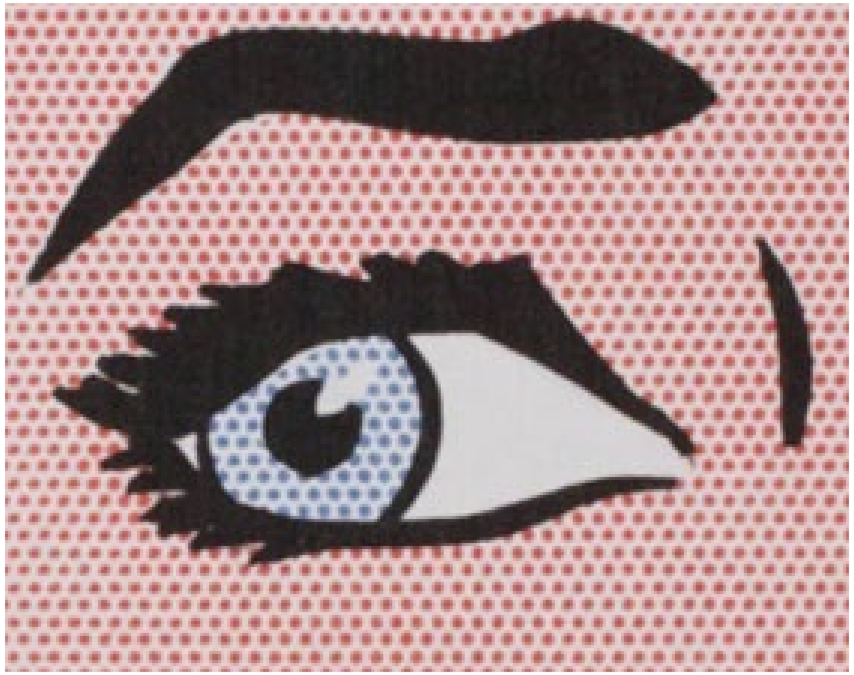
Absorption photometry of patterned deposits on IMPROVE PTFE filters

Glacier NP, October 2023



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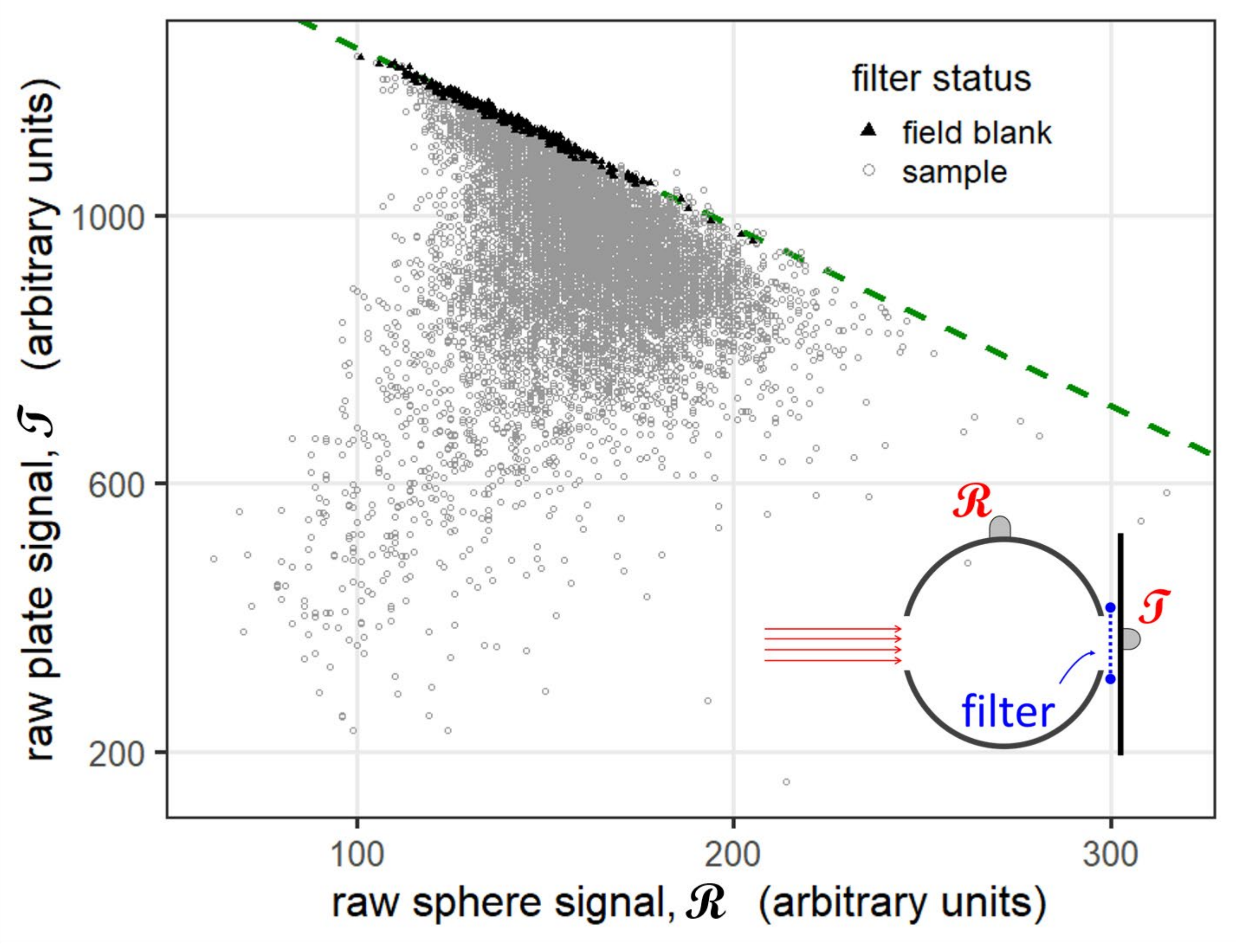
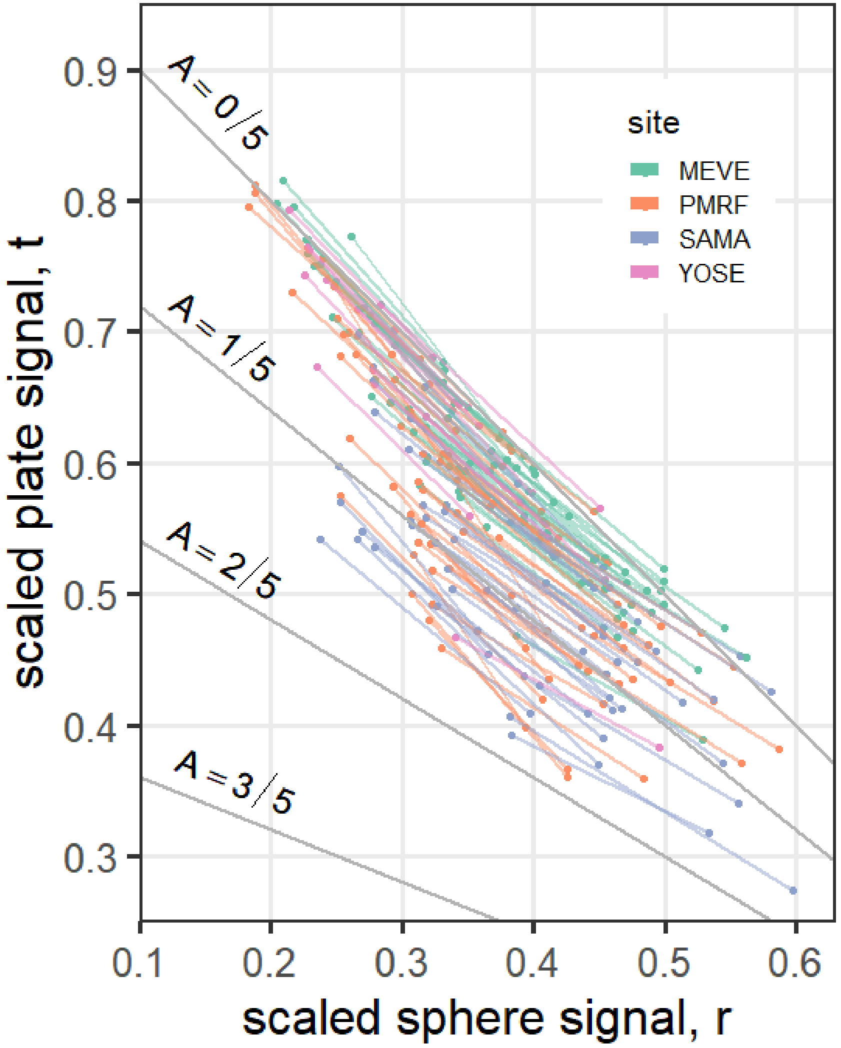
- Measuring sample absorptance with HIPS
- **Estimating aerosol absorption from sample absorptance**
  - Beer-Lambert theory and its fine print
  - Absorbing cross-sections, deposited uniformly
  - An optical model for pixelated deposits
  - Pixelation-induced uncertainty
- Relevance of pixelation in rural and urban haze monitoring
  - The rural-oriented IMPROVE Regional Haze network
  - Reconciling HIPS analyses of urban IMPROVE with early results for CSN



Unscaled data from HIPS. The scatter-plot shows routine IMPROVE network data from 285 field blanks and 9753 active 24-hr samples collected from October 2019 through April 2020. The dashed green line shows the ordinary least-squares (OLS) regression relationship determined by the field blanks.



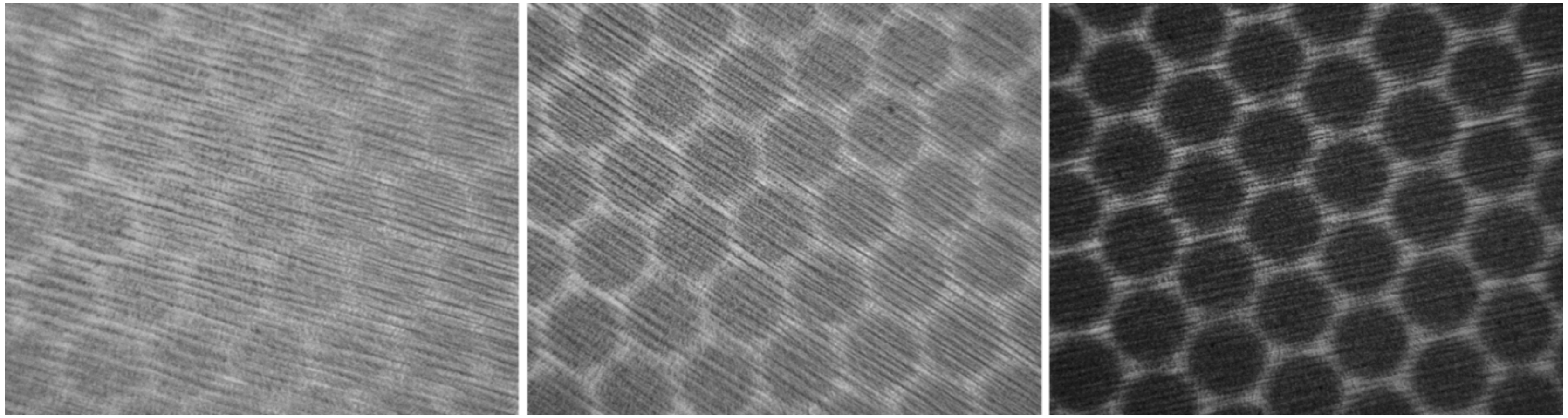
Scaled data from HIPS for 127 pairs of collocated IMPROVE samples from 2005-2021, selected to have both well-matched sample volumes and disparate optical readings. $A = 1 - \frac{t}{1-r}$.

Absorptance, $A = 1 - \frac{t}{1-r}$, is the absorbed fraction of incident radiative power, ${}^{P_{abs}}/_{P_{LASER}}$.

Transmittance, $T = \frac{t}{1-r}$, is the transmitted fraction of incident radiative power, ${}^{P_{tran}}/_{P_{LASER}}$.

($P_{LASER} = P_{abs} + P_{tran}$ is corrected for losses to reflectance.)

We have previously shown that these HIPS measurements are precise, consistent in reanalyses decades later , and – for uniform 'deposits' of absorbing gelfilm – accurate. Our problem is that IMPROVE deposits are not generally uniform:



$A = 7\%$ $A = 29\%$ $A = 47\%$

Area of filter support screen covered by holes: $\theta = 63.8\ \%$ (McDade et al., 2009).

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We want to consider aerosol absorption as an extensive property like mass or moles, one whose subsystem quantities are additive. For sufficiently fine particulate matter, we can identify this property with the sum, $\chi_{sample} = \sum_{p \in sample} \sigma_p$, of the absorbing cross sections σ_p belonging to our sample's particles, p.

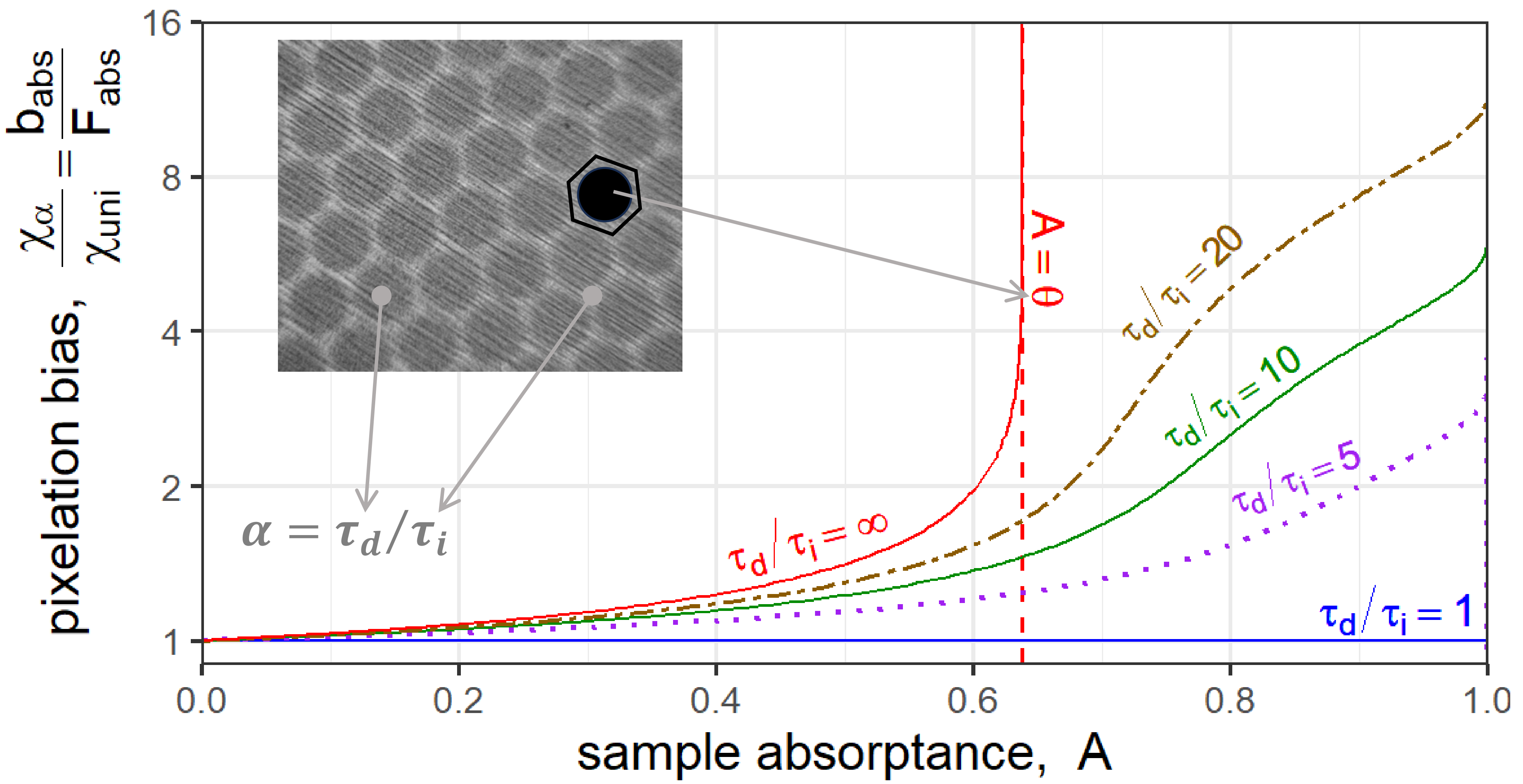
In these terms, what we want to know is the concentration of these absorbing cross sections in our original 3-D volume V of sampled air, $b_{abs} = {}^{\chi}/_{V}$. (Mm^{-1} = mm^2/m^3)

What we directly observe is a 2-D array of deposited particles in the sampled filter area, f. (mm^2)

We've always assumed that this 2-D sample deposit is **uniform**. When this is true, Beer's Law assures us that its areal density ${}^{\chi}/_{f}$ is given by $log_e(T^{-1}) = \boldsymbol{\tau}_{abs}$, which we call the absorption optical depth. (dimensionless)

And we know our sample's transmittance from the HIPS measurement: $T = 1 - A = \frac{t}{1-r}$.

So we claim that $b_{abs} = {}^{\chi}/_{V} = {}^{f\tau_{abs}}/_{V} = \frac{f}{V} log_e(T^{-1}) = \frac{f}{V} log_e\left(\frac{1-r}{t}\right) = Fabs$.



Expected bias in estimated sample cross-sections introduced by intermediate amplitudes $\boldsymbol{\alpha = \tau_d/\tau_i}$ of pixelation. Note that the bias plotted on the y-axis is the multiple by which the filter absorption coefficient Fabs reported by IMPROVE is <u>low</u> relative to the absorption coefficient b_{abs} of the *in situ* aerosol.

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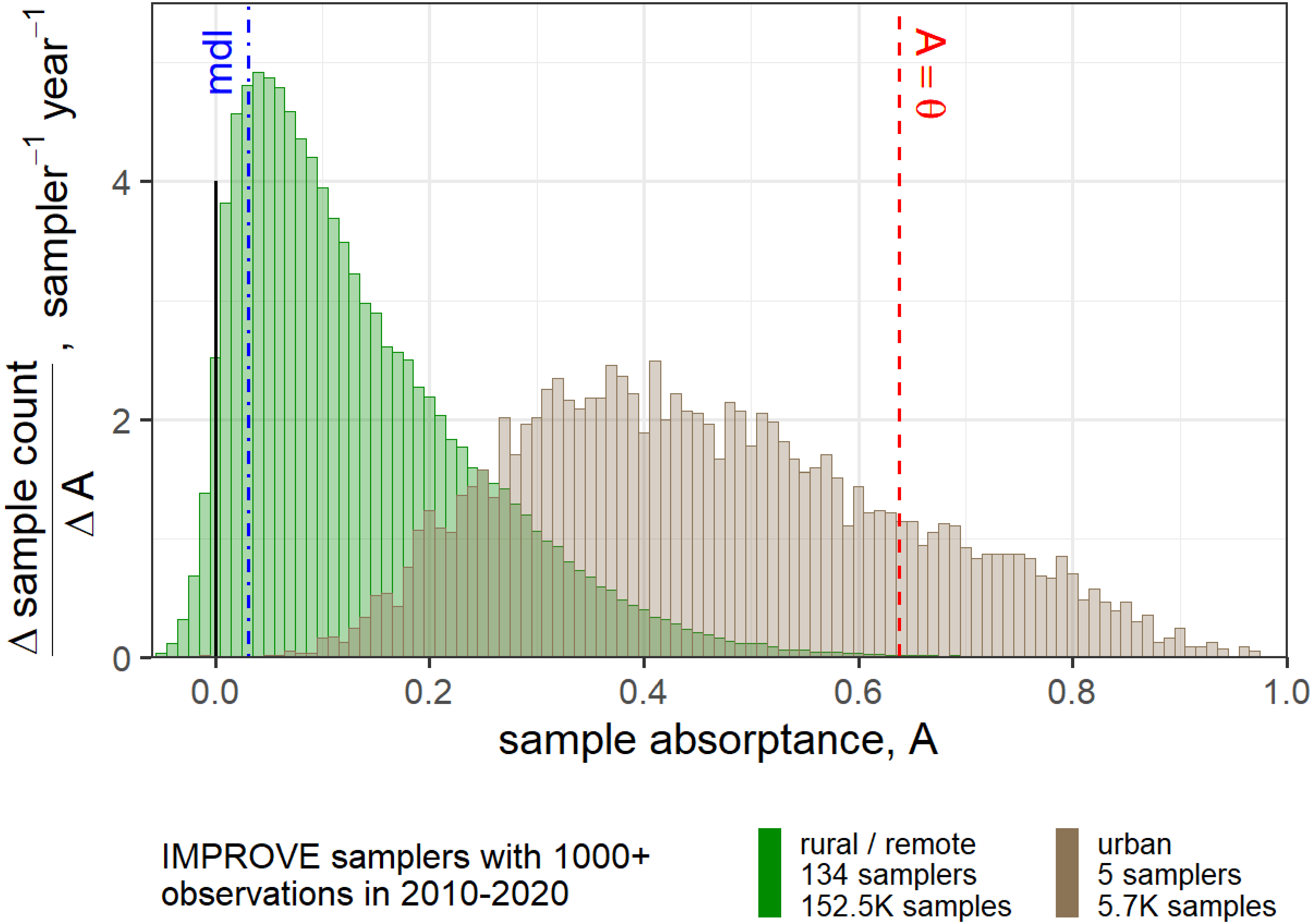
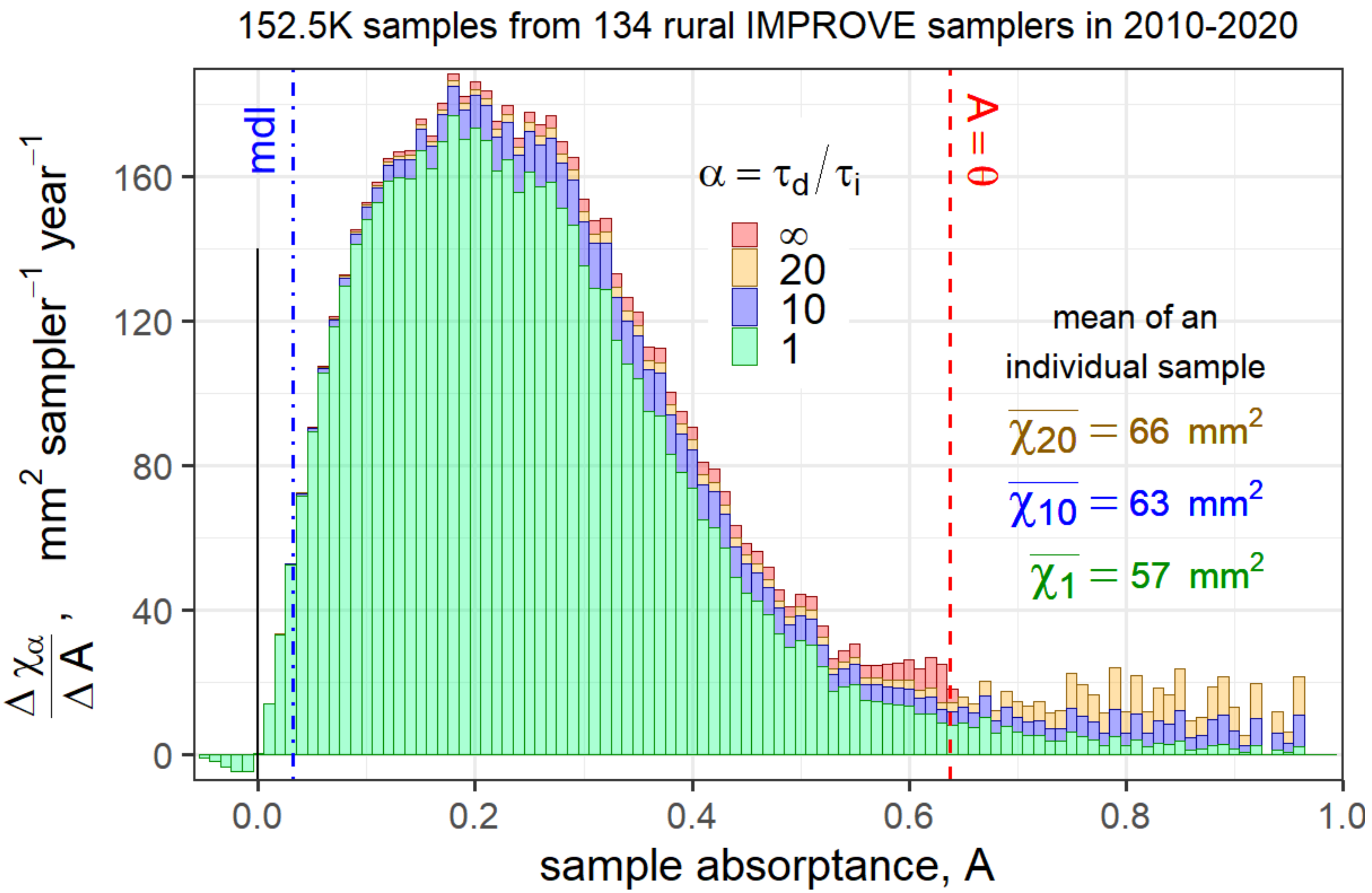
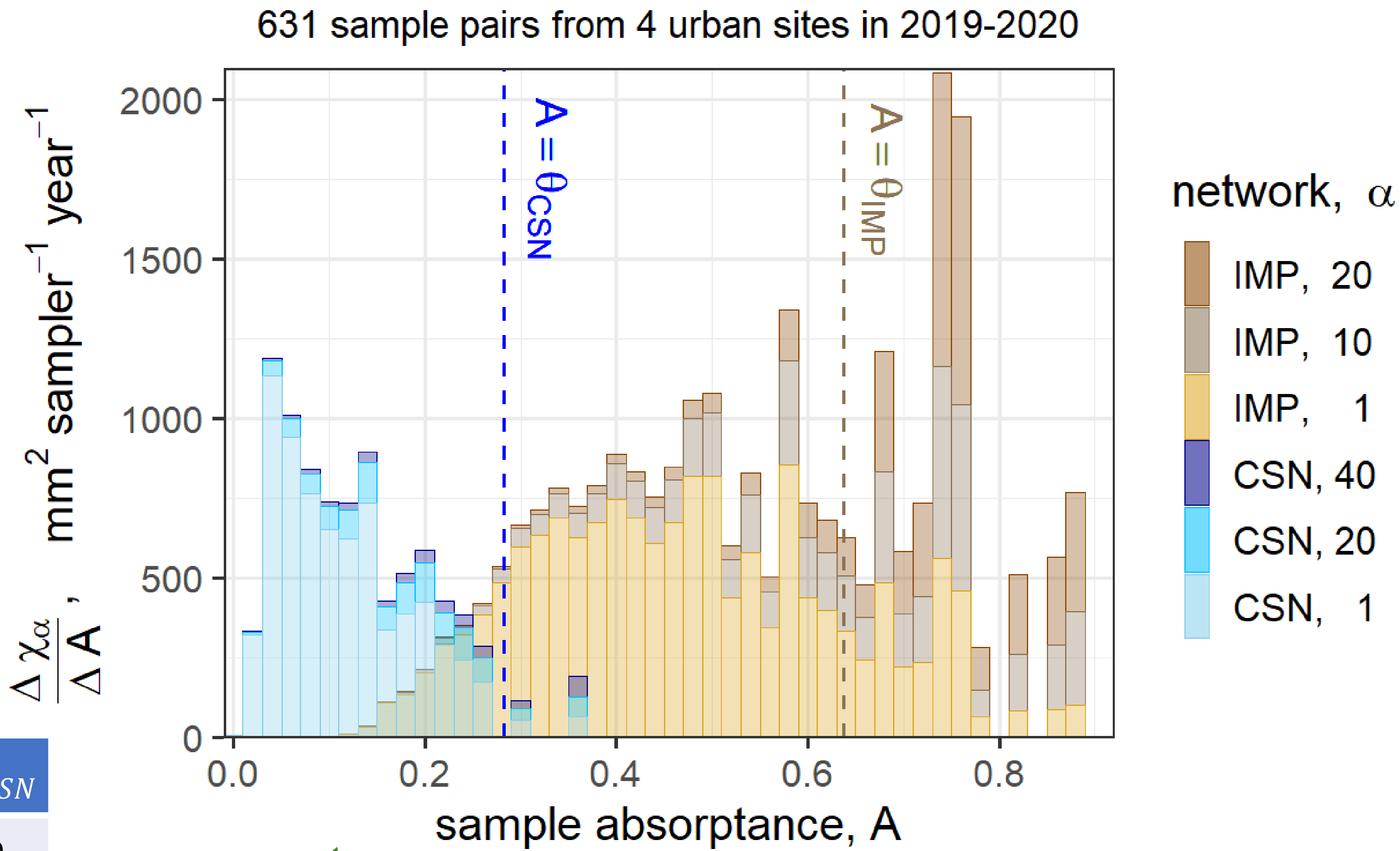
Sample frequency distributions recorded over an 11-year period at IMPROVE sites with good sample recovery. Histograms distinguish samples from rural and urban locations and separately tabulate their respective counts, as distributed by measured sample absorptance in bins of uniform width $\Delta A = 1/100$.



Alternative interpretations of the rural sample frequency distribution shown in slide 11. Each of four different histograms shows a distribution of absorbing cross sections recovered from measured sample absorptances on the assumption that all samples are pixelated with a common amplitude, $\alpha = 1, 10, 20, \infty$. The histograms recede from the viewer in order of increasing amplitude, with the one in front showing the default results for uniform deposits ($\alpha = 1$). Full pixelation ($\alpha = \infty$) cannot produce absorptances above the pixelation limit.



Distributions of absorbing cross-sections χ_α recovered from measured sample absorptances A as in slide 12. Separate but overlapping histograms distinguish the HIPS analyses of collocated samples from two independent monitoring networks with differing sampling protocols. Absorptance bins are of uniform width $\Delta A = 1/50$. Three cross-sections are estimated from each network's reported $Fabs$ for each sample, corresponding to three different assumed pixelation amplitudes.

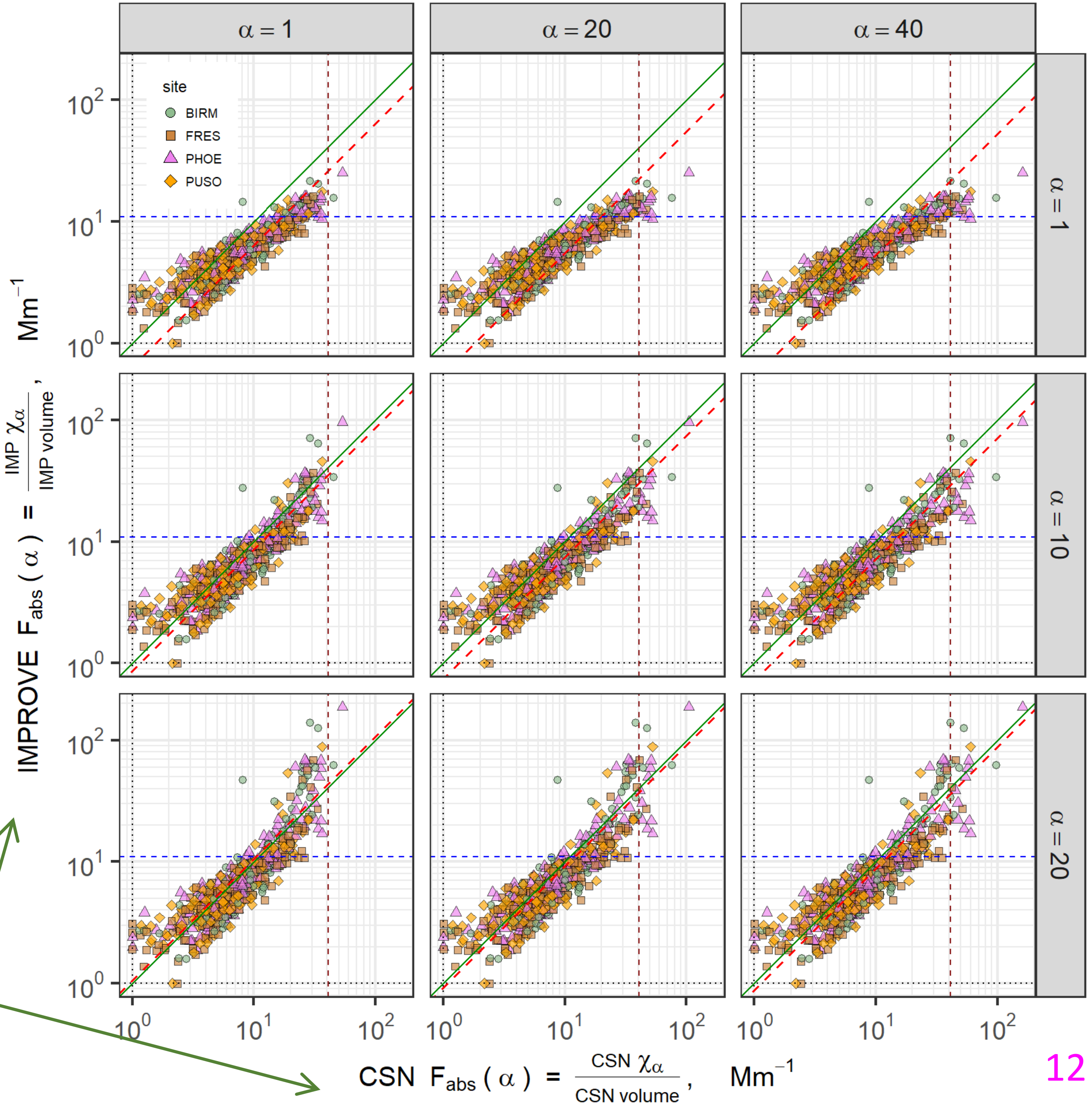


Parameter	α	$IMPROVE$	CSN	$IMP/_{CSN}$
V_{sample} (m^3)	-	32.8	9.65	3.40
χ_{sample} (mm^2) $= V_{sample} F_{abs}$	1	197	91	2.16
	10	266	100	2.66
	20	327	105	3.11
	40	444	110	4.03

absorbing cross-sections χ_α (estimated)

Network estimates of urban absorption coefficients for three different amplitudes of assumed sample pixelation. Sloping solid green lines show the locus of agreement expected between networks. Sloping dashed red lines indicate the ratios of network-mean absorption estimates $F_{abs} = {}^{\chi}/_{V}$. Horizontal and vertical dashed lines indicate the upper limits of absorption reportable for fully pixelated deposits ($\alpha = \infty$) at network-nominal sample volumes.

absorption coefficients $Fabs(\alpha)$
(estimated)



Complete triples of HIPS measurements at Phoenix, Arizona, from paired IMPROVE samplers PHOE1 and PHOE5 collocated with one CSN sampler. Observations are plotted as triangular symbols at the coordinates reported by default for uniform sample deposits. Horizontal bars indicate reported 1σ uncertainties of the CSN observations. Curved solid lines identified near the top of the figure show expected loci of agreement between IMPROVE and CSN at specified amplitudes for deposit pixelation.