Summary of Reprocessing 2016 IMPROVE Data with New Integration Threshold

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1. Background

UC Davis (2017) reported that the 10% percentile and median elemental carbon (EC) values for January-June 2016 were lower than those of 2011-2015 (Figure 1). The mass absorption efficiency (f_{Abs}/EC), defined as the ratio of HIPS-derived filter optical absorption coefficients (f_{Abs} in Mm^{-1}) to IMPROVE_A EC concentration, appears to have increased during the first half of 2016 (Figure 2). Differences between the first half of 2016 and prior full years were larger for the 10% and 50% percentiles than for the 90% percentiles. Organic carbon (OC) percentile values for 2016 were similar to those of prior years (Figure 3).

OC, EC, TC, $PM_{2.5}$, and f_{Abs} over 2011–2016 measured in the IMPROVE network were downloaded from the Federal Land Manager Environmental Database (CIRA, 2017). Figures 4 and 5 show monthly 10%, 50%, 90%, and average of $PM_{2.5}$ concentrations and f_{Abs}, respectively. Both 2016 $PM_{2.5}$ and f_{Abs} had the lowest values among 2011–2016, particularly from January to September. Lower $PM_{2.5}$ concentrations would partially contribute to lower EC and OC in Figures 1 and 3.

Since January 2016, carbon analysis of the IMPROVE and Chemical Speciation Network (CSN) were completed with the DRI Model 2015 multiwavelength carbon analyzers, while the DRI Model 2001 carbon analyzers were used in earlier years. There are two main design differences between Model 2001 and Model 2015: 1) Model 2001 uses a single laser (633 nm) while Model 2015 uses seven lasers (i.e., 405, 445, 532, 635, 780, 808, and 980 nm) for optical monitoring; and 2) Model 2001 uses a flame ionization detector (FID) for carbon detection, while the Model 2015 uses a nondispersive infrared (NDIR) CO_2 detector. The carbon integration signal for the Model 2015 is calculated as the product of the CO_2 concentration (ppm) and NDIR flow rate (200 mL/min). This report:

- Re-examines the IMPROVE comparison data between Model 2015 and Model 2001;
- Evaluates the Model 2015 signal integration threshold in relation to the Model 2001 threshold;
- Compares 2016 IMPROVE data with different Model 2015 signal integration thresholds.

2. Re-examine the IMPROVE Comparison Data between Model 2015 and Model 2001

Prior to replacement of the aging Model 2001 with the Model 2015, ~1,000 IMPROVE samples from the IMPROVE network (October 2014 to December 2015) were analyzed by both models to verify their comparability. Figure 6 compares the OC, EC, TC, and carbon fraction concentrations by the two instruments with Model 2015 NDIR integration threshold set to 2. During initial examination of equivalence, the linear regressions were forced through zero. The slopes of linear regressions forced through the origin for OCR, OCT, ECR, ECT, and TC were within 0.95–1.05 with coefficients of determination (R^2) ≥ 0.94. All carbon fractions except OC1 and EC3 had slopes within ±15% from unity. Based on these results, it was concluded that the Model 2015 carbon data were equivalent to the Model 2001 and the IMPROVE Steering Committee approved replacement of the aging units.

3. Examine the appropriateness of Model 2015 signal integration threshold

During the Model 2015 analyzer development, different NDIR integration thresholds were compared to reduce effects of NDIR noise and drift. After analysis of blanks, calibration standards, as well as IMPROVE and Fresno samples, a threshold value of 2 (ppm × mL/min) was chosen. However, this integration threshold was not compared to the carbon-equivalent threshold of the FID on the Model 2001 as the difference was believed to be negligible.

Figure 7 compares Model 2015 thermograms of sucrose calibration solutions containing 1 and 18 μg carbon (per punch), corresponding to 0.22 and 4.0 $\mu gC/m^3$ for IMPROVE samples. For the 1 μg carbon case (Figure 7a), with a threshold of 2, all carbon fractions except OC3 were set to zero, truncating the low-level carbon signals of OC1, OC2, and OC4. For the 18 μg carbon case (Figure 7b), most carbon signals were above 2. Therefore, a threshold of 2 did not result in a significant truncation of the carbon integration signal. The nonzero carbon signal at the EC3 stage, is likely an artifact since sucrose should not produce EC3. The Model 2001 used an FID threshold value of 1 to remove noise. This threshold translates to 0.72 (ppm × mL/min) for an equivalent amount of carbon for the Model 2015. Figure 7 also shows that a threshold value of 0.72 reduces truncation while keeping noise level low. To maintain threshold consistency between the Models 2001 and 2015, the IMPROVE data for year 2016 was reprocessed with a threshold value of 0.72. For signals measured at sample oven temperatures above 800 °C, a higher threshold value of 2.0 was used because more noise occurs at higher temperatures.

4. Comparison of Model 2015 Signal Integration Threshold 0.72 vs. 2.0

Figure 8 compares all 2016 IMPROVE samples for carbon using thresholds of 0.72 (new) and 2.0 (original). Linear regressions with intercept set to zero and nonzero are both shown. While the slopes differ <±5% from unity and coefficients of determination (R^2) are close to 1 for most carbon fractions, there are positive intercepts when the regressions are not forced through the origin. To better illustrate the effect of the lower threshold at lower concentrations, Figure 9 compares concentrations from a subset of samples with TC <~100 μg/filter (95% of total samples). The higher carbon values with the new threshold of 0.72 are evident from the >1 slopes and positive intercept for most carbon fractions. Most of these values are below the standard deviation of the field blanks, however, so the absolute change is insignificant.

Table 1 compares the 10%, 50%, and 90% percentile carbon concentrations (after subtraction with monthly median blank levels) as well as annual averages of the 2016 IMPROVE data with thresholds of 0.72 and 2.0. Lowering threshold from 2.0 to 0.72 causes TC concentrations to increase by 0.036 $\mu g/m^3$ (32%) for 10% percentile, 0.094 $\mu g/m^3$ (16%) for 50% percentile, 0.117 $\mu g/m^3$ (6%) for 90% percentile, and 0.080 $\mu g/m^3$ (8%) for the annual average. Lowering the threshold causes EC concentrations to increase by 0.010 $\mu g/m^3$ (100%) for 10% percentile, 0.031 $\mu g/m^3$ (59%) for 50% percentile, 0.038 $\mu g/m^3$ (13%) for 90% percentile, and 0.026 $\mu g/m^3$ (20%) for the annual average.

Table 2 lists the concentrations of blank samples collected in 2016, analyzed with a threshold of 0.72. The sample concentration increases by lowering the threshold (i.e., the y-x column in Table 1) are 24–56% of average blank levels and are lower than the lower quantifiable limits (LQL; three times the field blank standard deviations) for OC and TC. The average EC concentration increase is comparable to the LQL for EC.

5. Evaluation of the 2011-2016 IMPROVE Data

OC, EC, and TC over 2011–2015 measured in the IMPROVE network were downloaded from the Federal Land Manager Environmental Database (CIRA, 2017). The monthly average EC, OC, TC, and mass absorption efficiency (f_{Abs}/EC) are plotted in Figures 10-13, respectively. The 2016 percentiles from the original submission with threshold value of 2.0 (2016-T2) and reprocessed data with threshold value of 0.72 (2016-T0.72) are also plotted. For the 2016 data, a constant sampling volume of 33.12 m^3 was assumed, and the monthly median blank concentrations were subtracted. Figure 10 shows that EC percentiles from 2016 with threshold 2.0 are lower than earlier years, and lowering threshold to 0.72 increases the EC concentration to be within the range of earlier years. Lowering threshold also increases OC and TC, but the relative changes are less than those of EC due to their higher concentrations. The mass absorption efficiency f_{Abs}/EC percentiles also have better agreement with the threshold of 0.72 than 2.0 (see also Figure 2).

The effect of changing the integration threshold makes frequency distributions of values more consistent with those from prior years. It has little effect on the absolute concentration, however, as the EC concentration differences before and after re-processing are within the reported uncertainty intervals.

6. References:

CIRA, (2017). Federal Land Manager Environmental Database (FED). Colorado State University, Fort Collins, CO. http://views.cira.colostate.edu/fed/

UCDavis, (2017). Interagency Monitoring of Protected Visual Environments (IMPROVE): Semiannual Quality Assurance Report. Air Quality Group, University of California, Davis.

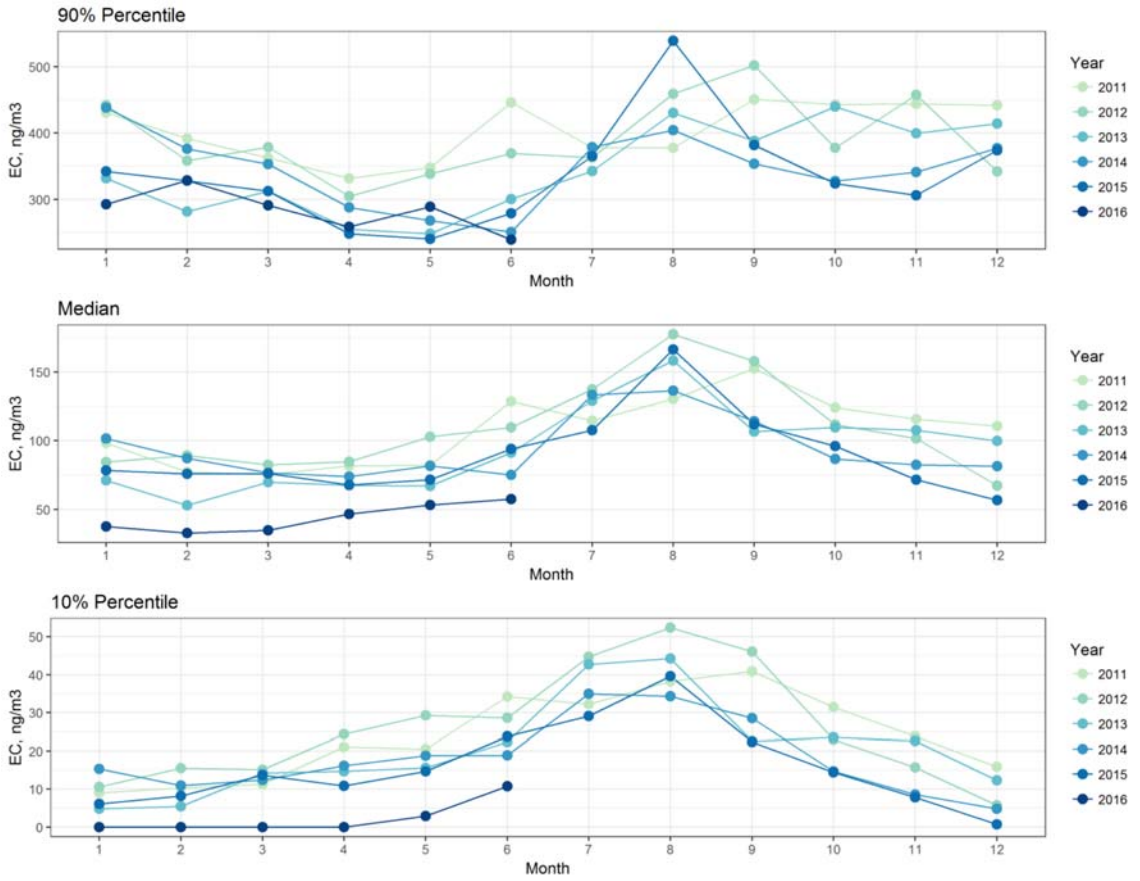

Figure 1. Comparison of EC concentrations in the IMPROVE network from 2011 to 2016 at 90%, 50% (median), and 10% percentiles (UCDavis, 2017).

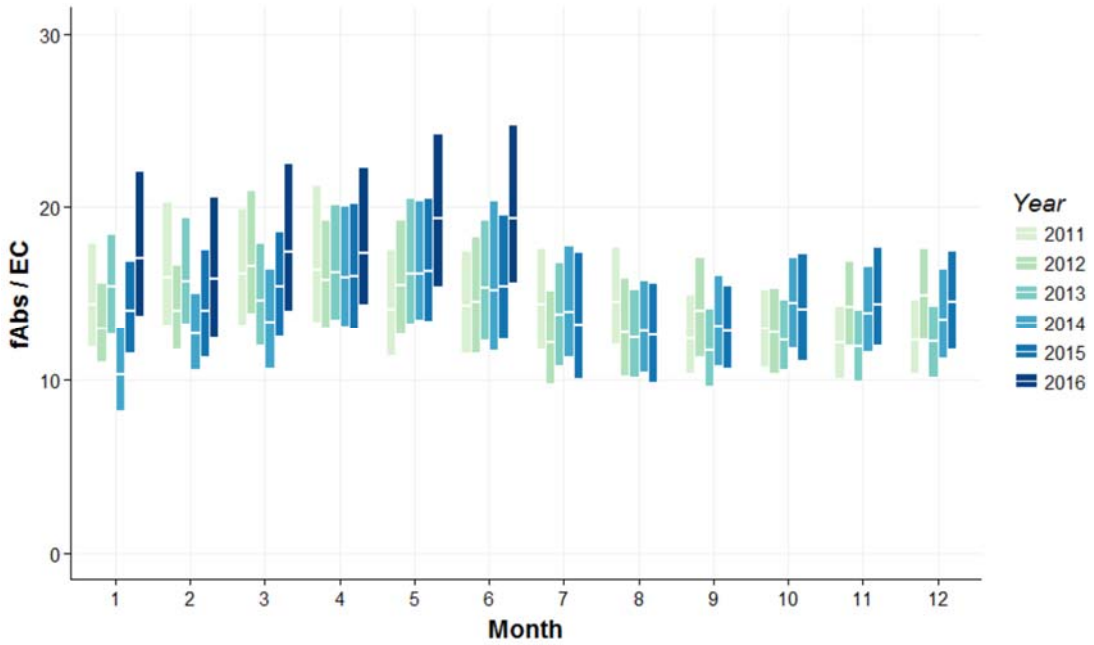

Figure 2. Comparison of the ratio of optical absorption coefficients (f_{Abs} measured by the hybrid integrating plate/sphere, in Mm^{-1}) and EC concentrations by thermal optical reflectance (in $\mu g/m^3$) in the IMPROVE network from 2011 to 2016 (UCDavis, 2017).

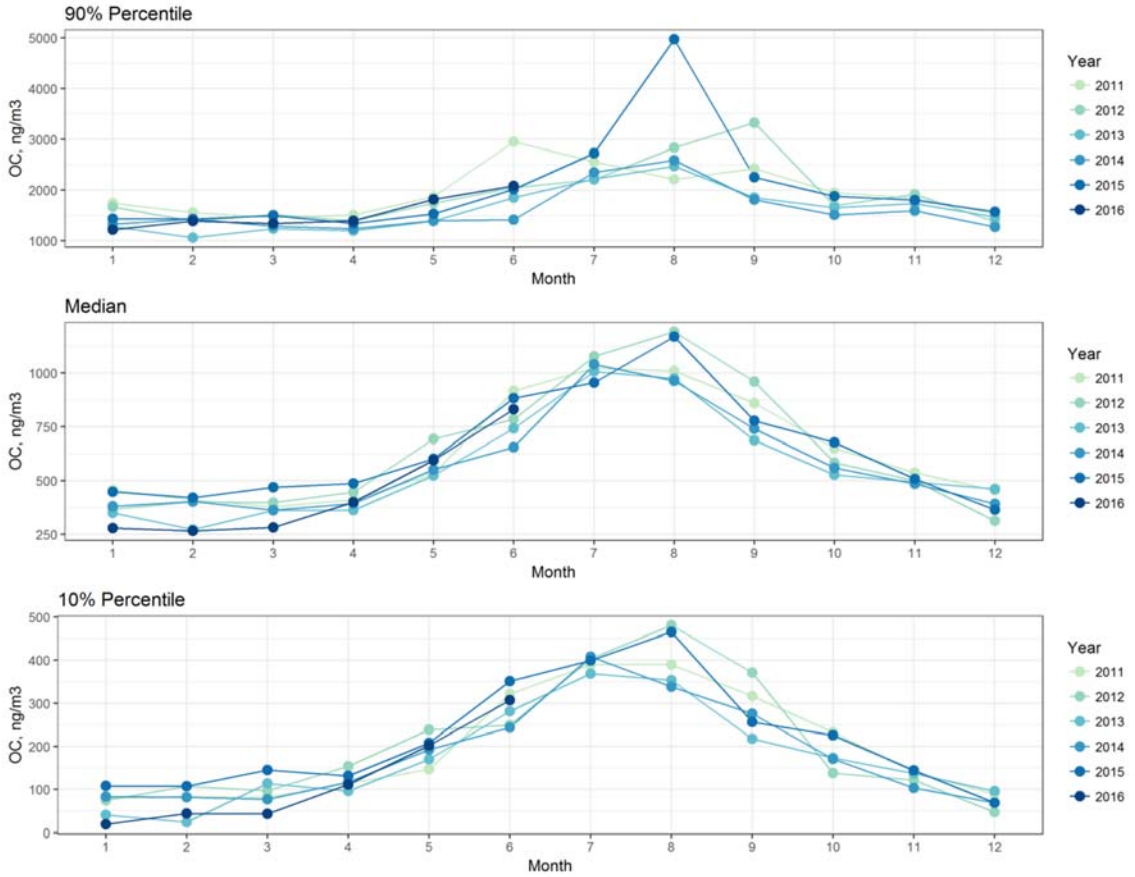

Figure 3. Comparison of OC concentrations in the IMPROVE network from 2011 to 2016 at 90%, 50% (median), and 10% percentiles (UCDavis, 2017).

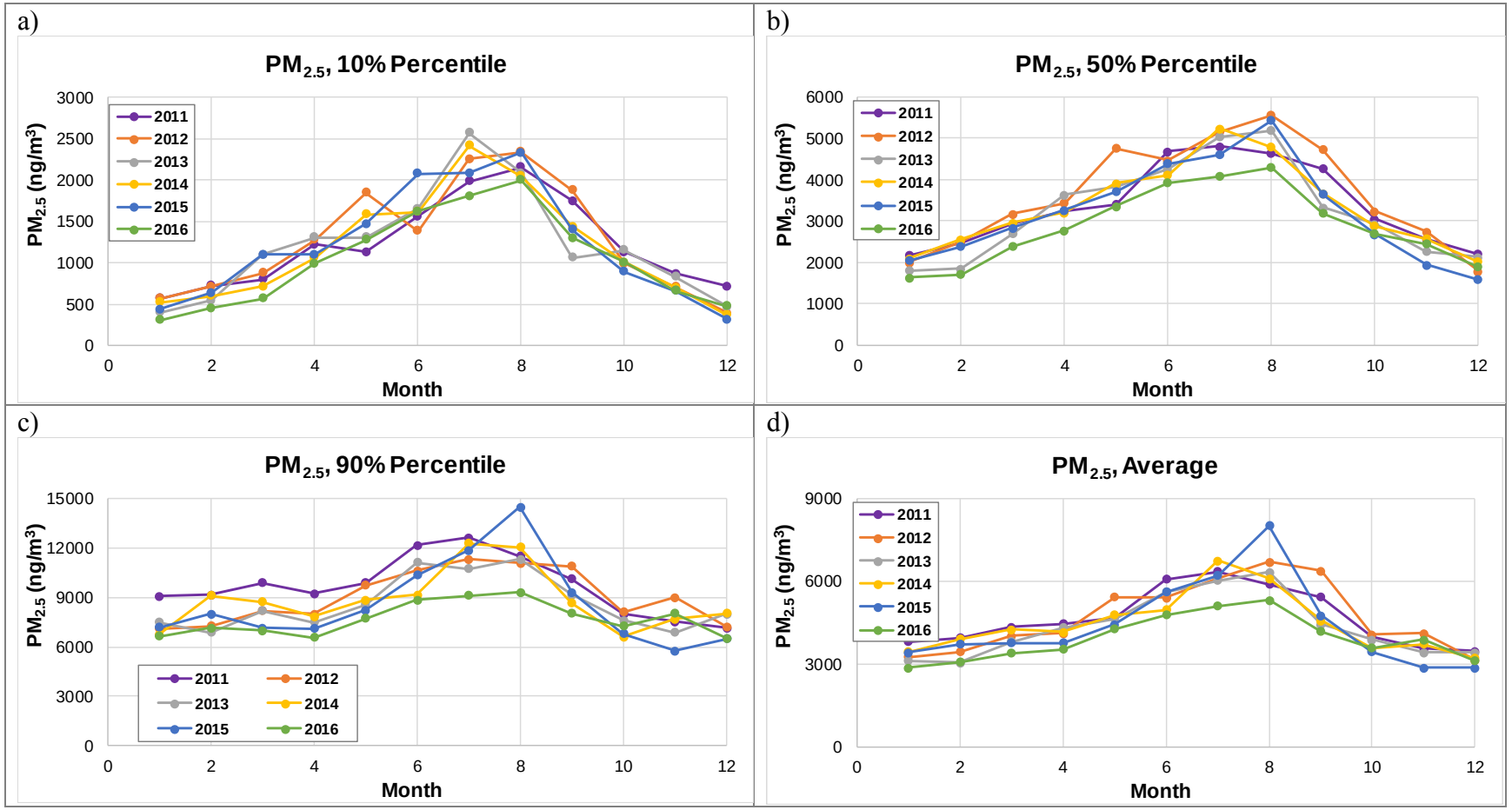

Figure 4. Comparison of $PM_{2.5}$ concentrations in the IMPROVE network from 2011 to 2016 at 10%, 50% (median), and 90% percentiles as well as monthly average in each year (CIRA, 2017).

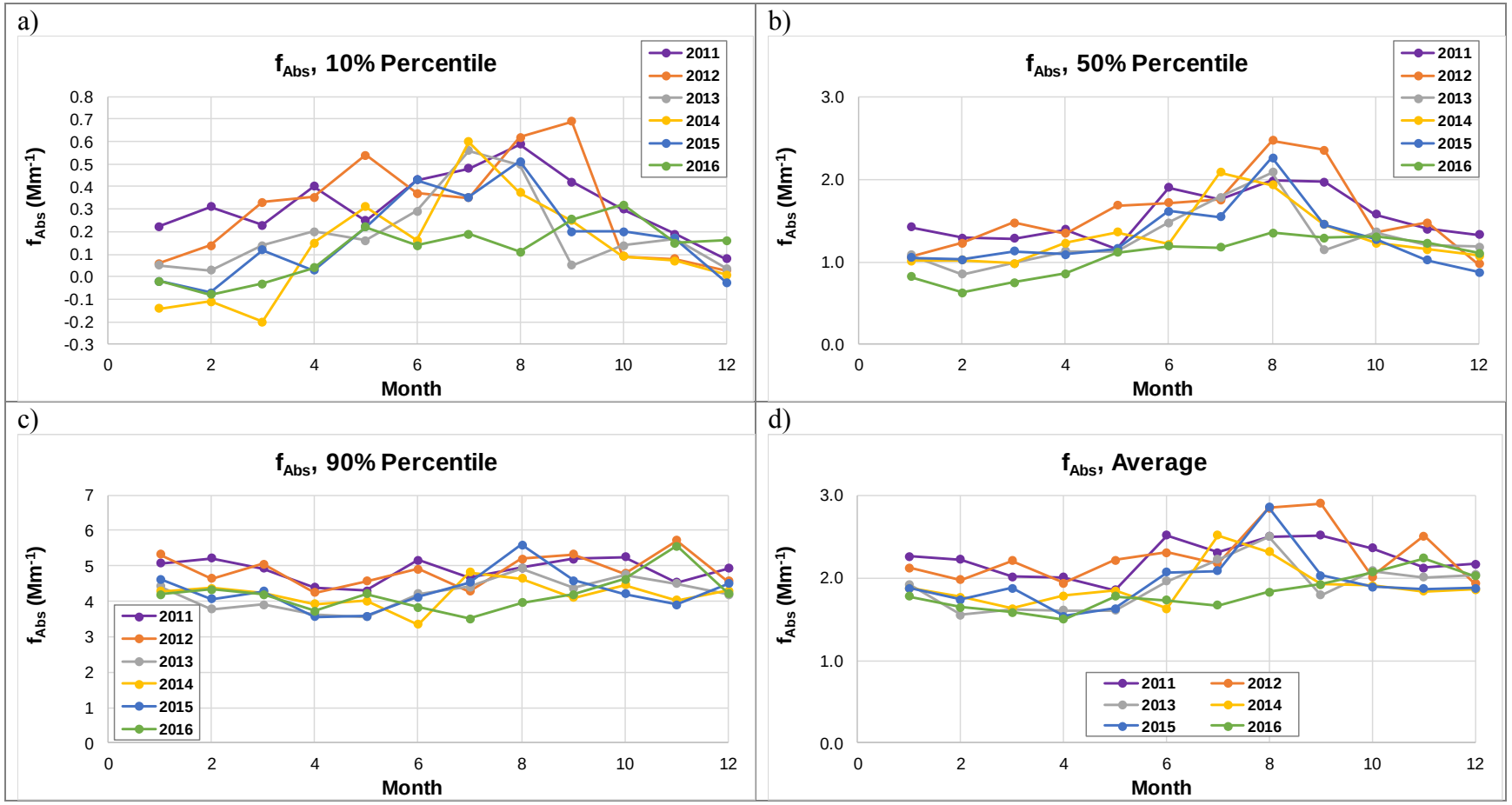

Figure 5. Comparison of optical absorption coefficients (f_{Abs}) in the IMPROVE network from 2011 to 2016 at 10%, 50% (median), and 90% percentiles as well as monthly average in each year (CIRA, 2017).

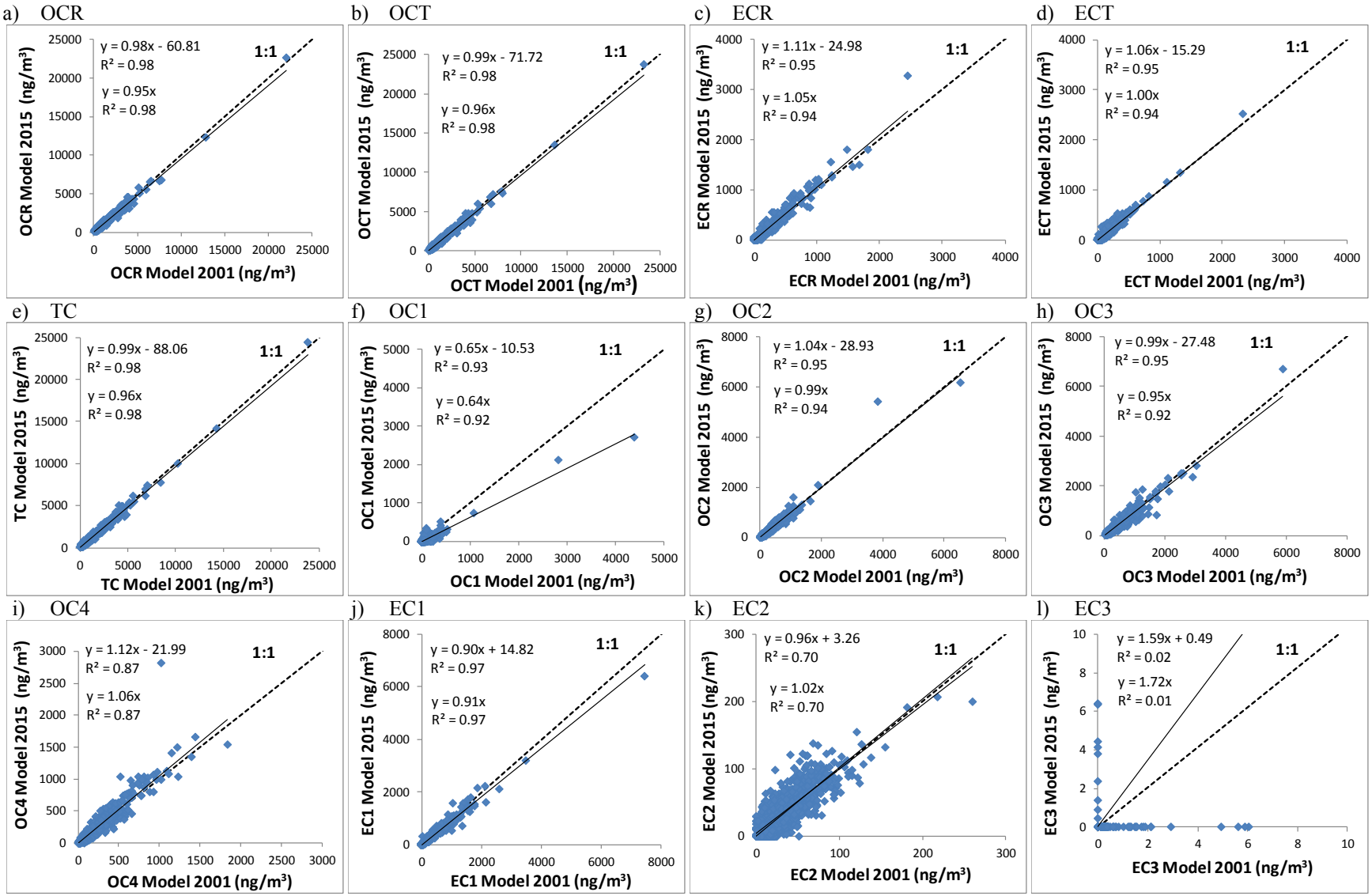

Figure 6. Comparison of Model 2015 vs. 2001 analysis for 1070 IMPROVE samples collected from October 2014 to December 2015. The Model 2015 NDIR signal integration threshold was set to 2 (ppm×mL/min).

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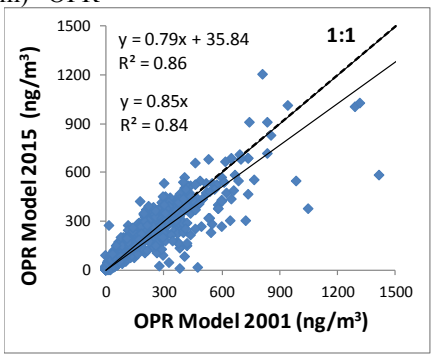


n) OPT

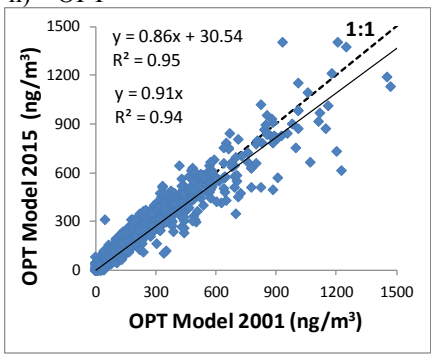
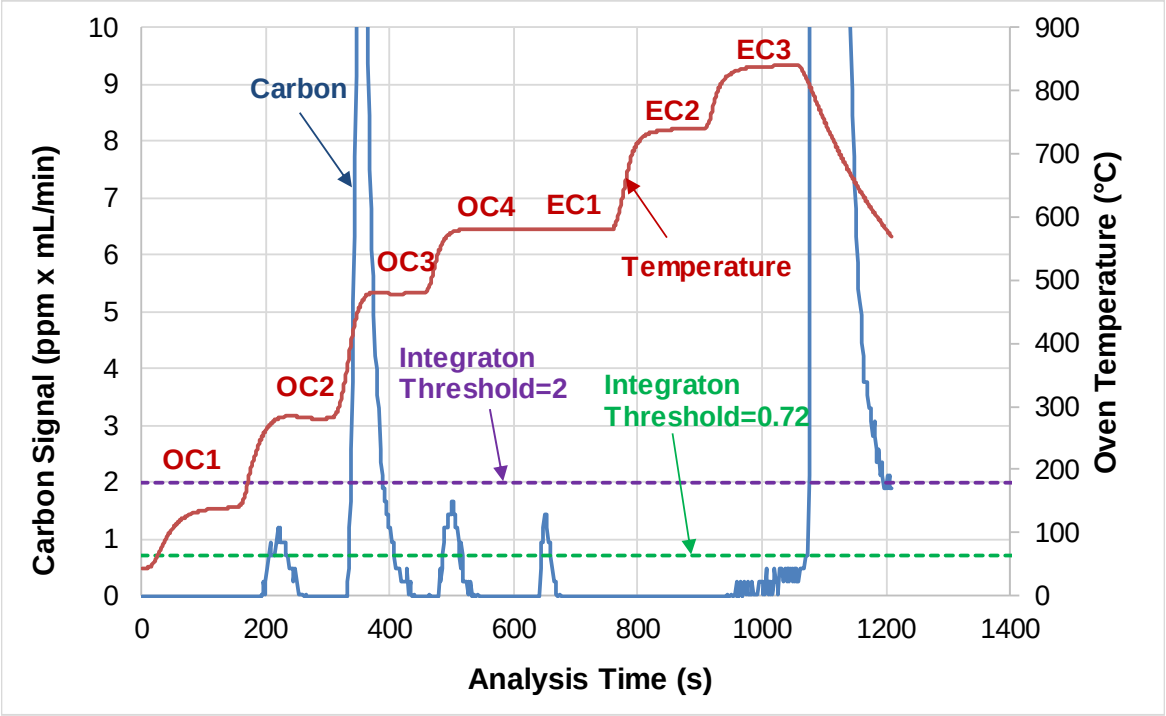


Figure 6 continued.

a) Thermogram of 1 µg carbon (10 µL of 100 ppm sucrose calibration solution)



b) Thermogram of 18 µg carbon (10 µL of 1800 ppm sucrose calibration solution)

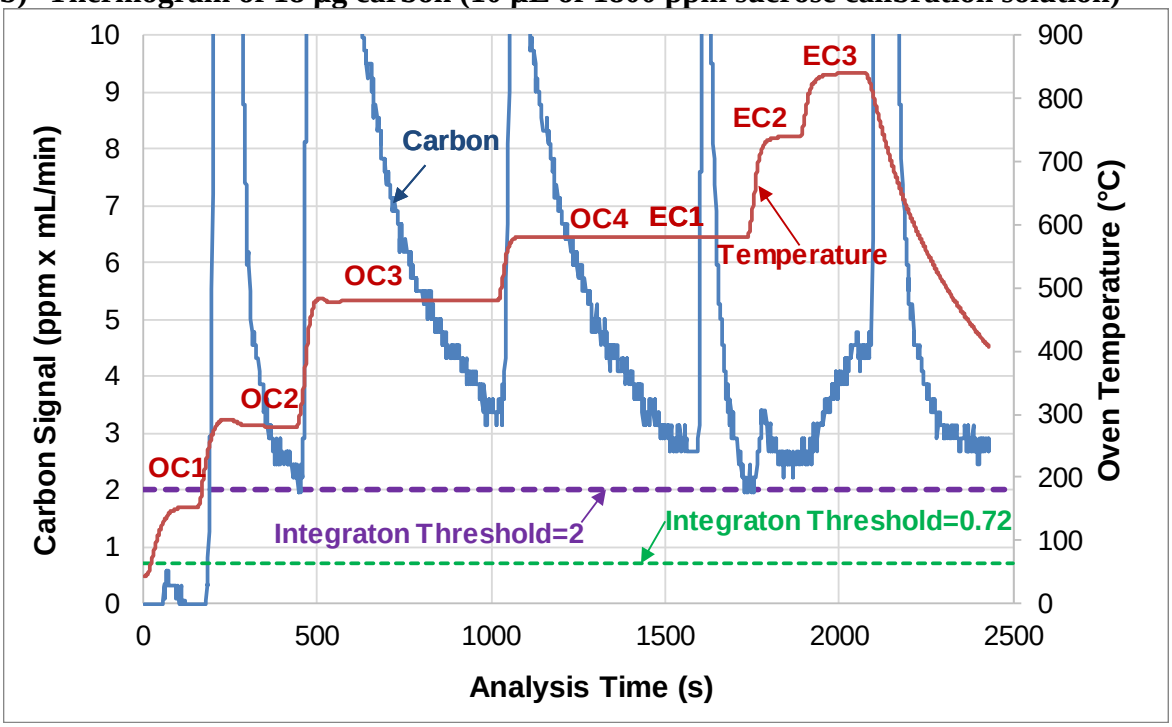


Figure 7. Model 2015 thermograms of sucrose solutions containing a) 1 and b) 18 µg carbon with left y-axis (carbon signal) zoomed in to 10 ppm × mL/min. The horizontal dash lines indicate carbon integration threshold of 2 and 0.72 ppm × mL/min.

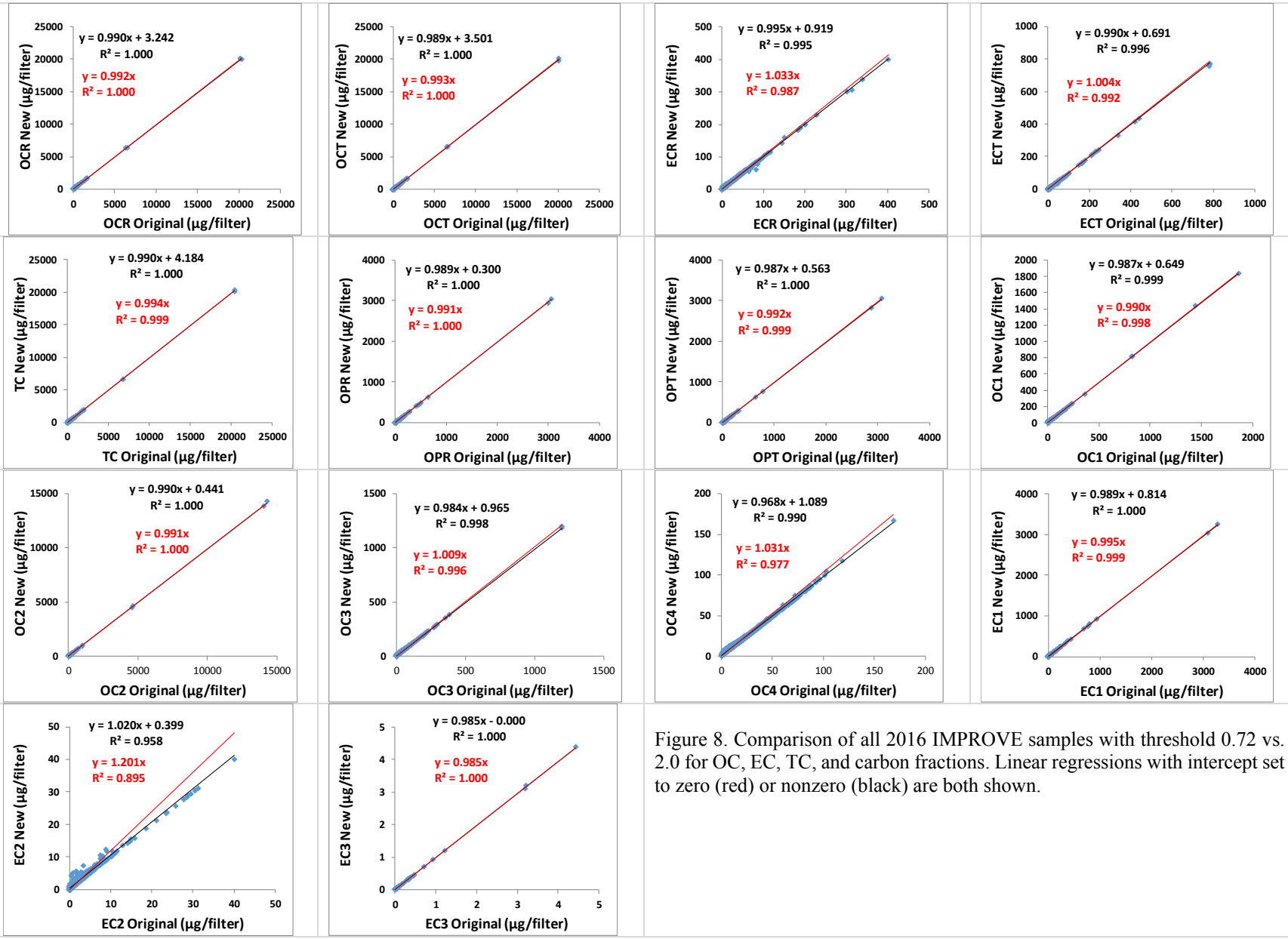


Figure 8. Comparison of all 2016 IMPROVE samples with threshold 0.72 vs. 2.0 for OC, EC, TC, and carbon fractions. Linear regressions with intercept set to zero (red) or nonzero (black) are both shown.

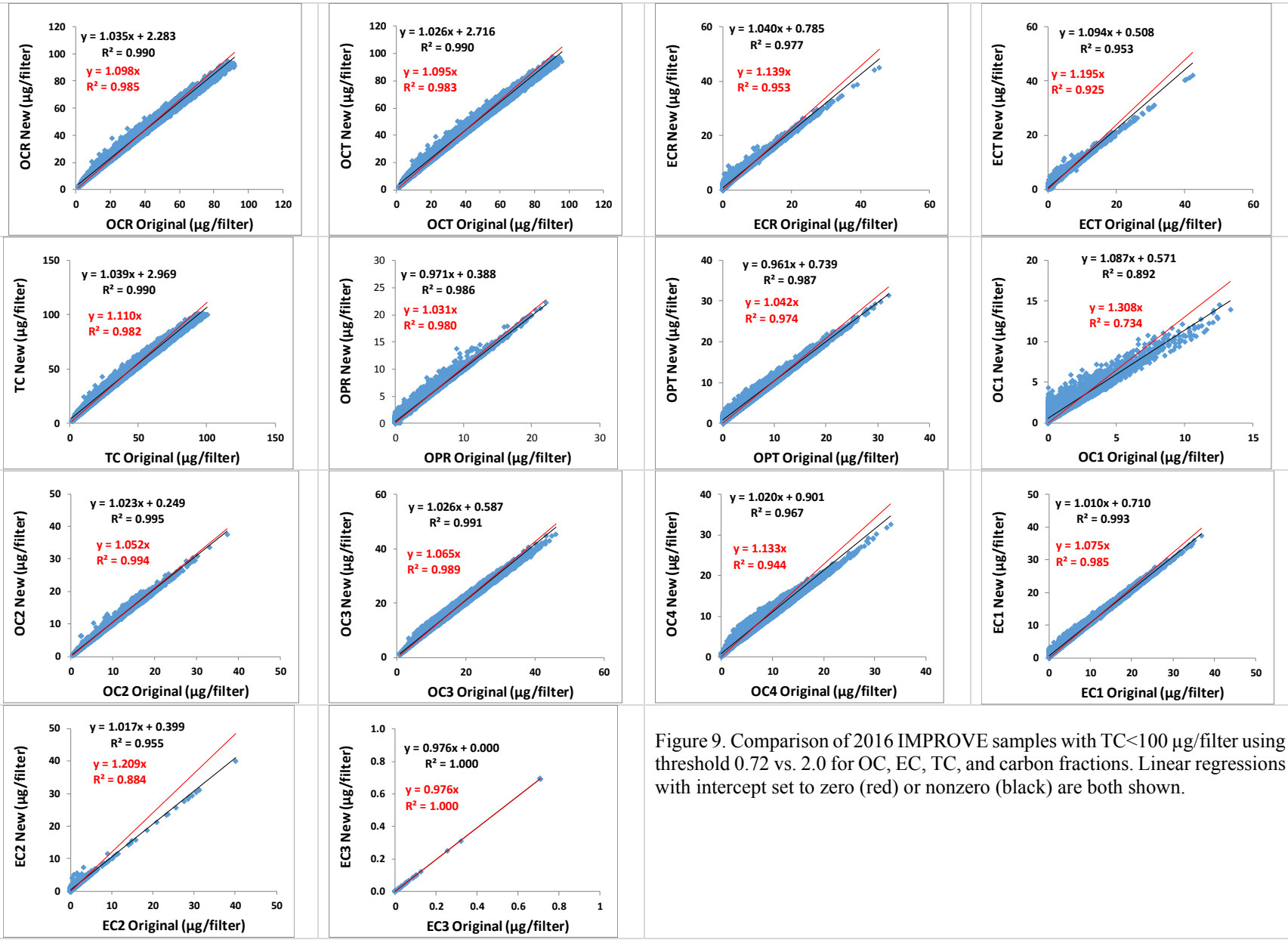


Figure 9. Comparison of 2016 IMPROVE samples with TC<100 µg/filter using threshold 0.72 vs. 2.0 for OC, EC, TC, and carbon fractions. Linear regressions with intercept set to zero (red) or nonzero (black) are both shown.

Table 1. Comparison of 2016 IMPROVE sample carbon concentrations (μg/m^3) using threshold 2.0 (x) and 0.72 (y).

Fractions	10% percentile				50% percentile				90% percentile				average			
	x	y	y-x	y/x	x	y	y-x	y/x	x	y	y-x	y/x	x	y	y-x	y/x
OC1	0.000	0.000	0.000	NA	0.000	0.001	0.001	NA	0.055	0.070	0.015	1.27	0.040	0.044	0.004	1.11
OC2	0.016	0.017	0.001	1.09	0.096	0.101	0.005	1.06	0.410	0.420	0.010	1.03	0.247	0.252	0.005	1.02
OC3	0.043	0.047	0.005	1.11	0.202	0.224	0.022	1.11	0.703	0.726	0.024	1.03	0.329	0.347	0.017	1.05
OC4	0.026	0.032	0.006	1.25	0.098	0.123	0.025	1.25	0.383	0.412	0.029	1.08	0.172	0.193	0.020	1.12
EC1	0.012	0.028	0.016	2.27	0.140	0.166	0.026	1.18	0.509	0.534	0.025	1.05	0.247	0.268	0.022	1.09
EC2	0.000	0.009	0.009	NA	0.029	0.041	0.011	1.38	0.064	0.077	0.013	1.21	0.033	0.044	0.011	1.33
EC3	0.000	0.000	0.000	NA	0.000	0.000	0.000	NA	0.000	0.000	0.000	NA	0.000	0.000	0.000	0.98
OPR	0.004	0.016	0.012	4.22	0.104	0.114	0.010	1.10	0.277	0.282	0.004	1.02	0.151	0.158	0.007	1.05
OC	0.103	0.126	0.023	1.22	0.523	0.590	0.067	1.13	1.746	1.832	0.086	1.05	0.928	0.983	0.055	1.06
EC	0.000	0.010	0.010	NA	0.052	0.083	0.031	1.59	0.302	0.340	0.038	1.13	0.129	0.155	0.026	1.20
TC	0.110	0.146	0.036	1.32	0.587	0.681	0.094	1.16	2.029	2.146	0.117	1.06	1.057	1.137	0.080	1.08

Table 2. 2016 IMPROVE field blank carbon concentrations (μg/m^3) using threshold 0.72.

Fraction	10% Percentile	50% Percentile	90% Percentile	Average	LQL*
OC1	0.009	0.027	0.050	0.030	0.058
OC2	0.027	0.043	0.068	0.046	0.058
OC3	0.048	0.078	0.125	0.084	0.121
OC4	0.000	0.009	0.023	0.011	0.029
EC1	0.000	0.000	0.006	0.002	0.018
EC2	0.000	0.000	0.009	0.003	0.016
EC3	0.000	0.000	0.000	0.000	0.000
OPR	0.000	0.000	0.001	0.001	0.014
OC	0.094	0.161	0.253	0.172	0.223
EC	0.000	0.000	0.011	0.004	0.024
TC	0.094	0.162	0.267	0.175	0.235

*LQL is defined as three times the field blank standard deviation.

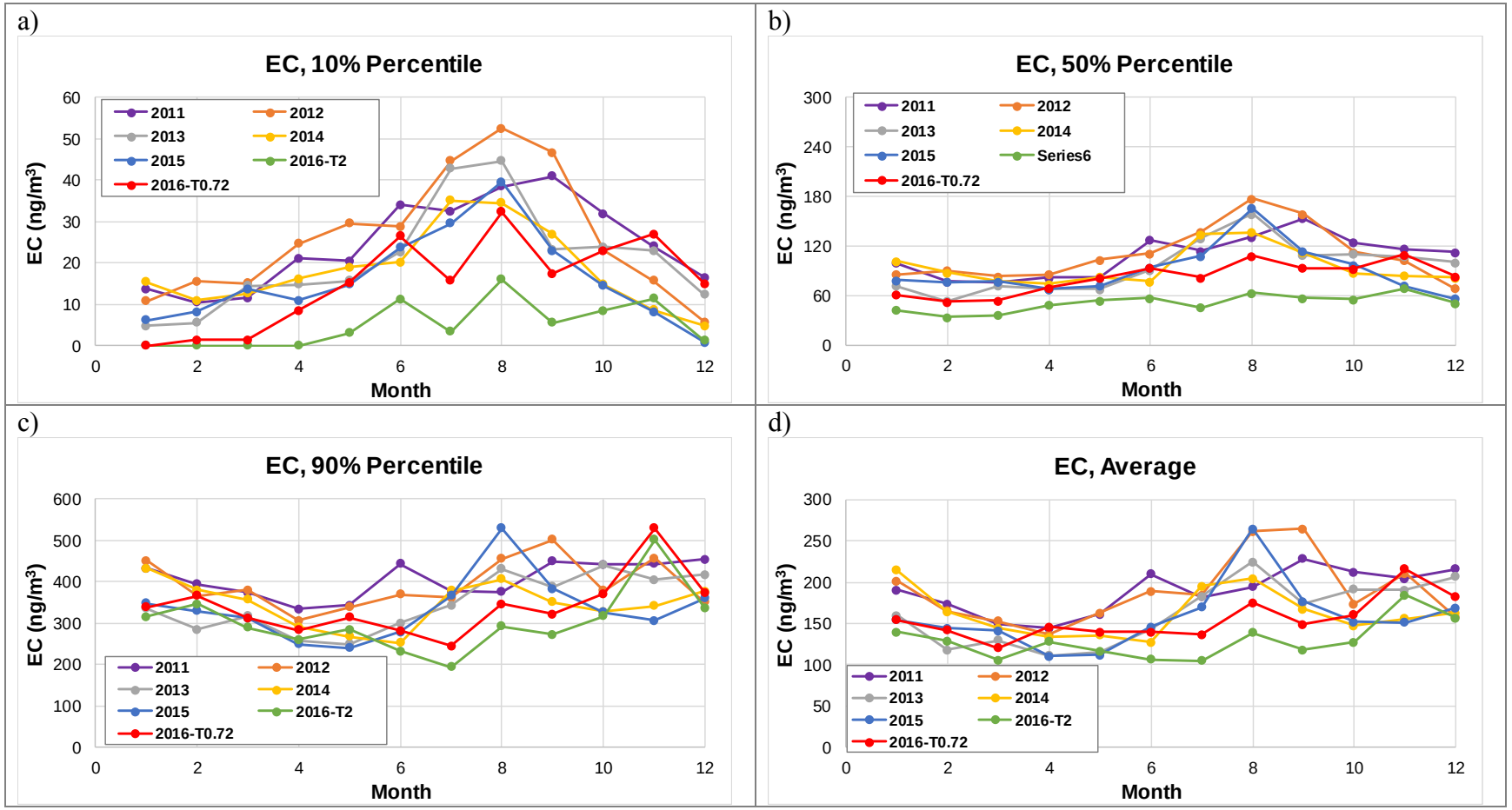


Figure 10. Comparison of EC concentrations in the IMPROVE network from 2011 to 2016 at 10%, 50% (median), and 90% percentiles as well as monthly average in each year. Both threshold values of 2.0 (2016-T2) and 0.72 (2016-T0.72) are plotted for the 2016 data.

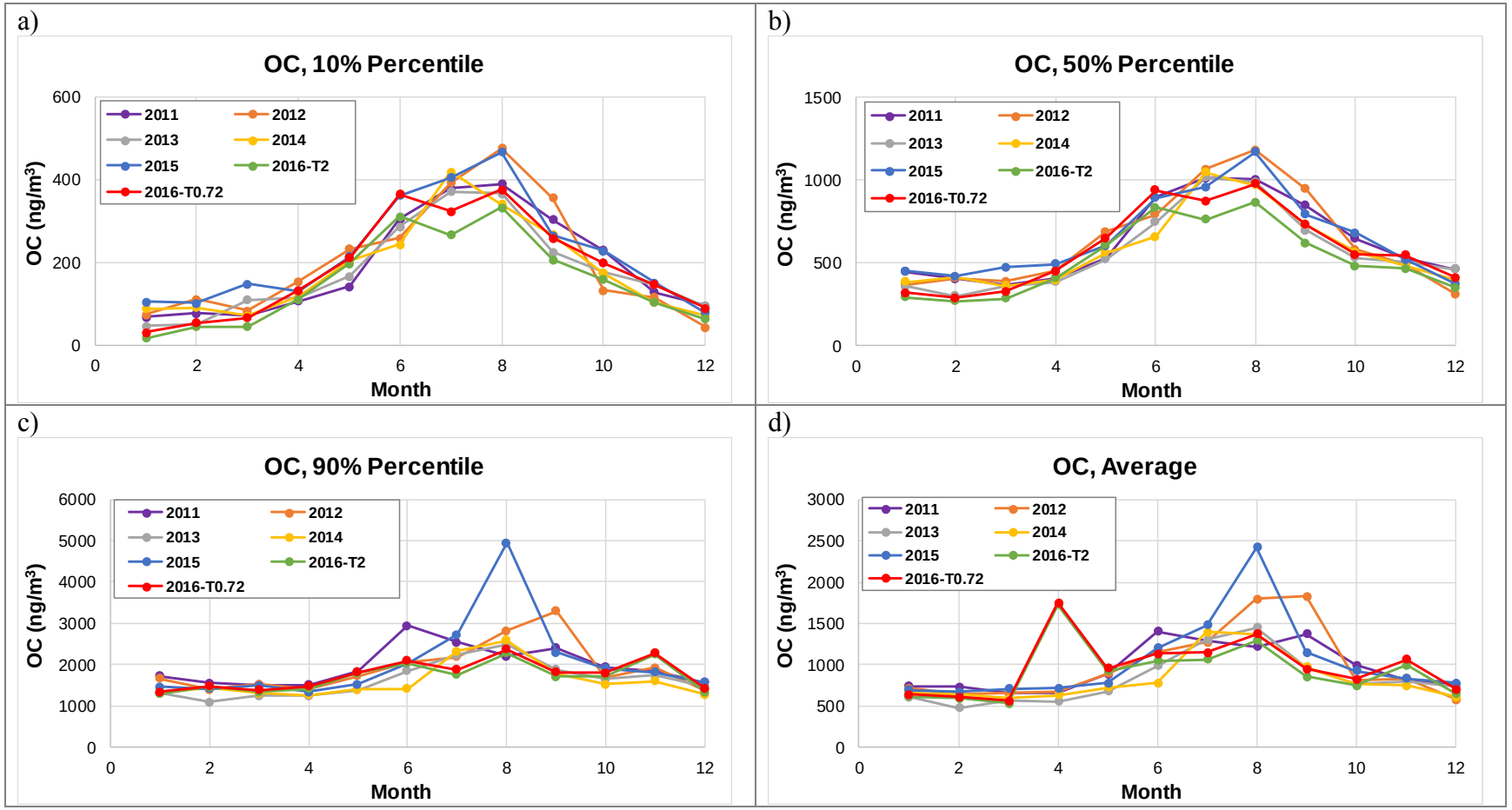


Figure 11. Comparison of OC concentrations in the IMPROVE network from 2011 to 2016 at 10%, 50% (median), and 90% percentiles as well as monthly average in each year. Both threshold values of 2.0 (2016-T2) and 0.72 (2016-T0.72) are plotted for the 2016 data.

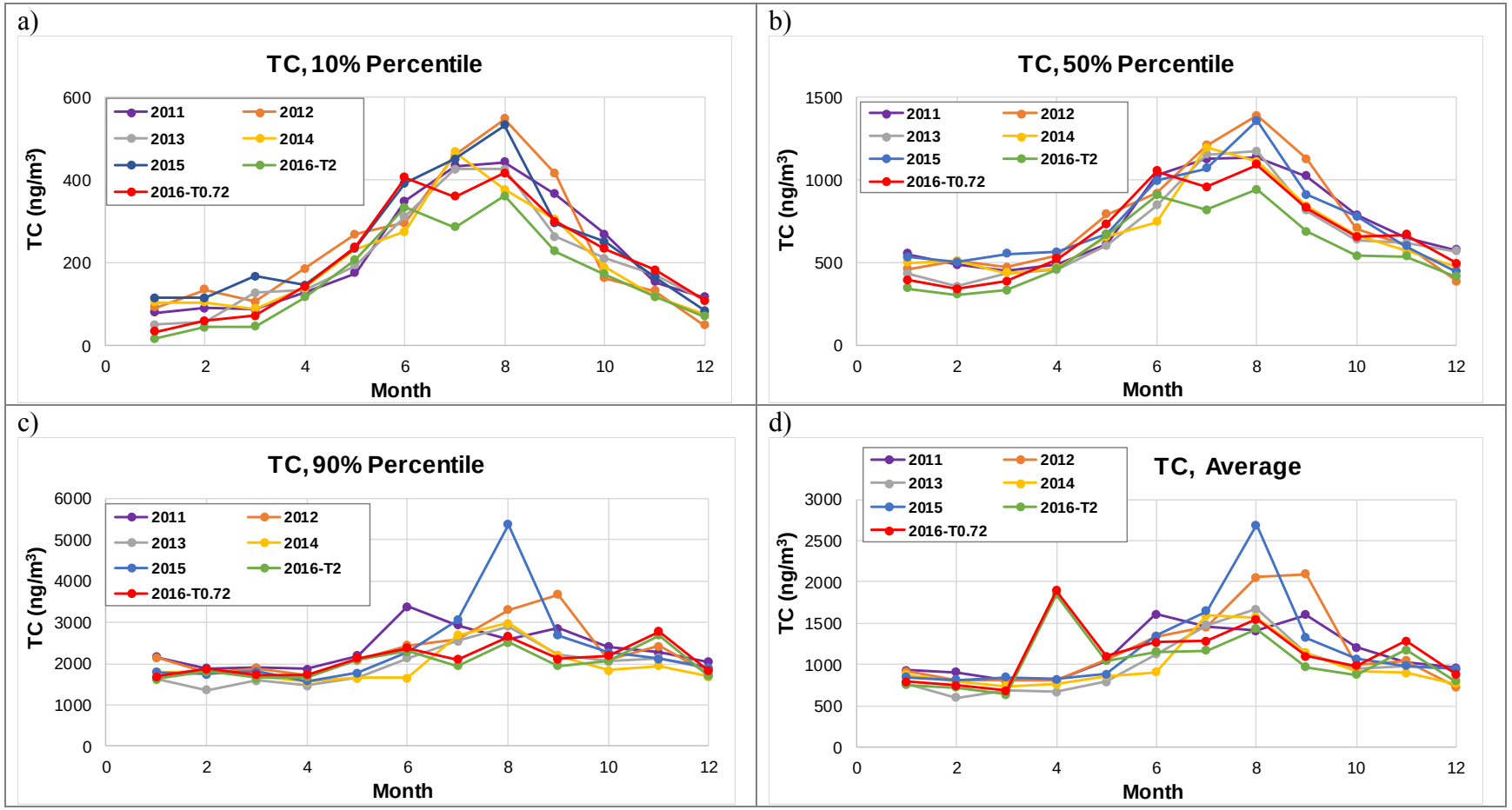


Figure 12. Comparison of TC concentrations in the IMPROVE network from 2011 to 2016 at 10%, 50% (median), and 90% percentiles as well as monthly average in each year. Both threshold values of 2.0 (2016-T2) and 0.72 (2016-T0.72) are plotted for the 2016 data.

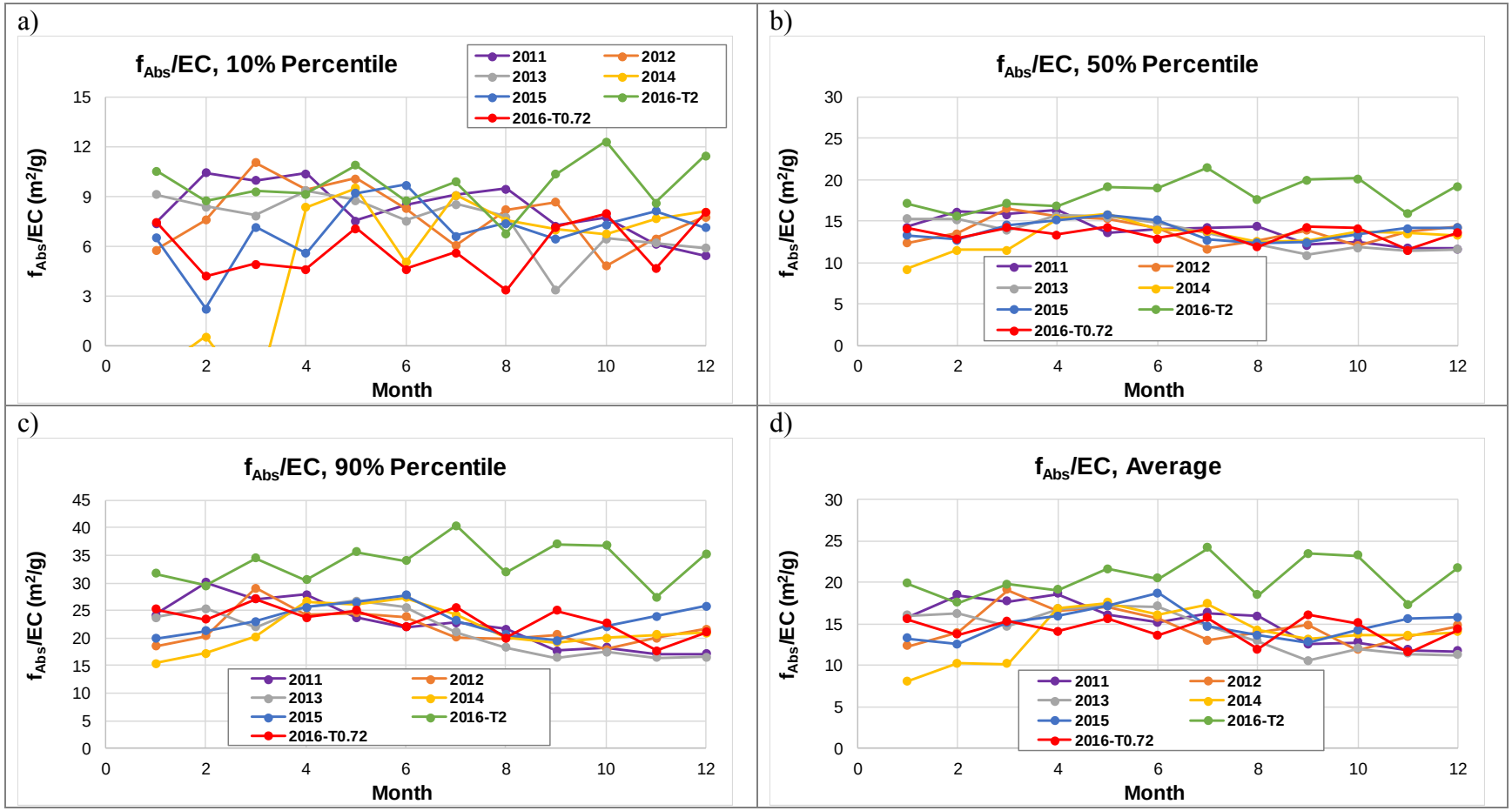


Figure 13. Comparison of mass absorption efficiency (f_{Abs}/EC) in the IMPROVE network from 2011 to 2016 at 10%, 50% (median), and 90% percentiles as well as monthly average in each year. Both threshold values of 2.0 (2016-T2) and 0.72 (2016-T0.72) are plotted for the 2016 data.