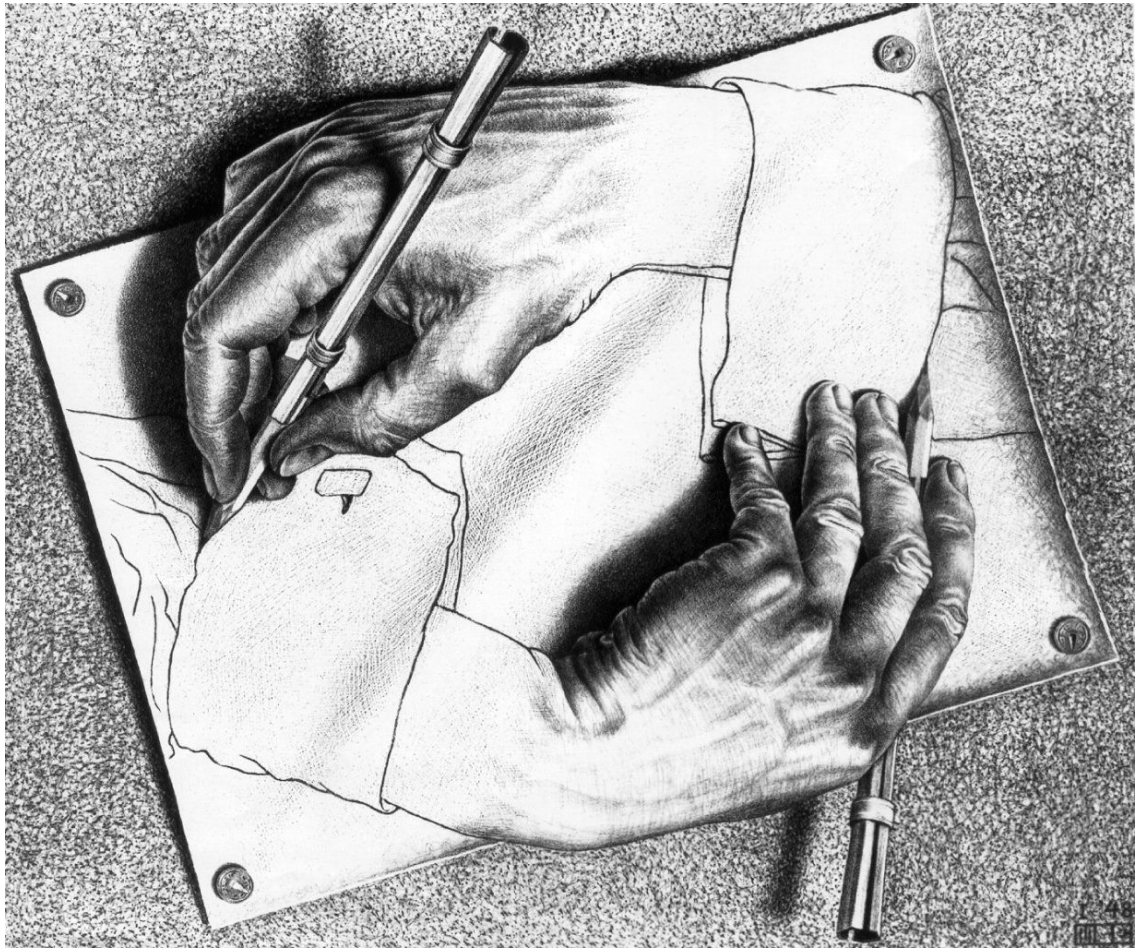
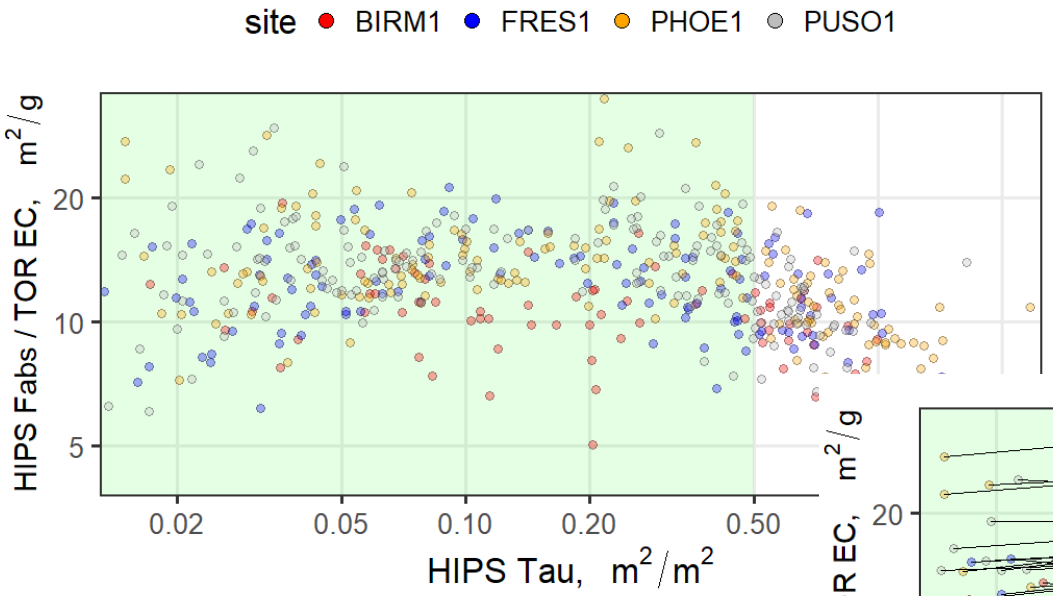
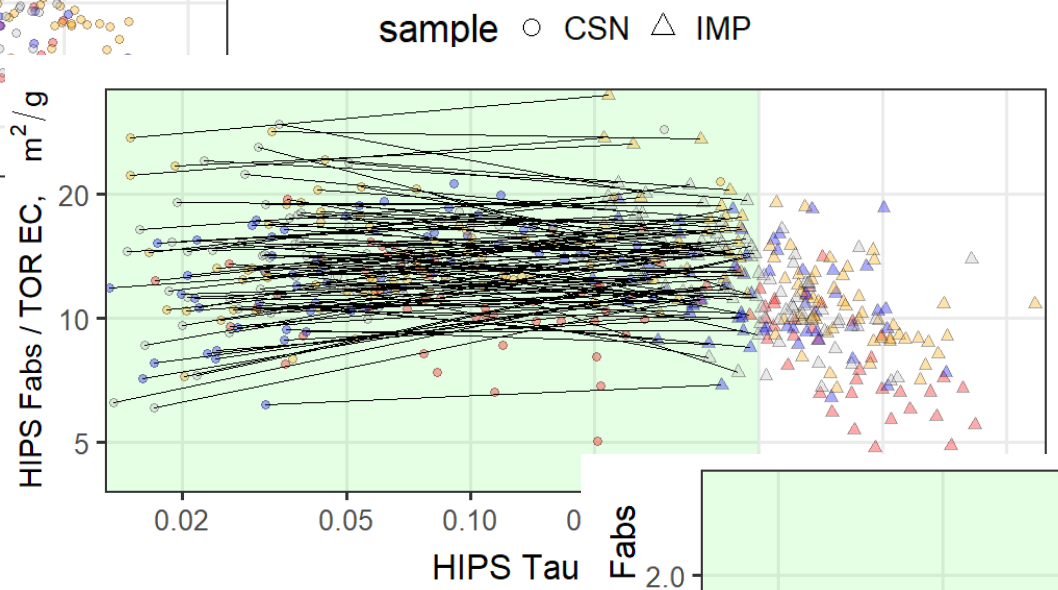
Loading effects, and the observed relationship between HIPS “light absorption” and TOR “light-absorbing carbon”

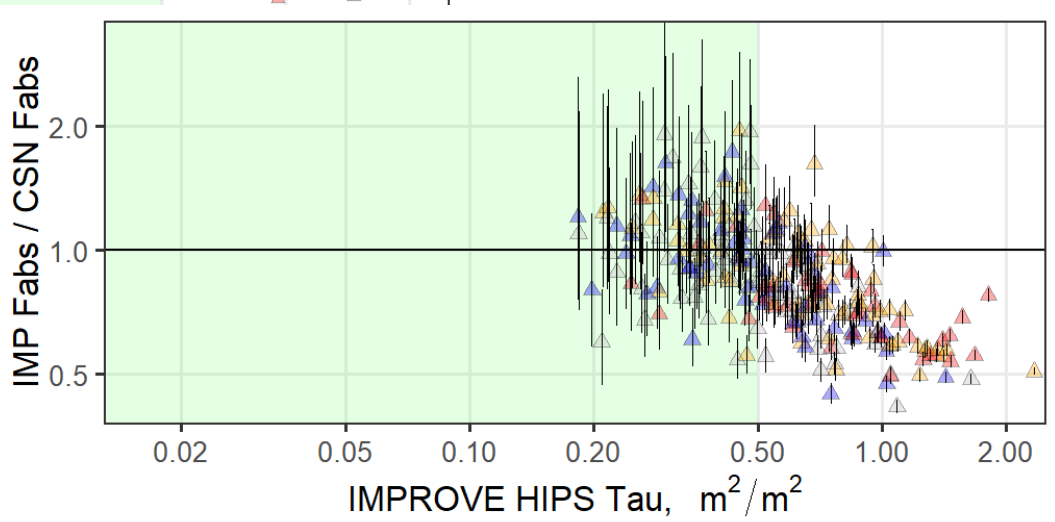


Presented to IMPROVE Steering Committee, 9 November 2021
by Warren White and the UCD Air Quality Monitoring Team



At last year's Steering Committee meeting, we confirmed Scott Copeland's suggestion of a diminished response by the HIPS Fabs measurement to *in-situ* aerosol absorption at high filter loadings, a so-called ***loading effect***.





From the 2020 Steering Committee Meeting:

http://vista.cira.colostate.edu/improve/wp-content/uploads/2020/10/Day1_9.-WHW_ISC_2020.pdf

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Particulate Matter Sample Deposit Geometry and Effective Filter Face Velocities

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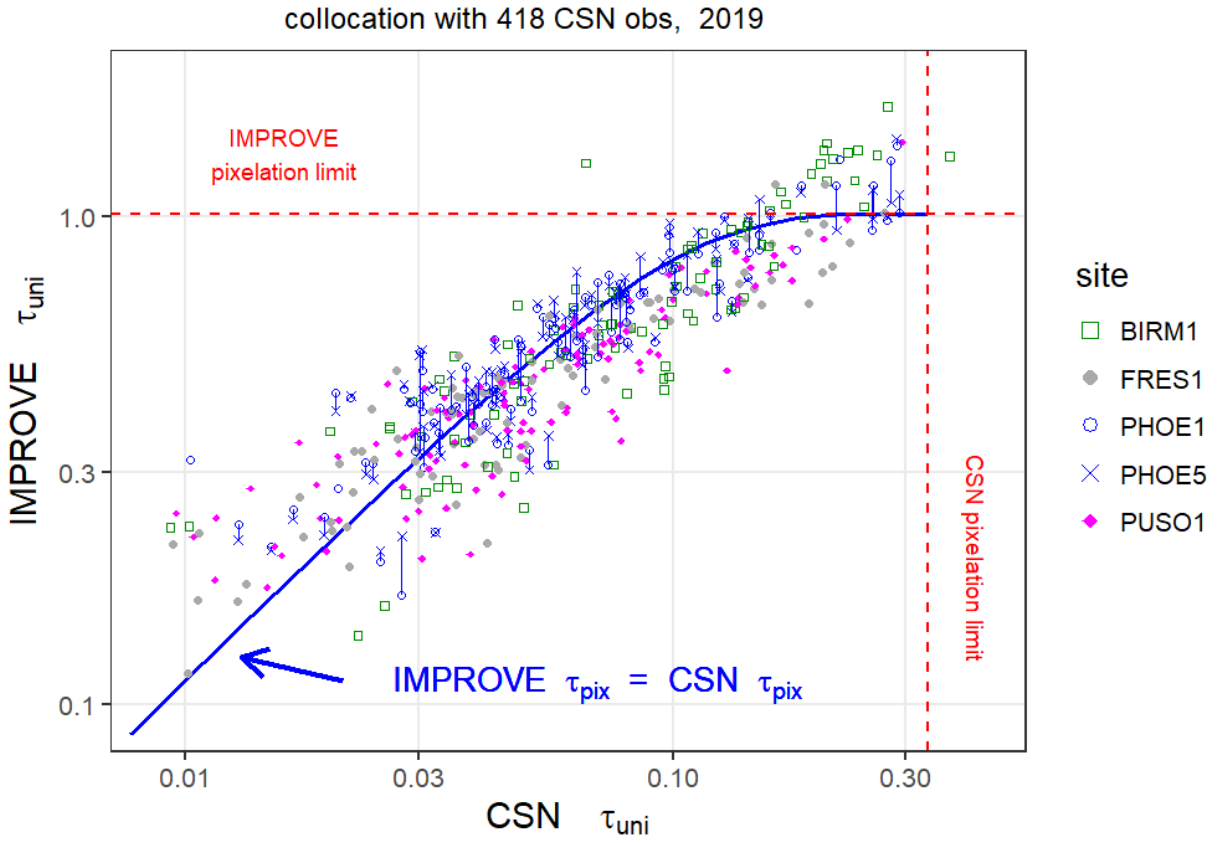
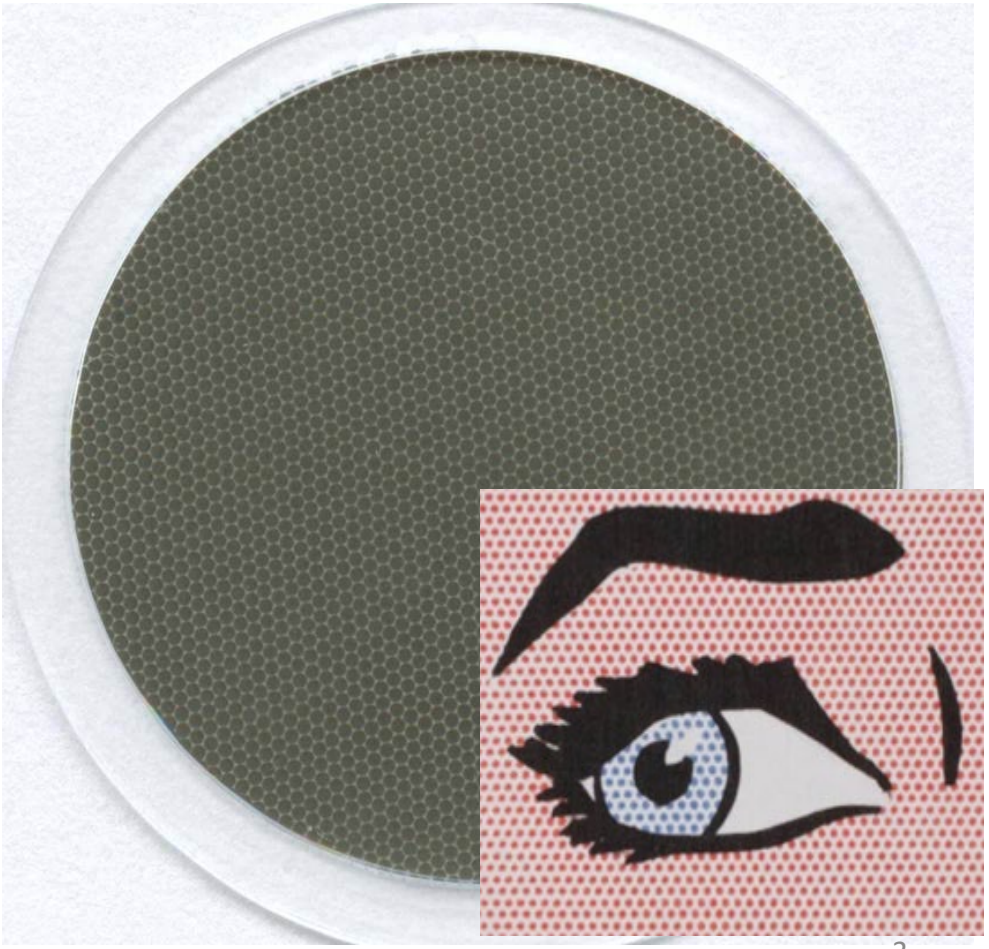
Crocker Nuclear Laboratory, University of California–Davis, Davis, CA

We subsequently traced this nonlinearity to the non-uniformity of IMPROVE sample deposits. The A-module samples analyzed by HIPS are visibly pixelated, shaped by perforated metal screens that support the PTFE membranes during sampling.

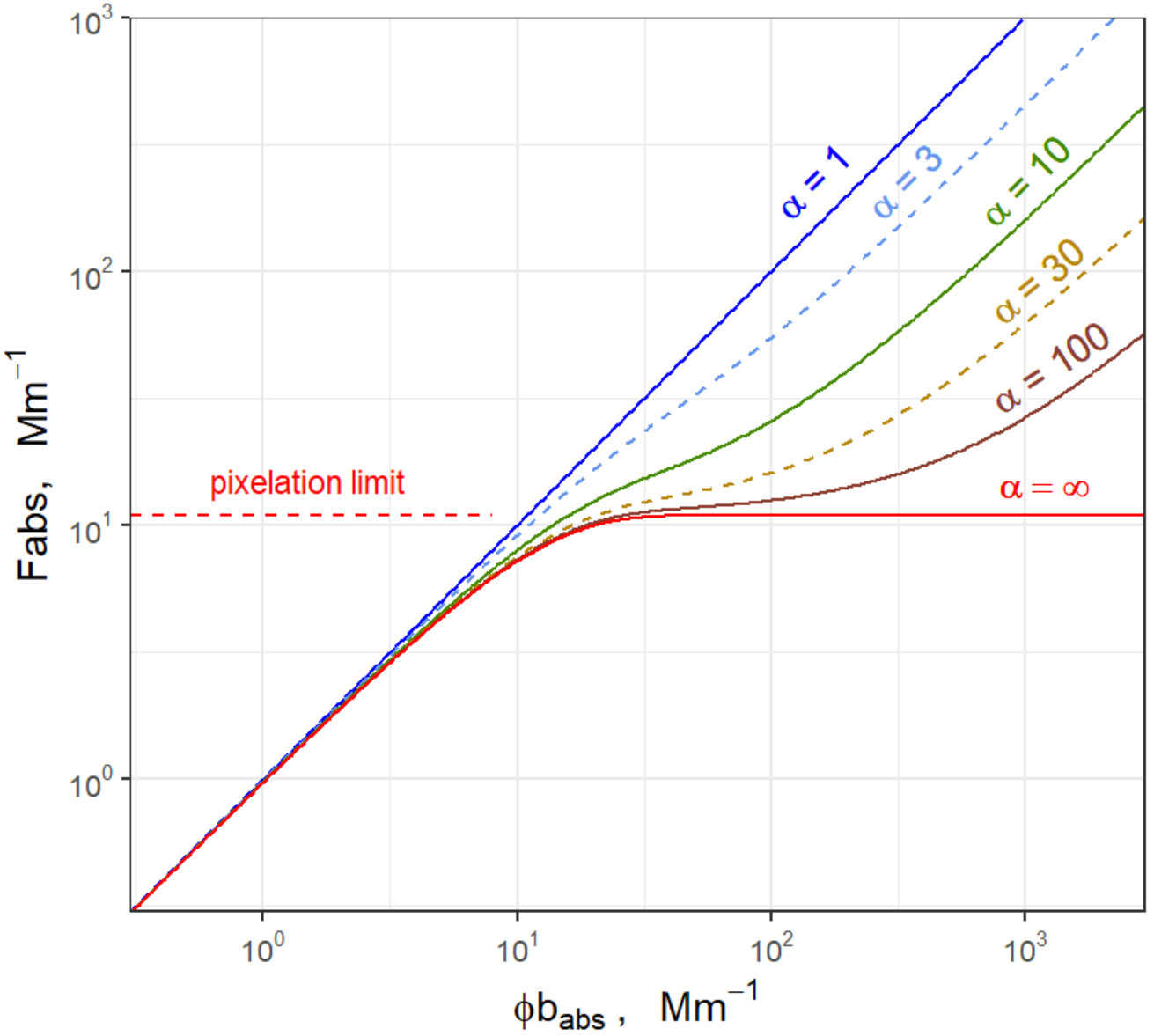




At the extreme of complete pixelation – where all deposition is restricted to discrete dots over the support screen's holes – the free transmittance of the clear interstitial area would place a hard upper bound, the ***pixelation limit***, on a filter sample's **mean absorption depth τ**. HIPS measures this τ as the basis for reporting a sample's filter absorption coefficient, Fabs.

Because observed HIPS values can exceed the pixelation limit, we will model the support screen's effect as one of preferential deposition rather than perfect segregation and exclusion. The resulting pattern appears as discrete dots of uniformly heavier deposit, separated by a interstitial background of uniformly lighter deposit. The ***pixelation amplitude*** α is characterized by the ratio of deposited absorption depths,

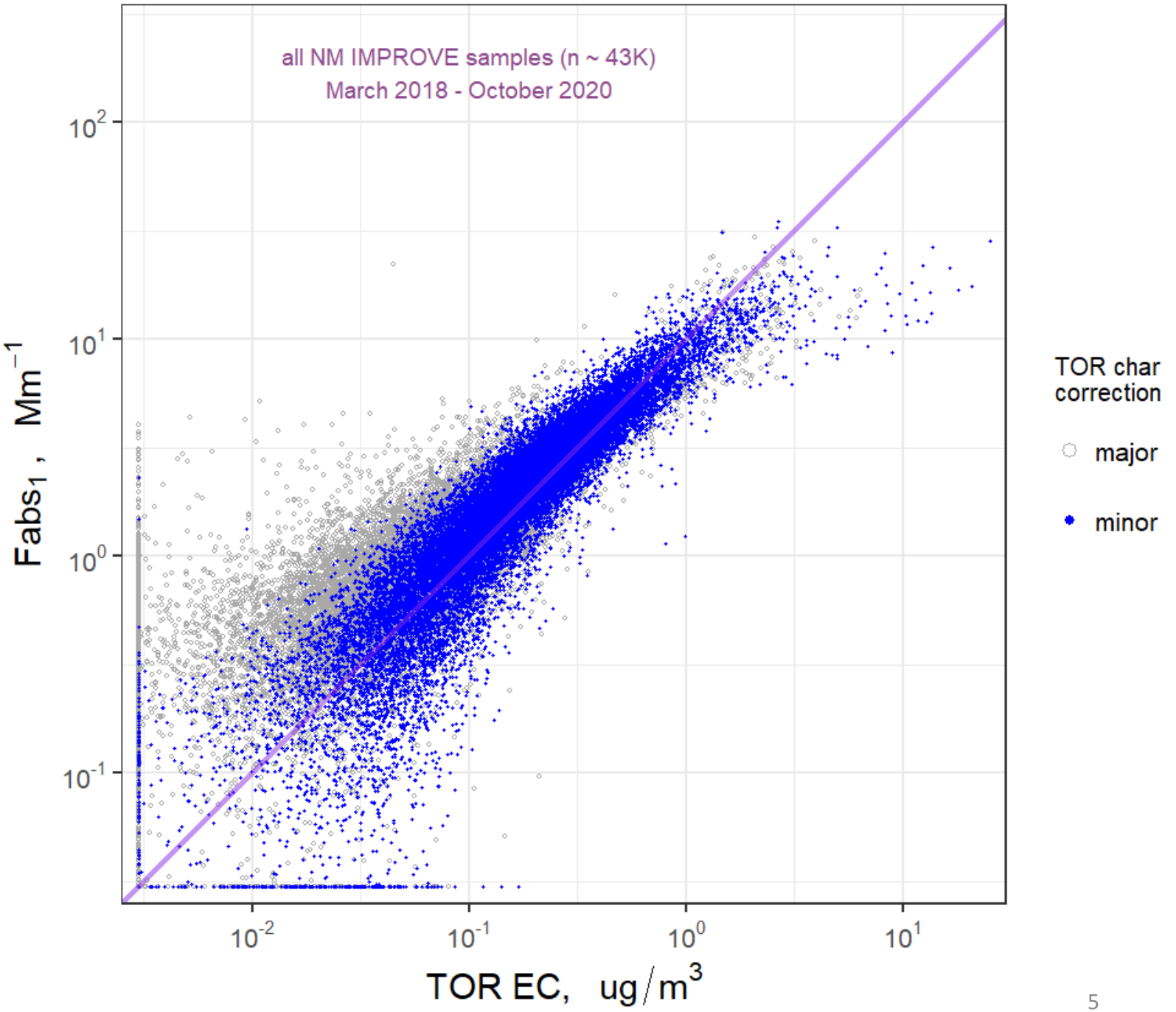
$$\alpha = dots \,/\, interstitial\ background.$$



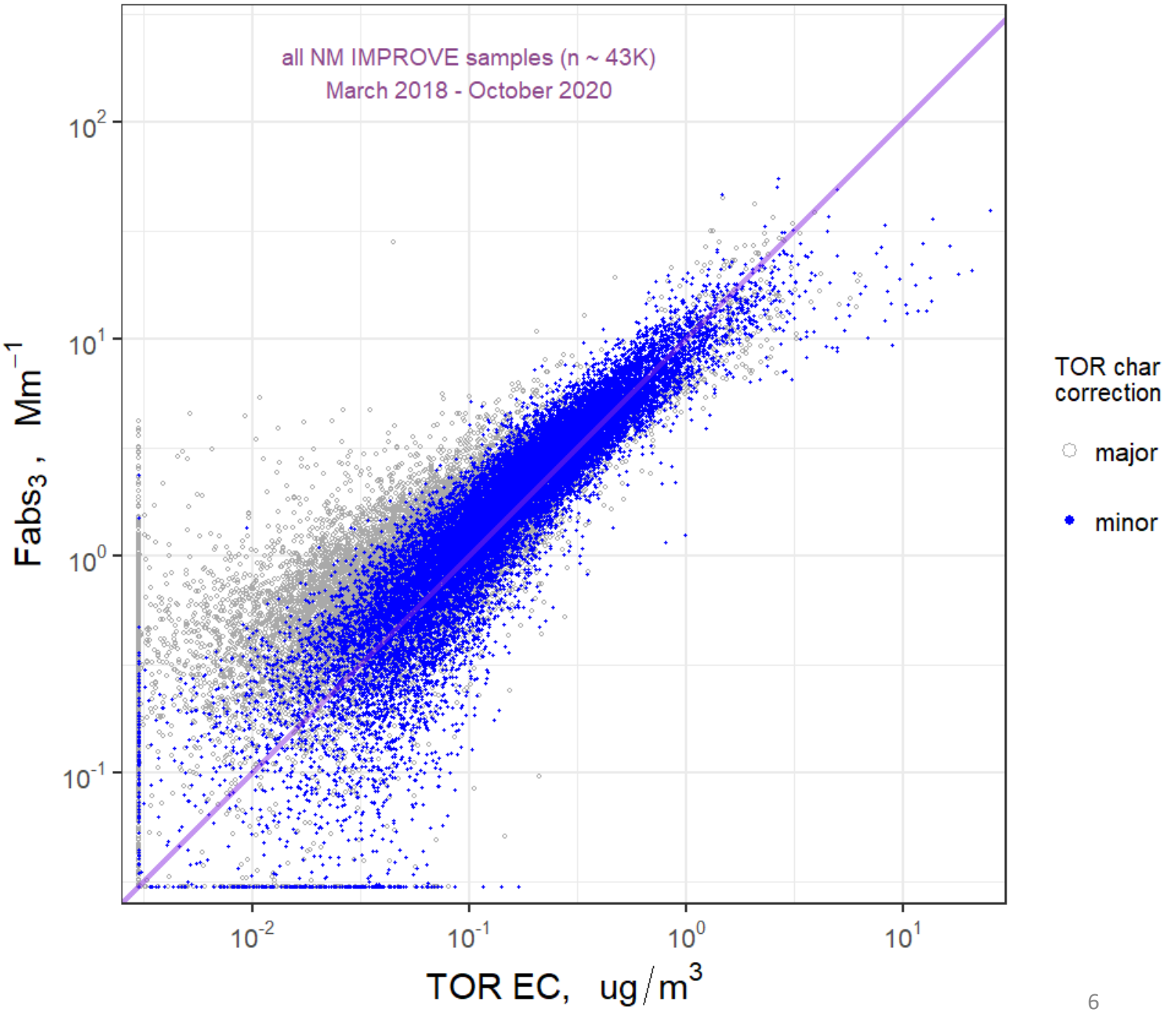
$1 \le \phi \le 2$ is the HIPS illumination factor.

The remainder of this presentation will compare network Fabs and EC data from 28 months of analysis by the current incarnations of HIPS and TOR. It will emerge that Fabs and EC generally show better agreement when the TOR correction needed for charring in the carbon analysis is not too large.

In this first comparison, Fabs is plotted as it is reported, which assumes the sample deposits to be uniform ($\alpha = 1$) .

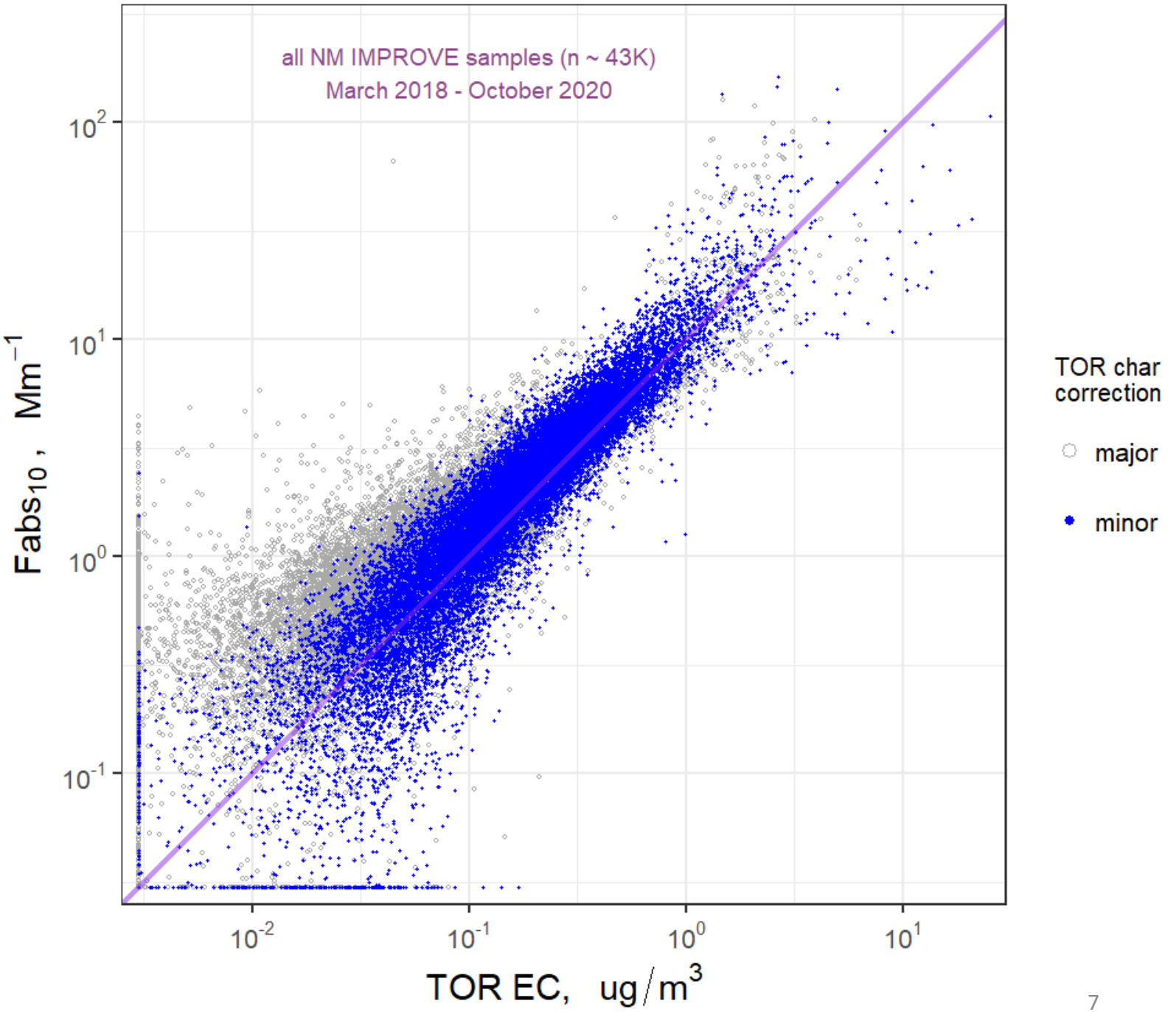


The difference in this comparison is that the amplitude of sample pixelation is now assumed to be $\alpha = 3$: the absorption depth of each deposited dot is 3x that of the interstitial background.

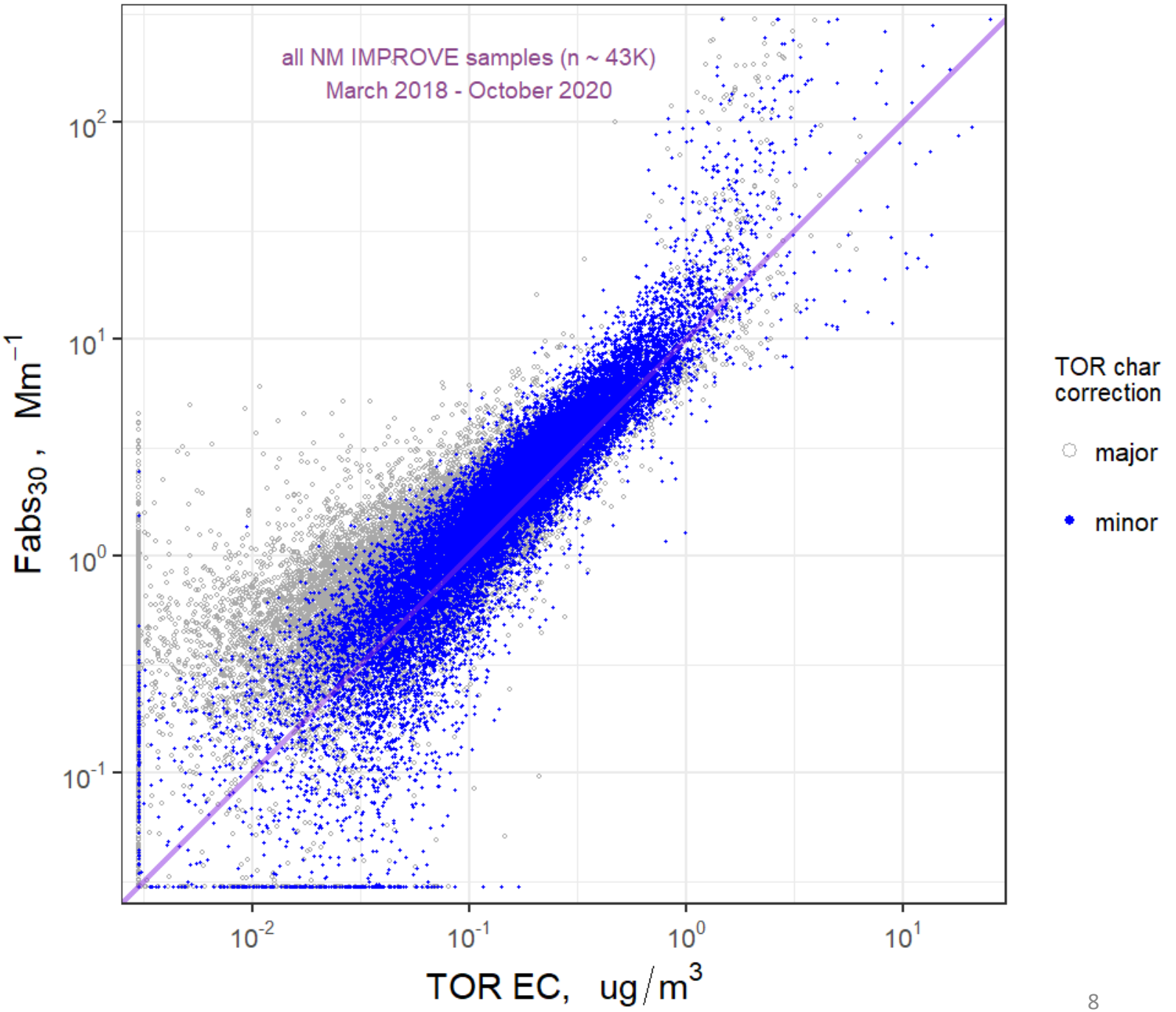


A value of $\alpha = 10$ seems fairly representative as a generic estimate for the pixelation amplitude.

It's worth noting that our "straightening" of the mean relationship comes at the expense of increasing the dispersion of individual heavily-loaded samples. It is these observations that are most sensitive to any errors in our measurements and interpretive model.



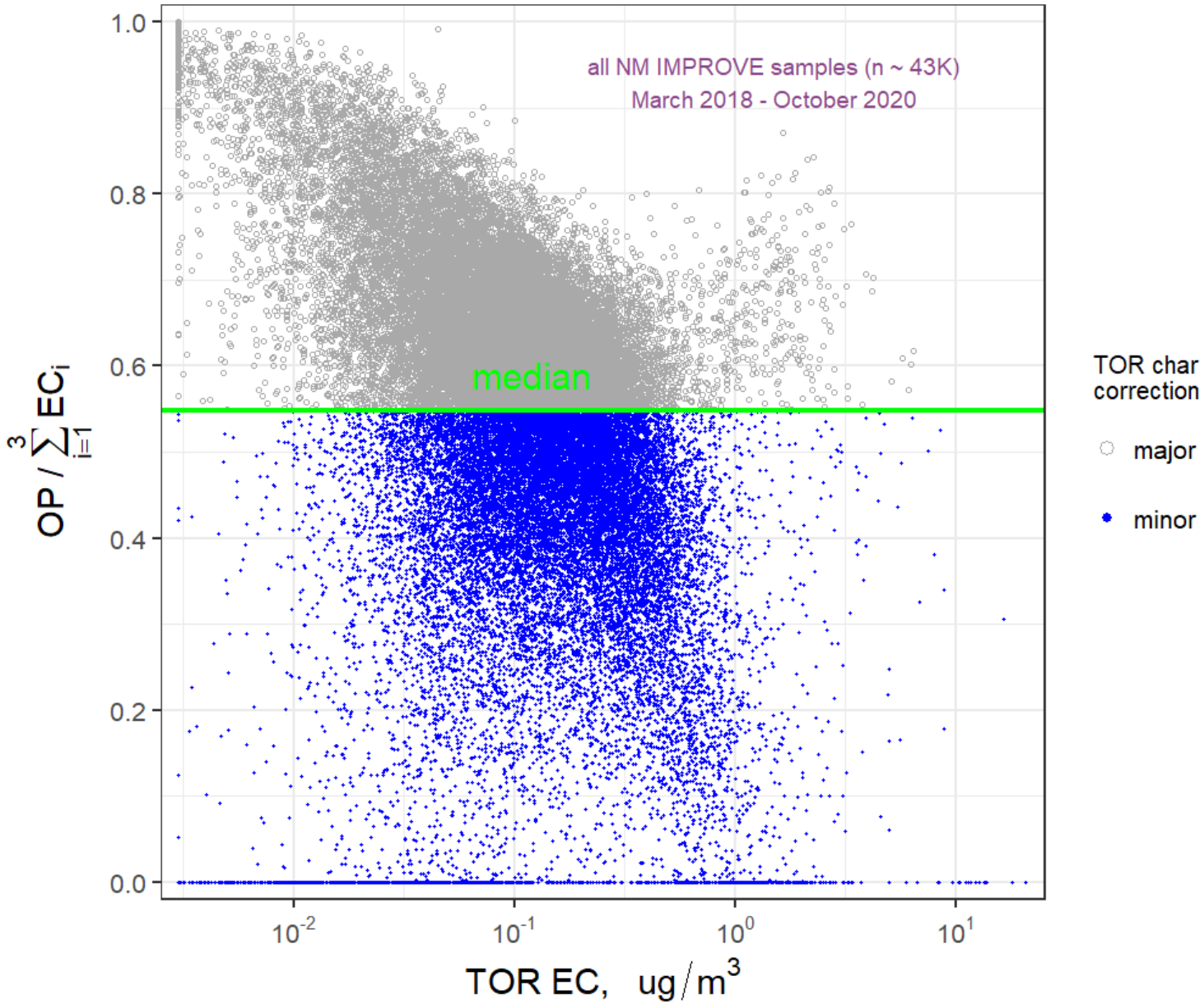
With sufficiently high pixelation amplitudes (describing nearly complete restriction of deposits to the dots over screen holes), we start to over-correct most samples for the HIPS loading effect. Even at this point, however, some samples still show less absorption than would be expected from the reported TOR EC.

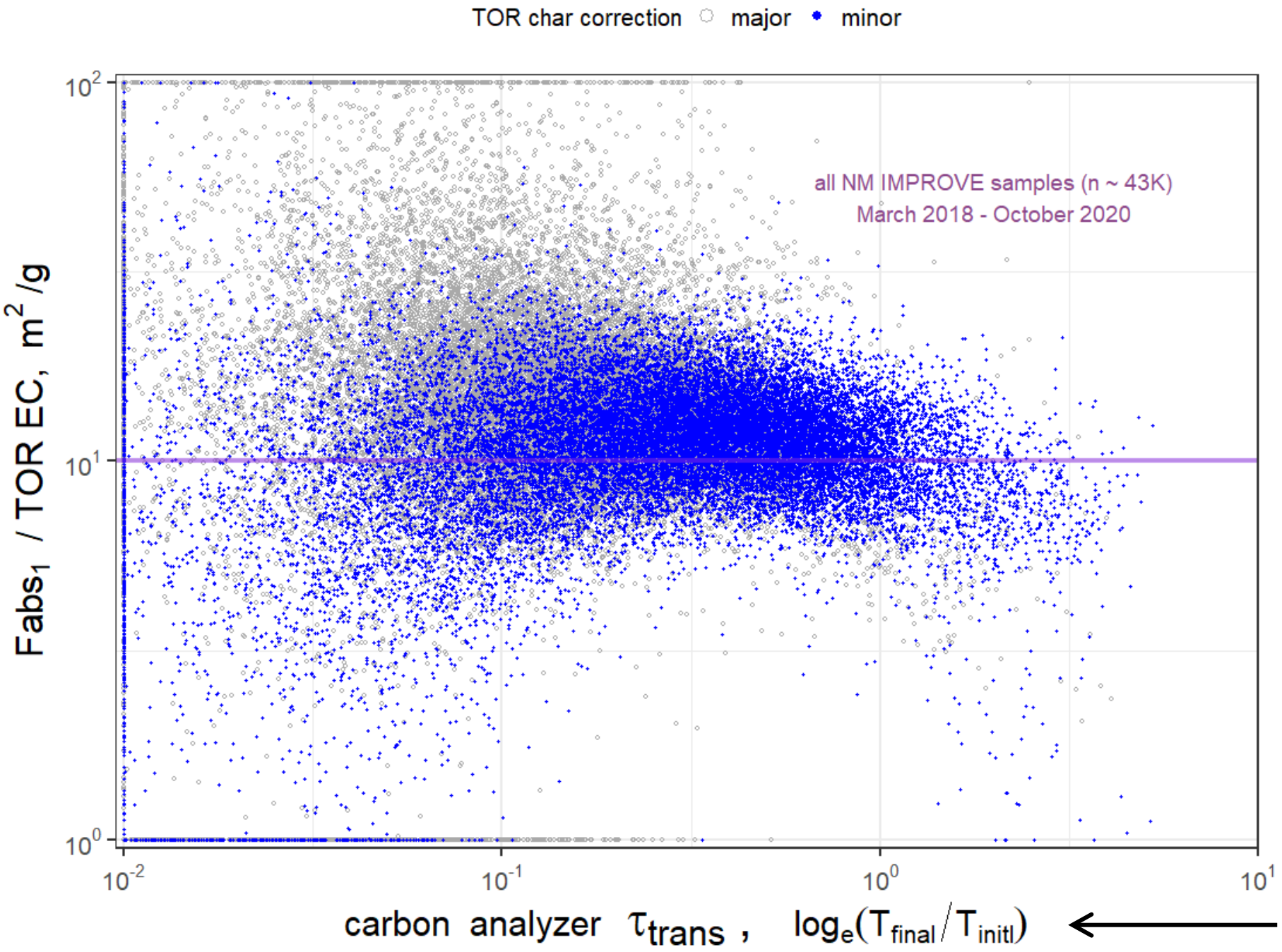


Here is an explanation of the color coding for the TOR char correction. In a naïve interpretation, the fractions OC1, …, OC4, evolving in pure He, represent organic compounds that directly volatilize under moderate heating; the fractions EC1, …, EC3, evolving after O_2 is added, represent the more refractory 'black' carbon that must be burnt off. OP is a correction term for the pyrolytic artifact 'EC' inadvertently converted from 'OC' by charring during the course of the analysis.

Charring is tracked by continuously monitoring the reflectance of the sample punch throughout the procedure. The OP correction is estimated as the carbon evolved in the presence of O_2 while the reflectance remains below its initial value.

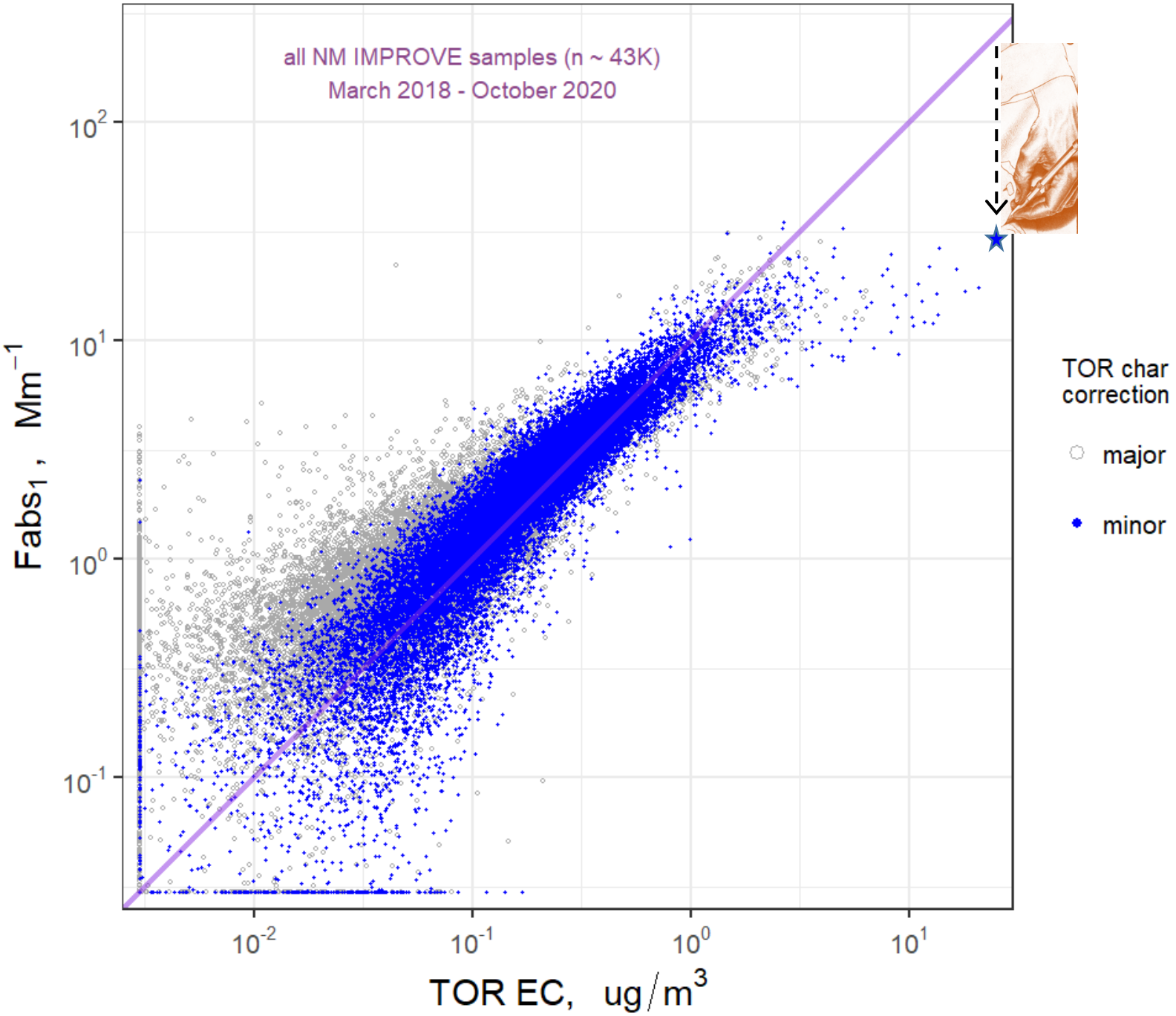
$$TOR\ EC = \sum_{i=1}^{3} EC_i - OP\ .$$





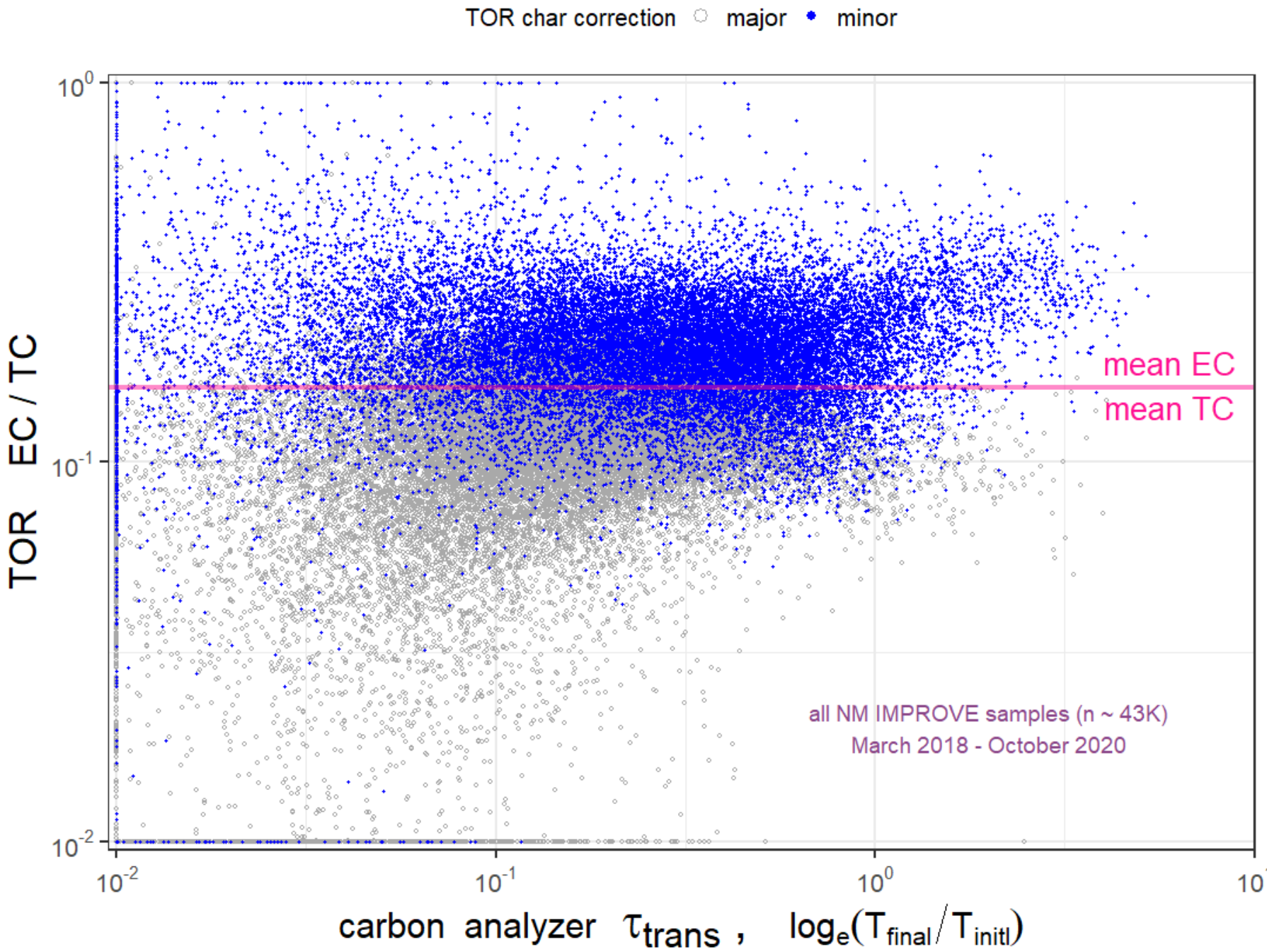
The observed relationship of raw absorption (uncorrected for pixelation effects) to reported TOR EC shows a decline in the apparent absorption cross-section per EC mass for the darkest sample filters, presumed to carry the most light-absorbing carbon.

Quartz-sample light attenuation, indicator for 'black carbon'.

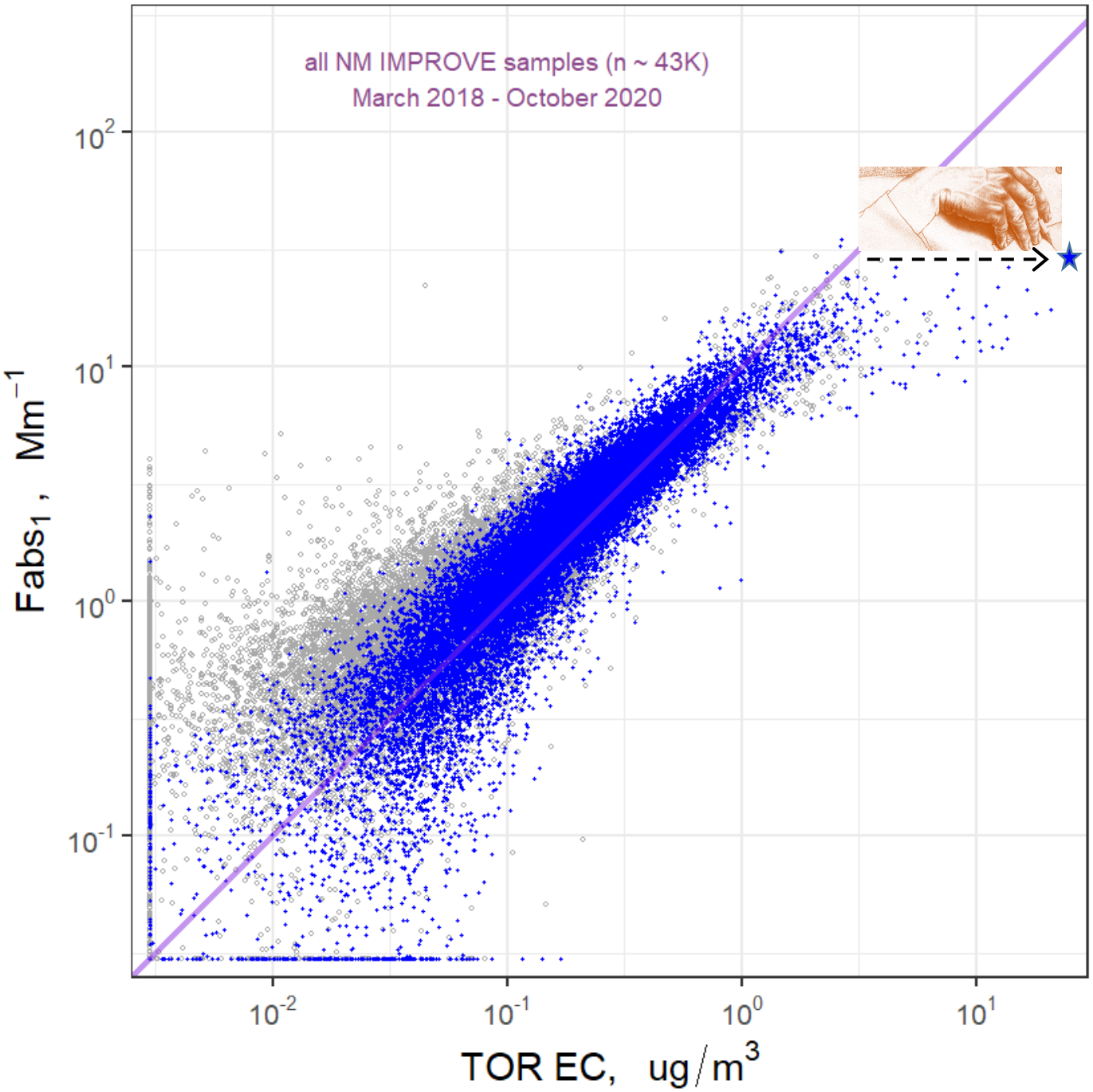


As already noted, some of this non-proportionality is explained by the pixelation of HIPS samples. The areas of lighter deposition remain relatively open 'windows', slowing the decrease in overall filter transmittance as overall loadings increase.

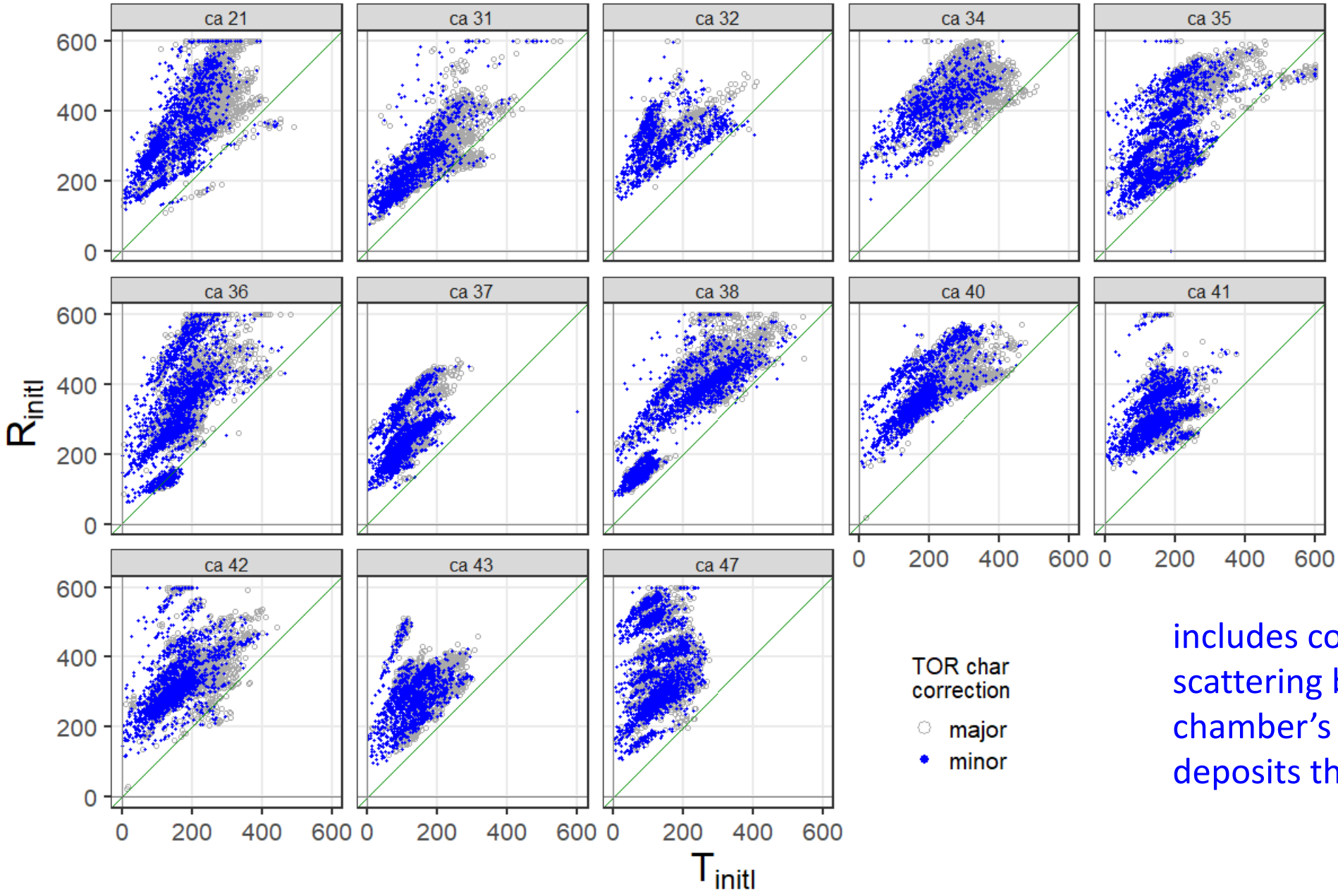
The existence of an identifiable mechanism for diminished HIPS response at high loadings prompted the exploration of loading effects in the HIPS measurement.



But the observed fraction of total carbon classified by TOR as "light-absorbing" EC exhibits a mirroring increase for the darkest samples. These are exactly the filters on which it is most difficult to track any further decline in reflectance during analysis, and such tracking underlies TOR's subtraction of the OP pyrolysis artifact from 'EC'.



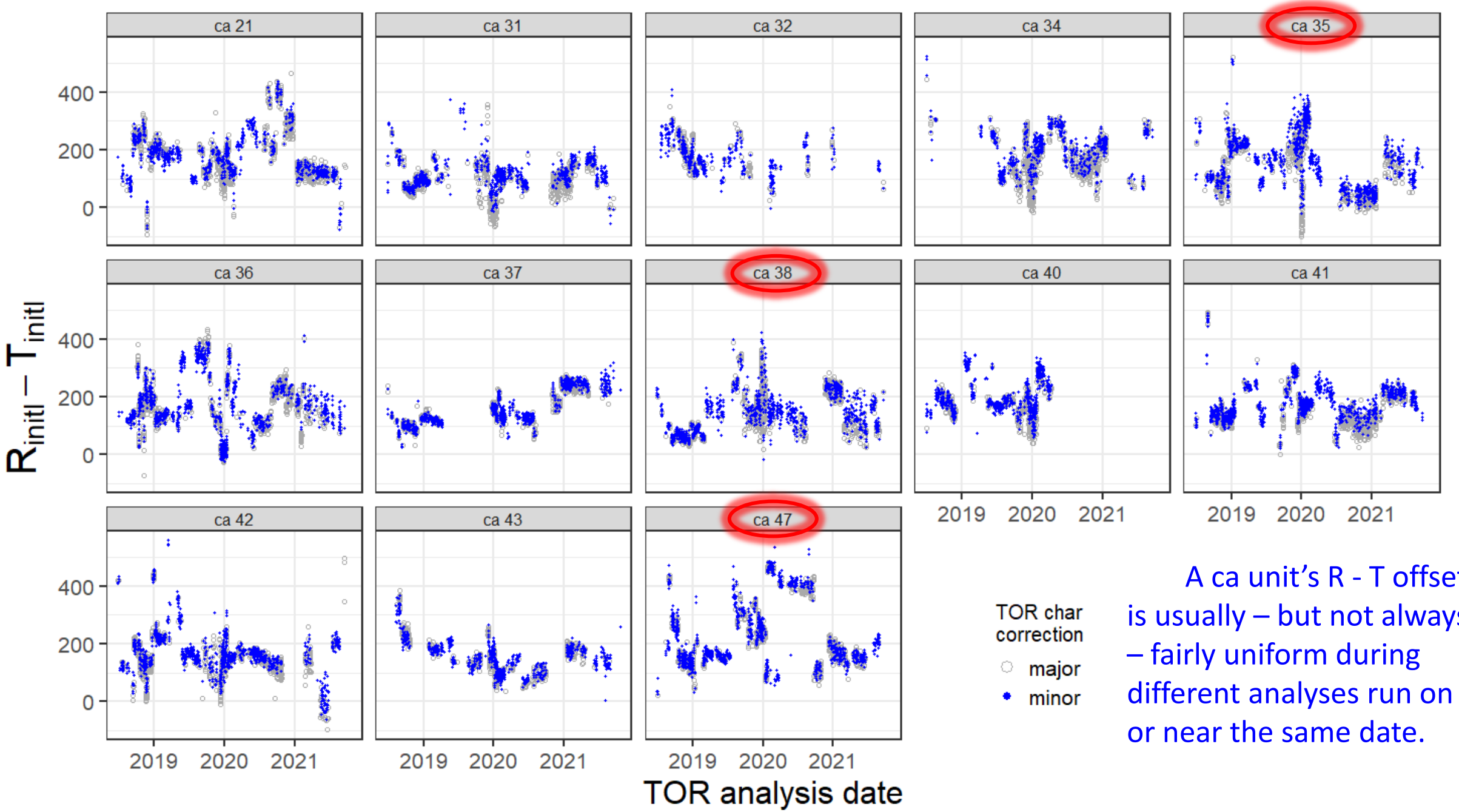
This symmetry prompts consideration also of possible loading effects in the TOR determination of light-absorbing EC. Under-estimation of the TOR char correction at high sample loadings can produce a similar distortion in the relationship between measured Fabs and measured TOR EC.



Here are the initial R (reflectance) and T (transmittance) readings ($\lambda = 635$ nm) from all the samples we've been looking at, broken out by individual carbon analyzer (ca) unit.

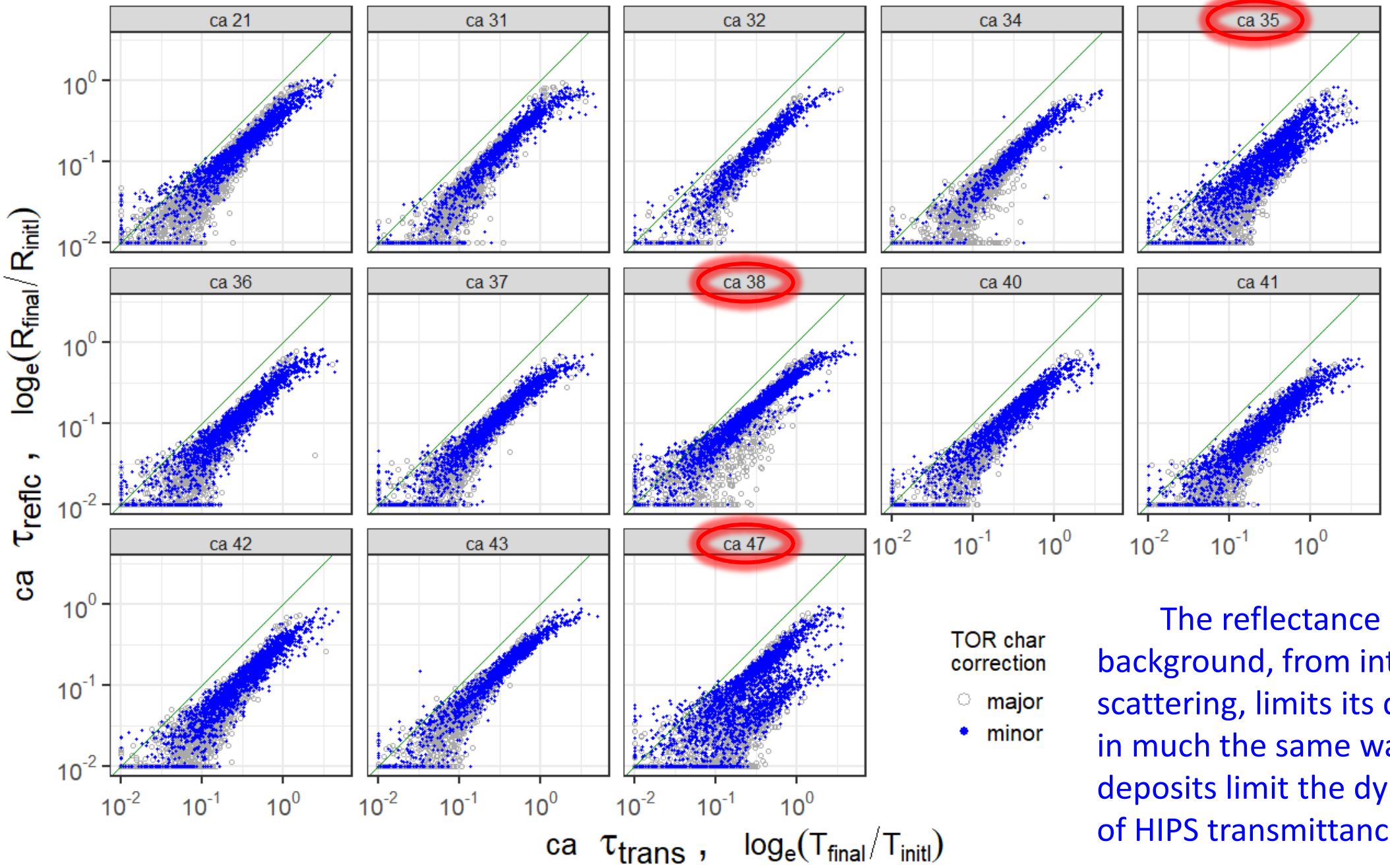
R is generally higher than T, even as T approaches zero, by an additive offset that includes contributions from internal scattering by the quartz sample chamber's surfaces and any foreign deposits they may have accumulated.

all NM IMPROVE samples (n ~ 43K), March 2018 - October 2020



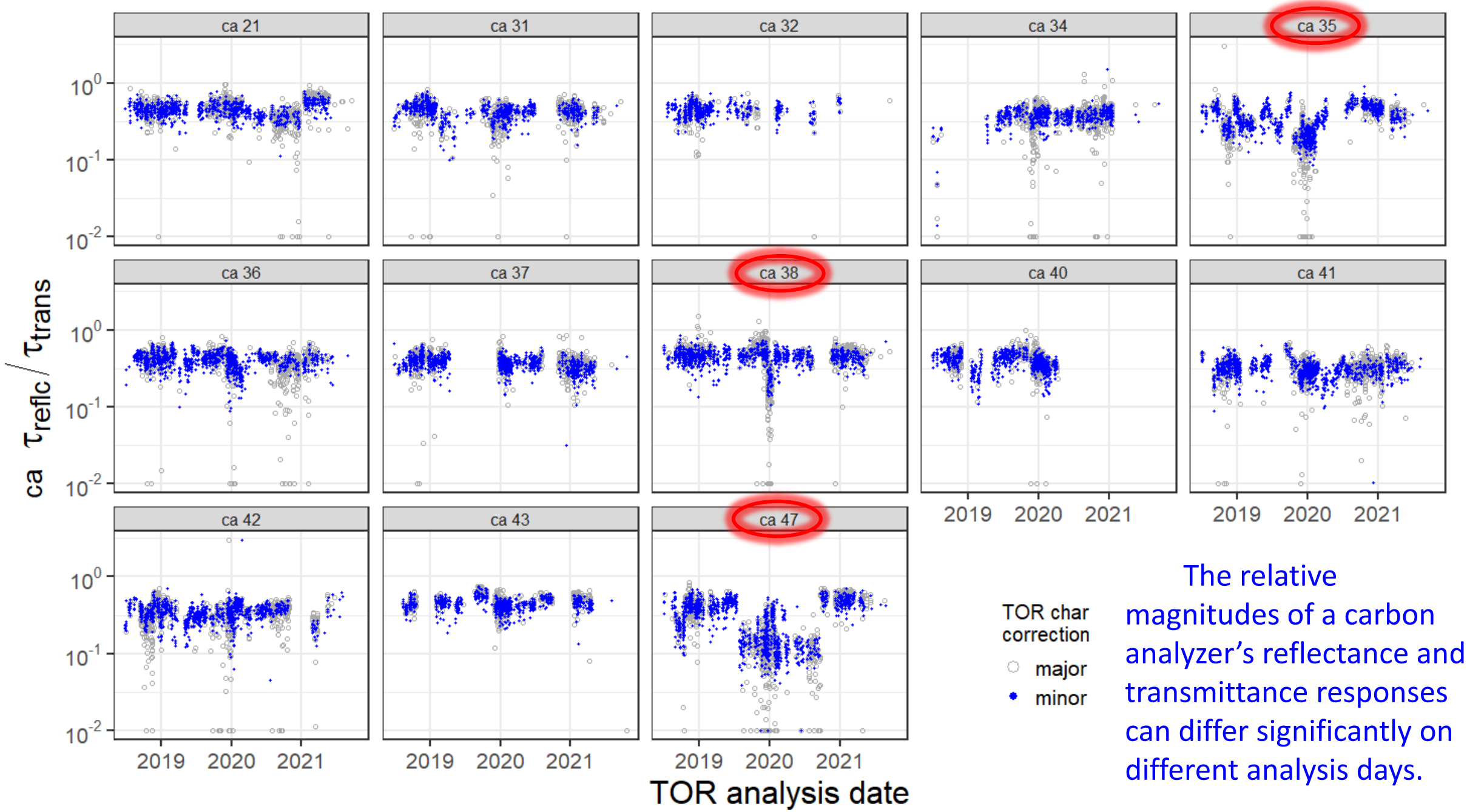
A ca unit's R - T offset is usually – but not always – fairly uniform during different analyses run on or near the same date.

all NM IMPROVE samples above median TC (n ~ 22K), March 2018 - October 2020



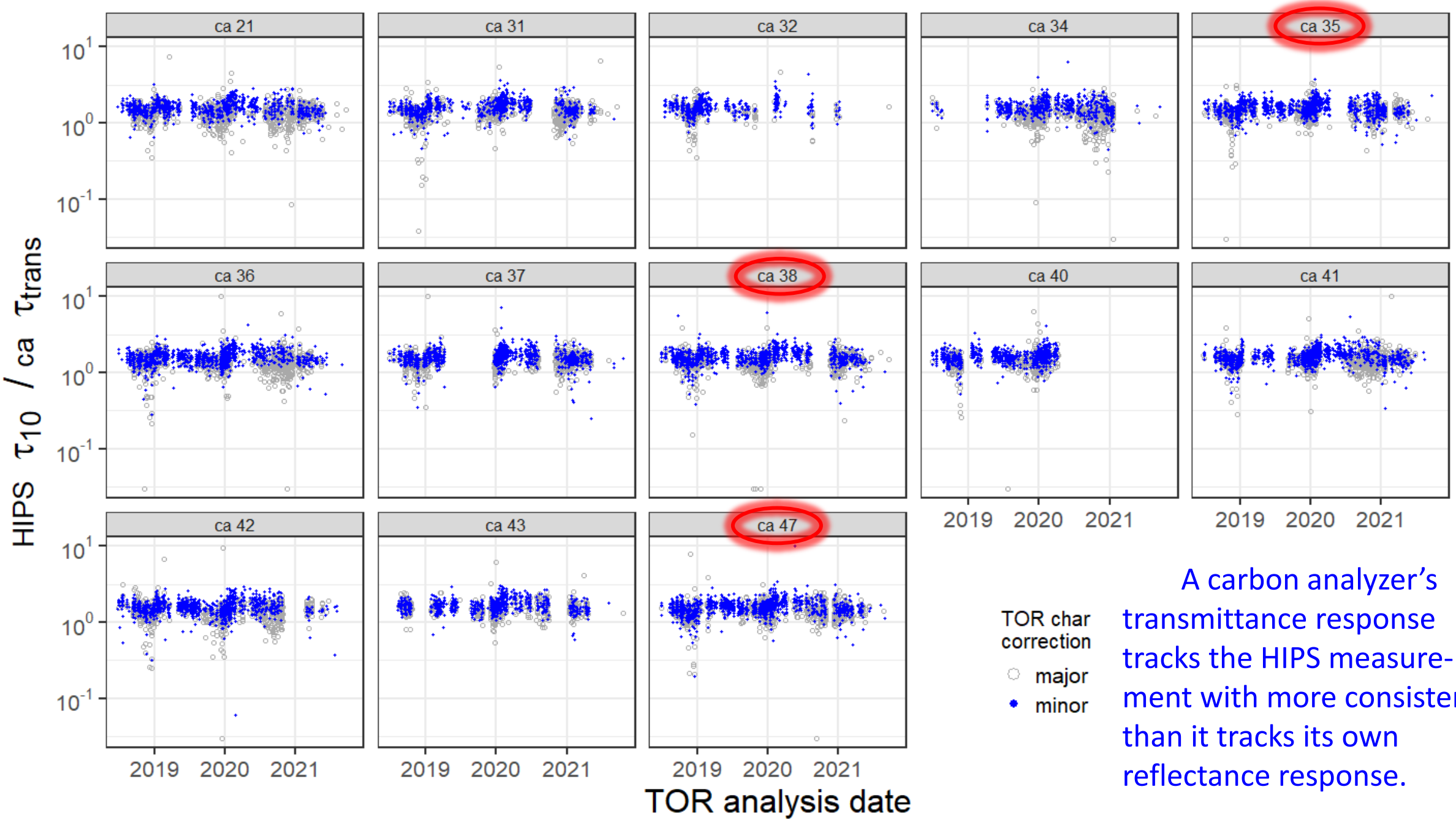
The reflectance signal's background, from internal scattering, limits its dynamic range in much the same way pixelated deposits limit the dynamic range of HIPS transmittance.

all NM IMPROVE samples (n ~ 43K), March 2018 - October 2020



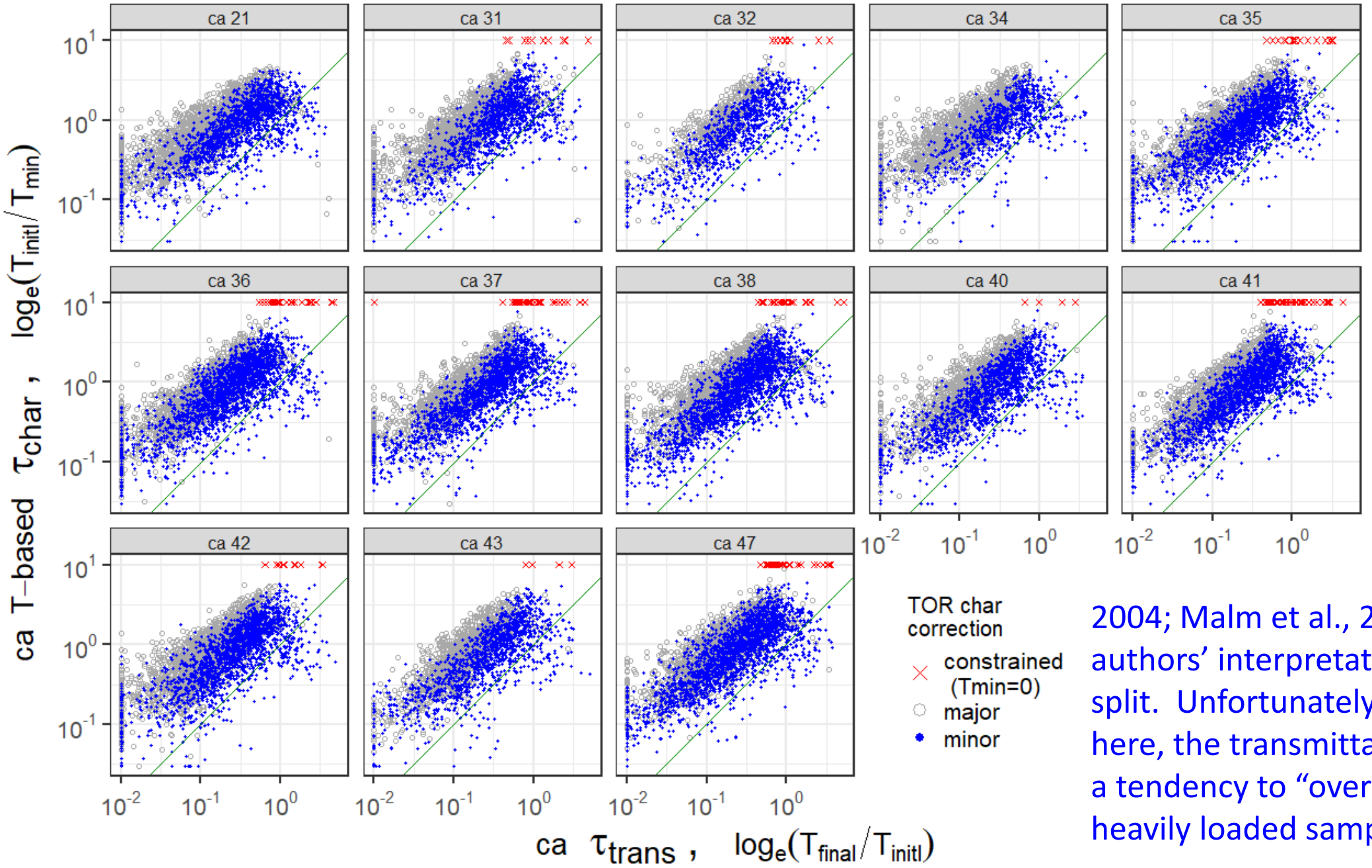
The relative magnitudes of a carbon analyzer's reflectance and transmittance responses can differ significantly on different analysis days.

all NM IMPROVE samples above median TC (n ~ 22K), March 2018 - October 2020



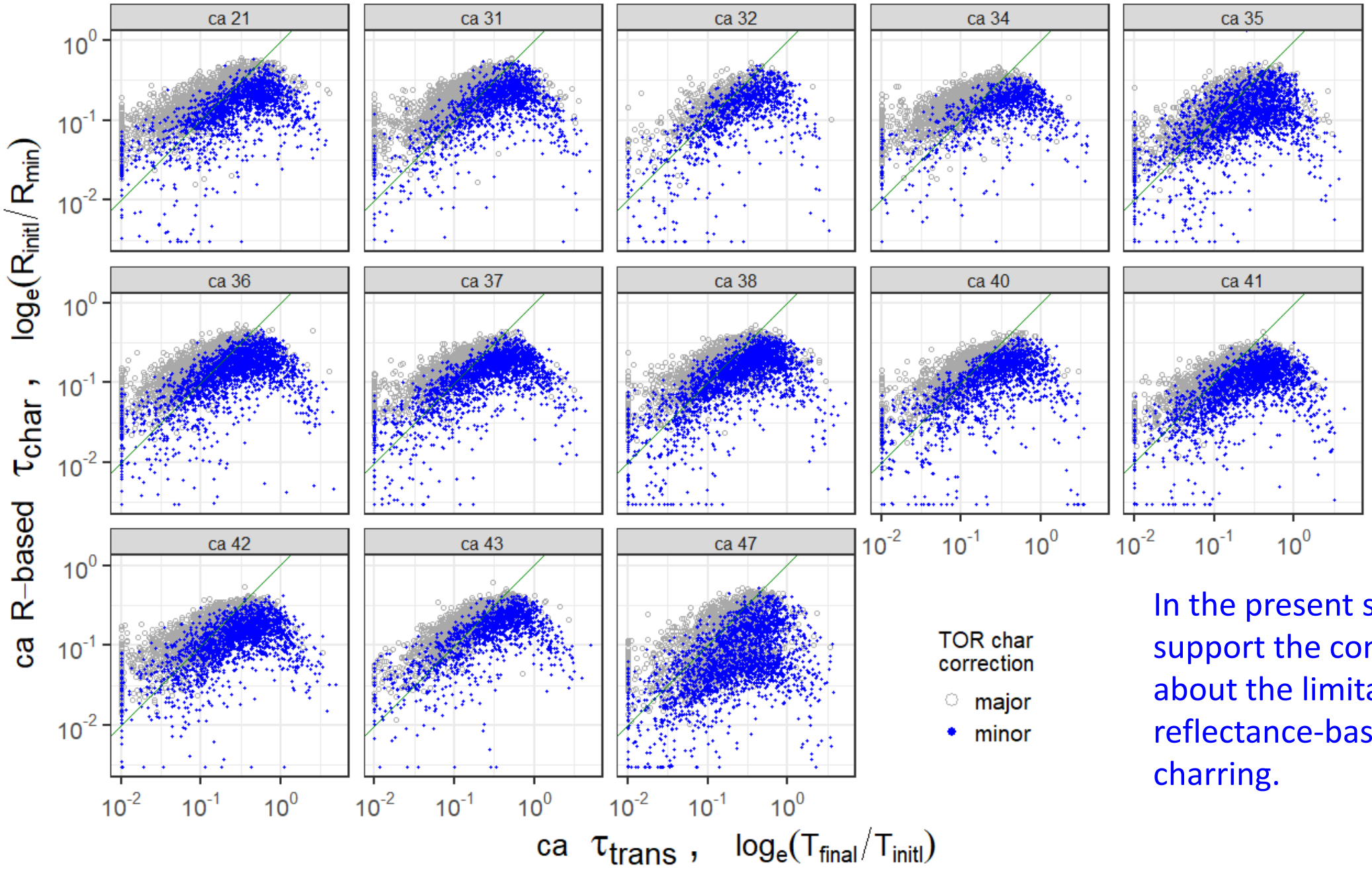
A carbon analyzer's transmittance response tracks the HIPS measurement with more consistency than it tracks its own reflectance response.

all NM IMPROVE samples above median TC (n ~ 22K), March 2018 - October 2020



The carbon analyzer's optical tracking signals can be used to estimate the absorption depths of, not only the sample itself, but also the char added during analysis. These estimates have been cited (e.g., Chow et al., 2004; Malm et al., 2020) to support authors' interpretations of the OC/EC split. Unfortunately for our purposes here, the transmittance estimate has a tendency to "over-range" for heavily loaded samples.

all NM IMPROVE samples (n ~ 43K), March 2018 - October 2020

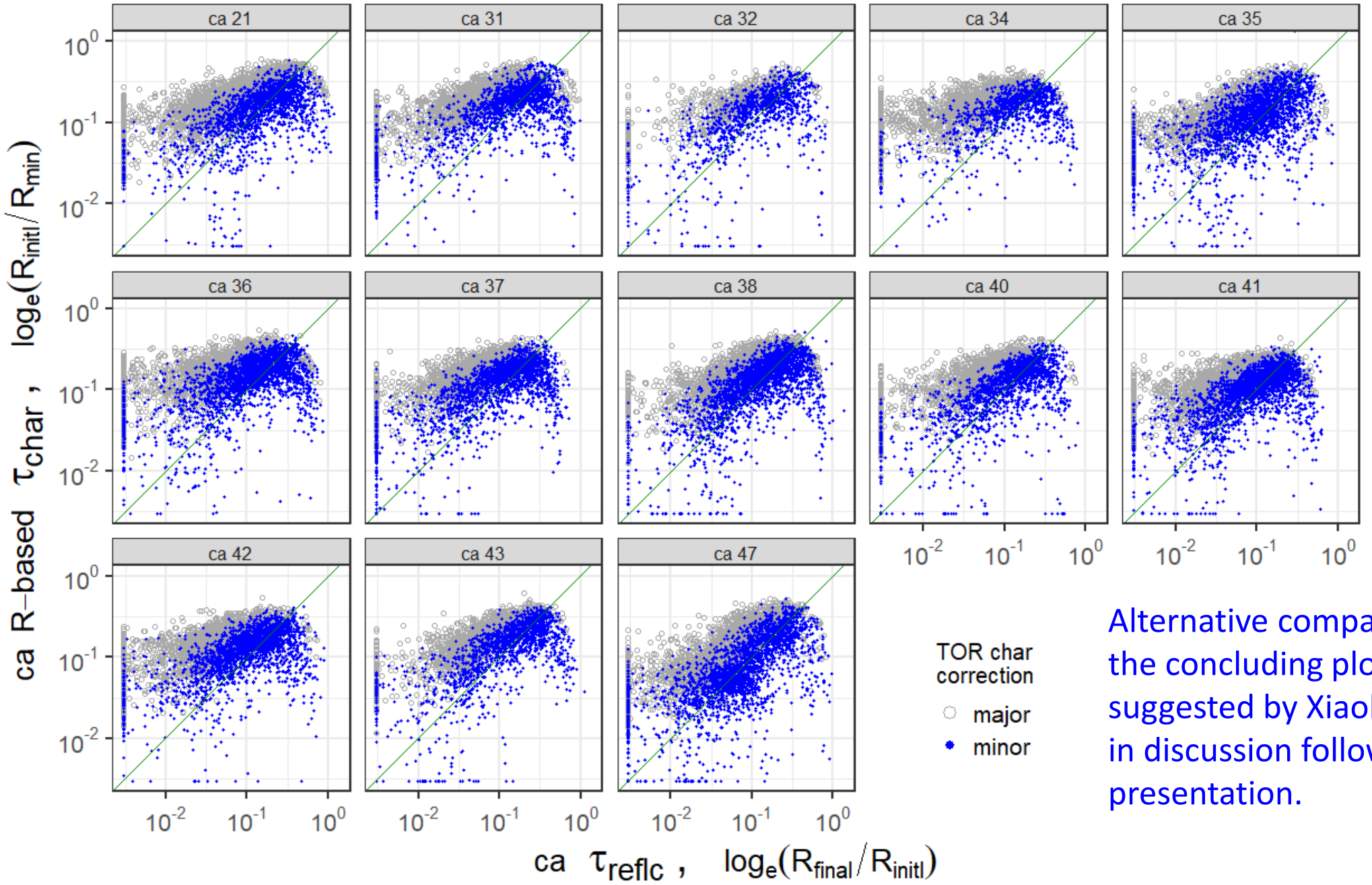


Buffered away from zero by their background offset, the reflectance estimates of char absorption depth remain at least nominally interpretable at high loadings.

In the present setting, they support the concerns raised here about the limitations of TOR's reflectance-based correction for charring.

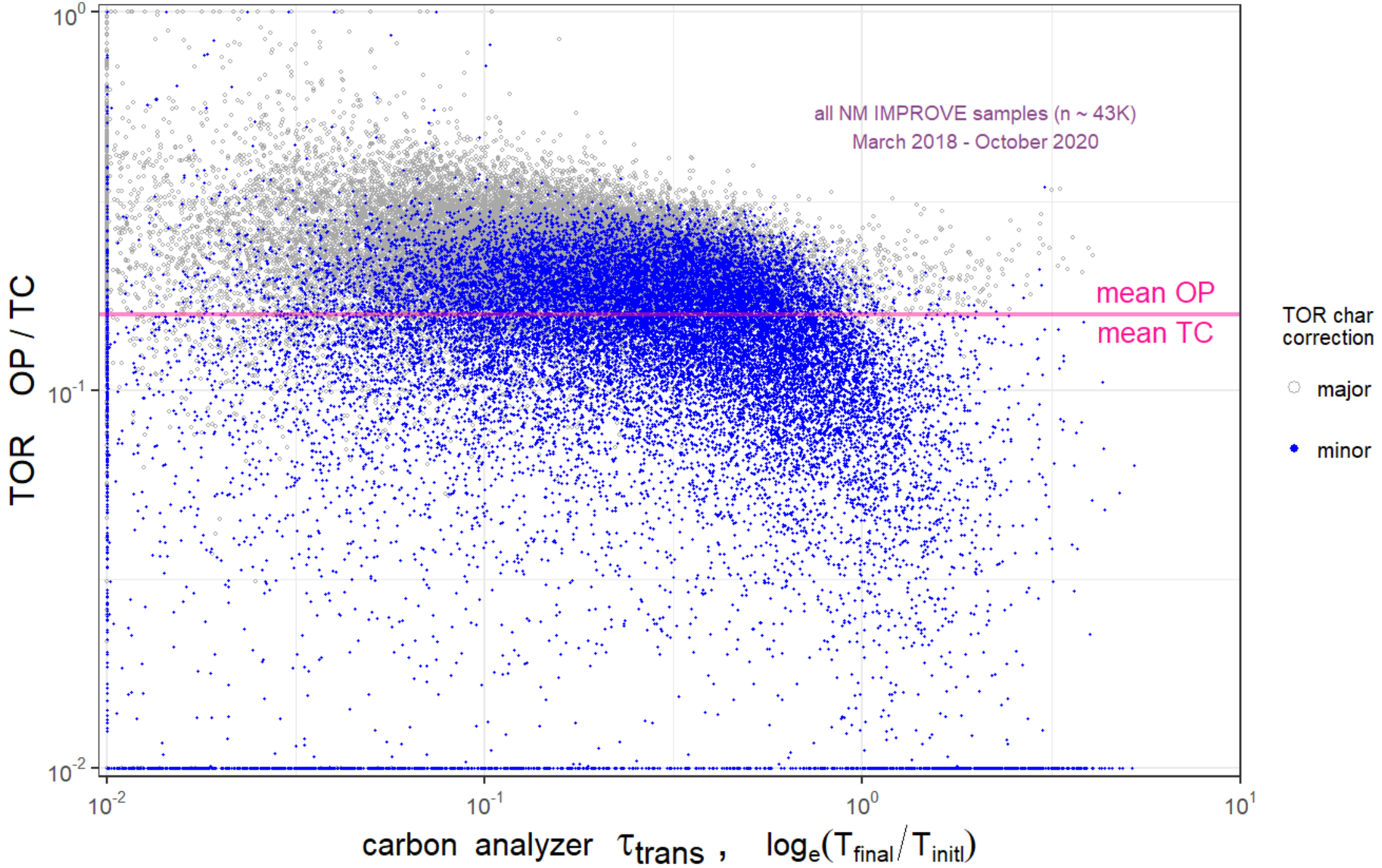
all NM IMPROVE samples (n ~ 43K), March 2018 - October 2020

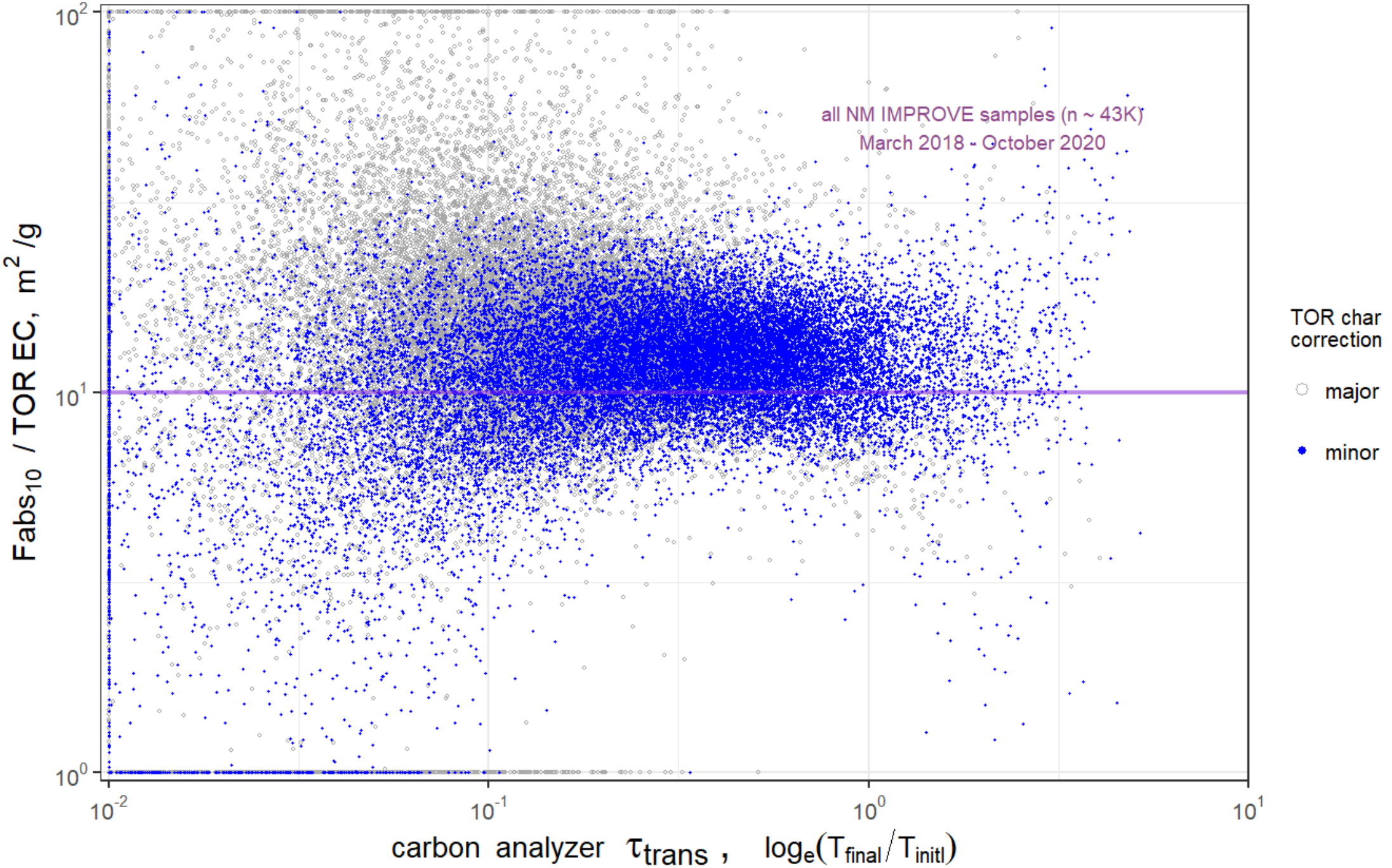
THANK YOU,
AND PLEASE DOWNLOAD AND PLAY WITH
THESE PLOTS YOURSELF,
ONCE THEY'RE POSTED AT CIRA!

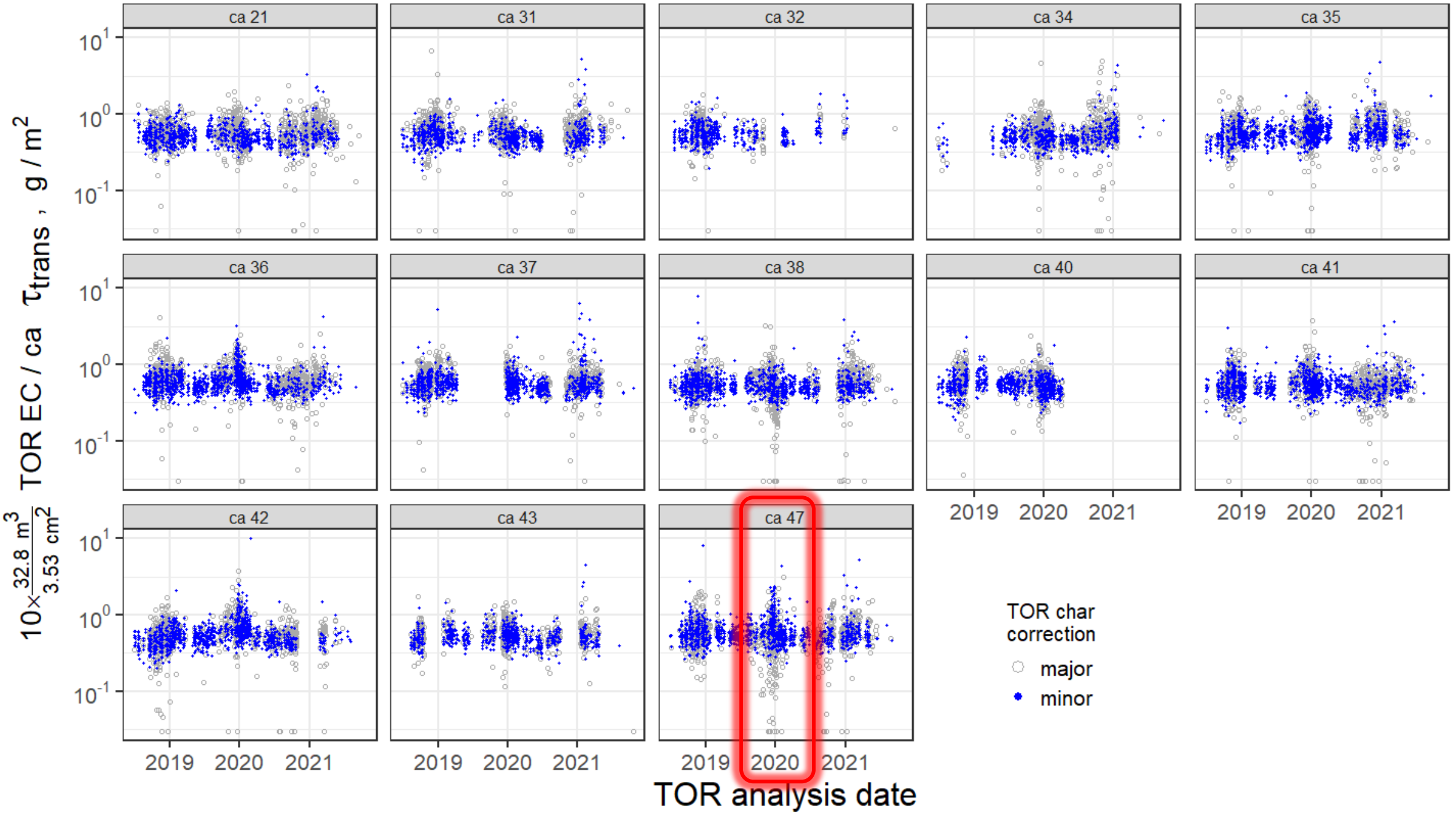


Alternative comparison for the concluding plot (slide 20), suggested by Xiaoliang Wang in discussion following presentation.

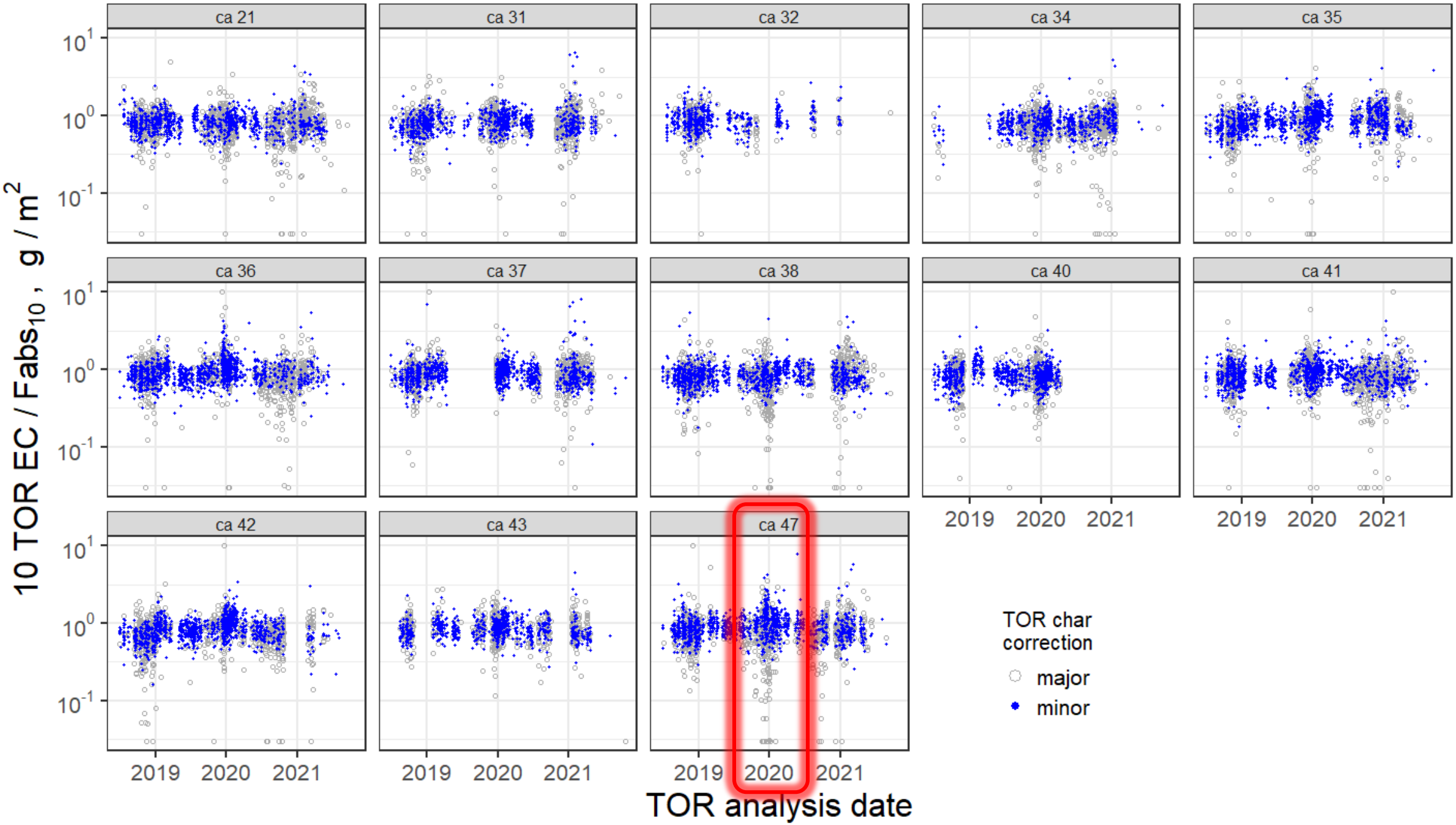
all NM IMPROVE samples (n ~ 43K), March 2018 - October 2020


all NM IMPROVE samples (n ~ 43K)
March 2018 - October 2020
mean OP
mean TC
TOR char correction
major
minor
TOR OP / TC
carbon analyzer τ_{trans} , $\log_e(T_{final}/T_{initl})$
10^0
10^{-1}
10^{-2}
10^1

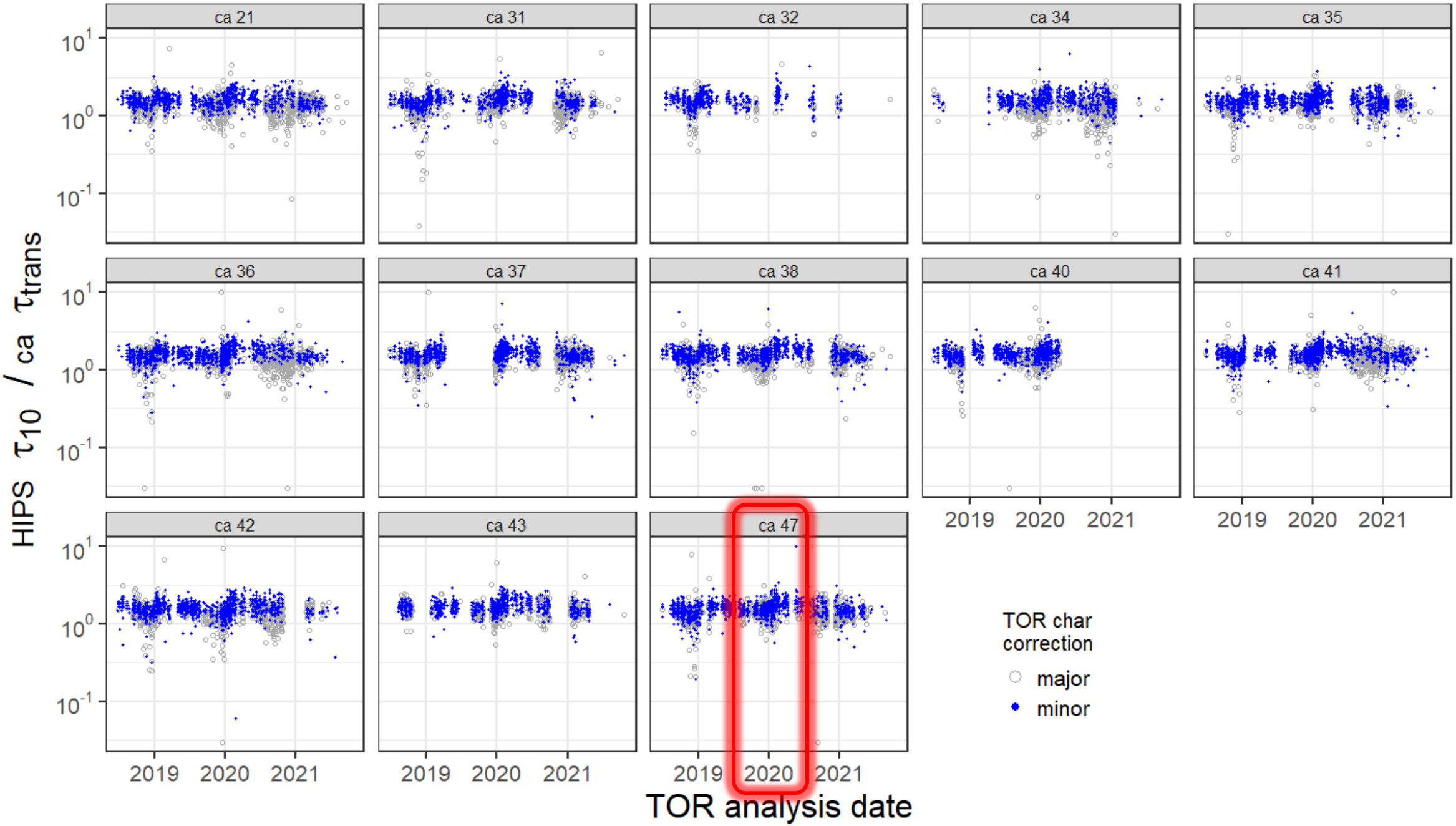

all NM IMPROVE samples (n ~ 43K)
March 2018 - October 2020
Fabs10 / TOR EC, m2/g
carbon analyzer τtrans , loge(Tfinal/Tinitl)
TOR char correction
major
minor



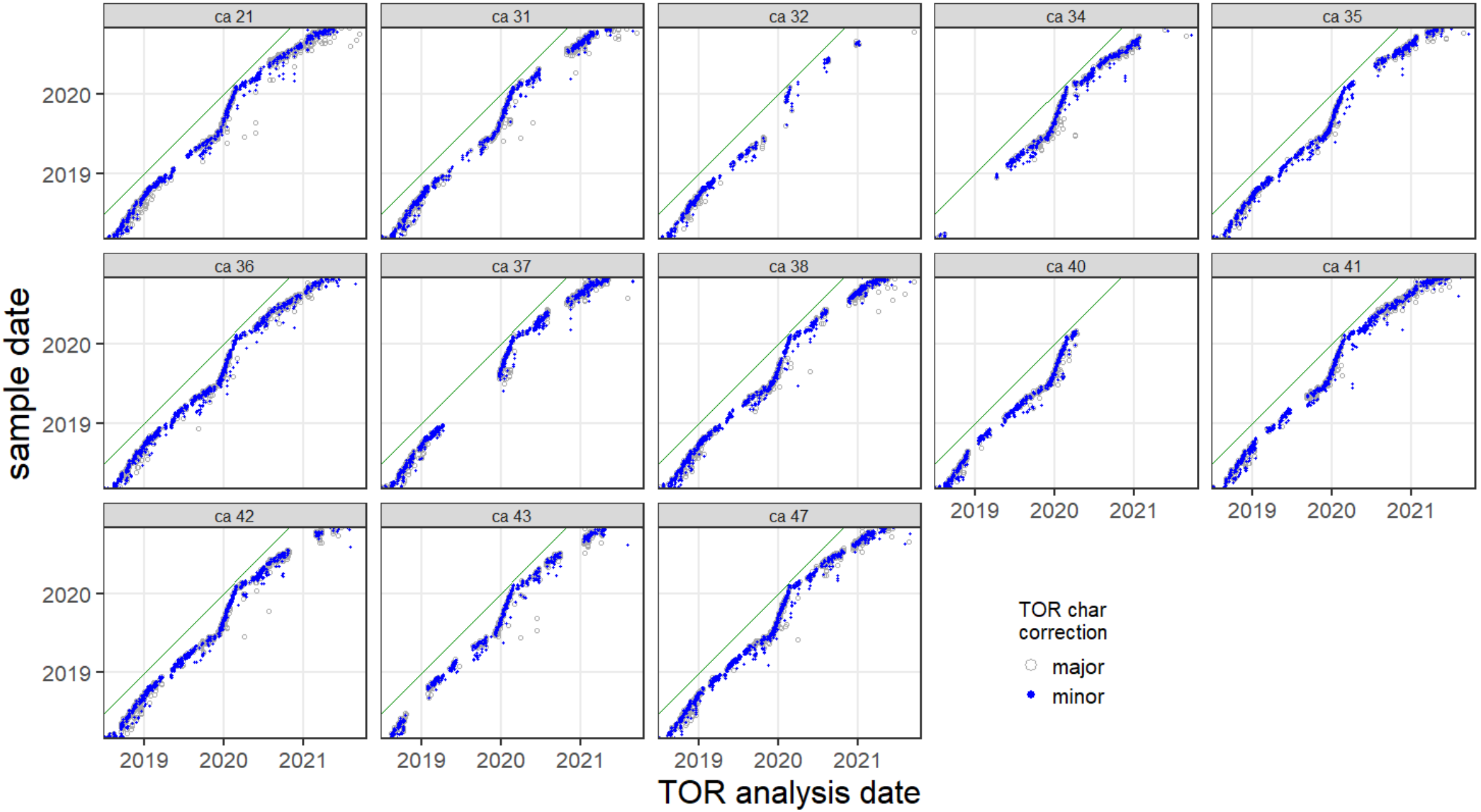
all NM IMPROVE samples above median TC (n ~ 22K), March 2018 - October 2020



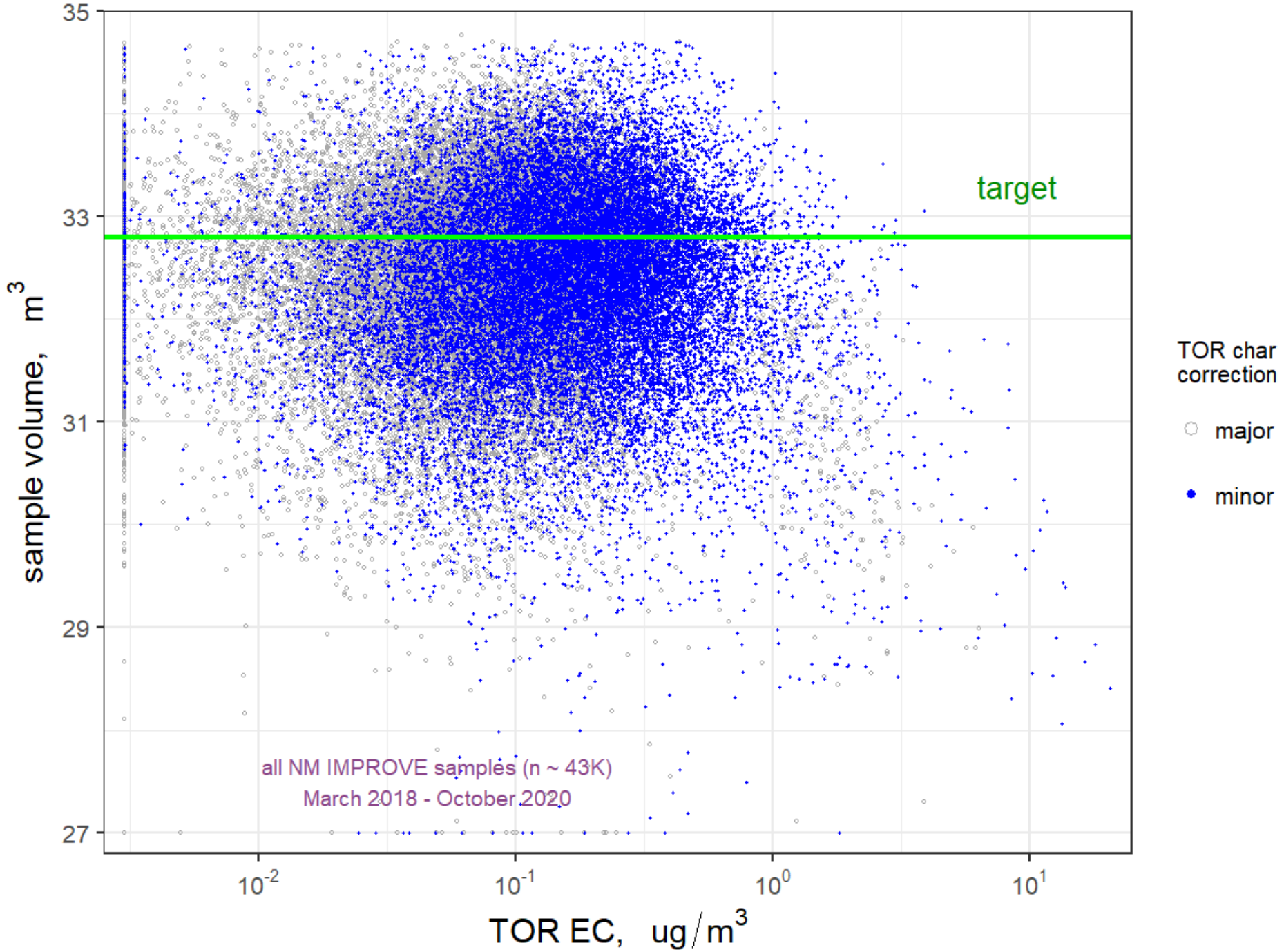
all NM IMPROVE samples above median TC (n ~ 22K), March 2018 - October 2020



all NM IMPROVE samples above median TC (n ~ 22K), March 2018 - October 2020



all NM IMPROVE samples above median TC (n ~ 22K), March 2018 - October 2020


35
33
31
29
27
target
sample volume, m3
all NM IMPROVE samples (n ~ 43K)
March 2018 - October 2020
10-2
10-1
100
101
TOR EC, ug/m3
TOR char correction
major
minor