

# Update of IMPROVE Carbon Analysis

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# Objectives

- Report status of IMPROVE carbon analyses
- Update on Model 2015 Multiwavelength Carbon Analyzer refinements
- Discuss thermogram processing to ensure long-term data consistency.

# Carbon Laboratory Operations

(July 2016 to June 2017 samples)

- Samples collected since 1/1/2016 have undergone multiwavelength analysis
- Received ~1,500 samples per month (~1,200 to 2,000 samples each month)
- Maintained 24 hours per day/5-7 days per week operation with 6-7 staff
- Analyzed ~15,100 IMPROVE samples (up to 2,700 per month)

# IMPROVE\_A Carbon Analyses

(July 2016 to June 2017 samples)

Sampling Period	Samples Received	Analysis Completion Date
7/1/16-12/31/16	9,200	Aug. 2017
<b>1/1/17-6/30/17*</b>	<b>8,962</b>	<b>Nov./Dec. 2017</b> (Estimate)

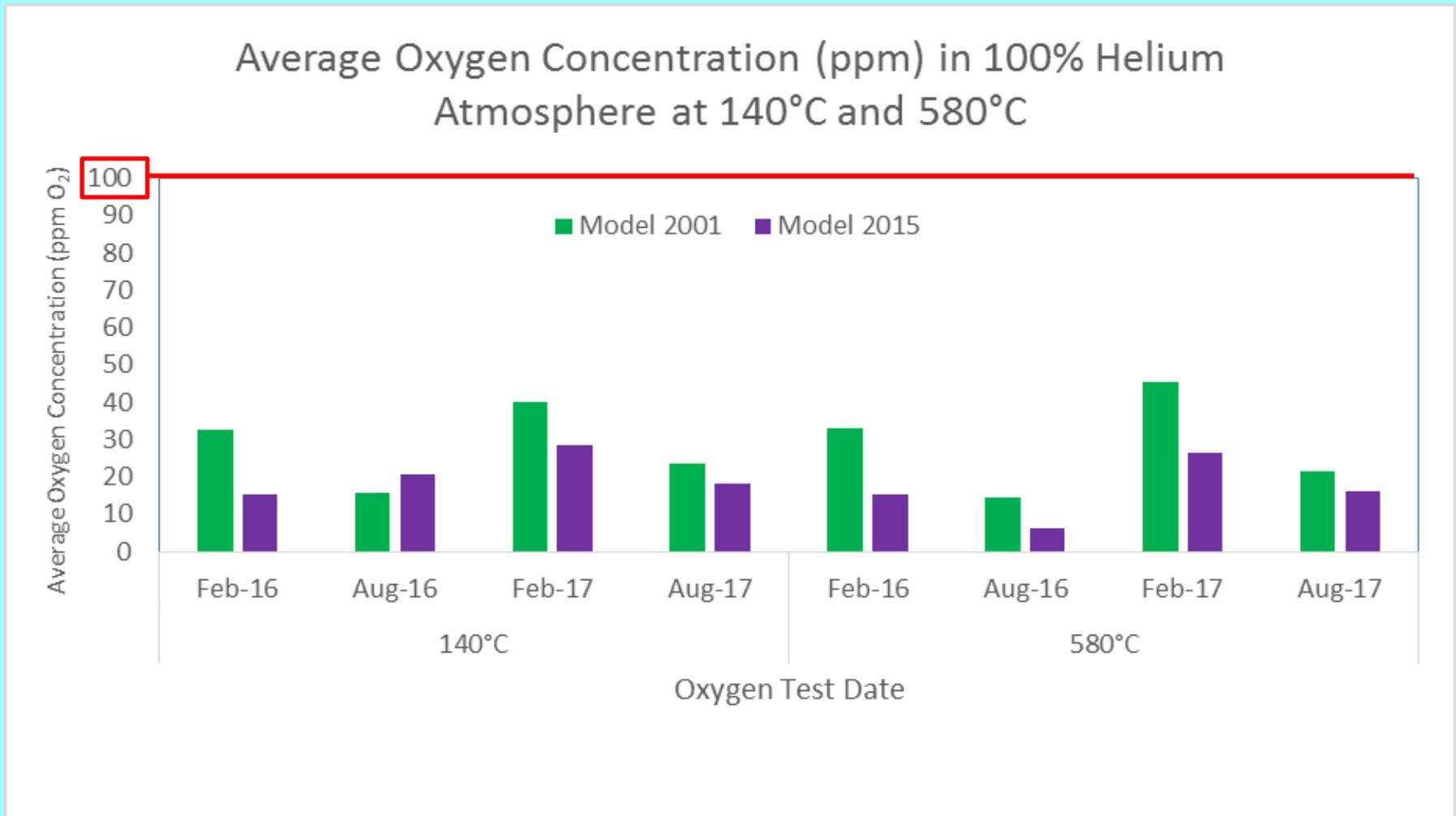
\*DRI has been analyzing and reporting samples by sample date rather than date received in order to speed up monthly data processing.

# Thirteen Model 2015 Multiwavelength Carbon Analyzers have been in operation since May 2017



(Magee Scientific, Berkeley, CA)

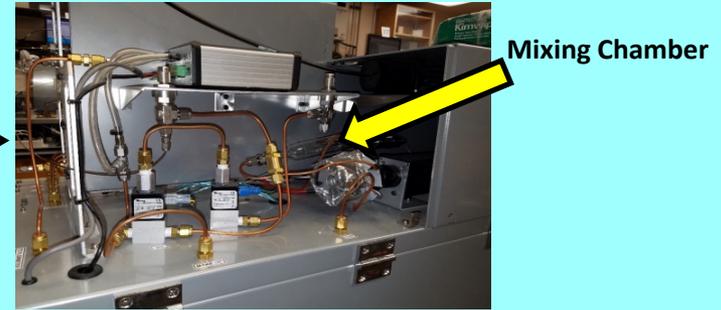
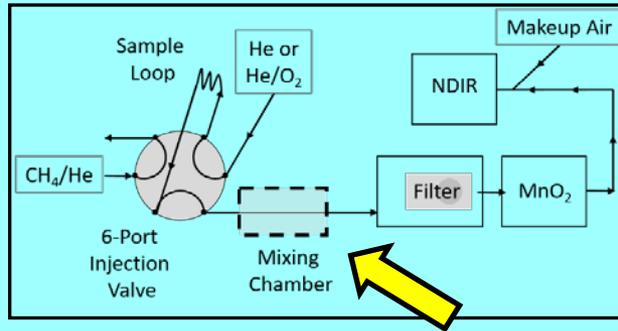
# O<sub>2</sub>\* in pure He remains low



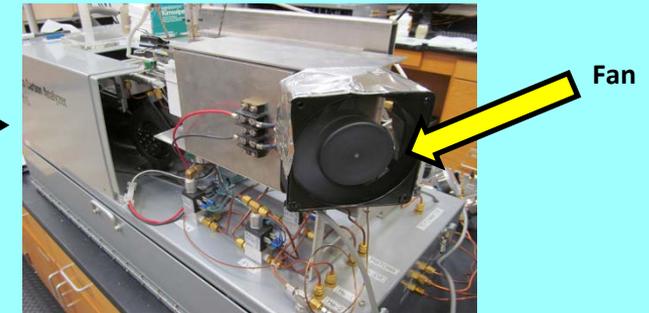
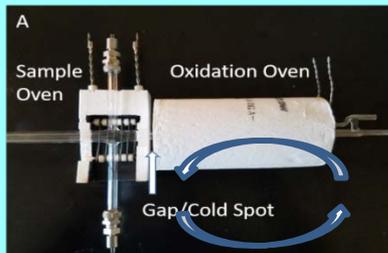
\*O<sub>2</sub> test limit is 100 ppm

# Model 2015 hardware was updated to increase throughput

- Add a mixing chamber to stabilize calibration peak

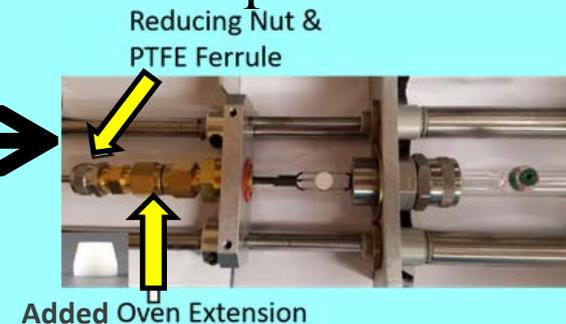
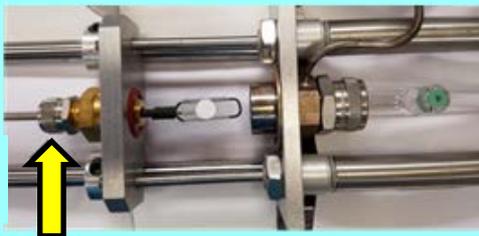


- Create convective flow in oxidation oven to minimize residual carbon deposits



- Separate Teflon ferrule from the sample boat to prevent residual Teflon deposition

Reducing Nut & PTFE Ferrule

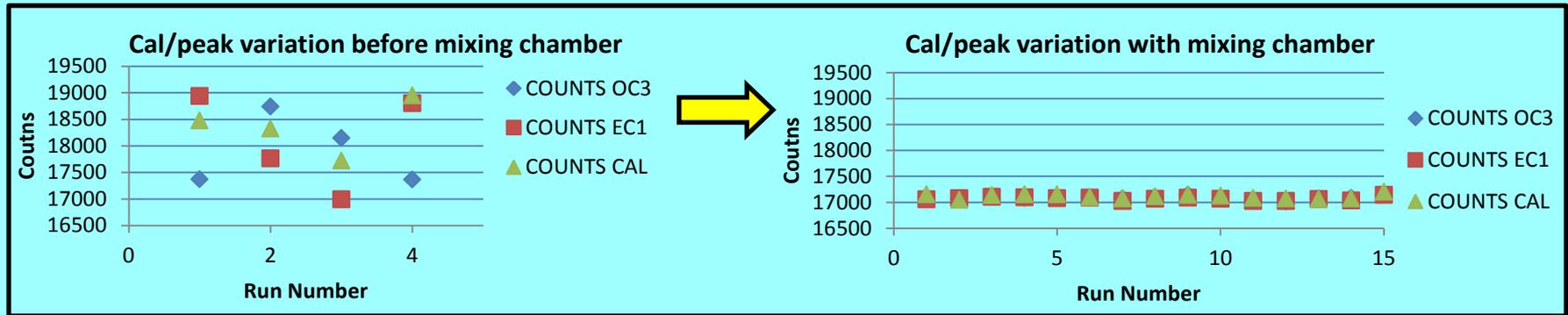


# Several types of mixing chambers were tested (50-65 ml in volume used to mix CO<sub>2</sub> with He)

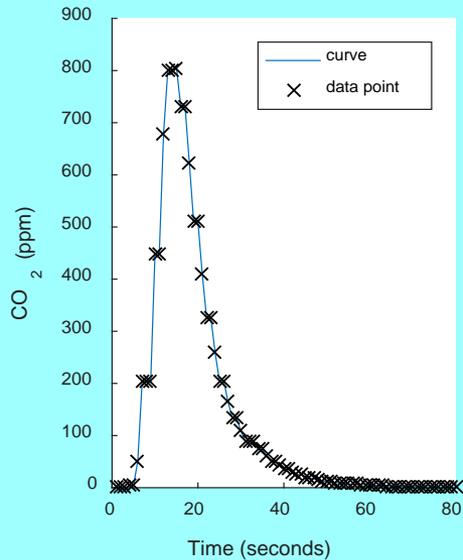


# Calibration peak areas are stabilized with a mixing chamber

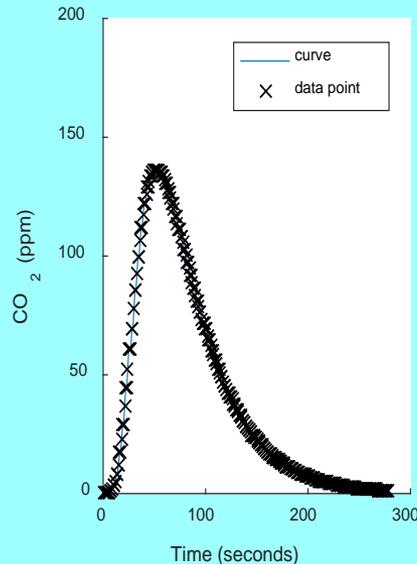
(Increases the duration of calibration peaks from 40 to 200 seconds, allowing for better detection by NDIR)



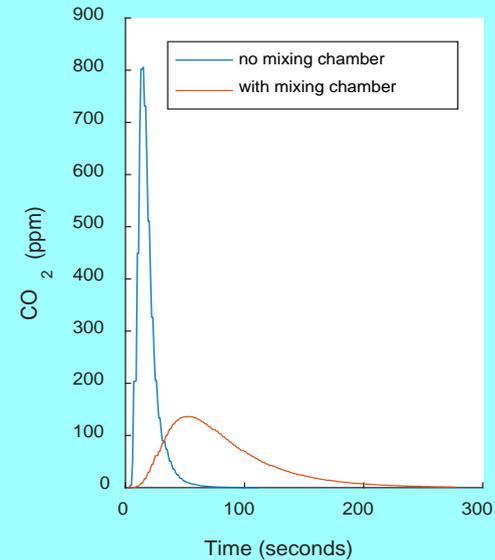
Cal peak w/o mixing chamber



Cal peak w/ mixing chamber

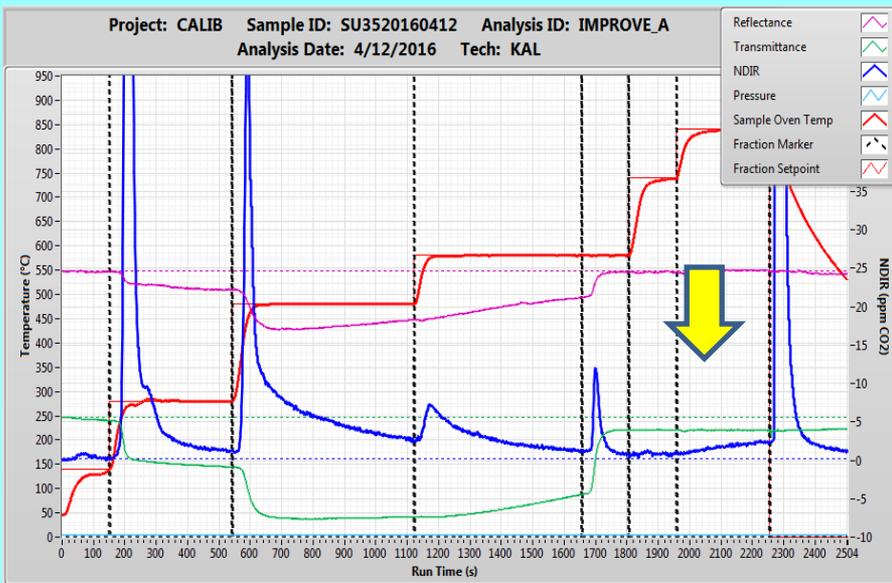


Both peaks shown together

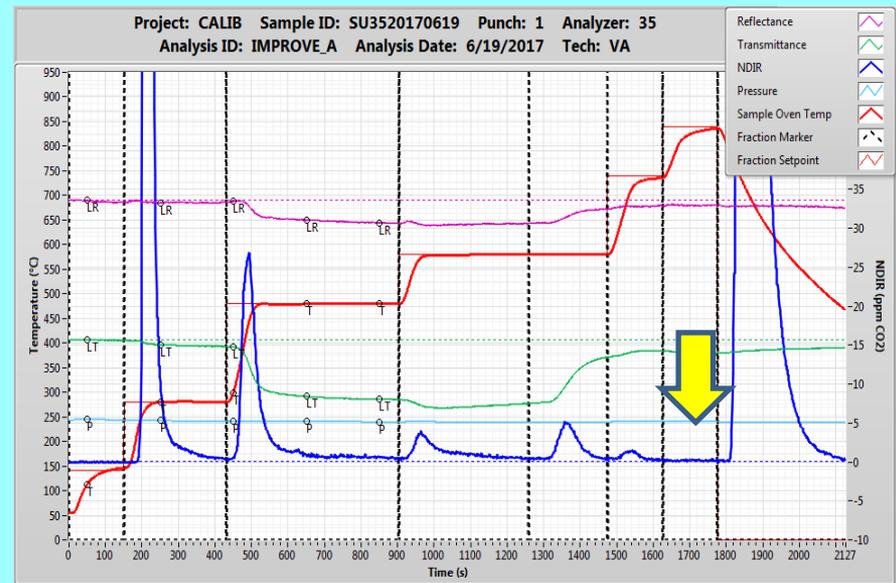


# Additional air circulation further stabilizes the baseline

## Without fan



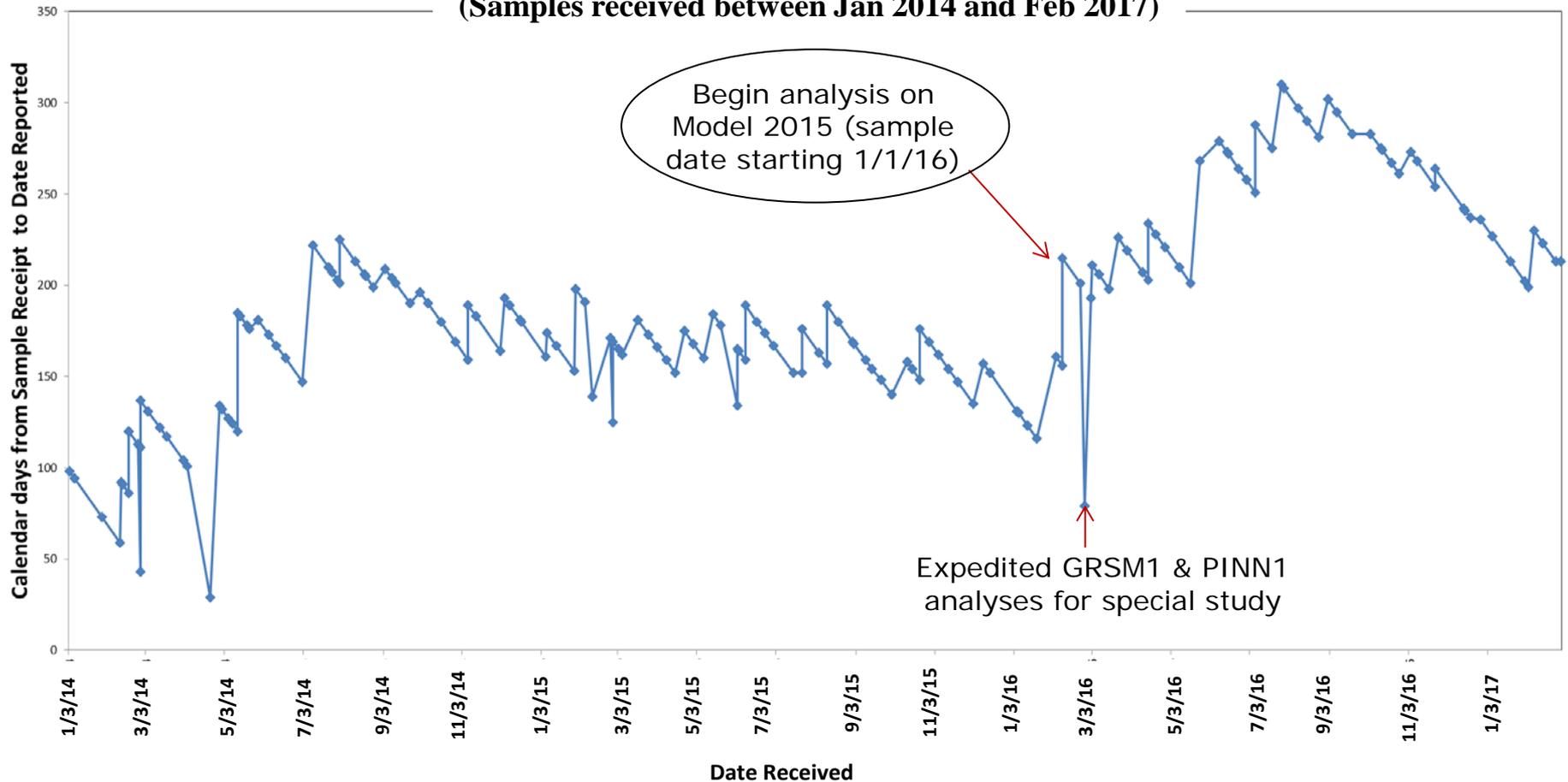
## With fan



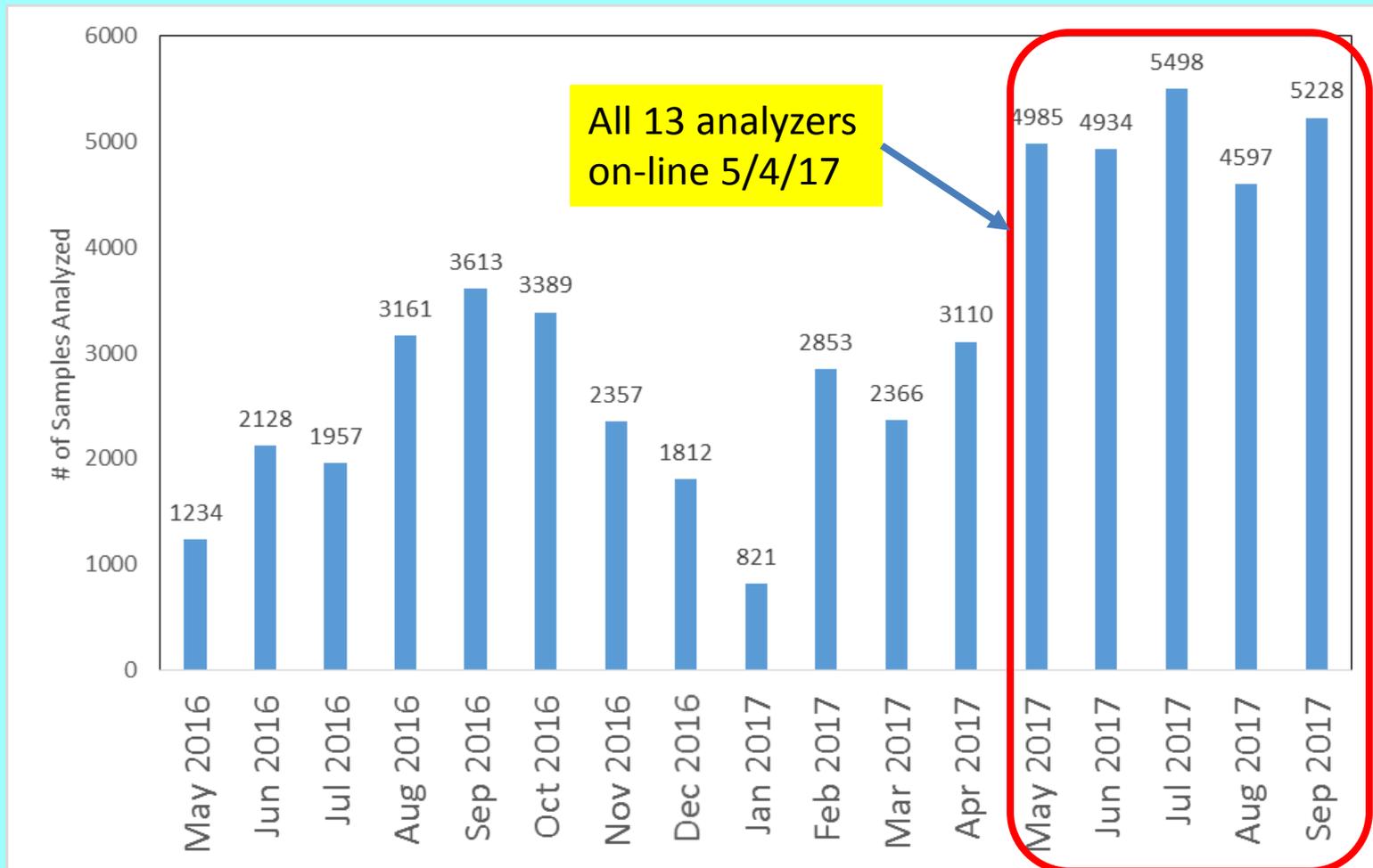
# IMPROVE carbon reporting time is improving with full integration of new analyzers

## Days from Sample Receipt to Report

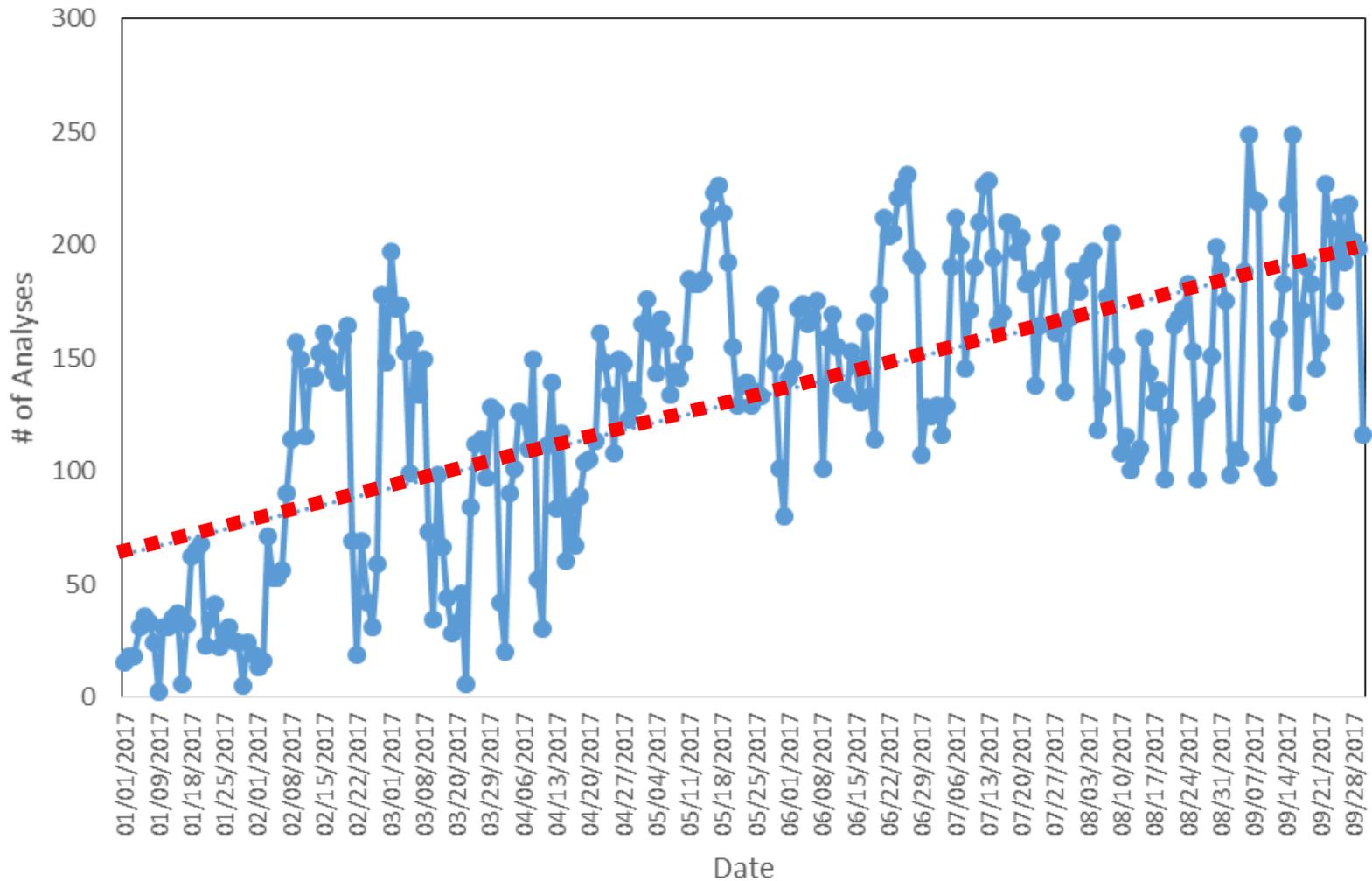
(Samples received between Jan 2014 and Feb 2017)



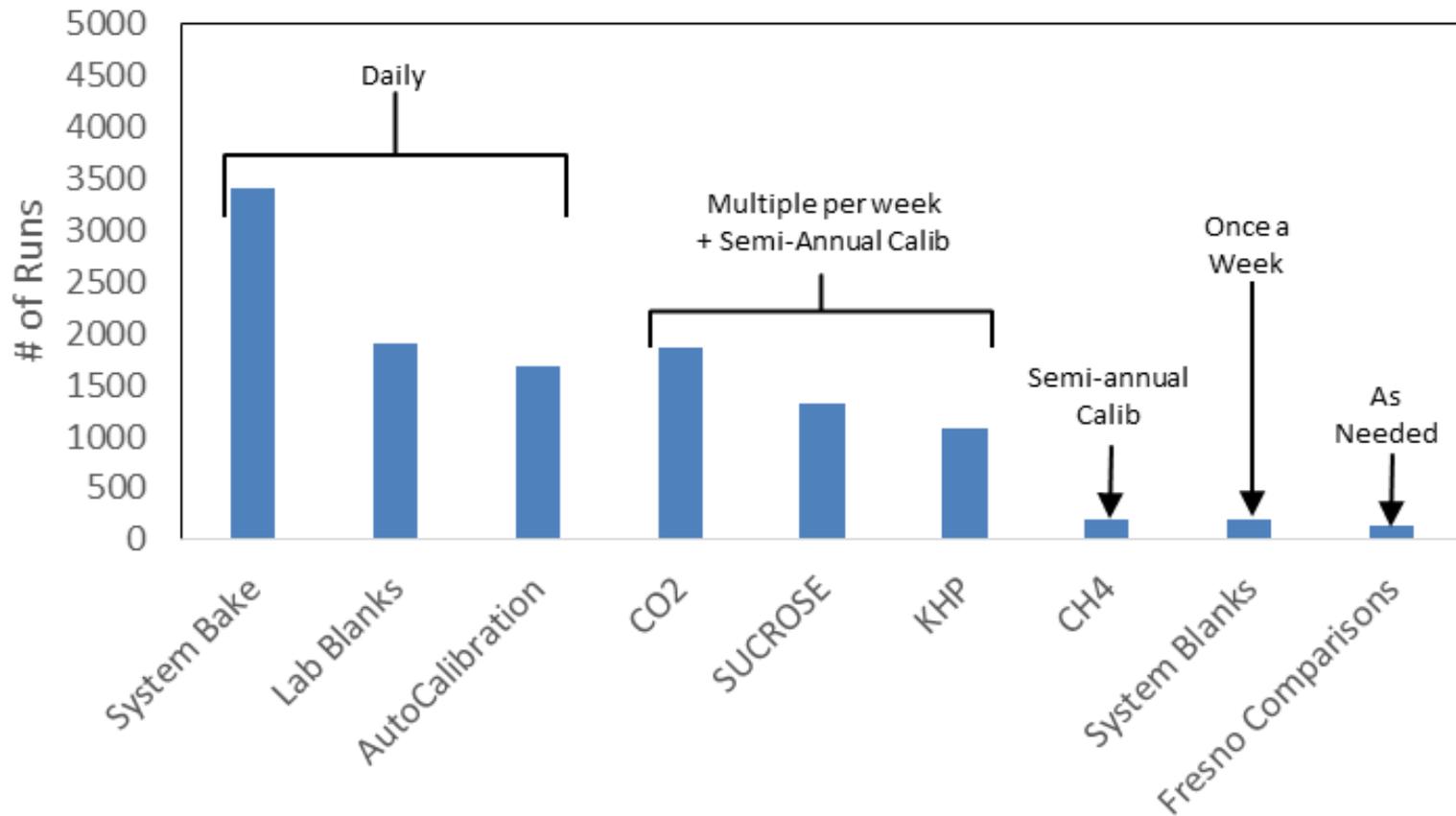
# Throughput averages 5000 analyses per month since May 2017



# Average daily output is on an upward trend (Jan-Sep 2017)

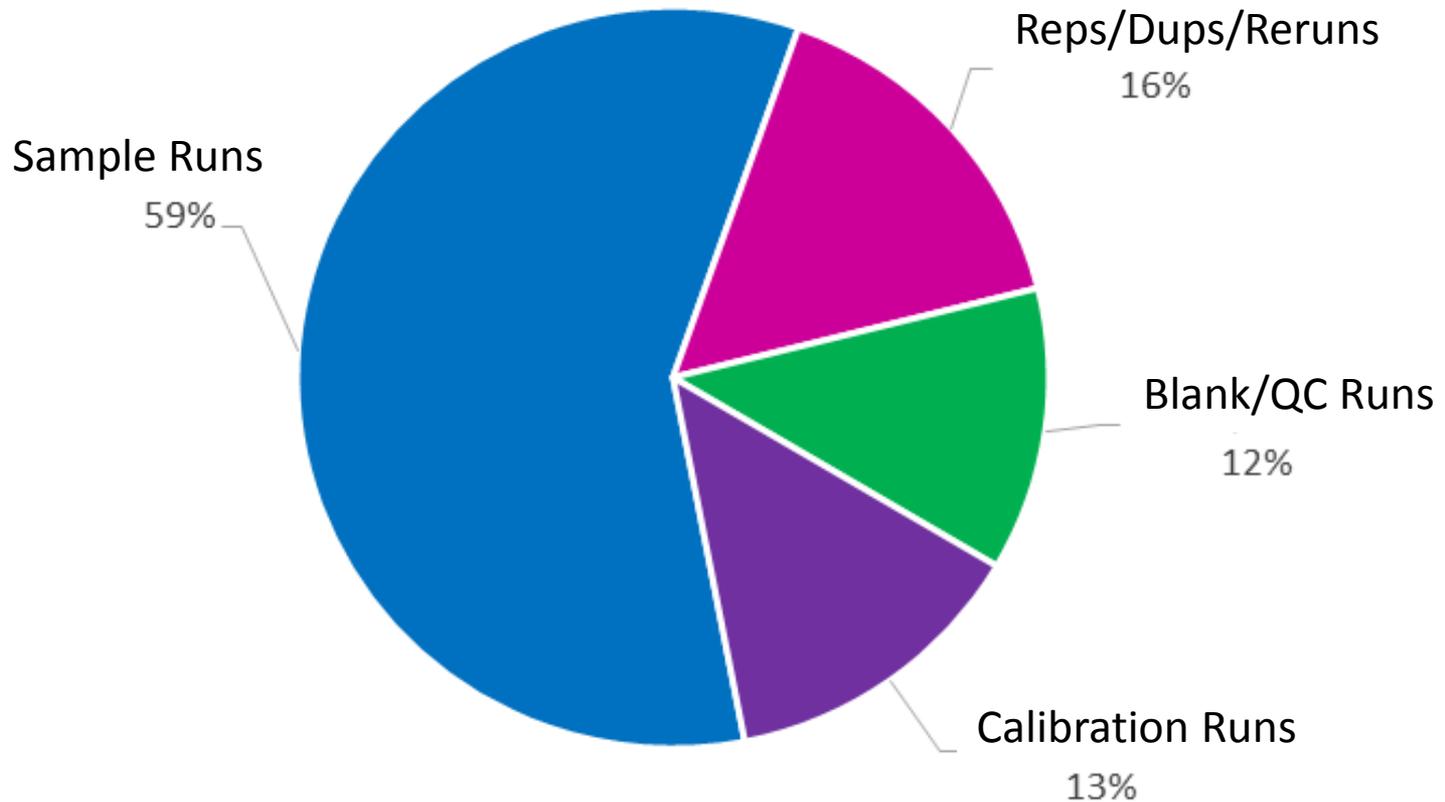


# Quality Control (QC) constitutes a large fraction of analyses (Jan-Sep 2017)



n=11,782 QC runs (average 43 per day for all instruments)

# Valid samples account for ~60% of total runs (Jan-Sep 2017)

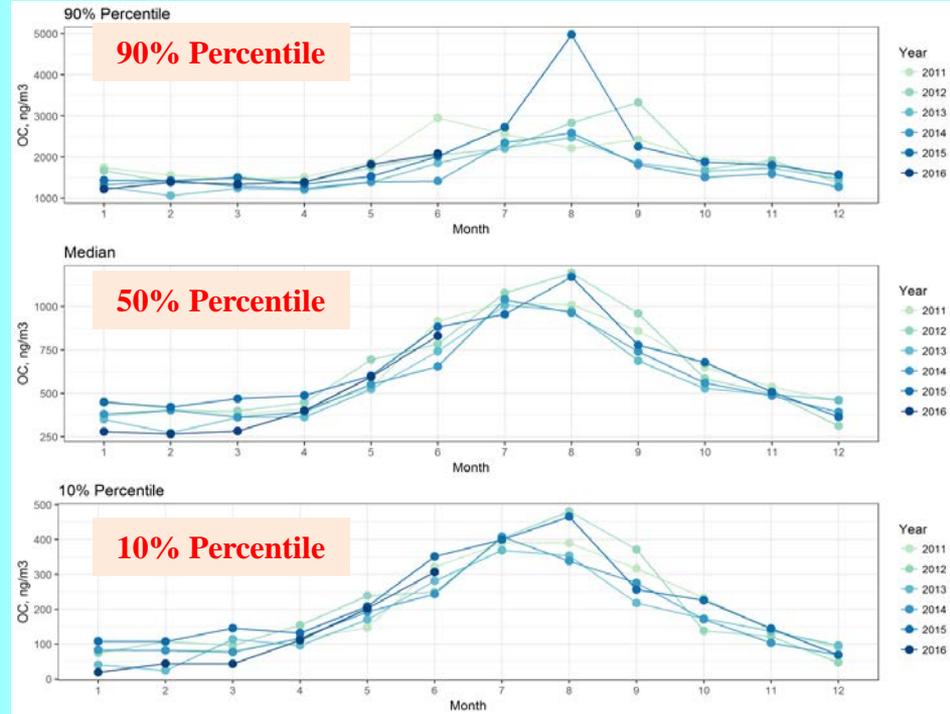
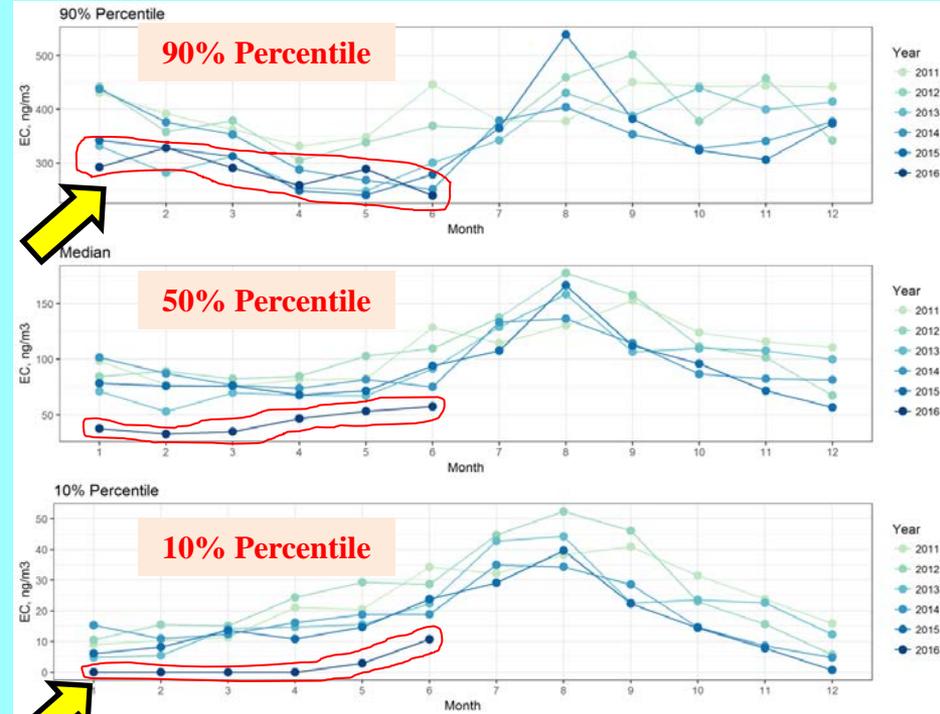


Sample Runs=26,676, Reps/Dups/Reruns=7,165, Blanks/QC Runs=5,644, Calibration Runs=6,138

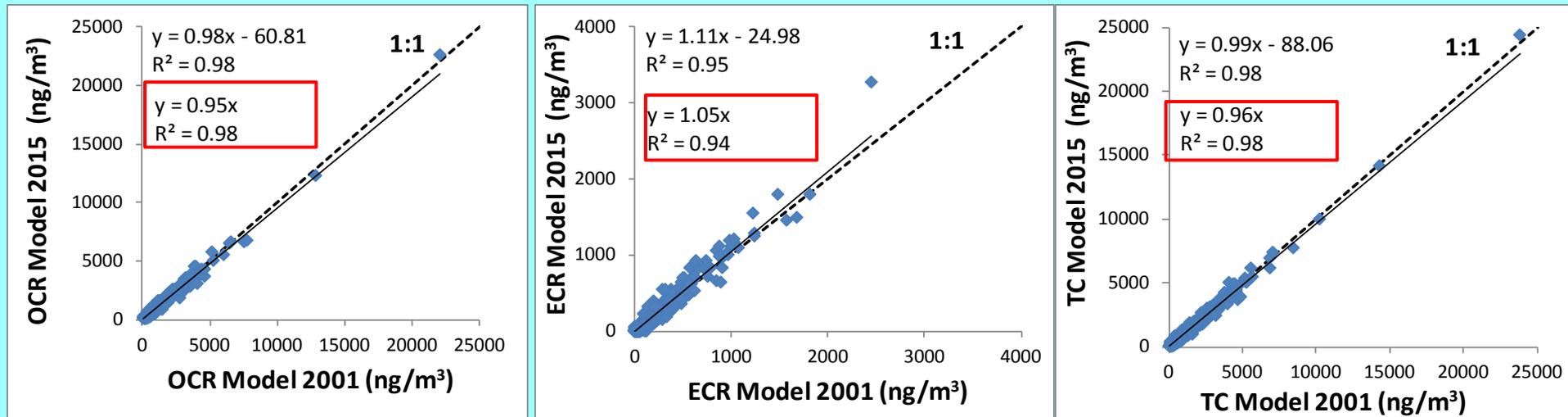
# EC 2016 percentiles are lower than in earlier years (2011-2016)

EC

OC



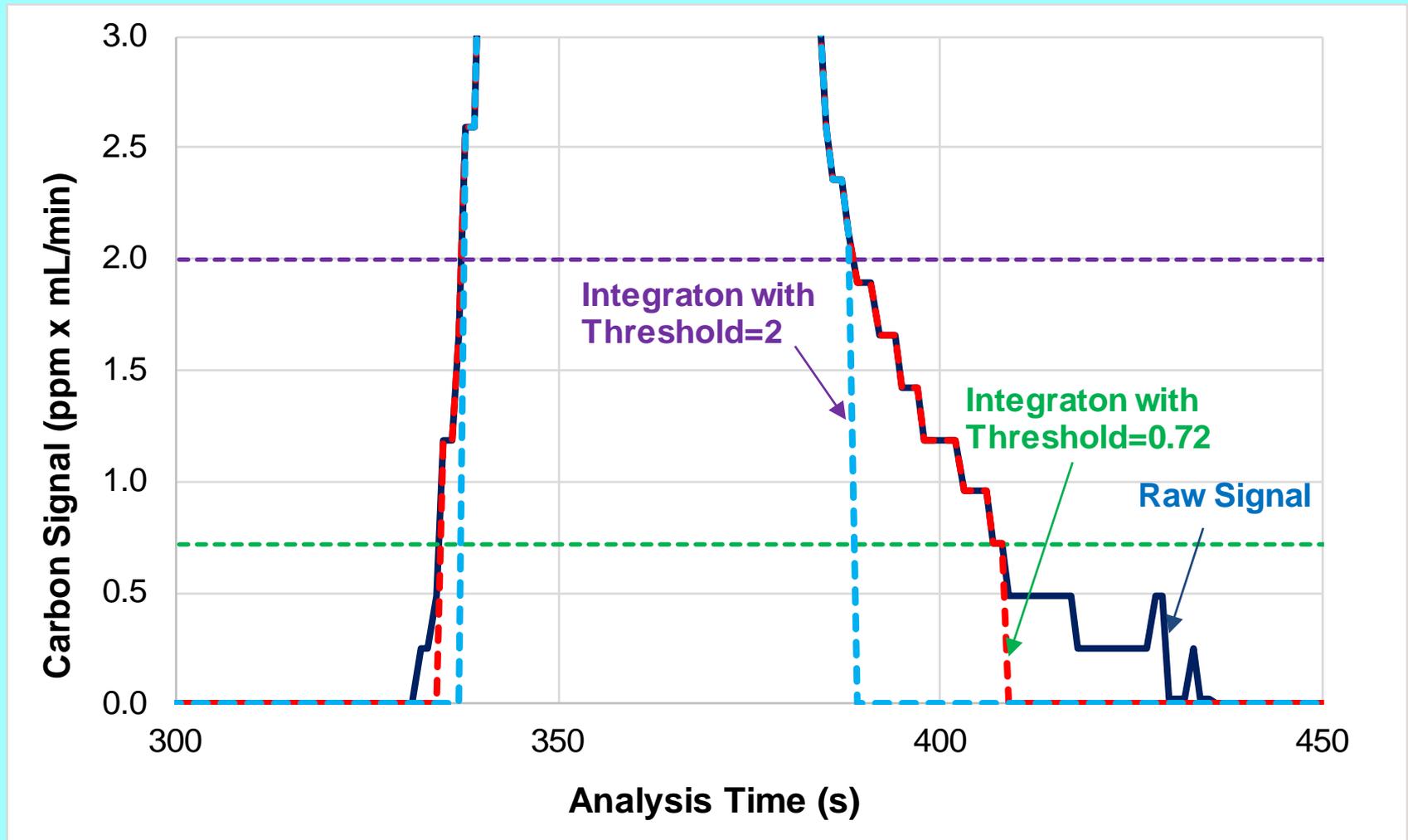
# Model 2001/2015 comparisons show small deviations at low EC concentrations (n = 1070)



Carbon	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
OCR	0.272	0.222	-0.050	0.82	0.656	0.577	-0.078	0.88	1.852	1.702	-0.150	0.92	0.941	0.861	-0.080	0.92
ECR	0.010	0.000	-0.010	0.00	0.074	0.054	-0.020	0.73	0.317	0.310	-0.008	0.98	0.135	0.125	-0.010	0.93
TC	0.284	0.228	-0.056	0.80	0.739	0.632	-0.108	0.85	2.130	1.975	-0.154	0.93	1.076	0.986	-0.090	0.92

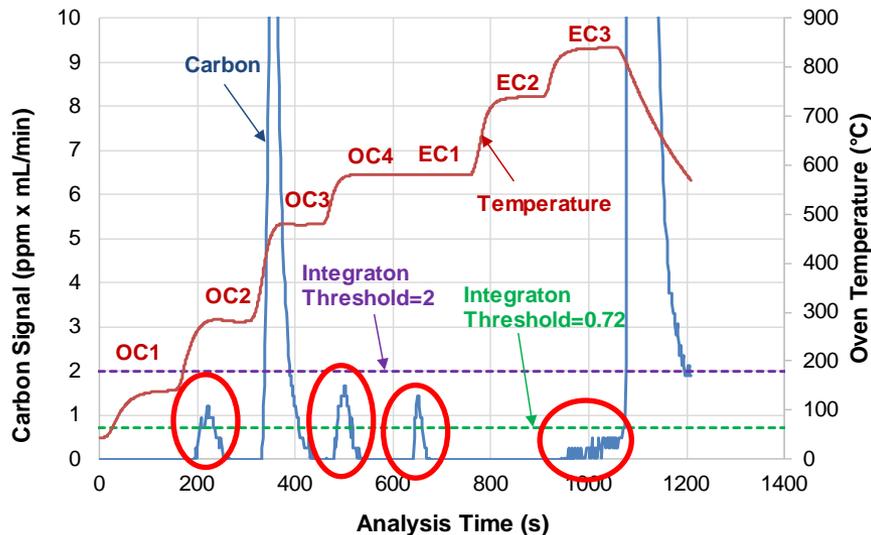
x (µg/m³): Model 2001; y (µg/m³) : Model 2015

# A 2001/2015 difference in peak integration thresholds might be the cause

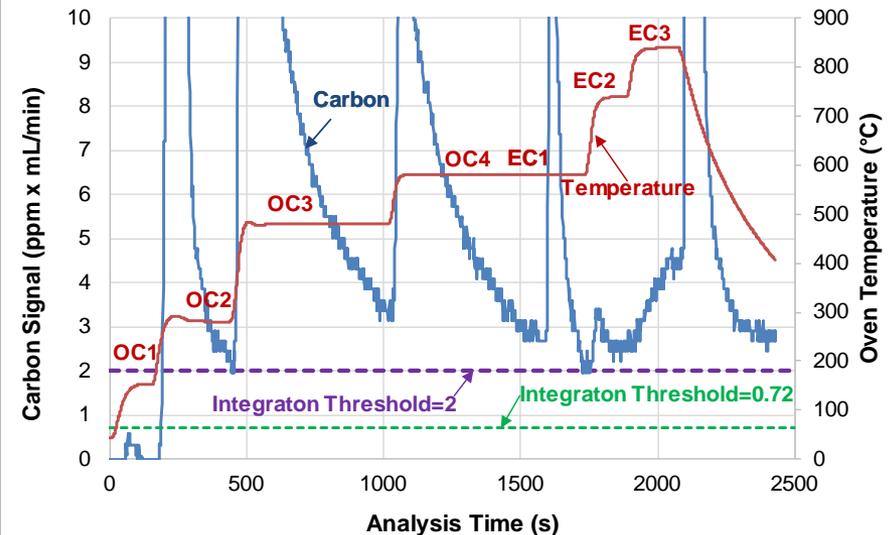


# Since carbon peaks are asymmetric, this may have an effect for signals near baseline

## Sucrose injection (0.22 $\mu\text{g}/\text{m}^3$ )



## Sucrose injection (4 $\mu\text{g}/\text{m}^3$ )

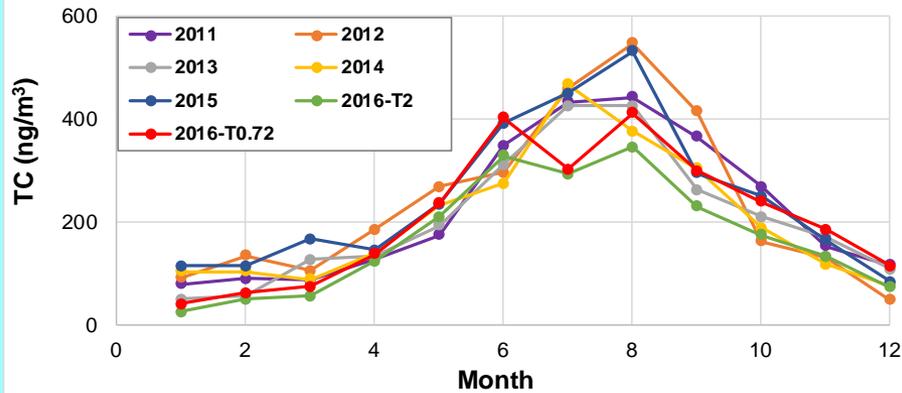


- A carbon signal threshold  $t = 2$  was used to reduce effects of NDIR noise/drift
- $t = 2$  for the Model 2015 cuts off more of the peak tail than did the Model 2001
- The Model 2001 has a  $t = 1$  for FID, which is equivalent to  $t = 0.72$  for Model 2015 NDIR

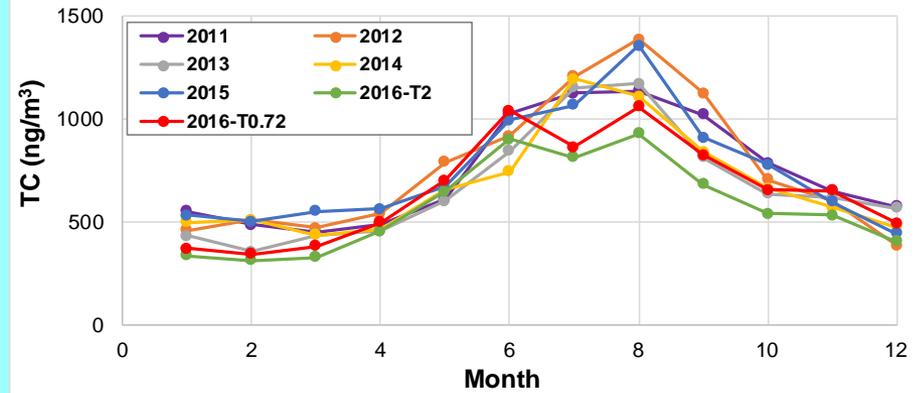
# Reprocessed IMPROVE thermograms with a 0.72 threshold show TC percentiles more comparable with those of Model 2001

## Total Carbon

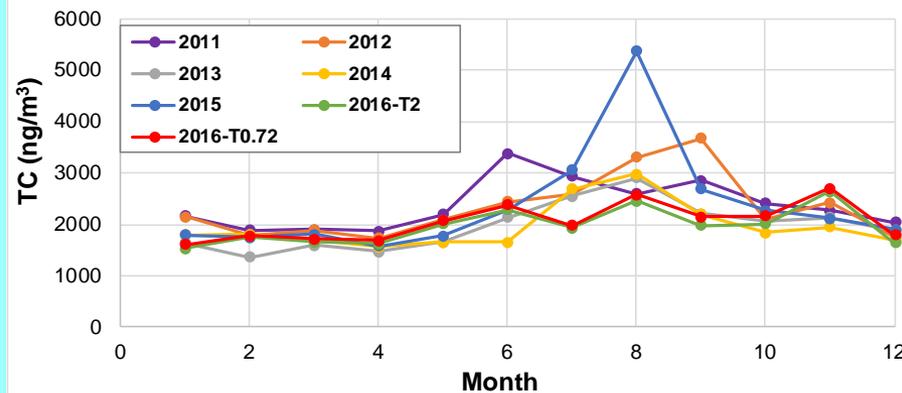
### TC, 10% Percentile



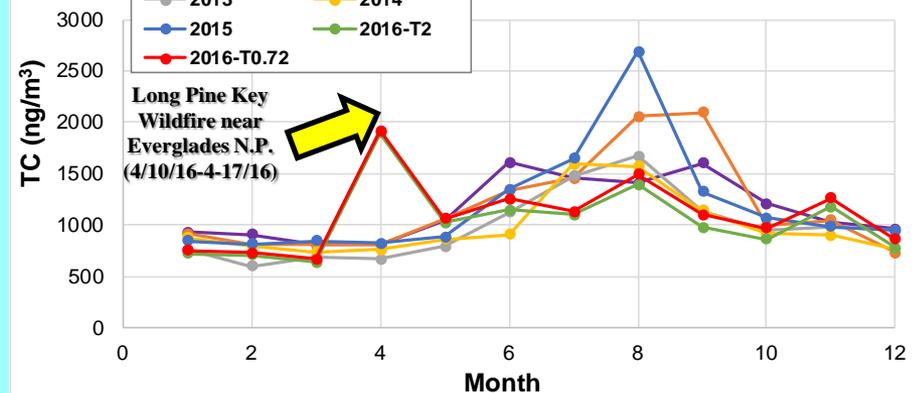
### TC, 50% Percentile



### TC, 90% Percentile



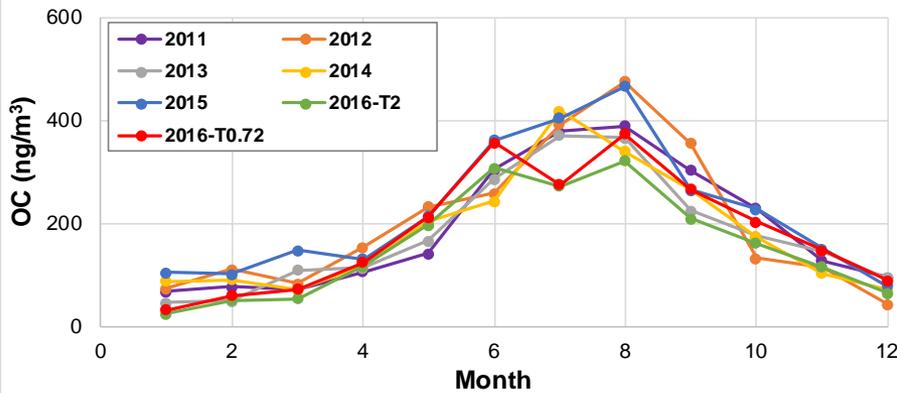
### TC, Average



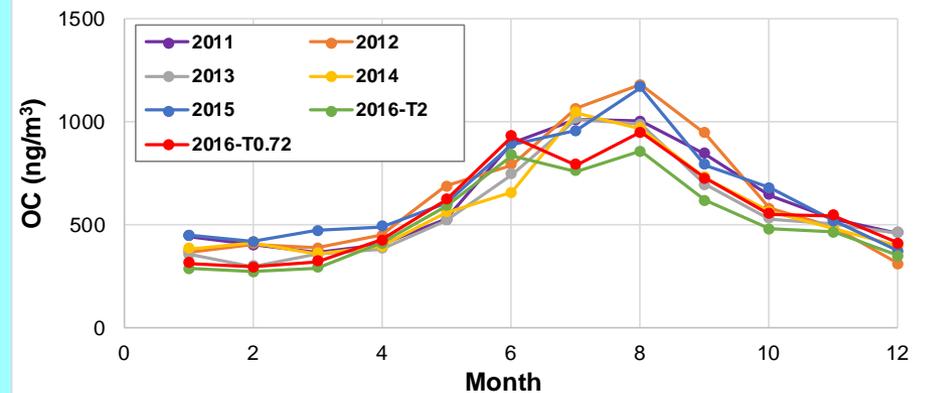
# Reprocessed IMPROVE thermograms with a 0.72 threshold show OC percentiles more comparable with those of Model 2001

## Organic Carbon

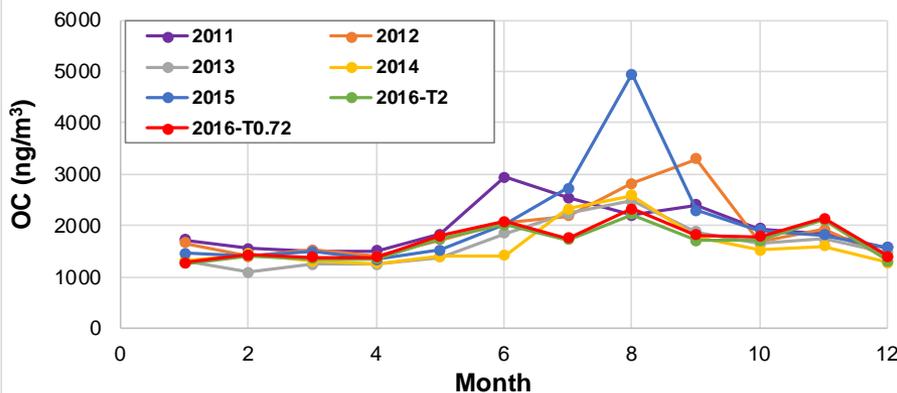
### OC, 10% Percentile



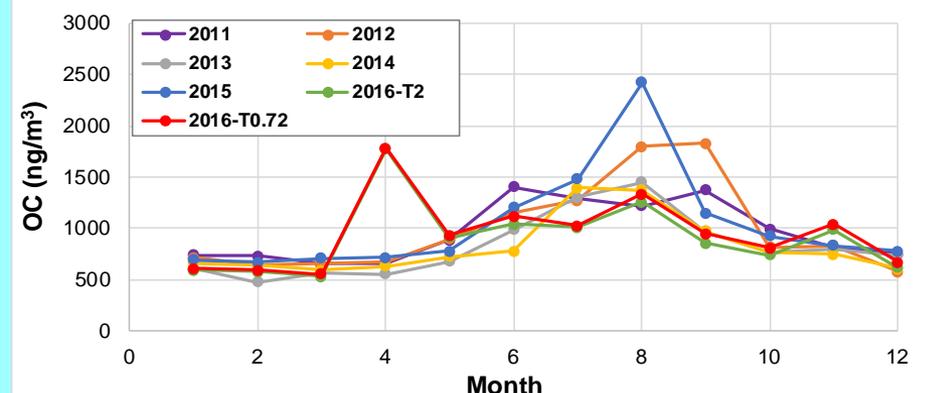
### OC, 50% Percentile



### OC, 90% Percentile



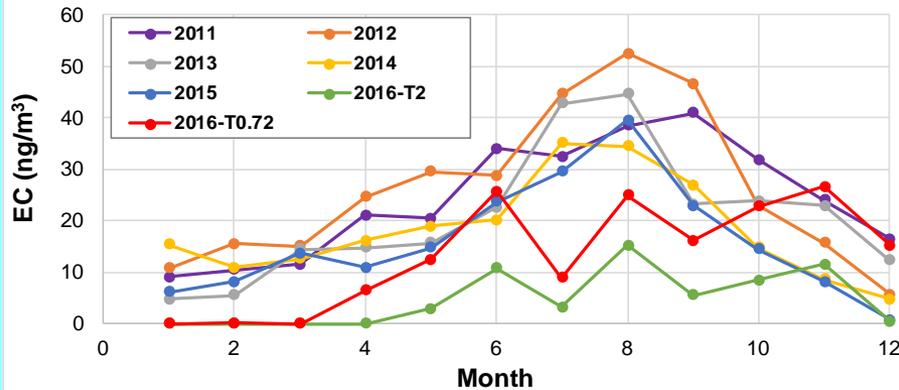
### OC, Average



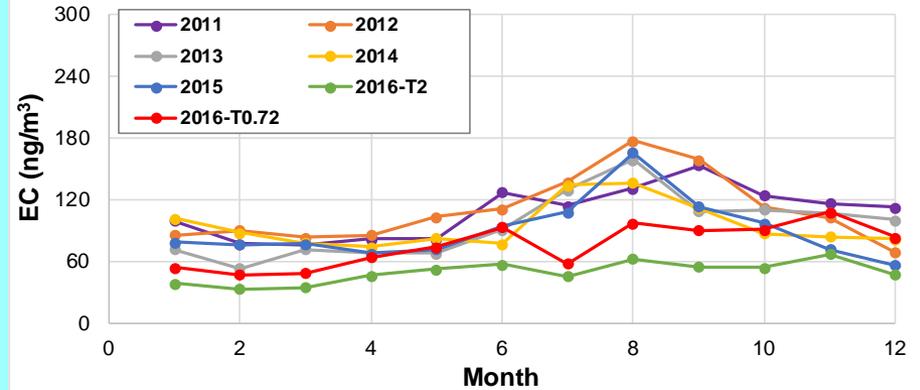
# Reprocessed IMPROVE thermograms with a 0.72 threshold show EC percentiles more comparable with those of Model 2001

## Elemental Carbon

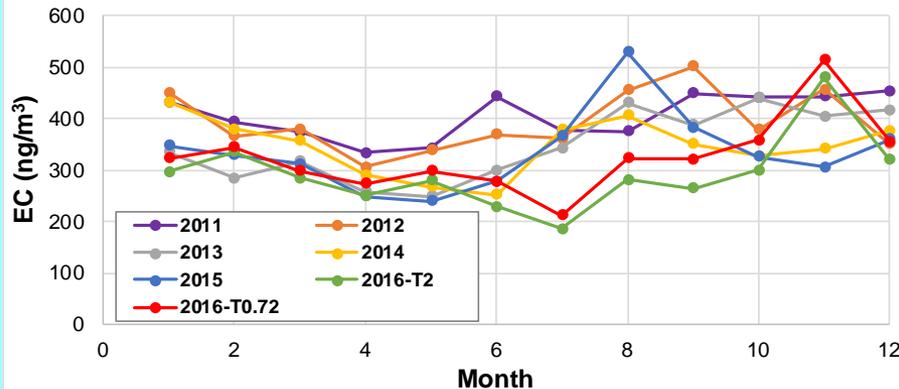
### EC, 10% Percentile



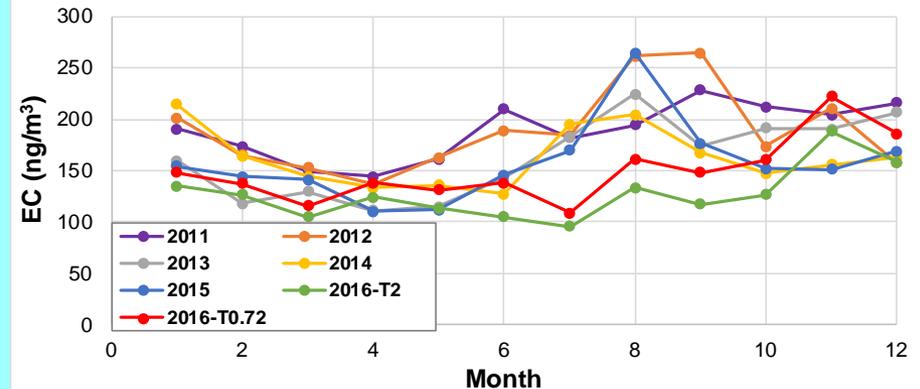
### EC, 50% Percentile



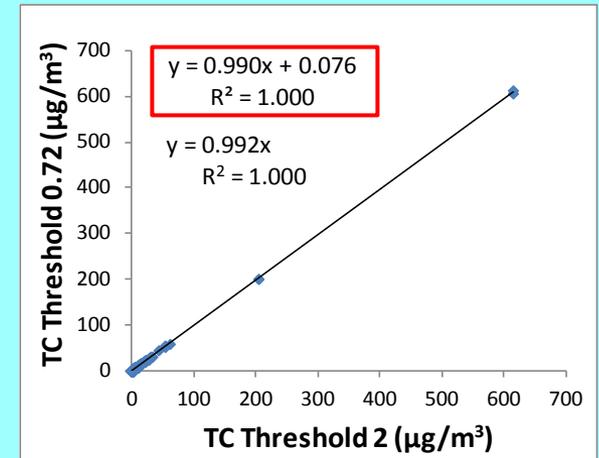
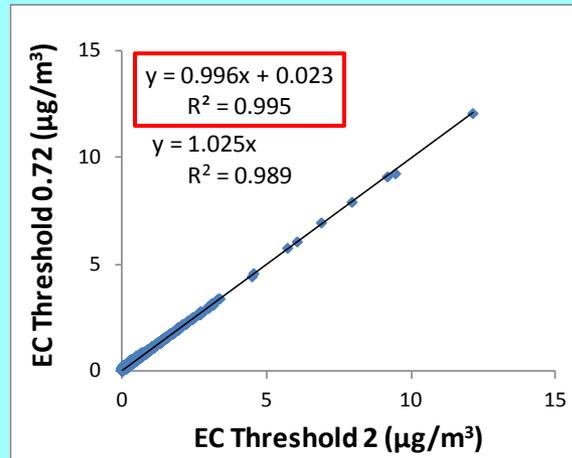
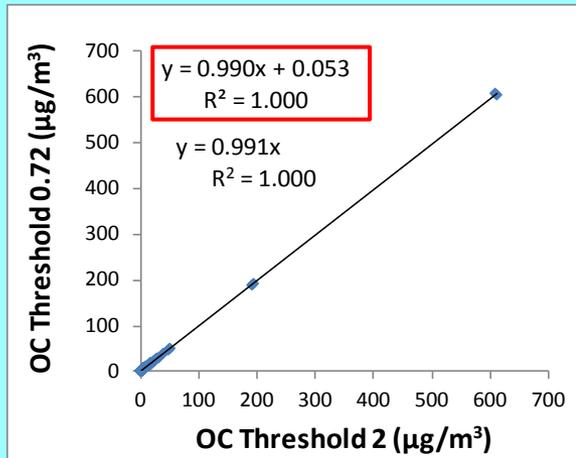
### EC, 90% Percentile



### EC, Average



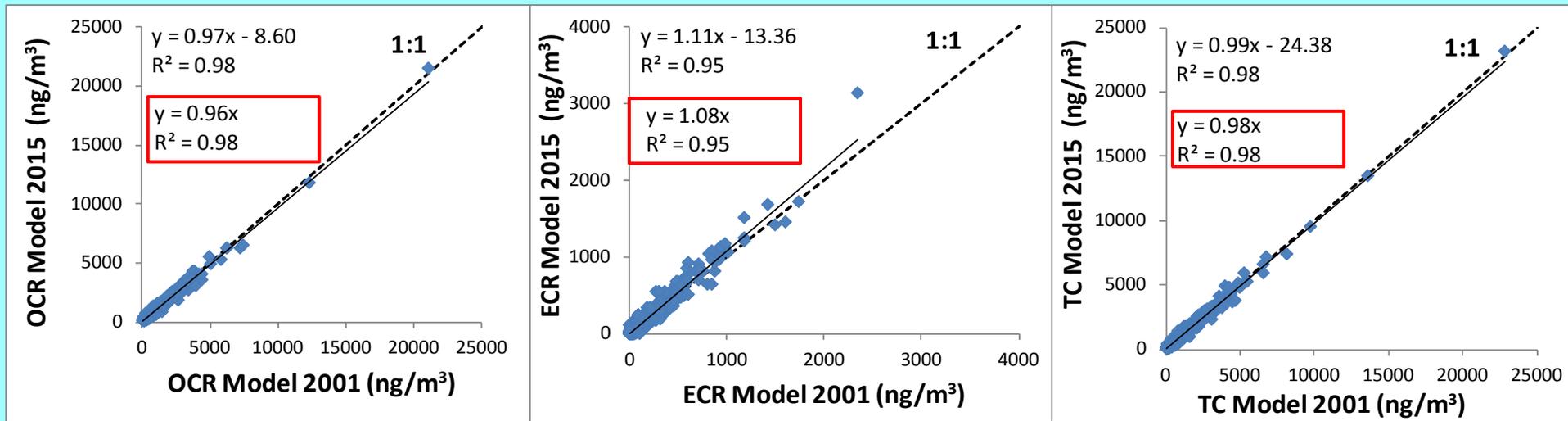
# Reduced threshold (from 2 to 0.72) increased OC by $\sim 0.05 \mu\text{g}/\text{m}^3$ and EC by $\sim 0.02 \mu\text{g}/\text{m}^3$ on average



Carbon	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
OCR	0.107	0.126	0.019	1.18	0.516	0.570	0.054	1.10	1.702	1.766	0.065	1.04	0.913	0.956	0.044	1.05
ECR	0.000	0.008	0.008	NA	0.051	0.077	0.026	1.52	0.290	0.323	0.034	1.12	0.127	0.149	0.022	1.18
TC	0.116	0.145	0.029	1.25	0.577	0.656	0.079	1.14	1.984	2.082	0.098	1.05	1.039	1.105	0.066	1.06

x ( $\mu\text{g}/\text{m}^3$ ): Model 2015 with t = 2; y ( $\mu\text{g}/\text{m}^3$ ): Model 2015 with t = 0.72 for OC1-EC2 and t = 2 for EC3

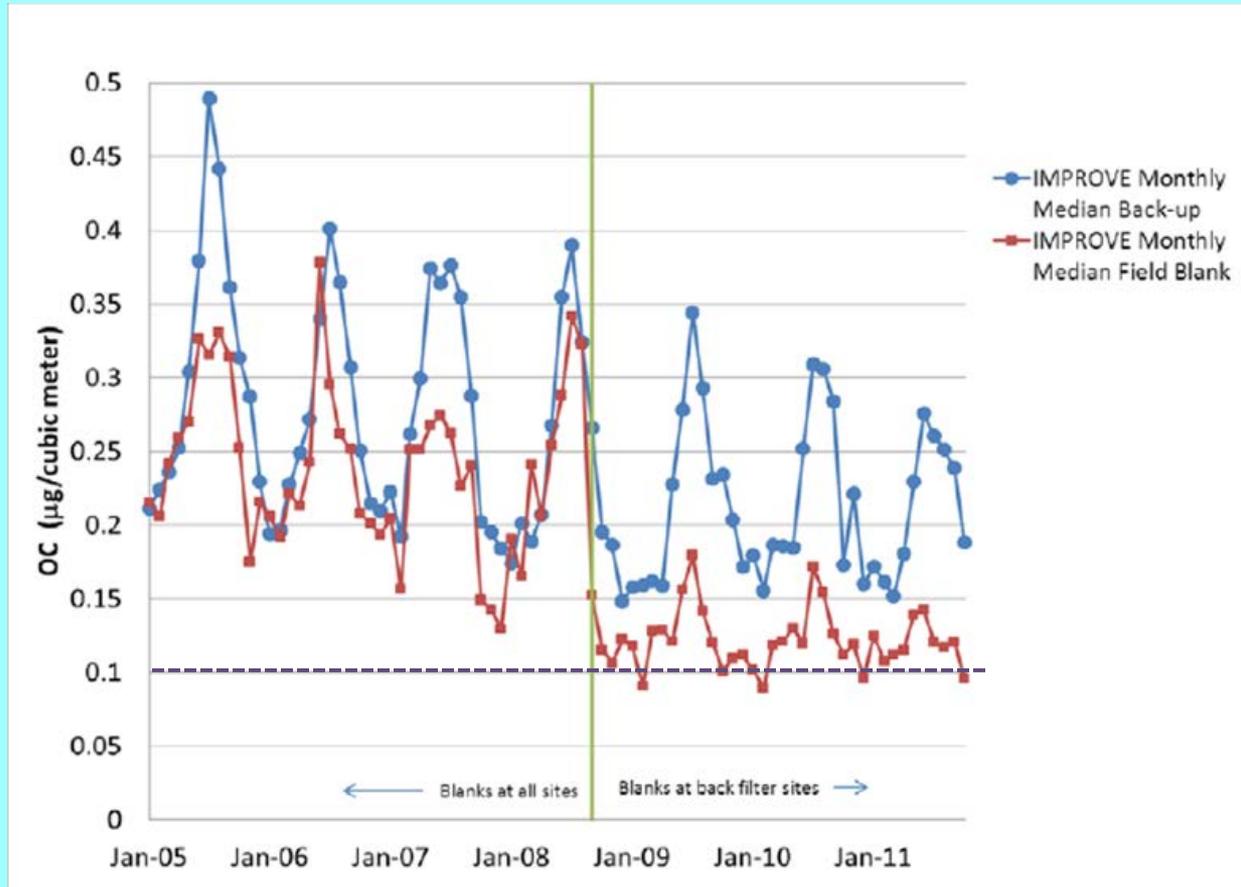
# Since IMPROVE EC levels are low to begin with, the lowest percentiles are most highly affected



Carbon	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
OCR	0.272	0.262	-0.010	0.96	0.656	0.626	-0.030	0.95	1.852	1.744	-0.108	0.94	0.941	0.903	-0.039	0.96
ECR	0.010	0.000	-0.009	0.01	0.074	0.069	-0.005	0.93	0.317	0.327	0.010	1.03	0.135	0.136	0.001	1.01
TC	0.284	0.267	-0.017	0.94	0.739	0.695	-0.045	0.94	2.130	2.028	-0.102	0.95	1.076	1.039	-0.037	0.97

x ( $\mu\text{g}/\text{m}^3$ ): Model 2001; y ( $\mu\text{g}/\text{m}^3$ ) : Model 2015

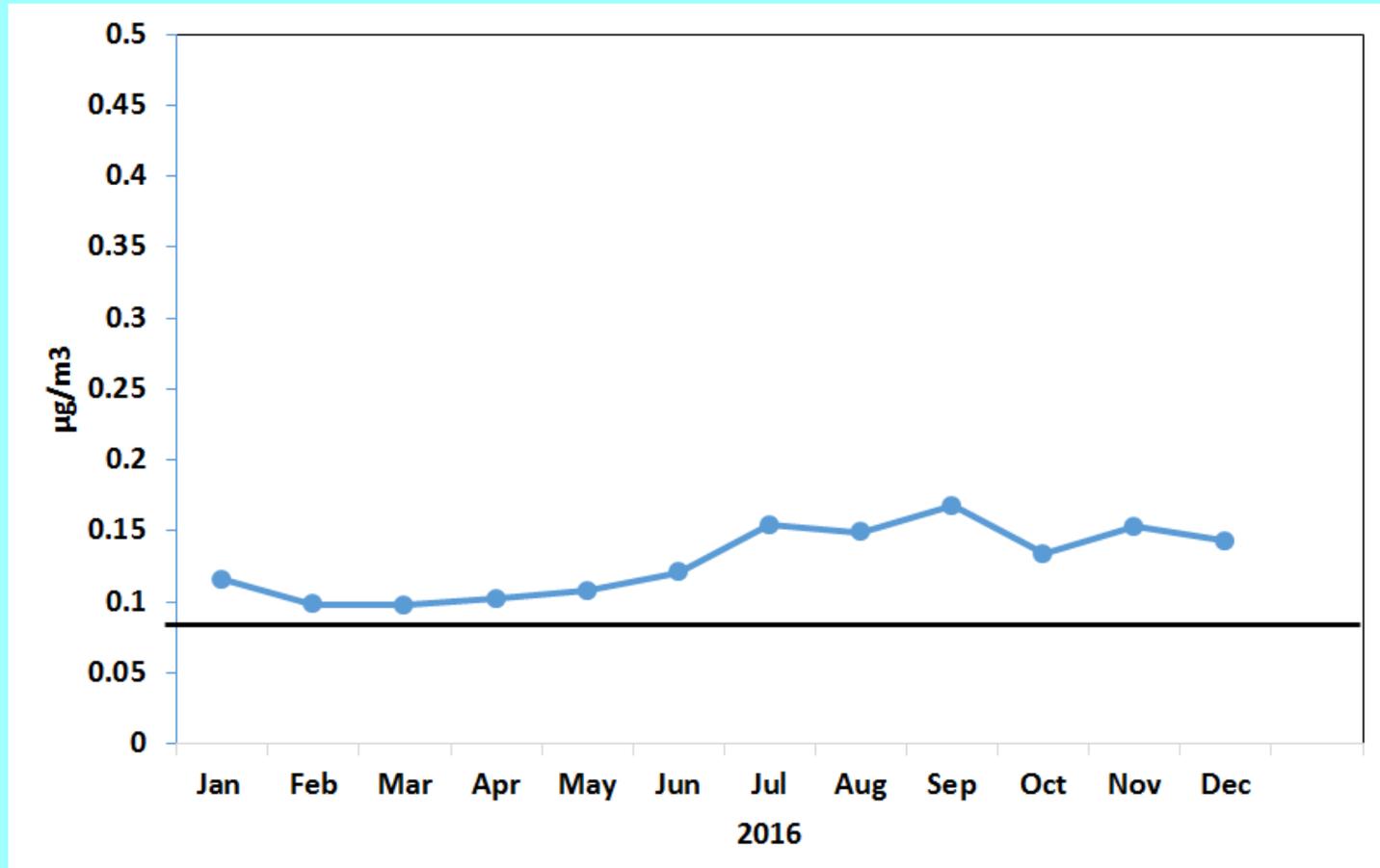
# Monthly median OC field blanks ranged from ~0.1 to 0.4 $\mu\text{g}/\text{m}^3$ (2005 – 2011)



Field blank OC concentrations decreased when filters began to be collected only at back-up filter sites (8/08). Double quartz field blanks were collected beginning 8/08. Prior to that time single field blanks were collected.

# 2016 monthly median OC ranged from ~0.1 – 0.17 $\mu\text{g}/\text{m}^3$

(average  $\pm$  standard deviation:  $0.13 \pm 0.025 \mu\text{g}/\text{m}^3$ )



# Conclusions

- Model 2015 analyzers have been integrated into the analysis system
- Throughput has increased to 5000 analyses per month
- Quality control constitutes 30% to 40% of all analyses
- Model 2001/2015 integration thresholds have a negligible effect on EC concentrations, but decrease many low values that are below lower quantifiable limits

# DRI publications and reports using the IMPROVE protocol

## 2016-2017

(n=21)

- Chen, L.-W.A., Han, Y.M., Chow, J.C., Watson, J.G., Cao, J.J., (2017). Black carbon in urban dust and surface soil particles: Refining optical measurement for environmental pollution survey. *Journal of Aerosol Science*, submitted.
- Dewangan, S., Pervez, S., Chakrabarty, R.K., Watson, J.G., Chow, J.C., Pervez, Y., Tiwari, S., Rai, J., (2016). Study of carbonaceous fractions associated with indoor PM<sub>2.5</sub>/PM<sub>10</sub> during Asian cultural and ritual burning practices. *Building and Environment*, 106, 229-236. <http://www.sciencedirect.com/science/article/pii/S036013231630213X>
- Gao, Y., Lee, S.C., Huang, Y., Chow, J.C., Watson, J.G., (2016). Chemical characterization and source apportionment of size-resolved particles in Hong Kong suburban area. *Atmospheric Research*, 170, 112-122.
- Han, Y.M., Chen, L.-W.A., Huang, R.J., Chow, J.C., Watson, J.G., Ni, H.Y., Liu, S.X., Fung, K.K., Shen, Z.X., Wei, C., Wang, Q.Y., Tian, J., Zhao, Z.Z., Prevot, A.S.H., Cao, J.J., (2016). Carbonaceous aerosols in megacity Xi'an, China: Implications of thermal/optical protocols comparison. *Atmospheric Environment*, 132, 58-68.
- Harrison, R.M., Khare, M., Chow, J.C., Watson, J.G., Pant, P., Khanna, I., Kanoje, M., Meena, M.L., (2016). Receptor modelling of fine air pollutants. UK-India Education and Research Initiative (UKIERI), Delhi, India.
- Hidy, G.M., Chow, J.C., Watson, J.G., (2017). Critical review summary: Air quality measurements—From rubber bands to tapping the rainbow. *EM*, 21,
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- Ho, S.S.H., Chow, J.C., Yu, J.Z., Watson, J.G., Cao, J.J., Huang, Y., (2017). Application of thermal desorption mass spectrometry for the analysis of environmental pollutants, Nollet, L.M.L., Lambropoulou, D. (Eds.), *Chromatographic Analysis of the Environment: Mass Spectrometry Based Approaches*, 4th Edition, Boca Raton, FL, pp. 77-106.
- Kleinman, M.T., Head, S.J., Morris, R.E., Stevenson, E.D., Altshuler, S.L., Chow, J.C., Watson, J.G., Hidy, G.M., Mueller, P.K., (2017). Critical review discussion: Air quality measurements: From rubber bands to tapping the rainbow. *Journal of the Air & Waste Management Association*, 67, 1159-11698.
- Liao, H.T., Yau, Y.C., Huang, C.S., Chen, N., Chow, J.C., Watson, J.G., Chou, C.C.-K., Wu, C.F., (2017). Source apportionment of urban air pollutants using constrained receptor models with a priori profile information. *Environmental Pollution*, 227, 323-333.
- Ni, H.Y., Tian, J., Wang, X.L., Wang, Q.Y., Han, Y.M., Cao, J.J., Long, X., Chen, L.-W.A., Chow, J.C., Watson, J.G., Huang, R.J., Dusek, U., (2017). PM<sub>2.5</sub> emissions and source profiles from open burning of crop residues. *Atmospheric Environment*, 169, 229-237.
- Pandey, A., Patel, S., Pervez, S., Tiwari, S., Yadama, G., Chow, J.C., Watson, J.G., Biswas, P., Chakrabarty, R.K., (2017). Aerosol emission factors from traditional biomass cookstoves in India: Insights from field measurements. *Atmospheric Chemistry and Physics*, 2017, accepted. 10.5194/acp-2017-291. <https://www.atmos-chem-phys-discuss.net/acp-2017-291/>
- Pervez, S., Chakrabarty, R.K., Dewangan, S., Watson, J.G., Chow, J.C., Matawle, J.L., (2016). Chemical speciation of aerosols and air quality degradation during the festival of lights (Diwali). *Atmospheric Pollution Research*, 7, 92-99. <http://www.sciencedirect.com/science/article/pii/S1309104215000380>
- Riggio, G.M., Wang, X.L., Cropper, P.M., Watson, J.G., Chow, J.C., (2017). Measuring the organic carbon to organic matter multiplier during thermal/optical carbon analysis. *Aerosol Science and Engineering*, submitted.
- Tian, J., Ni, H.Y., Cao, J.J., Han, Y.M., Wang, Q.Y., Wang, X.L., Chen, L.-W.A., Chow, J.C., Watson, J.G., Wei, C., Sun, J., Zhang, T., Huang, R.J., (2017). Characteristics of carbonaceous particles from residential coal combustion and agricultural biomass burning in China. *Atmospheric Pollution Research*, 8, 521-527.

# **DRI publications and reports using the IMPROVE protocol**

## **2016-2017**

### **(n=23)**

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