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 progress of multiwavelength data upload
- Illustrate brown carbon (BrC) algorithm in Model 2015

Carbon Laboratory Operations
(July 2015 to June 2016 samples)

- Received ~1,600 samples per month (~1,200 to 2,400 samples each month)
- Maintained 24 hours per day/5-7 days per week operation with 6-7 staff
- Analyzed ~18,200 IMPROVE samples (up to 2,200 per month)

IMPROVE_A Carbon Analyses
(July 2015 to June 2016 samples)

Sampling Period	**Samples Received**	**Analysis Completion Date**
7/1/15-12/31/15	9,024	May 2016
1/1/16-6/30/16*	9,200	Est. January 2017

***Samples collected as of 1/1/16 are being analyzed on the Model 2015 Multiwavelength Carbon Analyzer (Magee Scientific, Berkeley, CA)

[a] Chow et al. (2007) *JAWMA*

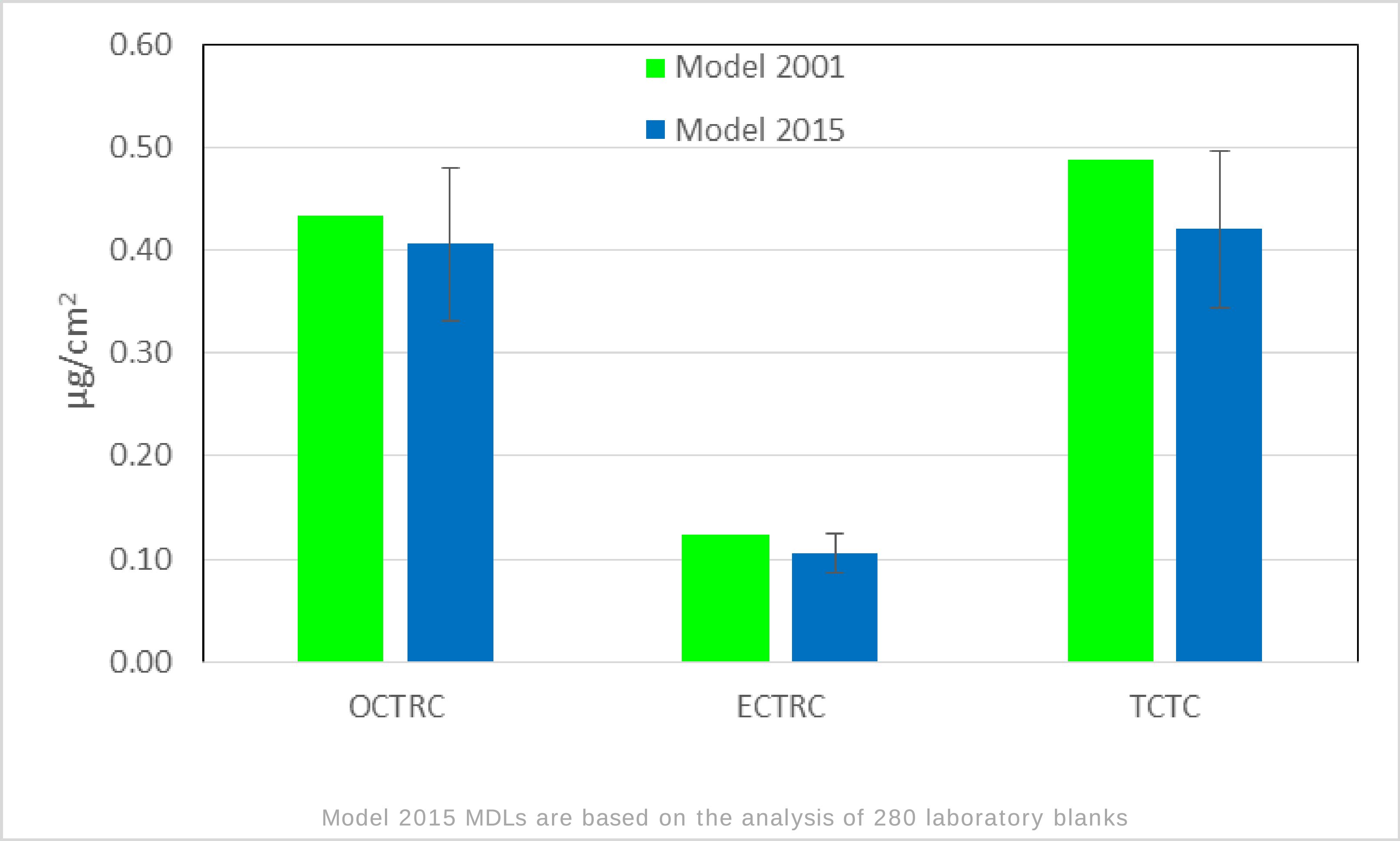
Operation of the Model 2015 Multiwavelength Carbon Analyzers

(10 DRI Model 2015 units as of October, 2016 [Magee Scientific, Berkeley, CA])

Transition from Model 2001 to Model 2015

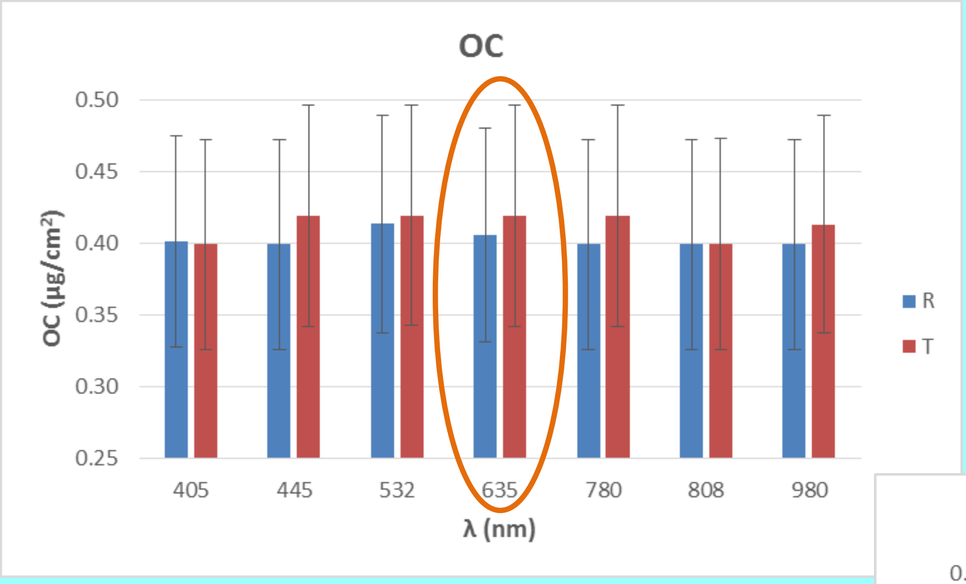
- Continue comparisons between Models 2001 and 2015 (Feb, 2015 – April, 2016)
- Start analyzing 2016 IMPROVE and CSN samples (May/June 2016)
- Instrument delivery by manufacturer was delayed (received 7 units from Magee Scientific, April – October, 2016)
- Anticipate ~13 operating units by the end of 2016

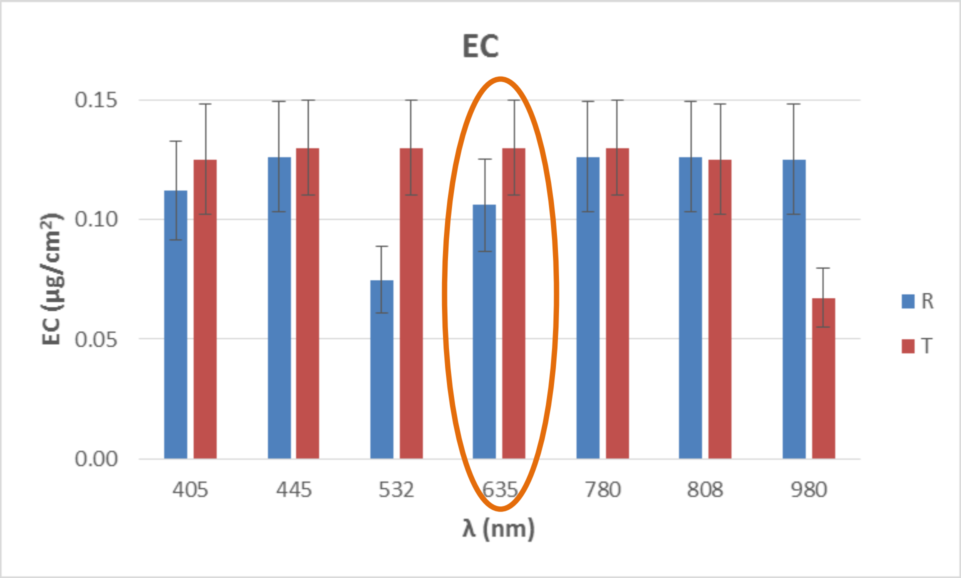
Comparable MDLs† between Models 2001 and 2015



† Minimum Detectable Limits at 635 nm are 5 – 15% lower for Model 2015

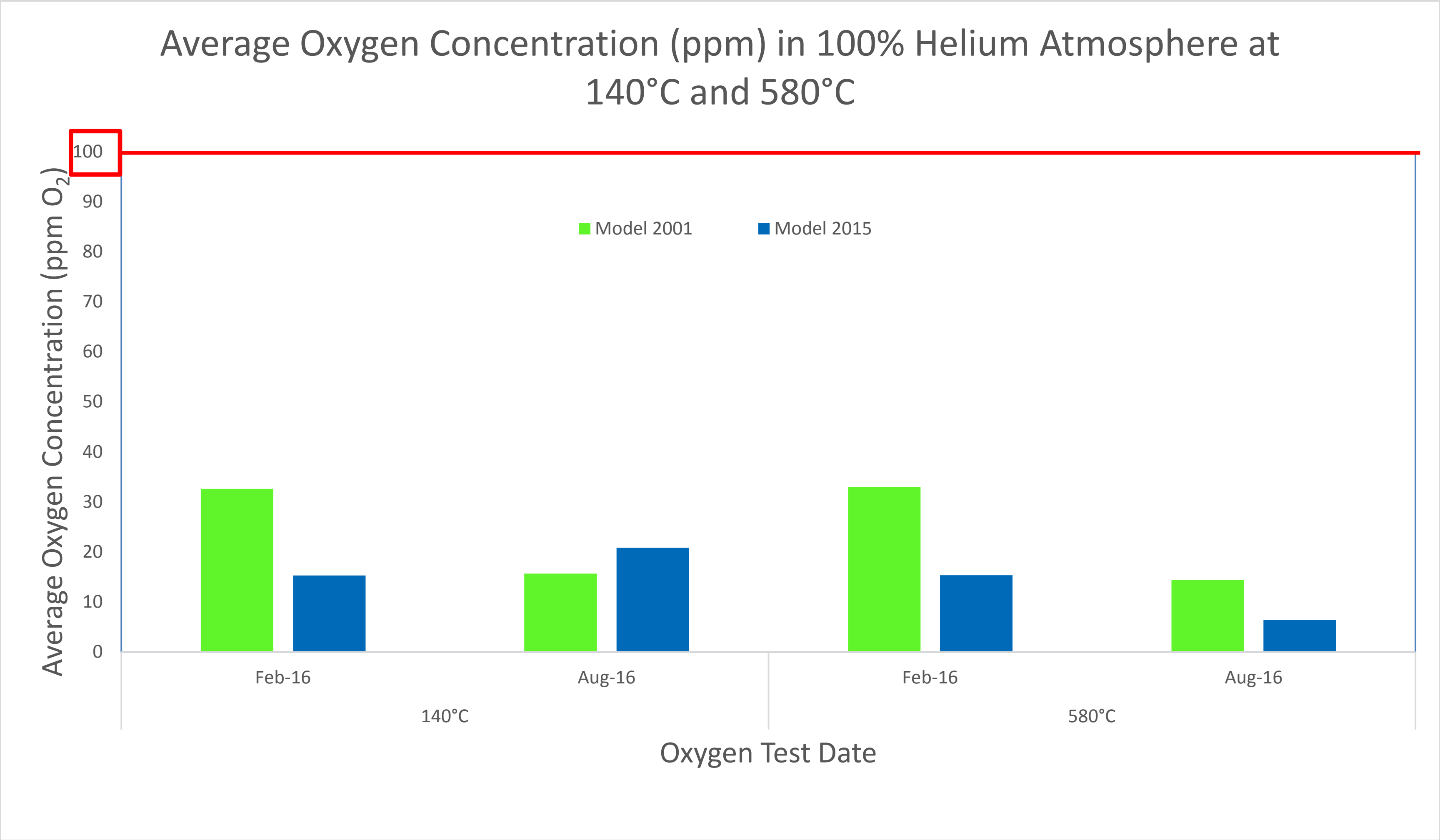
Similar MDLs found among the 7 wavelengths





MDLs are based on the analysis of 280 laboratory blanks

Traceable O_2* in pure He remains low



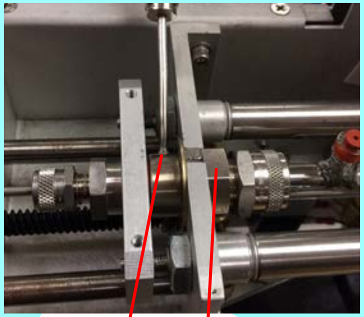
*O_2 test limit is 100 ppm

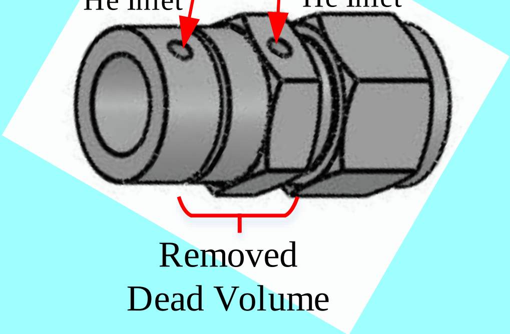
Model 2015 has been in stable operation. Refinements are made for operational efficiency

Minimize oxygen trap at the helium inlet

Strengthen the oven sidearm

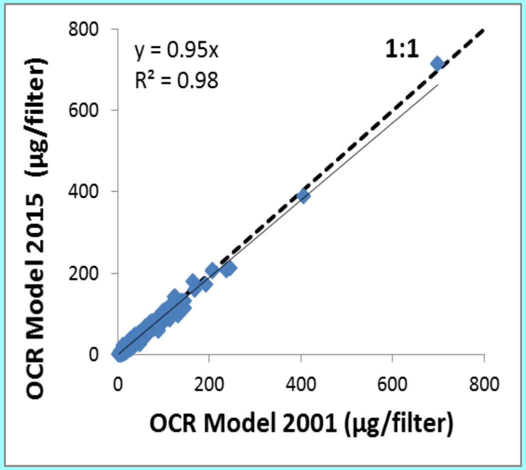
Stabilize calibration gas volume

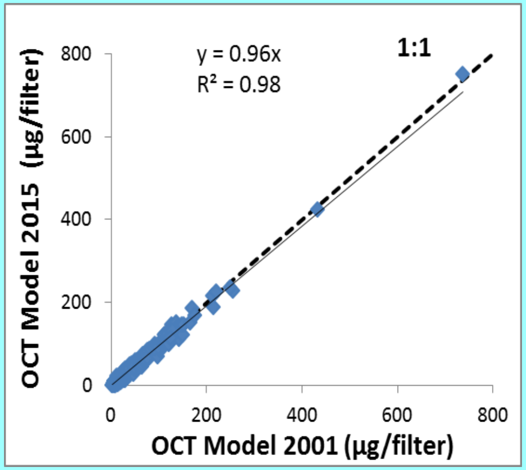




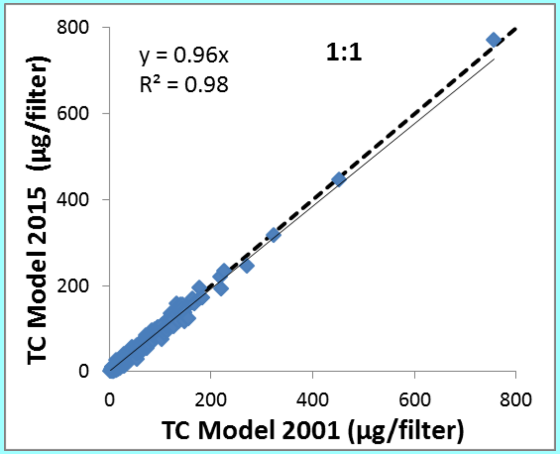
OC and EC are equivalent between Models
(Feb. 2015 – April 2016, n=1070)

OC

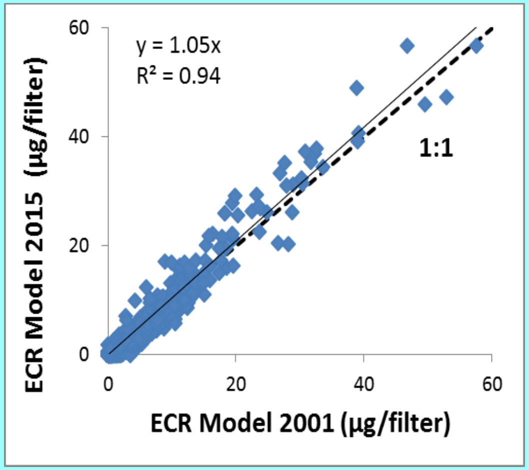


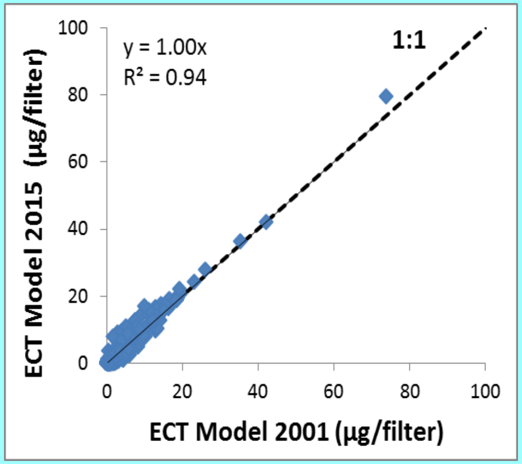


TC



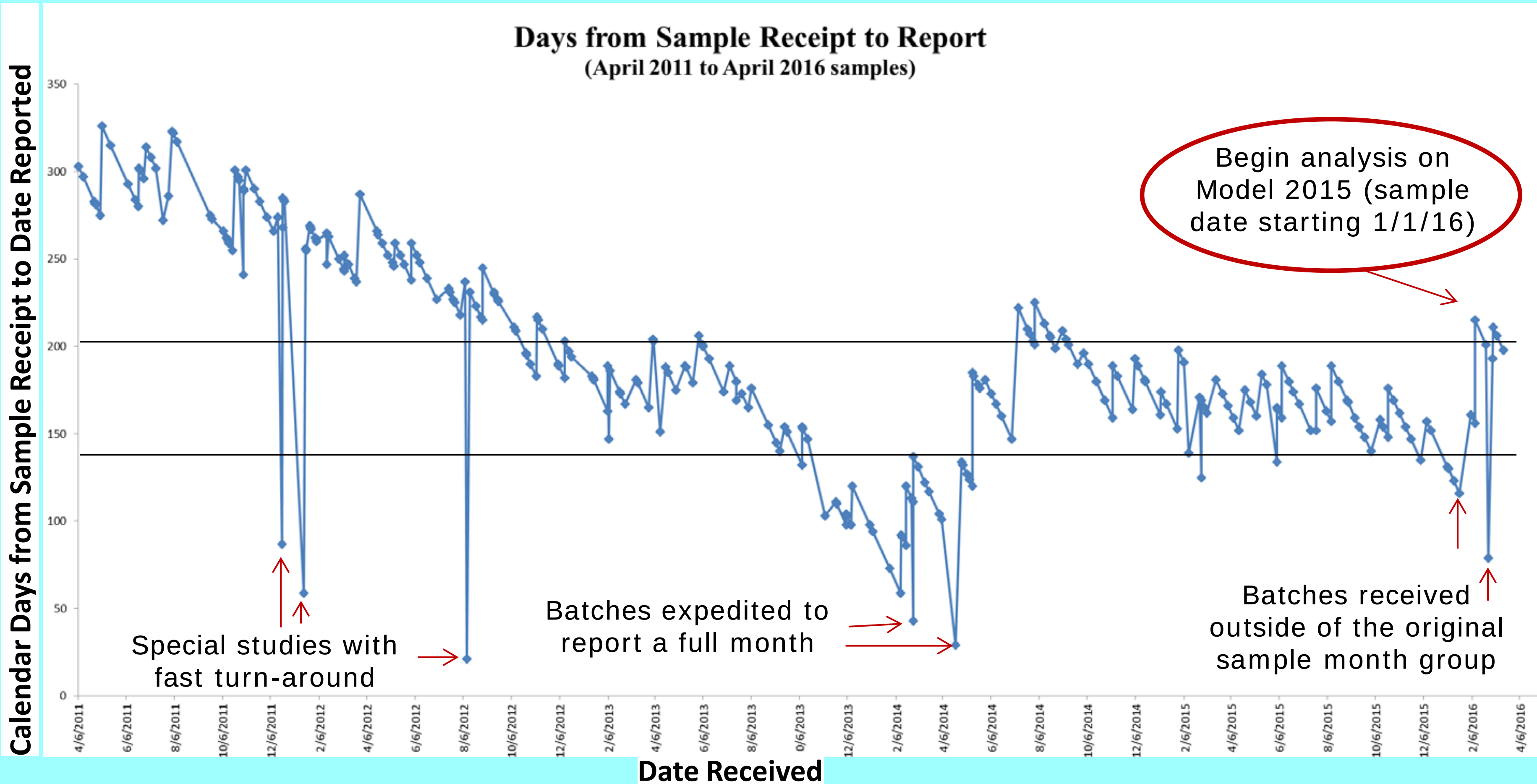
EC



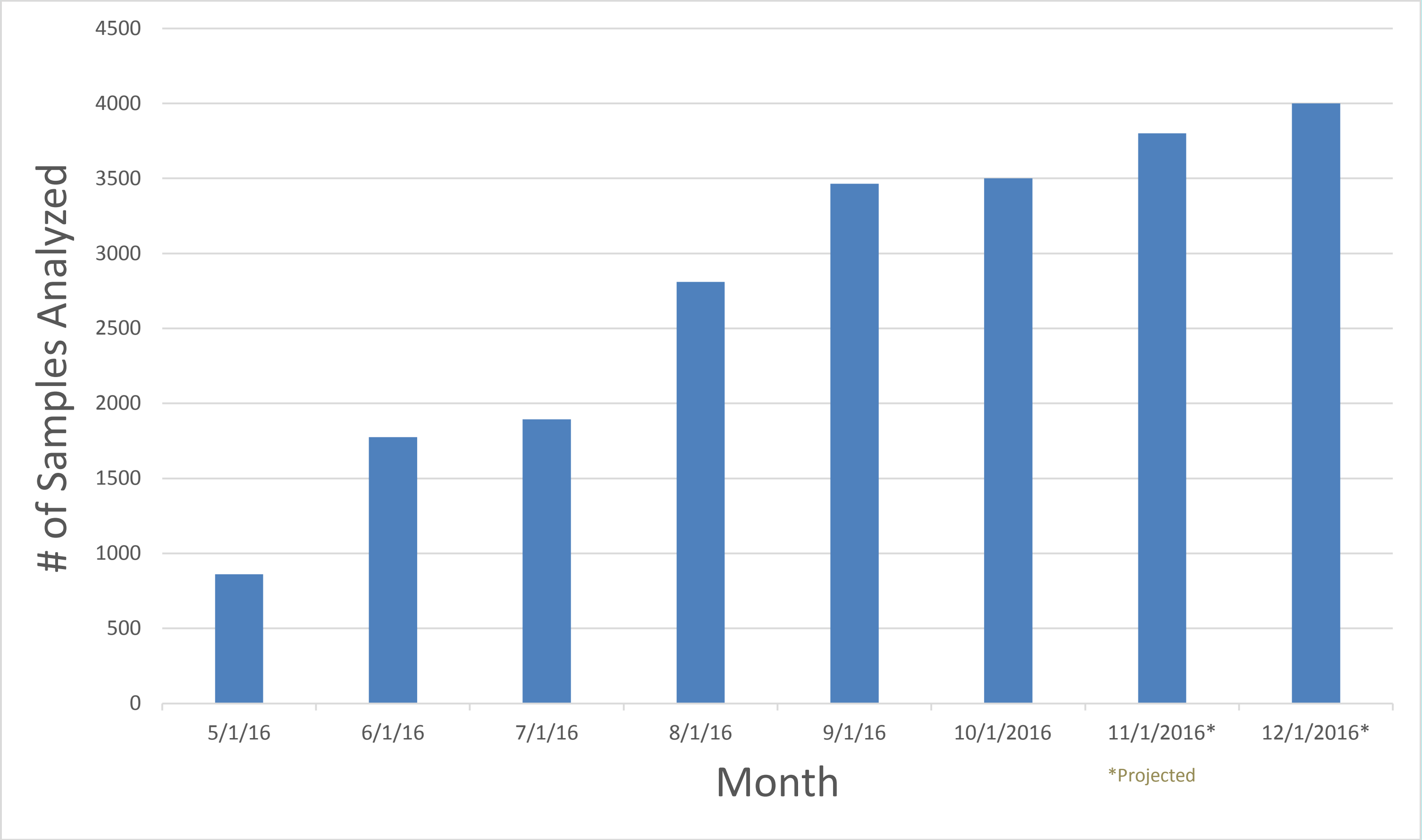


*IMPROVE samples collected for Oct 2014 – Dec. 2015

IMPROVE carbon reporting time has fluctuated between 140 and 200 days
(varied during initial transition to Model 2015)



Sample throughput will double with full instrumentation (~4,000/month)



*plan to eliminate backlogs by June, 2017

Seven wavelength data have been delivered to U.C. Davis*

Network	Sample Collection Date	Data Delivery Date
IMPROVE	1/1/16-3/7/16	9/30/16
CSN	1/1/16-3/25/16	8/3/16

Includes 142 parameters: total carbon, carbon fractions, OC, EC, and OP by reflectance/transmittance (R/T) (i.e., LRFINL, LTFINL, LRINIT, LTINIT, LRMIN, and LTMIN) for each wavelength (λ=405, 445, 532, **635**, 780, 808, 980)

**To be uploaded to Federal Land Manager Environmental Database for IMPROVE and to AQS for CSN

New Seven Wavelength Database Parameters*

Carbon Parameters (in µg/filter)

	New DRI Code Value Parameter	New Parameter Description	New DRI Code Uncertainty	Notes
	OC405TRC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tor_WL405	OC405TRU	
	OC445TRC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tor_WL445	OC445TRU	
	OC532TRC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tor_WL532	OC532TRU	
OCR	**OC635TRC**	**Oc Csn_Rev Unadjusted Pm2.5 Lc Tor_WL635**	**OC635TRU**	**Prev "OCTRC"**
	OC780TRC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tor_WL780	OC780TRU	
	OC808TRC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tor_WL808	OC808TRU	
	OC980TRC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tor_WL980	OC980TRU	
	OC405TTC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tot_WL405	OC405TTU	
	OC445TTC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tot_WL445	OC445TTU	
	OC532TTC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tot_WL532	OC532TTU	
OCT	**OC635TTC**	**Oc Csn_Rev Unadjusted Pm2.5 Lc Tot_WL635**	**OC635TTU**	**Prev "OCTTC"**
	OC780TTC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tot_WL780	OC780TTU	
	OC808TTC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tot_WL808	OC808TTU	
	OC980TTC	Oc Csn_Rev Unadjusted Pm2.5 Lc Tot_WL980	OC980TTU	
	EC405TRC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tor_WL405	EC405TRU	
	EC445TRC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tor_WL445	EC445TRU	
	EC532TRC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tor_WL532	EC532TRU	
ECR	**EC635TRC**	**Ec Csn_Rev Unadjusted Pm2.5 Lc Tor_WL635**	**EC635TRU**	**Prev "ECTRC"**
	EC780TRC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tor_WL780	EC780TRU	
	EC808TRC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tor_WL808	EC808TRU	
	EC980TRC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tor_WL980	EC980TRU	
	EC405TTC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tot_WL405	EC405TTU	
	EC445TTC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tot_WL445	EC445TTU	
	EC532TTC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tot_WL532	EC532TTU	
ECT	**EC635TTC**	**Ec Csn_Rev Unadjusted Pm2.5 Lc Tot_WL635**	**EC635TTU**	**Prev "ECTTC"**
	EC780TTC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tot_WL780	EC780TTU	
	EC808TTC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tot_WL808	EC808TTU	
	EC980TTC	Ec Csn_Rev Unadjusted Pm2.5 Lc Tot_WL980	EC980TTU	
	OP405TRC	Op Csn_Rev Unadjusted Pm2.5 Lc Tor_WL405	OP405TRU	
	OP445TRC	Op Csn_Rev Unadjusted Pm2.5 Lc Tor_WL445	OP445TRU	
	OP532TRC	Op Csn_Rev Unadjusted Pm2.5 Lc Tor_WL532	OP532TRU	
OPR	**OP635TRC**	**Op Csn_Rev Unadjusted Pm2.5 Lc Tor_WL635**	**OP635TRU**	**Prev "OPTRC"**
	OP780TRC	Op Csn_Rev Unadjusted Pm2.5 Lc Tor_WL780	OP780TRU	
	OP808TRC	Op Csn_Rev Unadjusted Pm2.5 Lc Tor_WL808	OP808TRU	
	OP980TRC	Op Csn_Rev Unadjusted Pm2.5 Lc Tor_WL980	OP980TRU	
	OP405TTC	Op Csn_Rev Unadjusted Pm2.5 Lc Tot_WL405	OP405TTU	
	OP445TTC	Op Csn_Rev Unadjusted Pm2.5 Lc Tot_WL445	OP445TTU	
	OP532TTC	Op Csn_Rev Unadjusted Pm2.5 Lc Tot_WL532	OP532TTU	
ORT	**OP635TTC**	**Op Csn_Rev Unadjusted Pm2.5 Lc Tot_WL635**	**OP635TTU**	**Prev "OPTTC"**
	OP780TTC	Op Csn_Rev Unadjusted Pm2.5 Lc Tot_WL780	OP780TTU	
	OP808TTC	Op Csn_Rev Unadjusted Pm2.5 Lc Tot_WL808	OP808TTU	
	OP980TTC	Op Csn_Rev Unadjusted Pm2.5 Lc Tot_WL980	OP980TTU	

Laser Parameters (Initial, Minimum, and Final R&T)

New Parameter	New Parameter Description	Notes	
LR405INIT	Laser_Reflect_Init_WL405		
LR405MIN	Laser_Reflect_Min_WL405		
LR405FINL	Laser_Reflect_Finl_WL405		
LR445INIT	Laser_Reflect_Init_WL445		
LR445MIN	Laser_Reflect_Min_WL445		
LR445FINL	Laser_Reflect_Finl_WL445		
LR532INIT	Laser_Reflect_Init_WL532		
LR532MIN	Laser_Reflect_Min_WL532		
LR532FINL	Laser_Reflect_Finl_WL532		
LR635INIT	**Laser_Reflect_Init_WL635**	**Prev "LRINIT" for IMPROVE**	
LR635MIN	**Laser_Reflect_Min_WL635**	**Prev "LRMIN" for IMPROVE**	Initial, Minimum, and Final by Reflectance
LR635FINL	**Laser_Reflect_Finl_WL635**	**Prev "LRFINL" for IMPROVE**	
LR780INIT	Laser_Reflect_Init_WL780		
LR780MIN	Laser_Reflect_Min_WL780		
LR780FINL	Laser_Reflect_Finl_WL780		
LR808INIT	Laser_Reflect_Init_WL808		
LR808MIN	Laser_Reflect_Min_WL808		
LR808FINL	Laser_Reflect_Finl_WL808		
LR980INIT	Laser_Reflect_Init_WL980		
LR980MIN	Laser_Reflect_Min_WL980		
LR980FINL	Laser_Reflect_Finl_WL980		
LT405INIT	Laser_Trans_Initial_WL405		
LT405MIN	Laser_Trans_Minimum_WL405		
LT405FINL	Laser_Trans_Finl_WL405		
LT445INIT	Laser_Trans_Initial_WL445		
LT445MIN	Laser_Trans_Minimum_WL445		
LT445FINL	Laser_Trans_Finl_WL445		
LT532INIT	Laser_Trans_Initial_WL532		
LT532MIN	Laser_Trans_Minimum_WL532		
LT532FINL	Laser_Trans_Finl_WL532		
LT635INIT	**Laser_Trans_Initial_WL635**	**Prev "LTINIT" for IMPROVE**	
LT635MIN	**Laser_Trans_Minimum_WL635**	**Prev "LTMIN" for IMPROVE**	Initial, Minimum, and Final by Transmittance
LT635FINL	**Laser_Trans_Finl_WL635**	**Prev "LTFINL" for IMPROVE**	
LT780INIT	Laser_Trans_Initial_WL780		
LT780MIN	Laser_Trans_Minimum_WL780		
LT780FINL	Laser_Trans_Finl_WL780		
LT808INIT	Laser_Trans_Initial_WL808		
LT808MIN	Laser_Trans_Minimum_WL808		
LT808FINL	Laser_Trans_Finl_WL808		
LT980INIT	Laser_Trans_Initial_WL980		
LT980MIN	Laser_Trans_Minimum_WL980		
LT980FINL	Laser_Trans_Finl_WL980		

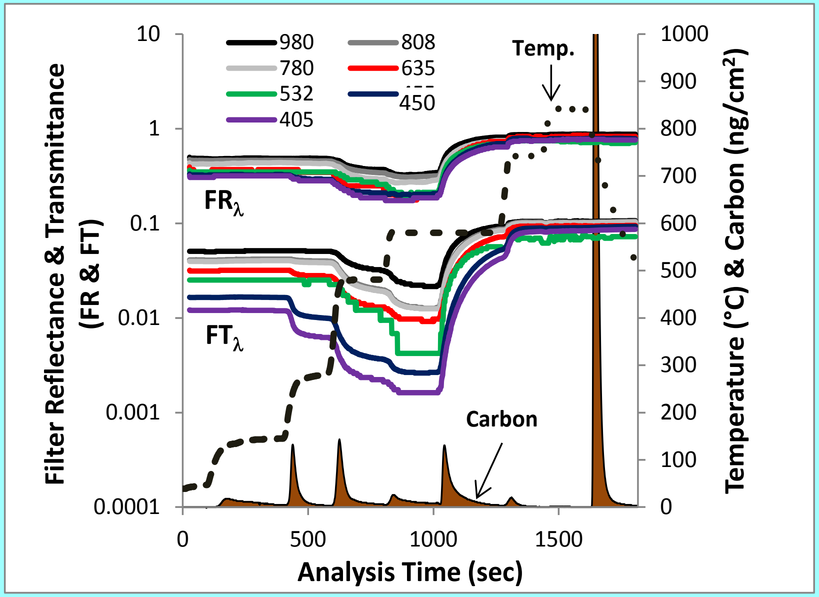
*Total of 142 parameters

Model 2015 reports the optical signal every second for the seven wavelengths*

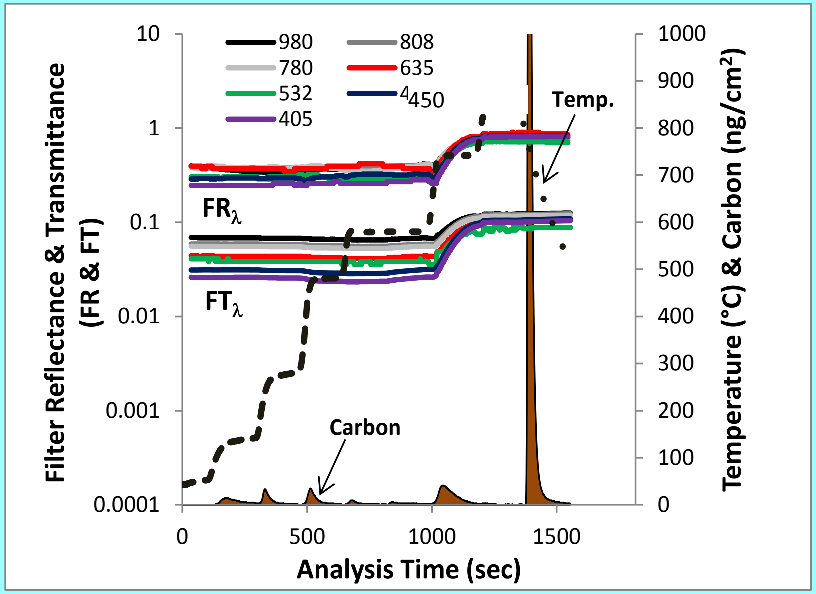
(starting 1/1/16)

After Optical Calibration

Fresno Ambient Sample



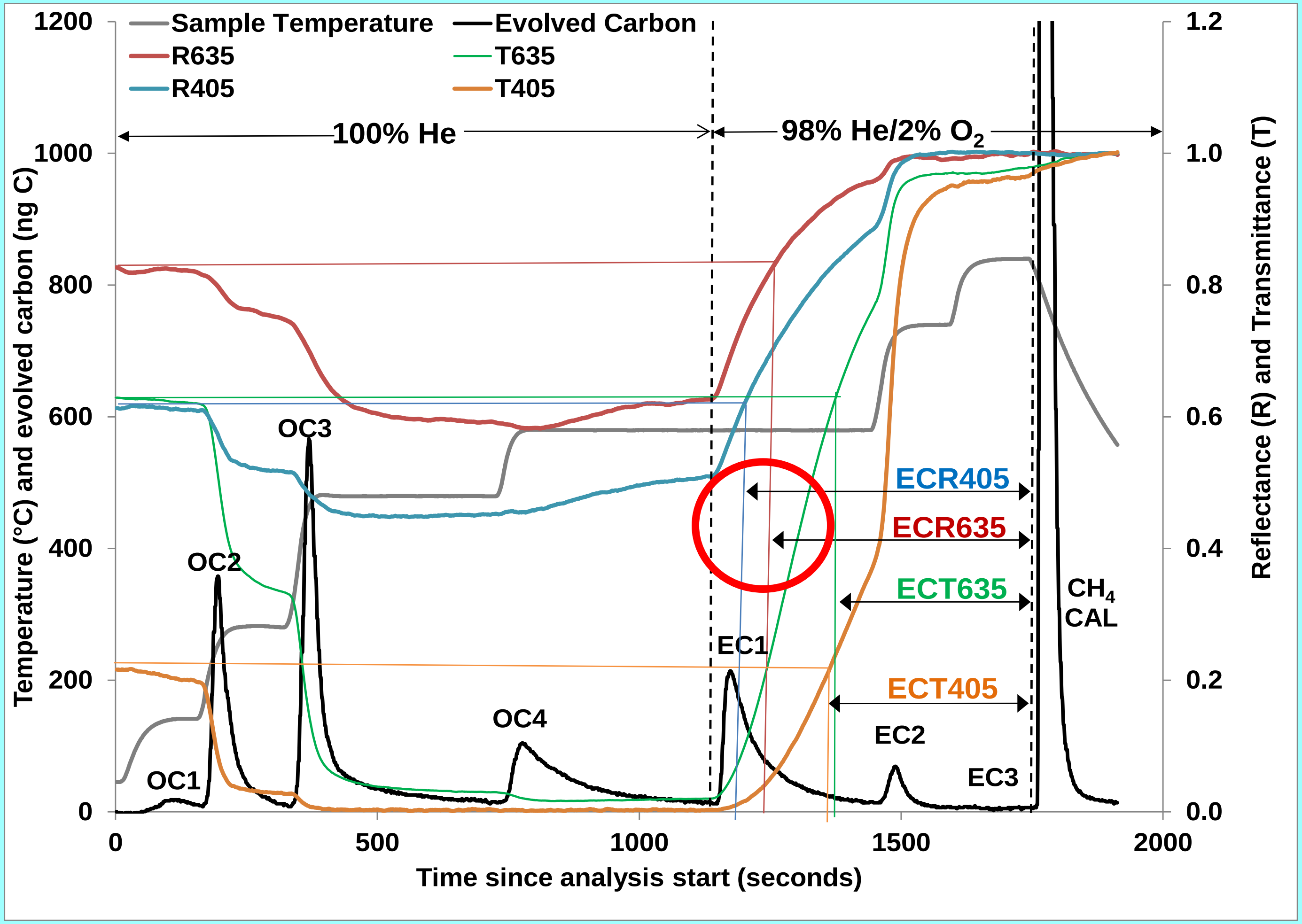
Diesel Exhaust



- FR = Filter reflectance
- FT = Filter transmittance
- $ATN(\lambda) = \ln(\frac{FT_{\lambda,f}}{FT_{\lambda,i}})$

*The DRI Model 2015 uses seven wavelengths (i.e., 405, 445, 532, 635, 780, 808, and 980 nm) to separate brown carbon (BrC) from black or elemental carbon

For wood smoke dominated samples[a] EC_{405} (i.e., ECR and ECT at 405 nm) exceeds EC_{635}

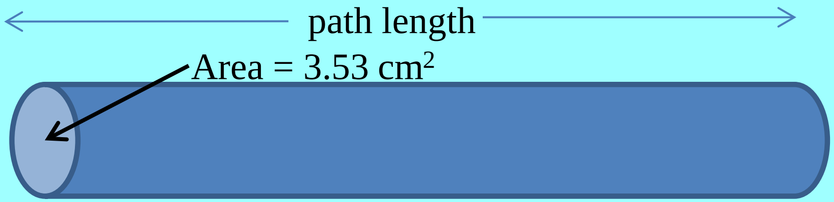


[a] IMPROVE samples from Buffalo Pass, CO, USA, using multiwavelength IMPROVE_A protocol

Two component model is used to separate BrC from BC

- $b_{ATN}(\lambda, Mm^{-1}) = b_{ATN\text{-}BC}(\lambda) + b_{ATN\text{-}BrC}(\lambda)$

- $b_{ATN}(\lambda, Mm^{-1}) = q_{BC} \times \lambda^{-AAE_{BC}} + q_{BrC} \times \lambda^{-AAE_{BrC}}$



Where:

-- $b_{ATN}(\lambda)$ = ATN(λ) ÷ path length*

-- ATN(λ) = $\ln(\frac{FT_{\lambda,f}}{FT_{\lambda,i}})$

-- $FT_{\lambda, f}$ and $FT_{\lambda, i}$ are the final and initial filter transmittance, respectively

-- $b_{ATN\text{-}BC}$ and $b_{ATN\text{-}BrC}$ are the fractions of BC and BrC, respectively; $b_{ATN}(\lambda) \propto \lambda^{-AAE}$

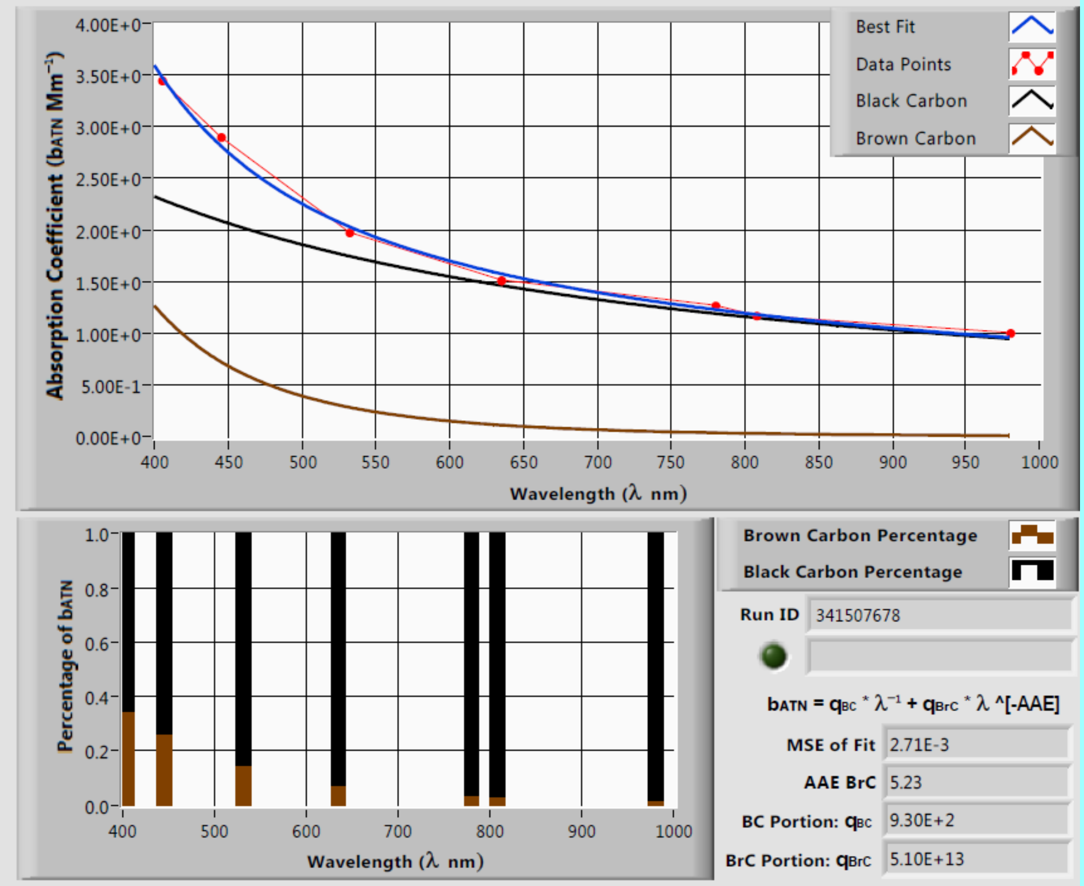
-- q_{BC} and q_{BrC} are fitting coefficients

-- AAE_{BrC} is the calculated Absorption Ångström Exponent for BrC, assuming $AAE_{BC} = 1$

* $b_{ATN}(\lambda)$ = filter light absorption (does not yet account for internal scattering within filter),
ATN(λ) = transmittance attenuation,
IMPROVE filter sight path length = ($33.12\ m^3 \div 3.53\ cm^2 \times 10^4\ m^2/cm^2$) = 93,824.36 m

BrC calculation is being implemented in Model 2015 software

(BrC contributed to 35% of EC at 405 nm)

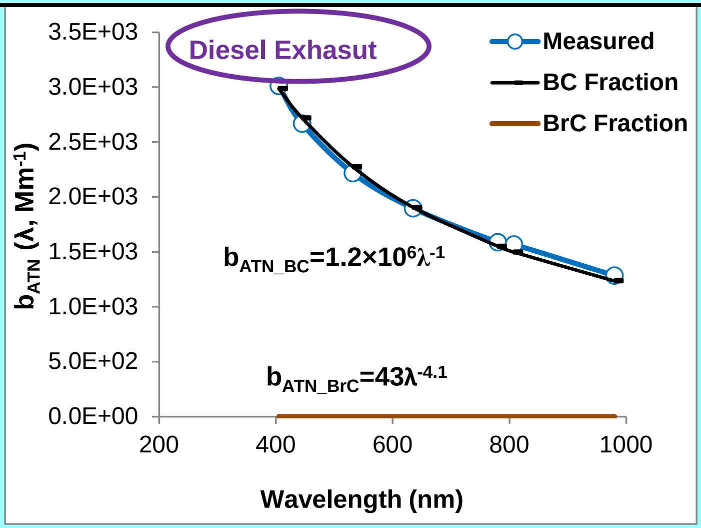


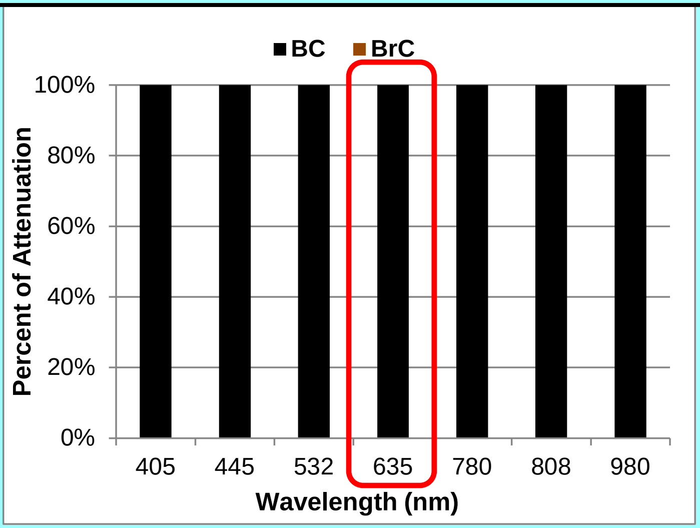
Sample collected on 4/18/16 from Everglades National Park (EVER site) in Florida

(TC=696.4 μg/filter [21.03 μg/m^3]; OC=675.7 μg/filter [20.4 μg/m^3]; EC=20.7 μg/filter [0.6 μg/m^3])

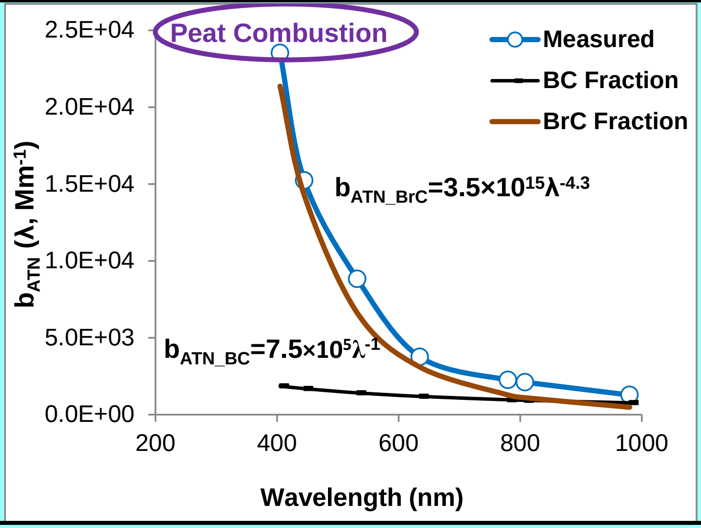
Attenuation spectra show distinguished differences between diesel exhaust and peat combustion samples

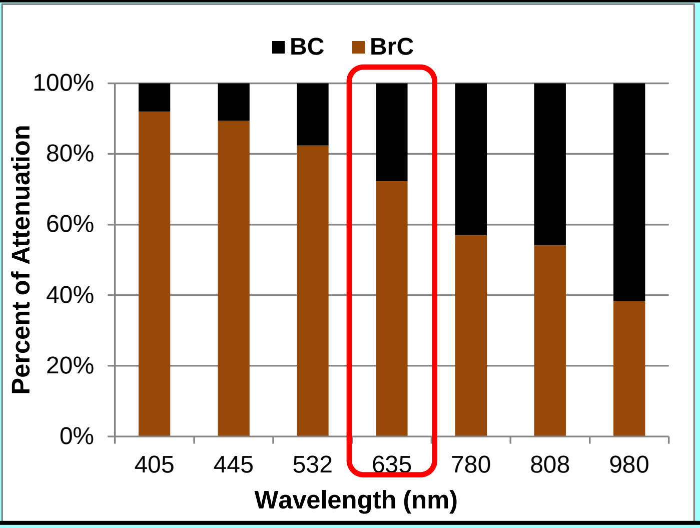
BC dominated diesel exhaust attenuation at all wavelengths





BrC dominated peat combustion emission attenuation at lower wavelengths

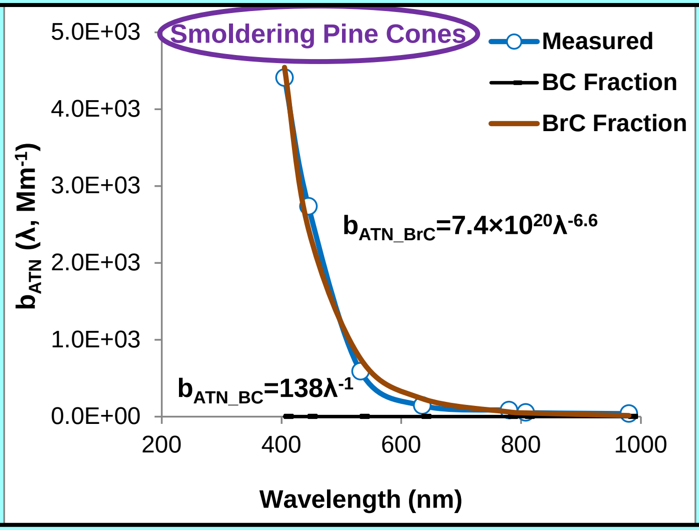


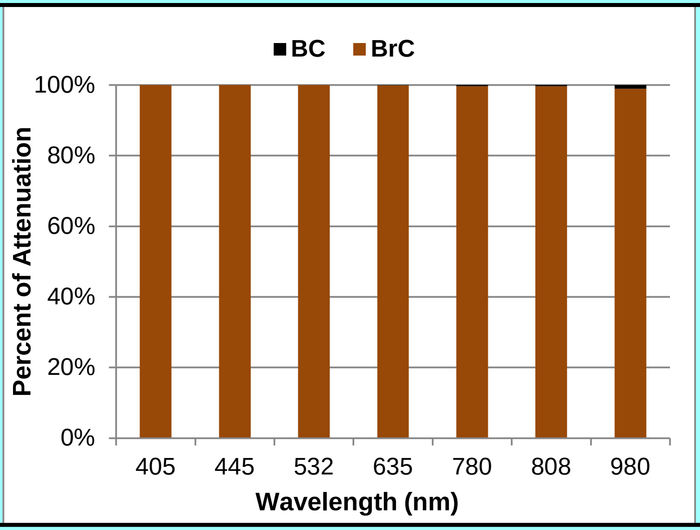


BrC-dominated smoldering- and BC-dominated flaming-phases of biomass burning

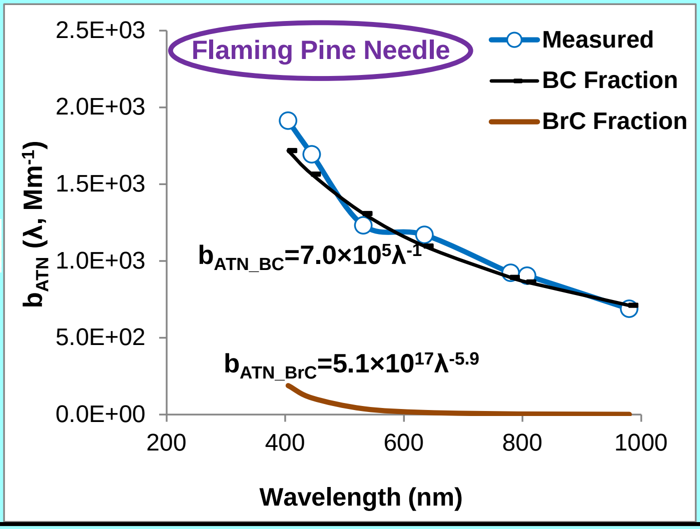
(Chamber Experiment, Reno, Nevada)

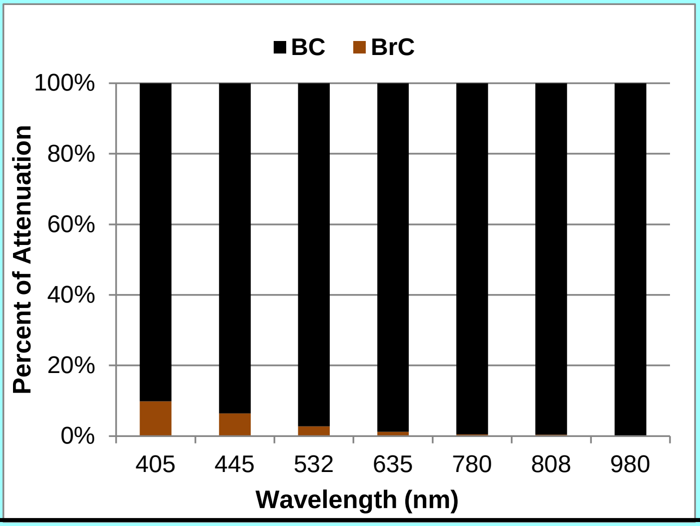
BrC dominated smoldering pine cone emissions





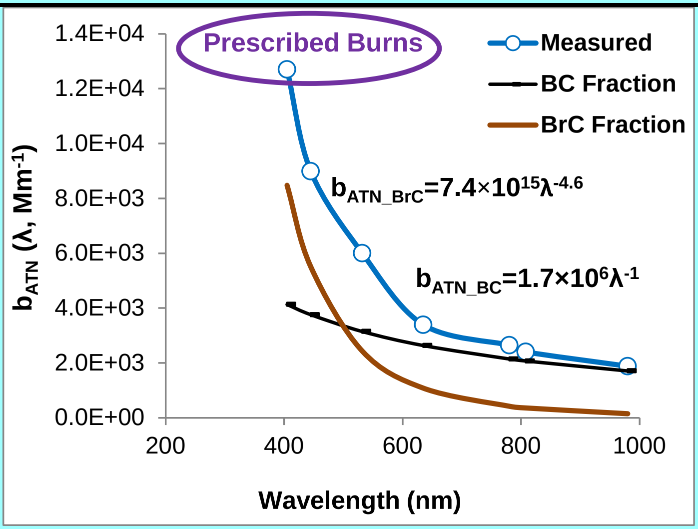
BC dominated flaming pine needle emissions

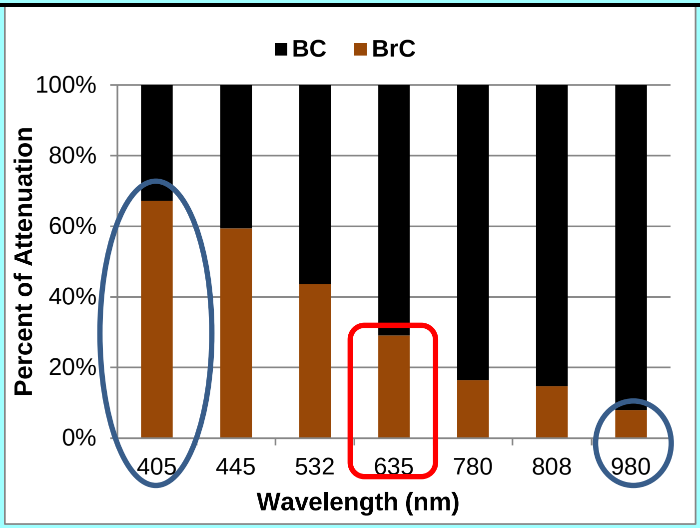




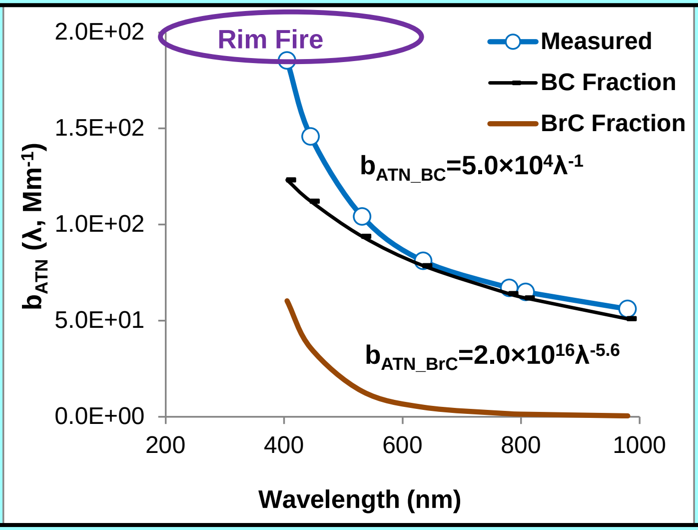
Prescribed burns and wildfires show a mixture of BrC and BC

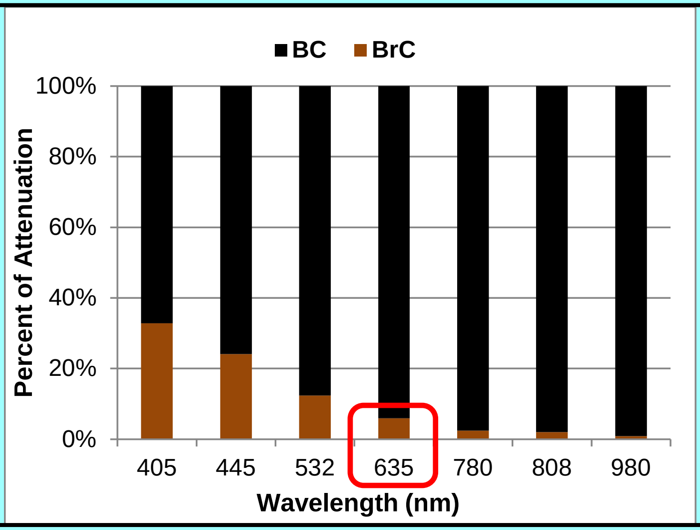
Attenuation by BrC varied from 67% (405 nm) to 8% (980 nm) in the prescribed burnings from Lake Tahoe Basin.





The 2013 Rim Fire emission sample was dominated by BC.





AAE* by 7 λ and 2 λ fit are similar

(BrC contributions to light attenuation vary with sources)

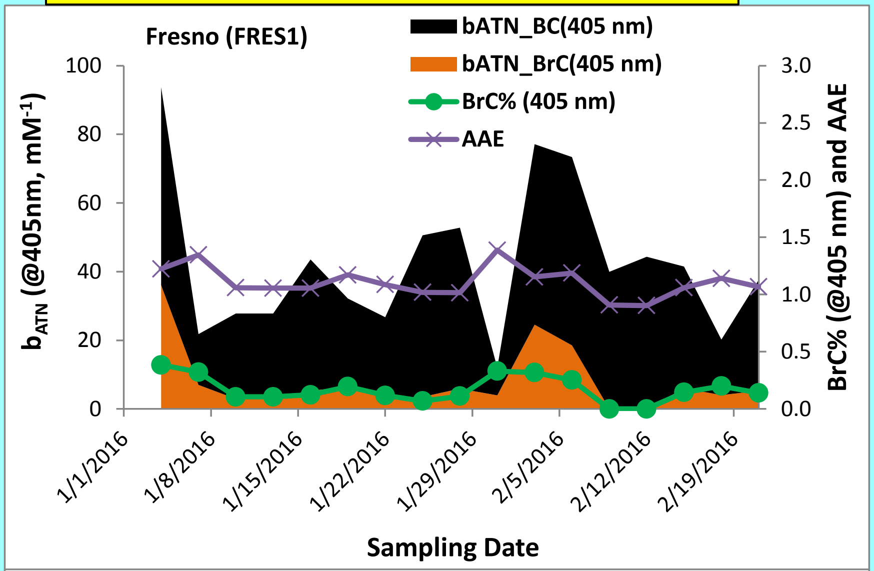
Sample	AAE_7λ fit	AAE_405_808 nm fit	b_{ATN}(@635 nm, Mm^{-1})	%b_{ATN_BrC} (@635 nm)
Diesel	0.94	0.95	1896	0.0%
Diesel	0.87	0.83	4749	0.0%
Diesel	0.90	0.92	4910	0.0%
Diesel	0.85	0.83	3389	0.0%
Diesel	0.98	1.06	860	1.3%
Diesel	0.88	0.91	2755	0.0%
Peat	9.05	11.35	159	99.9%
Peat	3.34	3.50	3751	72.3%
Pine Cone	5.73	6.43	143	99.9%
Pine Needle	1.09	1.09	1169	1.2%
Rim Fire	1.34	1.52	81	5.9%
Tahoe Wood	1.81	1.94	900	82.0%
Tahoe Wood	2.17	2.41	3392	29.1%
Tahoe Wood	3.06	3.30	729	99.9%
Tahoe Wood	2.68	2.76	1030	99.9%

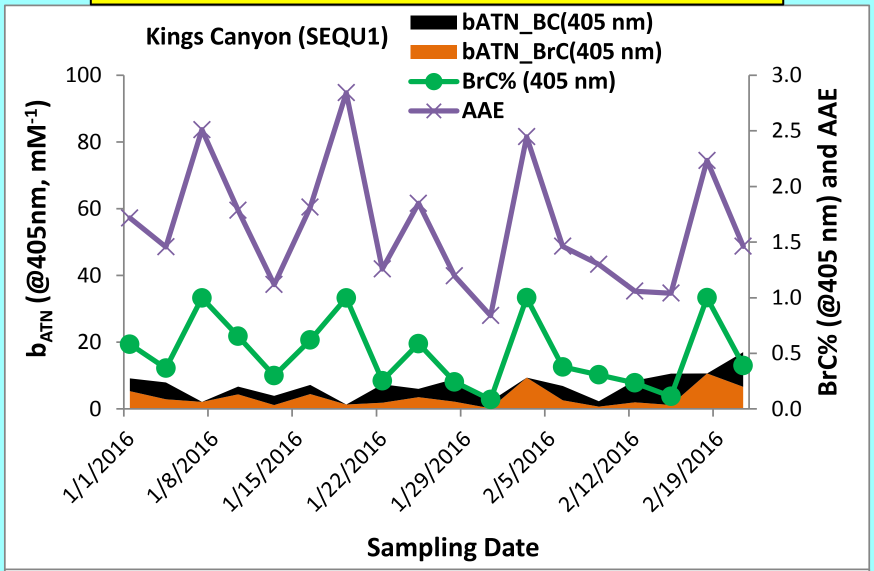
*AAE: Absorption Ångström Exponent

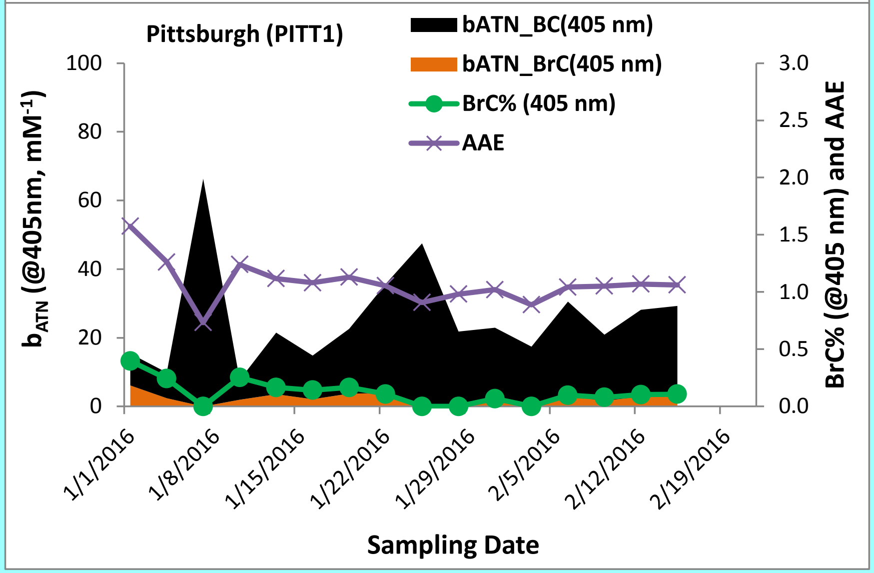
Abundance of BrC is more apparent in rural than urban sites

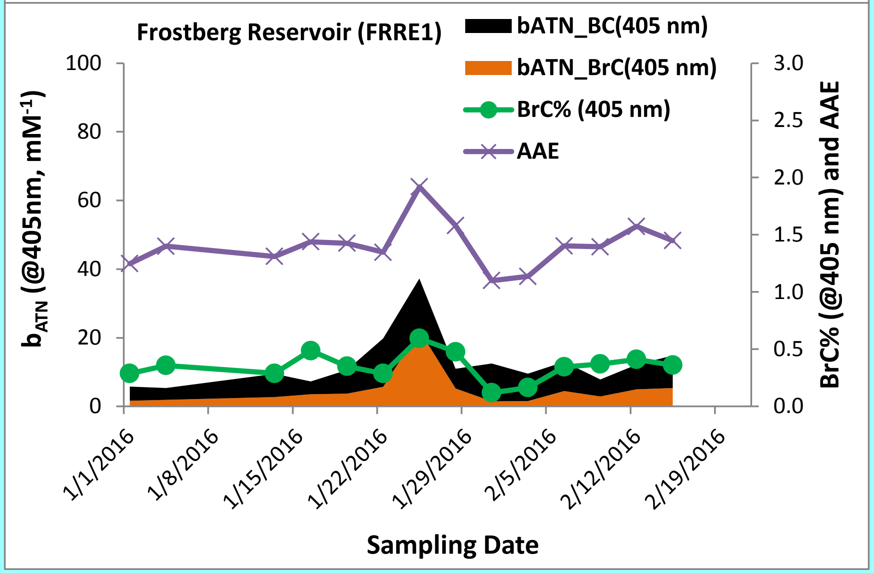
Collocated IMPROVE and CSN Sites

IMPROVE Sites

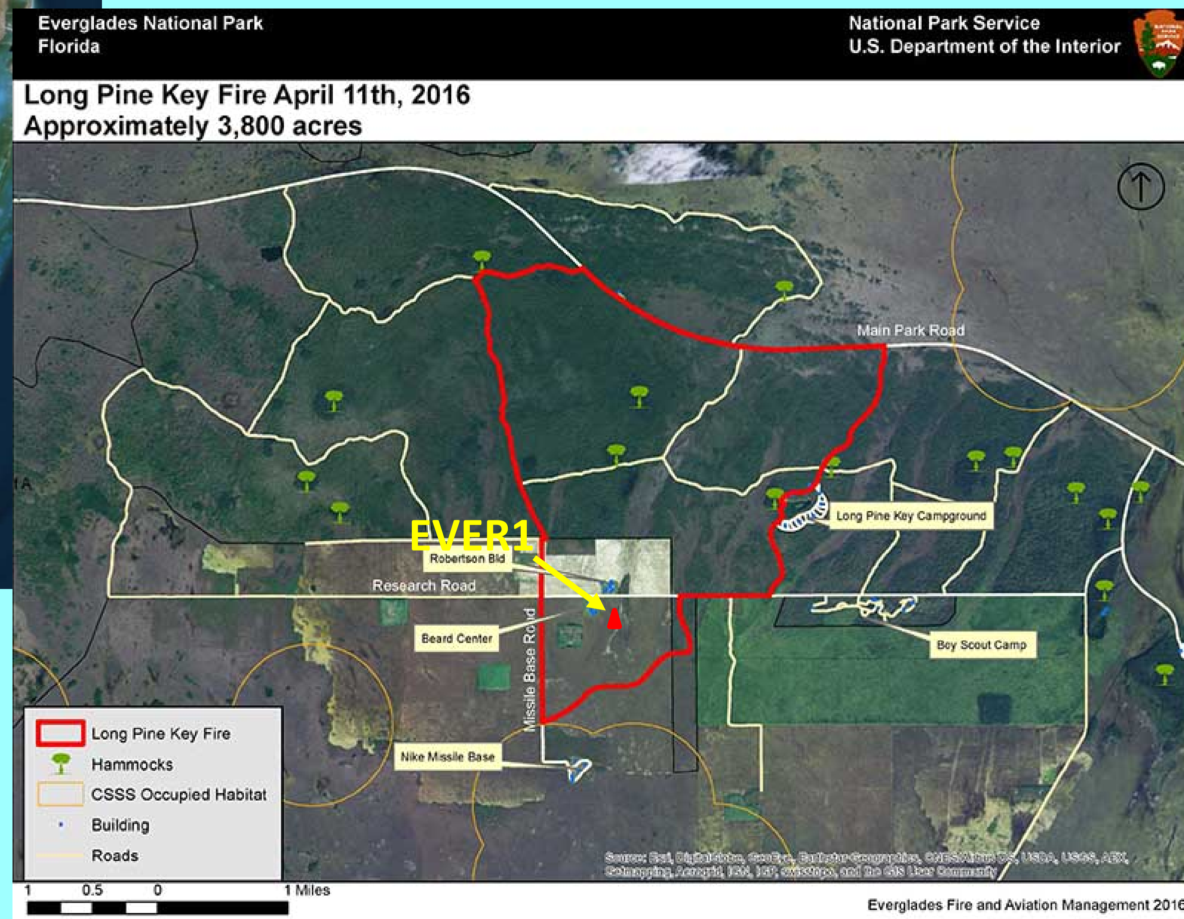




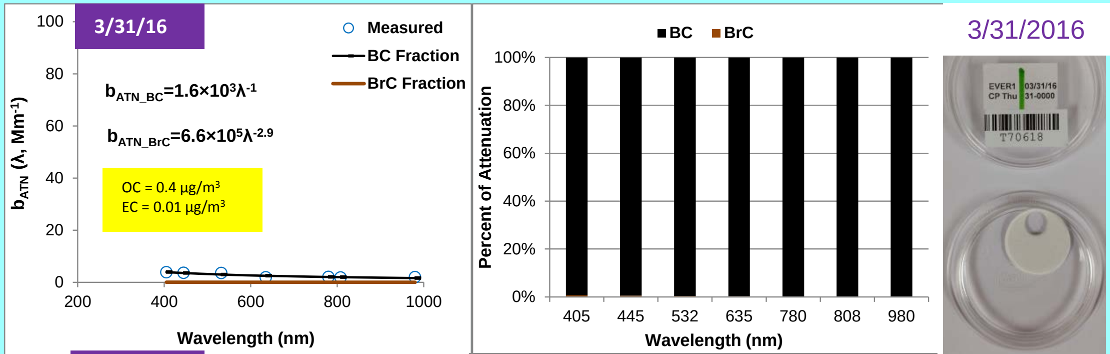


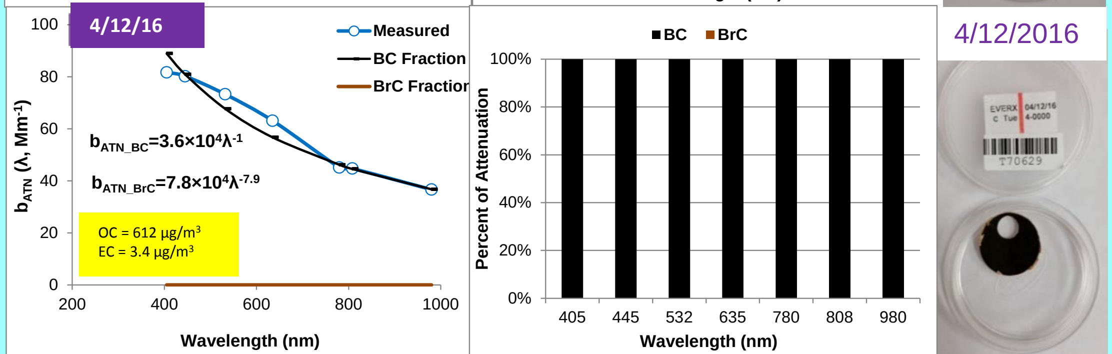


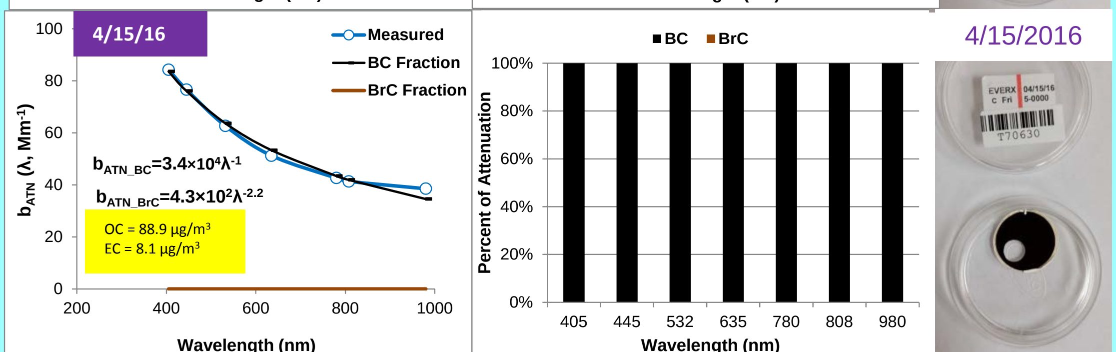
Forest fire event
Long Pine Key Wildfire
(EVER site, 4/10 – 4/17/16)

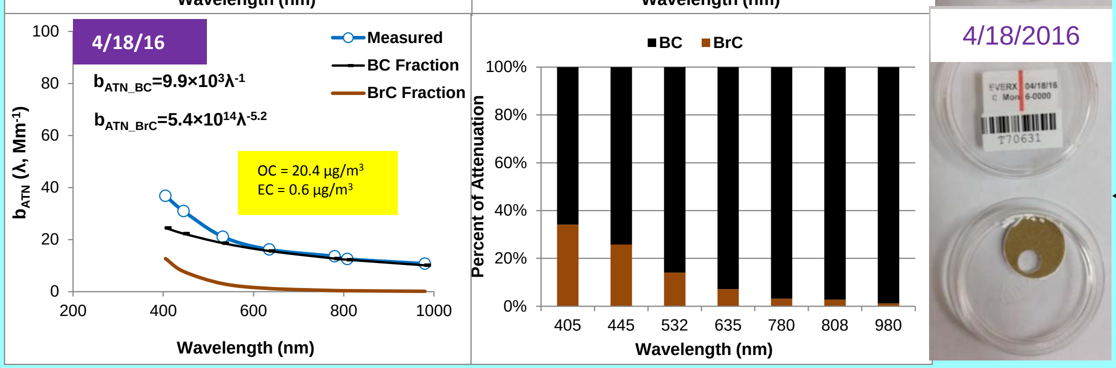


Elevated OC and EC found at EVER site during and after fire









Elevated BrC found after wildfire was 100% contained on 4/17/16

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