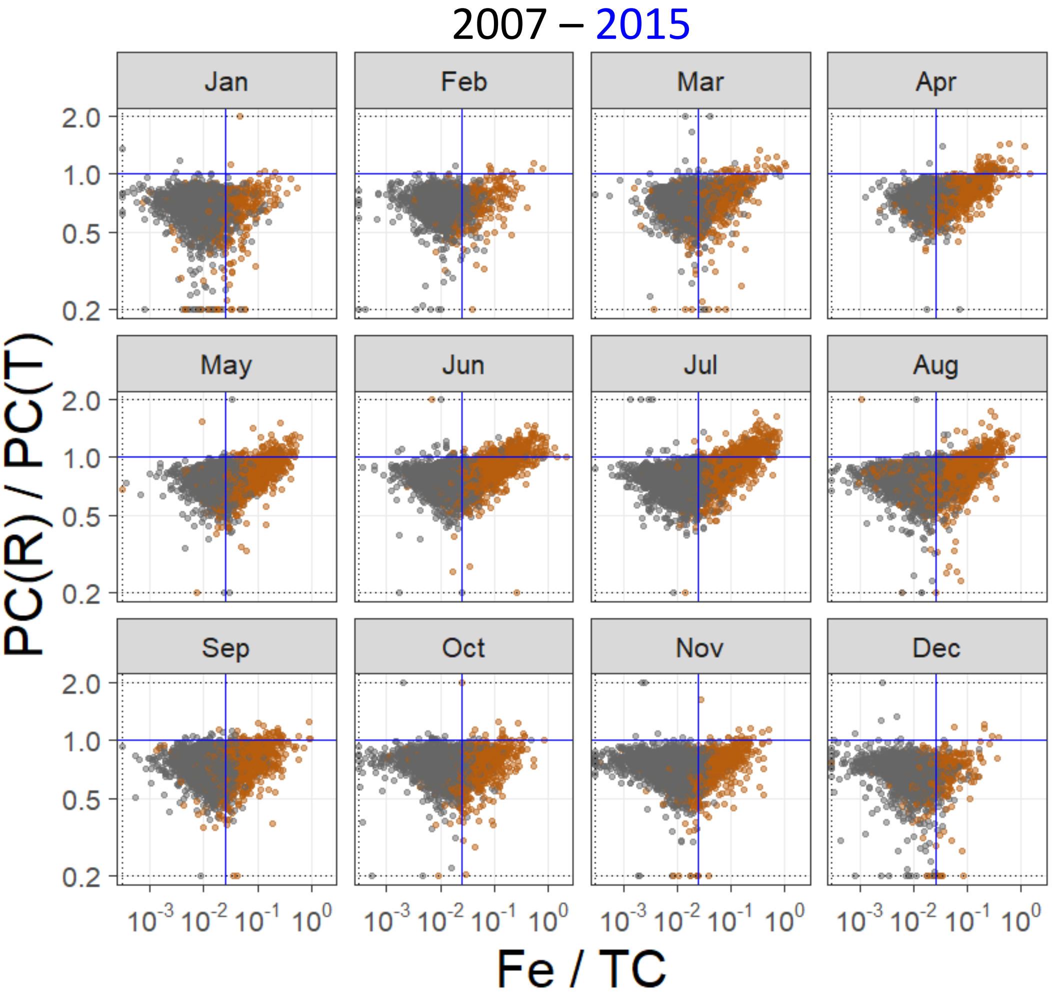
How does Fe influence the TOR EC split? And why is this influence limited to spring and summer? One potentially relevant modulation is the seasonal variation in the organic aerosol's volatility distribution and phase partitioning. These factors affect the depth distribution of the total carbon collected and its likelihood of interacting with the presumably solid particles expected to carry Fe.



Ratio of pyrolysis corrections from R and T signals

As a final observational note, the dependence of the TOR EC/TC split on Fe content is insensitive to whether this content is expressed as a filter loading of the element or as a composition relative to total carbon.

The compositional framing facilitates comparisons with some experimental aerosols.



“Despite the knowledge of the catalytic effect of certain minerals on soot oxidation, the feasibility of thermo-optical methods for the quantification of EC and OC in aerosol samples is rarely questioned.”

H. Bladt et al., *Journal of Aerosol Science 70* (2014) 26–35

TPD [temperature-programmed desorption] experiments of soot collected on quartz fiber filters were conducted … without external O_2. For this purpose, N_2 (≥99,9990%, Air Liquide, France) was additionally purified by an oxygen absorber to give N_2 with <1 ppm O_2. …
[E]mission of CO and CO_2 could be observed for all soot types containing Fe. At 56% (m/m) Fe content, soot could even be completely combusted [at temperatures attained in the OC3 stage of IMPROVE_A.]

H. Bladt et al., Impact of Fe Content in Laboratory-Produced Soot Aerosol on its Composition, Structure, and Thermo-Chemical Properties. *Aerosol Science and Technology 46* (2012) 1337–1348

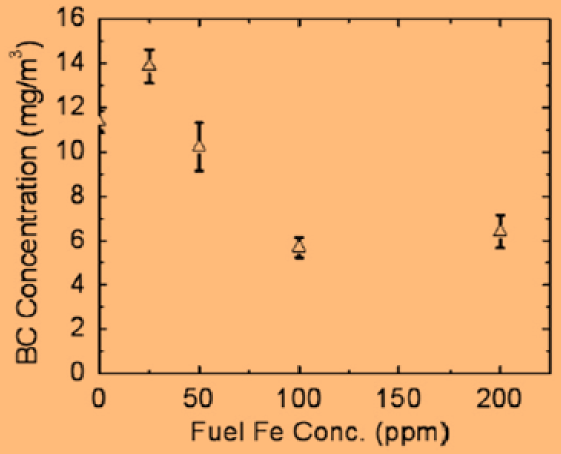
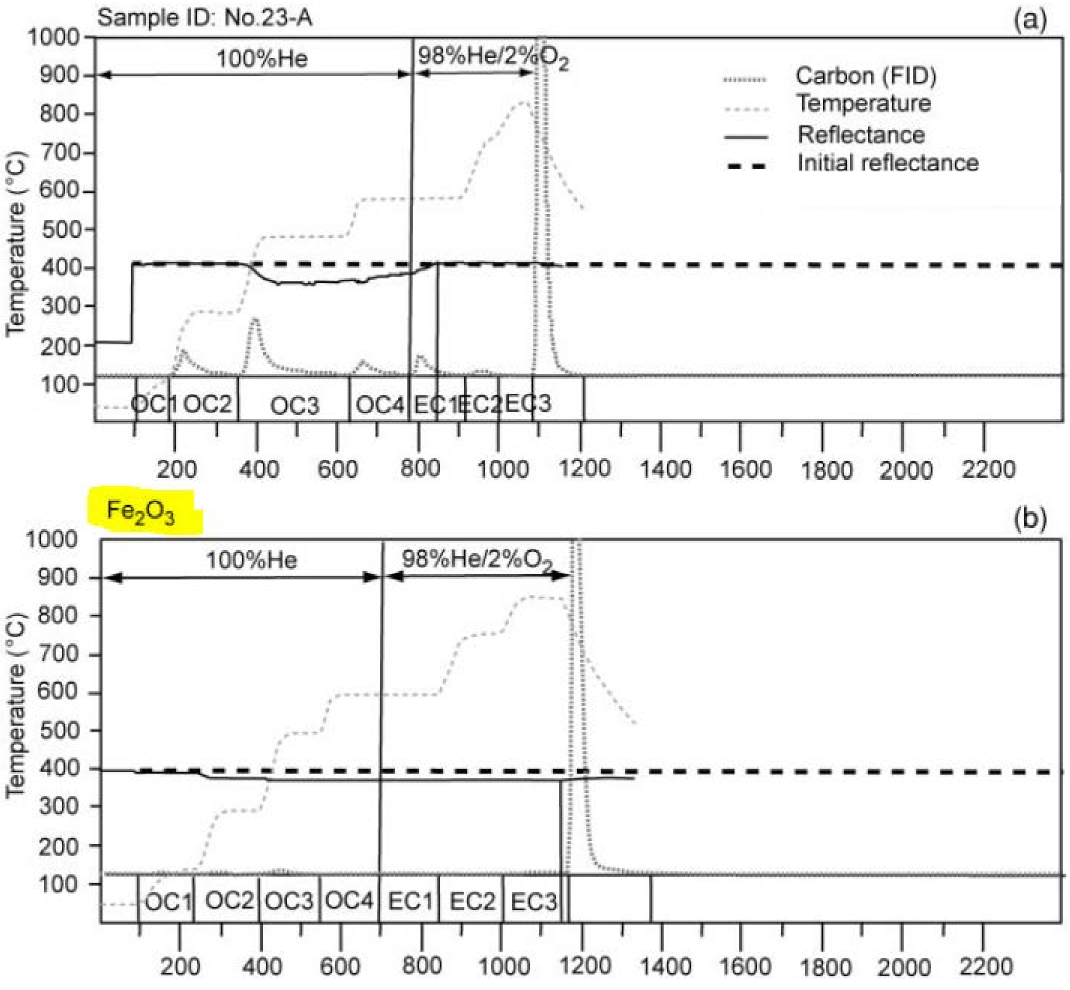


Fig. 5. Effect of Fe addition on BC concentration as measured by aethalometer.

D.G. Nash et al., Environmental implications of iron fuel borne catalysts and their effects on diesel particulate formation and composition. *Journal of Aerosol Science 58* (2013) 50–61



All filter samples were analyzed for OC and EC by a Desert Research Institute (DRI) Model 2001 Thermal/ Optical Carbon Analyzer following the IMPROVE TOR protocol … . … **dust on the filter results in the FID division being postponed or inefficient**. As a consequence, over-estimated OC and underestimated or even negative EC values are produced.

FIG. 2. Example thermograms of No. 23-A (Non-Dust Group) … from ice core samples … and pure hematite: (a) the laser signal decreases at 450◦C and returns back after O_2 is injected; (b) the optical change of Fe_2O_3 when combusted for the second time …

M. Wang et al., The Influence of Dust on Quantitative Measurements of Black Carbon in Ice and Snow when Using a Thermal Optical Method. *Aerosol Science and Technology 46* (2012) 60–69