

**A Non-destructive,  
Inexpensive Method  
for Predicting  
TOR OC and EC  
in IMPROVE and CSN  
using  
Infrared Spectra**



**Ann M. Dillner\***,  
Andrew T. Weakley\*,  
Giulia Ruggeri §,  
Matteo Reggente §,  
Satoshi Takahama §

\*University of California, Davis, USA

§Swiss Federal Institute of Technology  
Lausanne (EPFL), Lausanne, Switzerland

NADP 2016

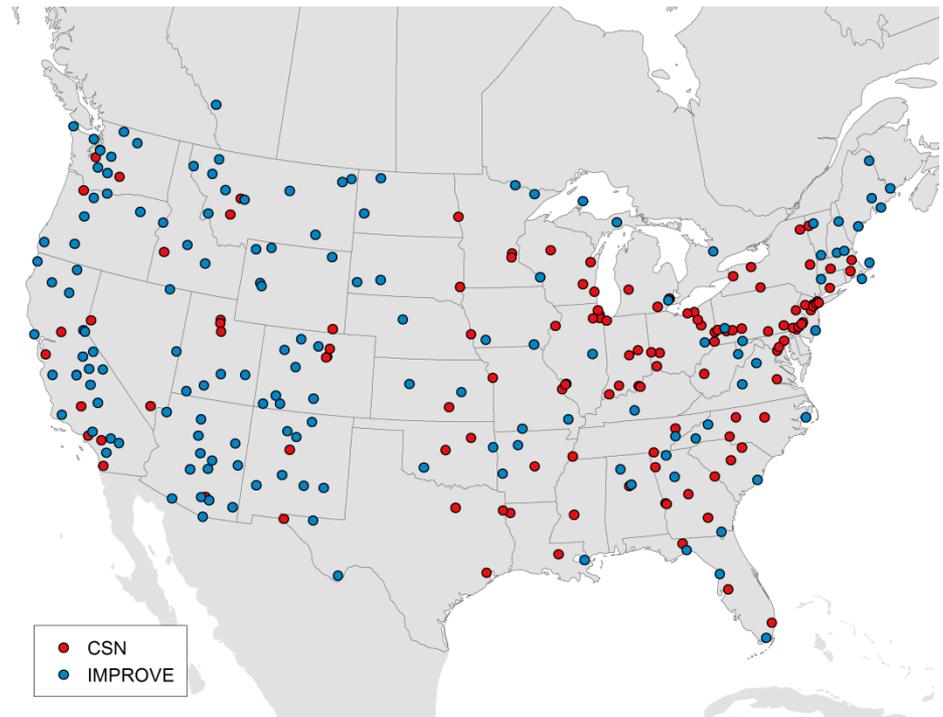
November 2, 2016

Santa Fe, New Mexico

---

# CSN and IMPROVE

- National particulate matter (PM) speciation networks
- CSN
  - health effects
  - Impact of control strategies
- IMPROVE
  - visibility at National Parks
  - Regional Haze Rule
- Both networks
  - Long term trends
  - Comparison to models
  - Sources



# IMPROVE and CSN Carbonaceous Aerosol Characterization

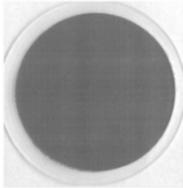
## Current Method

- Thermal optical reflectance (TOR)
  - Organic carbon (OC)
  - Elemental carbon (EC)
- Quartz filter
  - Destructive to sample
- IMPROVE-like sampler
- Long-time series of data
  - Beginning 2007-10 for CSN
  - Beginning 1988 for IMPROVE

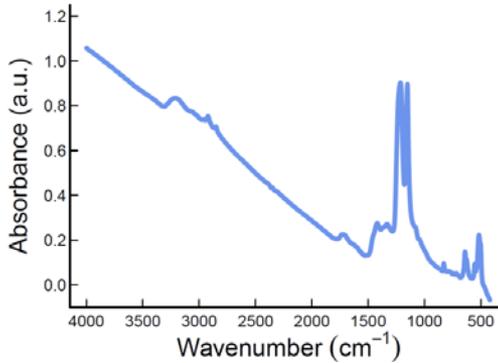
## Alternative Approach

- Infrared Spectroscopy (FT-IR)
  - Predict TOR OC and EC
- PTFE (Teflon) filters
  - Routinely collected for elements, mass, absorption
  - Non-destructive analysis
  - Move toward single channel sampling
- Existing samplers
- Continue TOR time-series
- Less expensive than TOR

# Characterizing Carbonaceous PM



ambient sampled  
teflon filter



FT-IR spectrum

TOR OC and EC  
calibrations

TOR OC, EC

This talk

Functional group  
calibrations

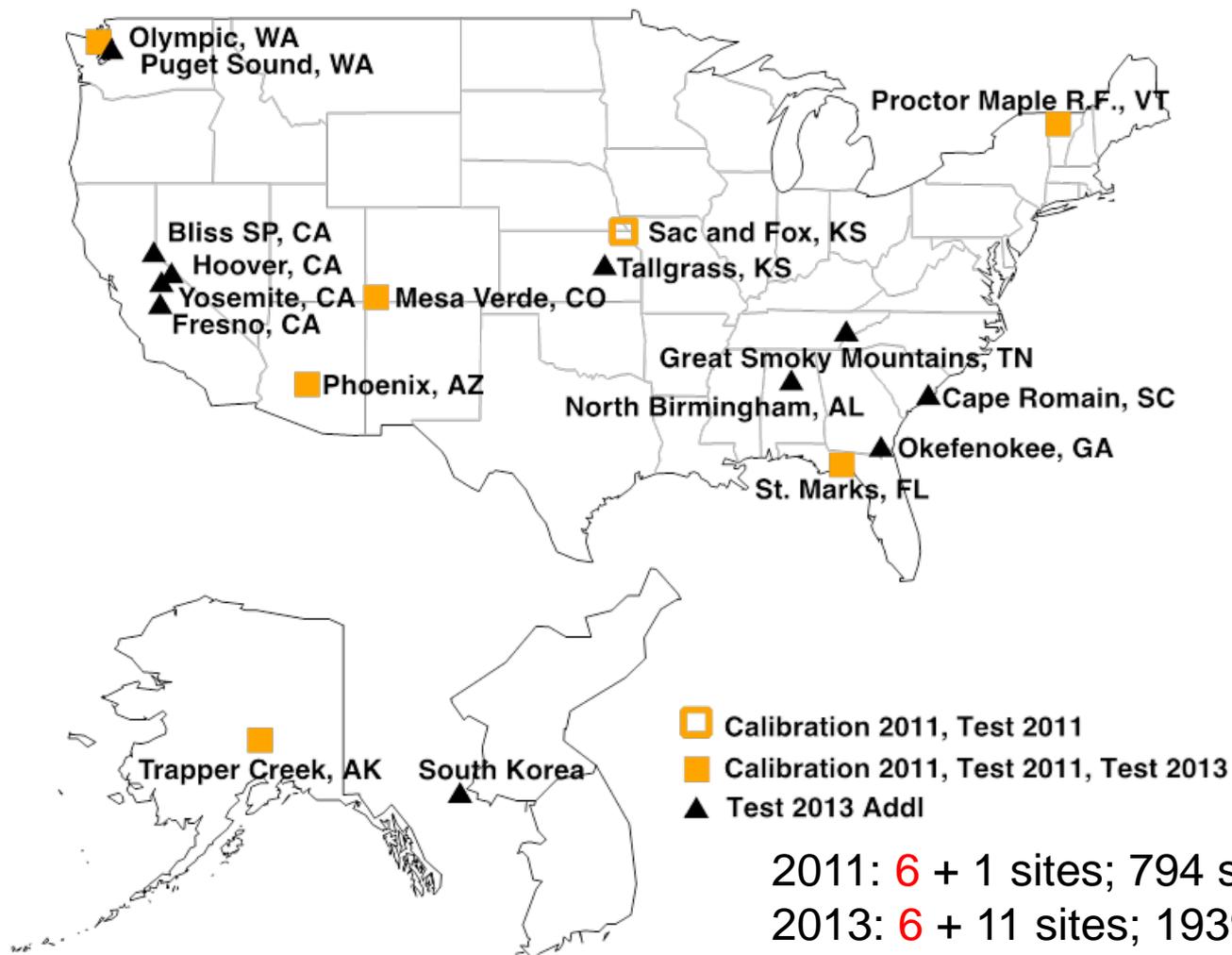
functional groups, OM, OM/OC, O/C

Poster session 6pm

Clusters/  
calibration

Source  
apportionment

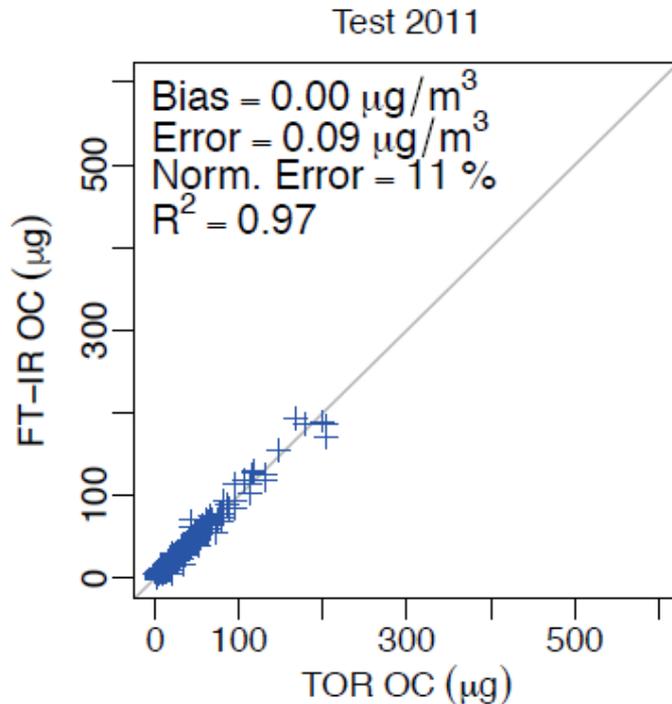
# IMPROVE 2011 and 2013



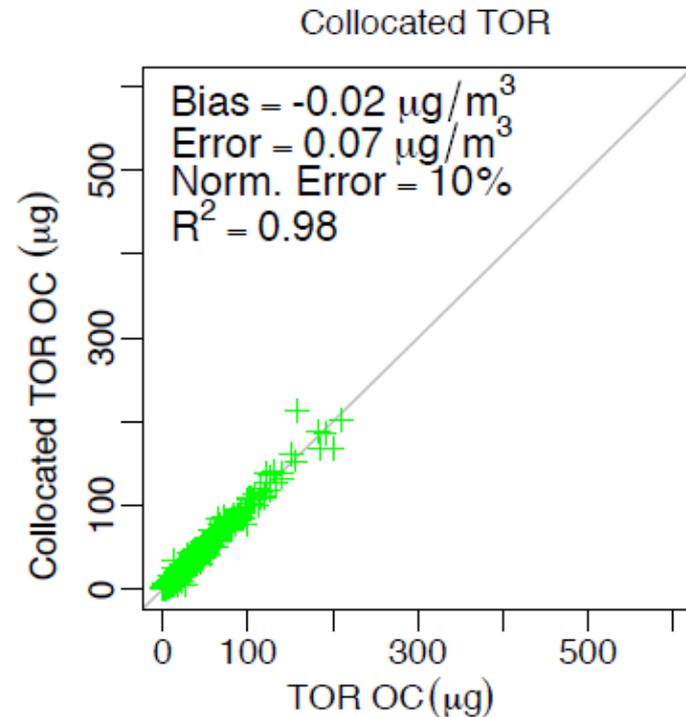
# Methods

- FT-IR spectra of Teflon samples
  - 5 minutes analysis time
  - Baseline corrected using automated program
- TOR OC and EC data from FED website
- Calibration
  - Inputs: spectra from 2/3 of 2011 samples and parallel TOR data
  - Model: Partial least squares (PLS) regression
    - Correlates spectra to TOR OC and EC
- Evaluation of calibration
  - 1/3 of 2011 sample spectra
  - all of 2013 sample spectra

# IMPROVE FT-IR OC



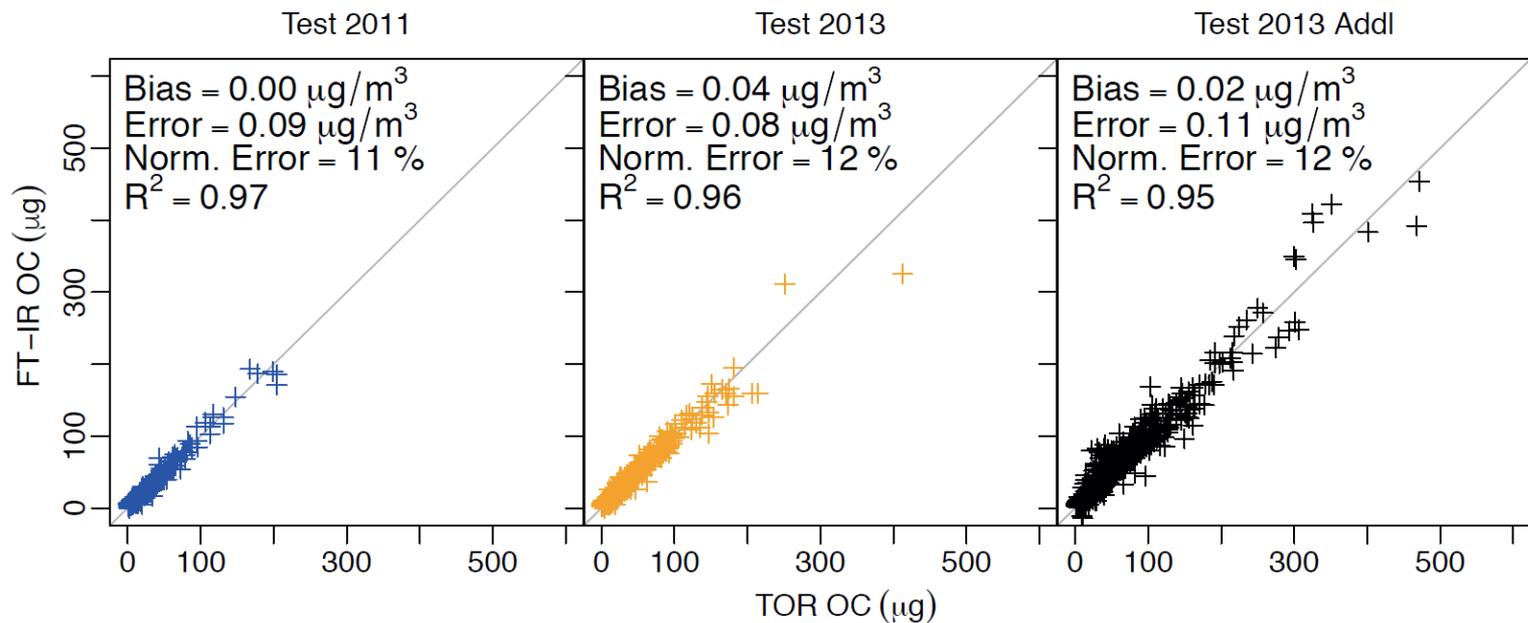
	FT-IR OC
MDL ( $\mu\text{g}/\text{m}^3$ )	0.14
% below MDL	3
precision ( $\mu\text{g}/\text{m}^3$ )	0.12



	TOR OC
MDL ( $\mu\text{g}/\text{m}^3$ )	0.05
% below MDL	2
precision ( $\mu\text{g}/\text{m}^3$ )	0.14

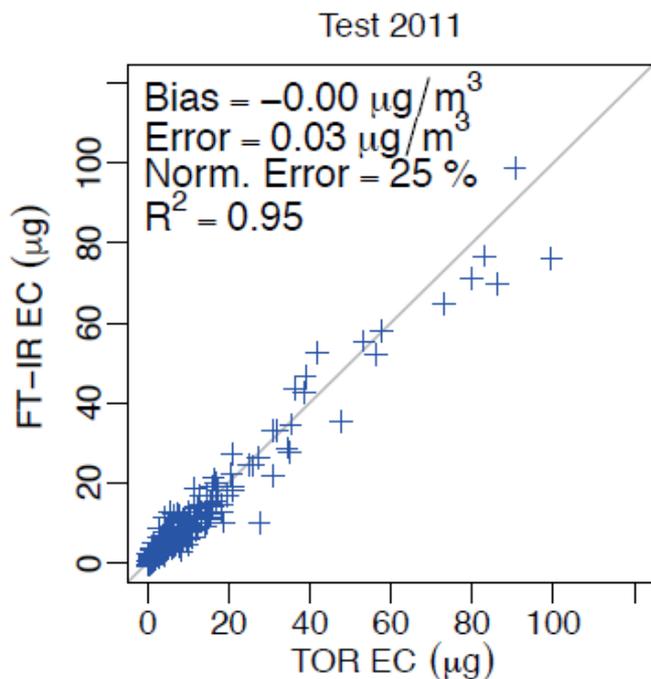
# IMPROVE FT-IR OC

extending predictions to different years and sites

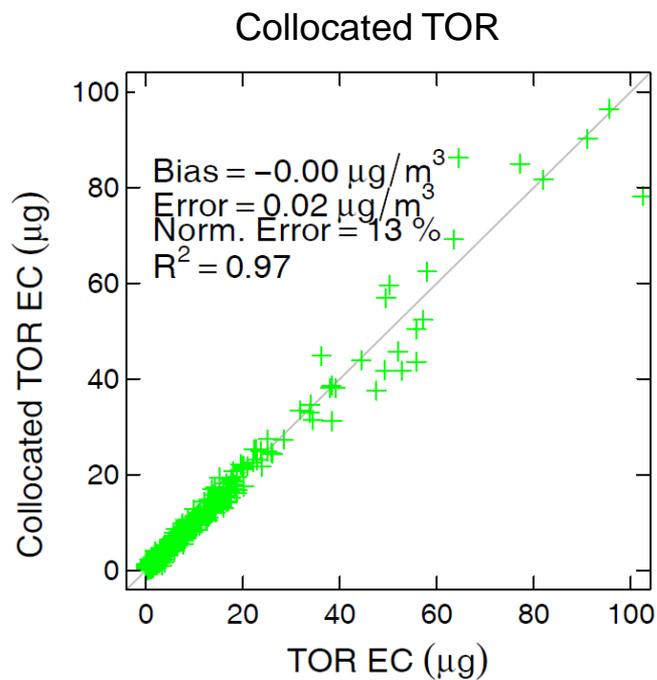


- Accurate predictions for different year
- Accurate predictions for different sites

# IMPROVE FT-IR EC



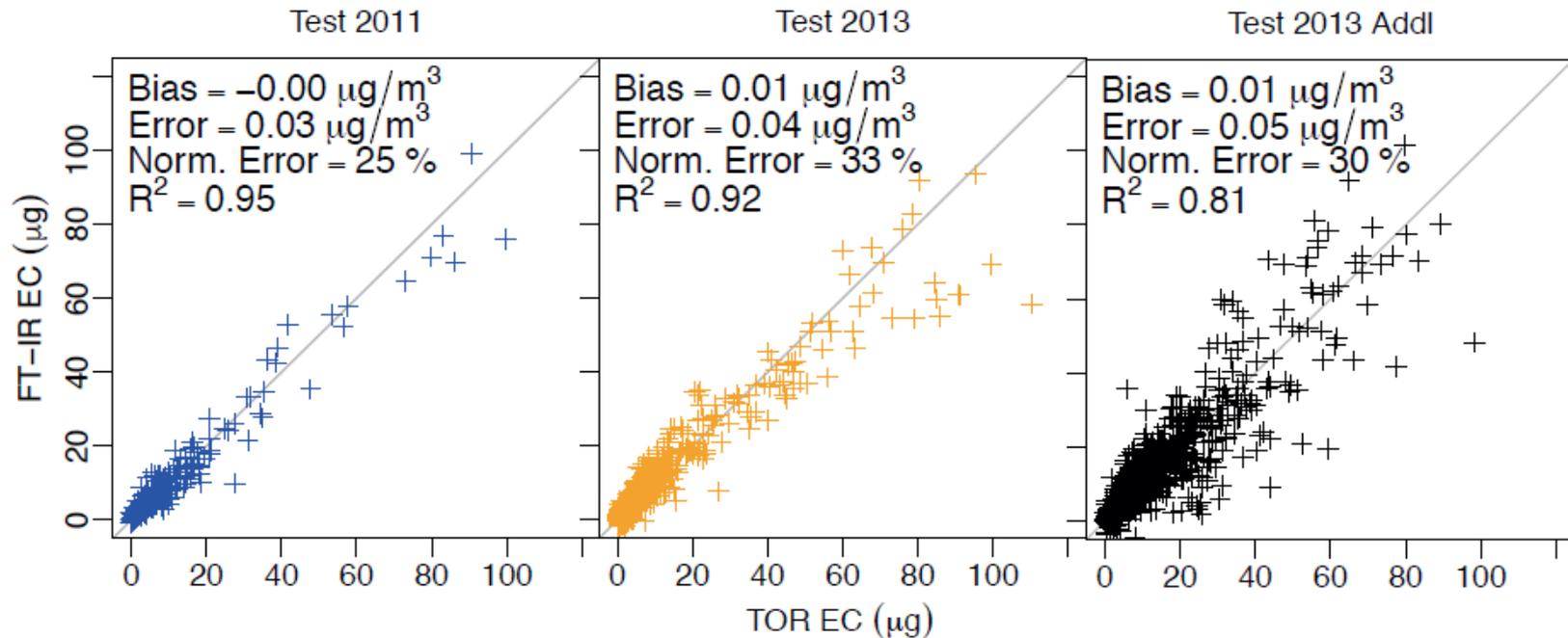
	FT-IR EC
MDL ( $\mu\text{g}/\text{m}^3$ )	0.01
% below MDL	1
precision ( $\mu\text{g}/\text{m}^3$ )	0.04



	TOR EC
MDL ( $\mu\text{g}/\text{m}^3$ )	0.01
% below MDL	3
precision ( $\mu\text{g}/\text{m}^3$ )	0.11

# IMPROVE FT-IR EC

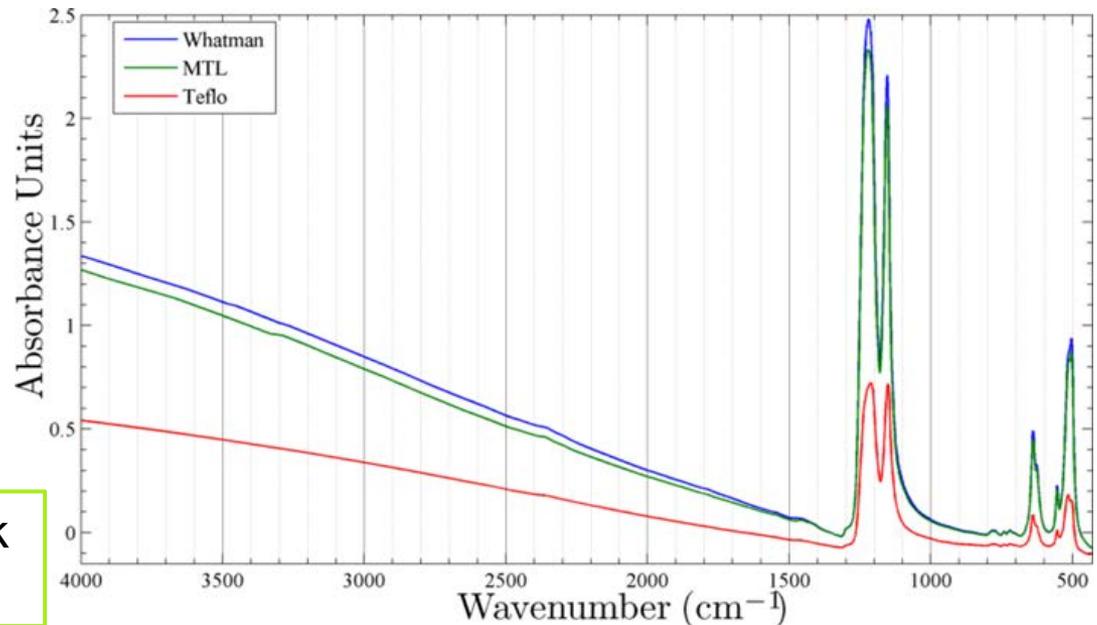
extending predictions to different years and sites



- Accurate predictions for different year
- Accurate but a bit noisier predictions for different sites

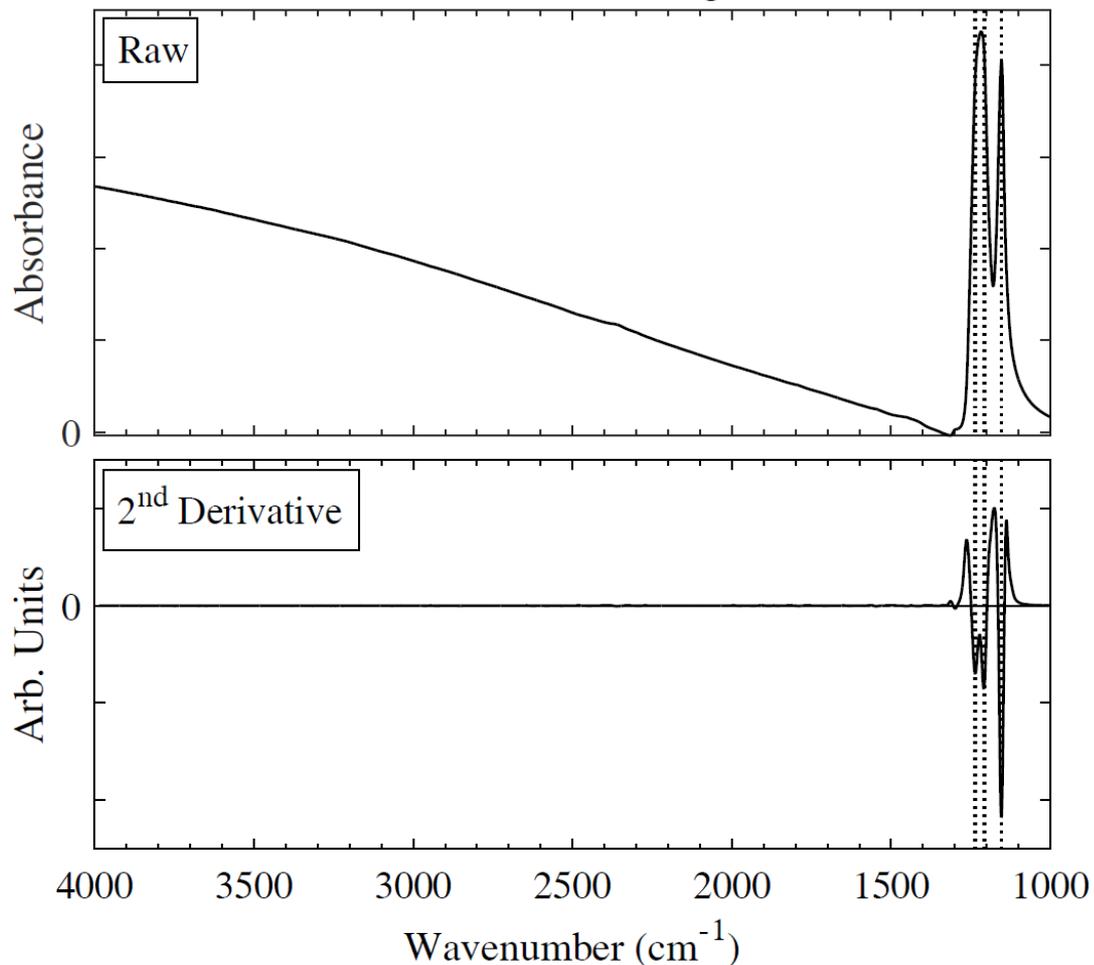
# New Questions with CSN

- Can we predict samples with ~5X lower aerial density?
- What functional groups is FT-IR using to predict OC and EC?
- Can we predict FRM filters from the CSN calibration?
  - CSN
    - 6.7 Ipm
    - Whatman
  - FRM
    - 16.7 Ipm
    - Mostly MTL



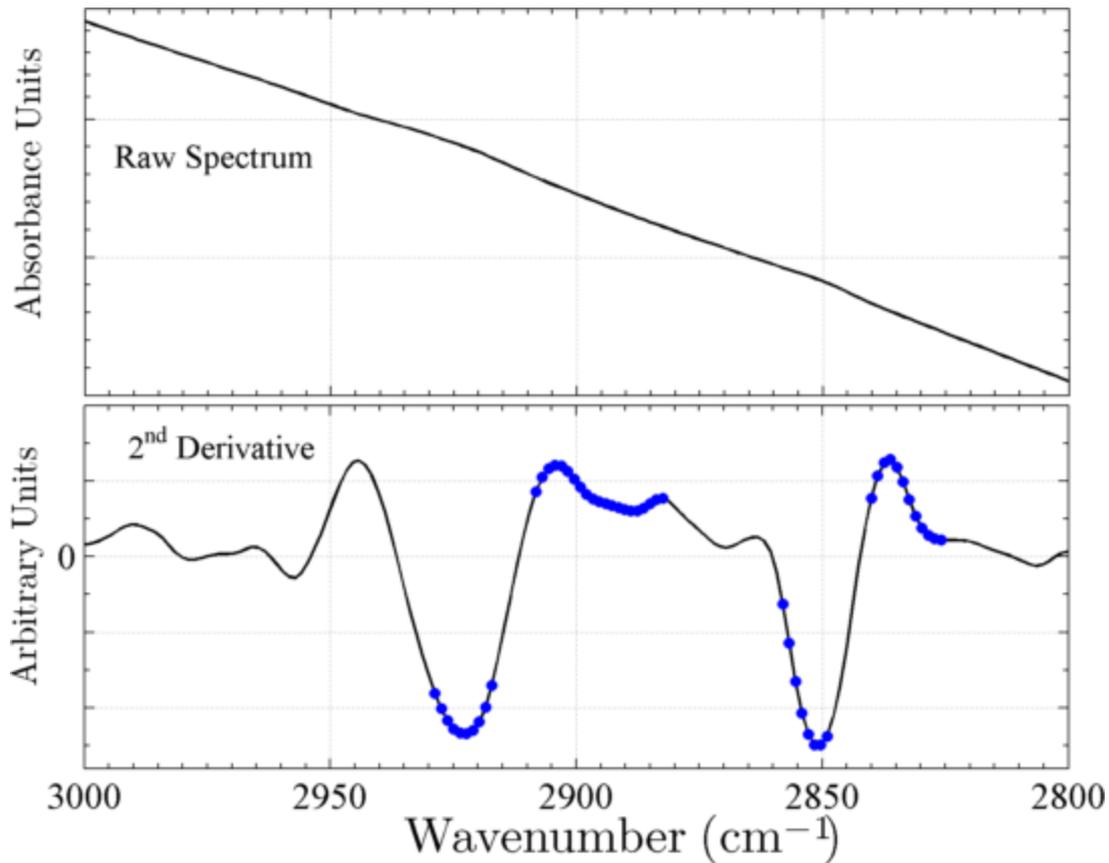
FRM is a mass only network  
with ~900 monitoring sites

# New Questions Need New Method: 2<sup>nd</sup> Derivative Spectra



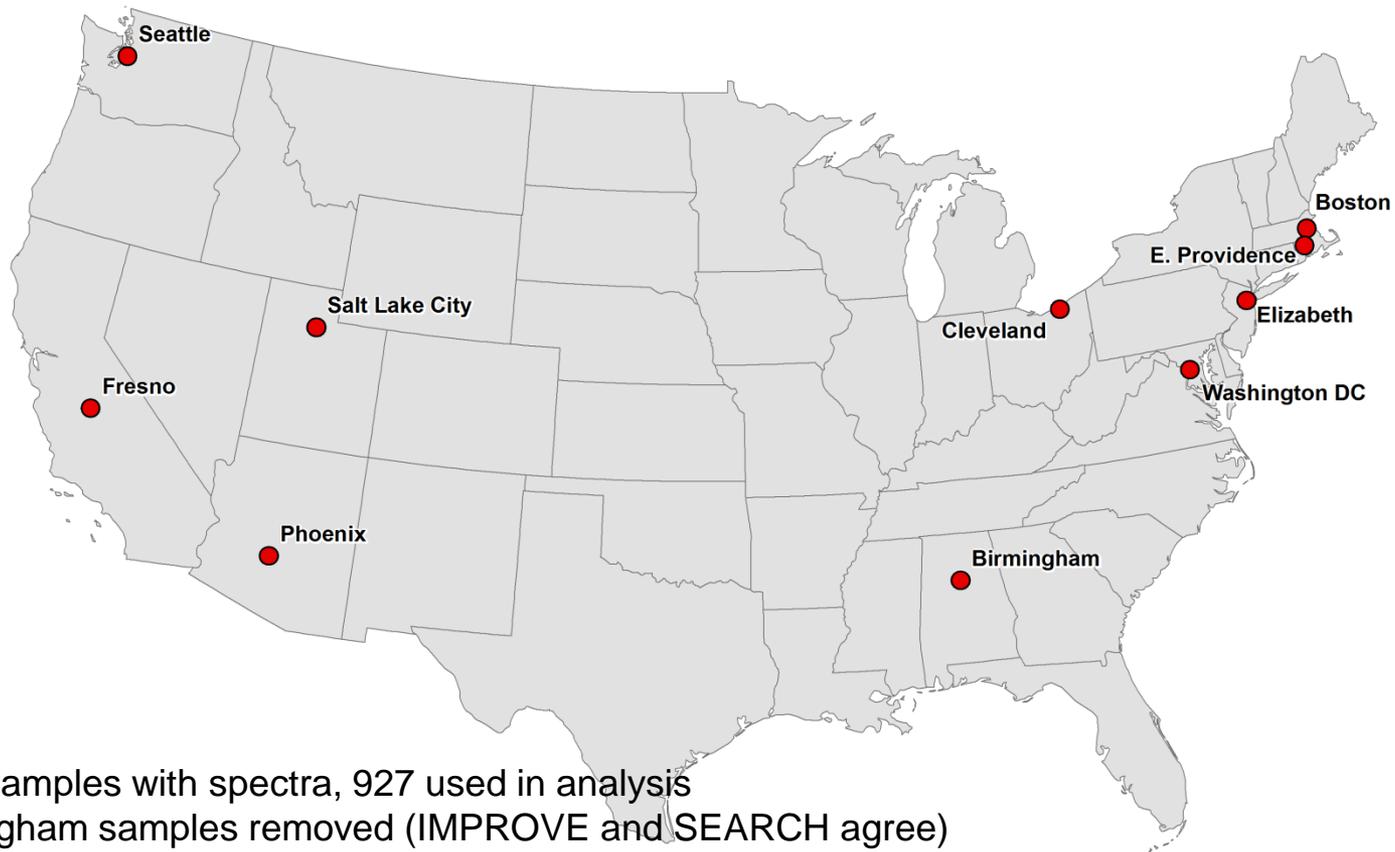
- Removes filter scattering from spectra

# New Questions Need New Method: 2<sup>nd</sup> Derivative Spectra



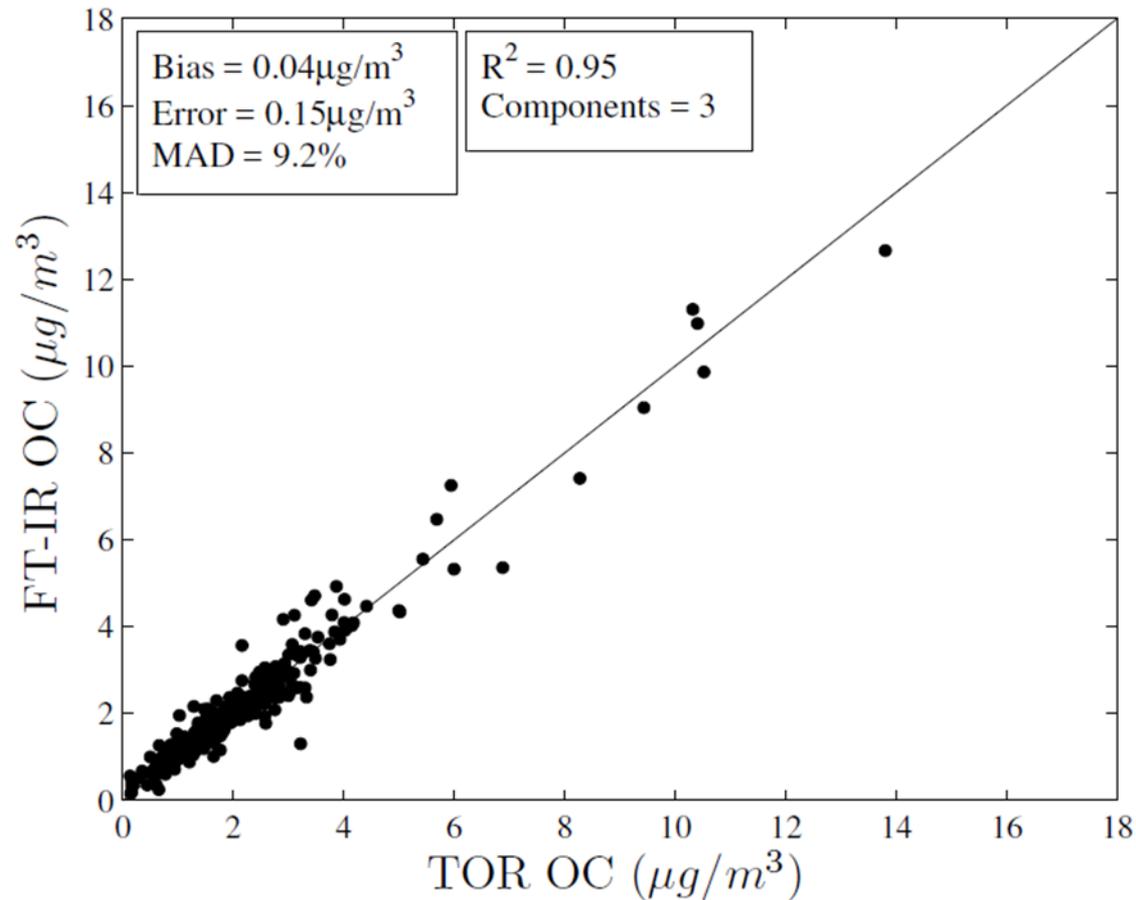
- Increases signal to background (filter) ratio

# CSN sites analyzed in 2013



1050 samples with spectra, 927 used in analysis  
Birmingham samples removed (IMPROVE and SEARCH agree)  
collocated Cleveland samples removed (maintenance record)

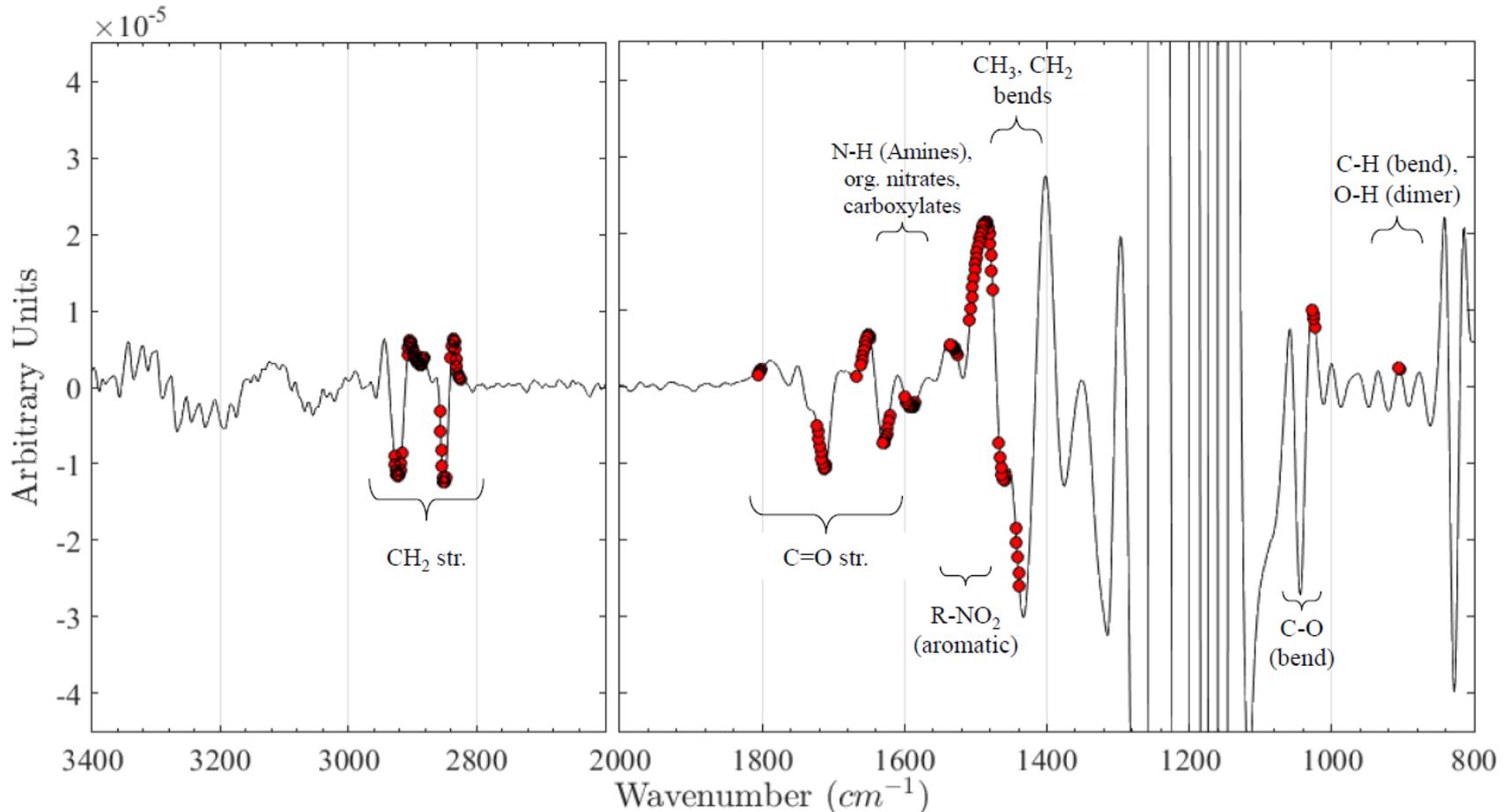
# Prediction of TOR OC using 2<sup>nd</sup> derivative spectra in CSN



## IMPROVE OC

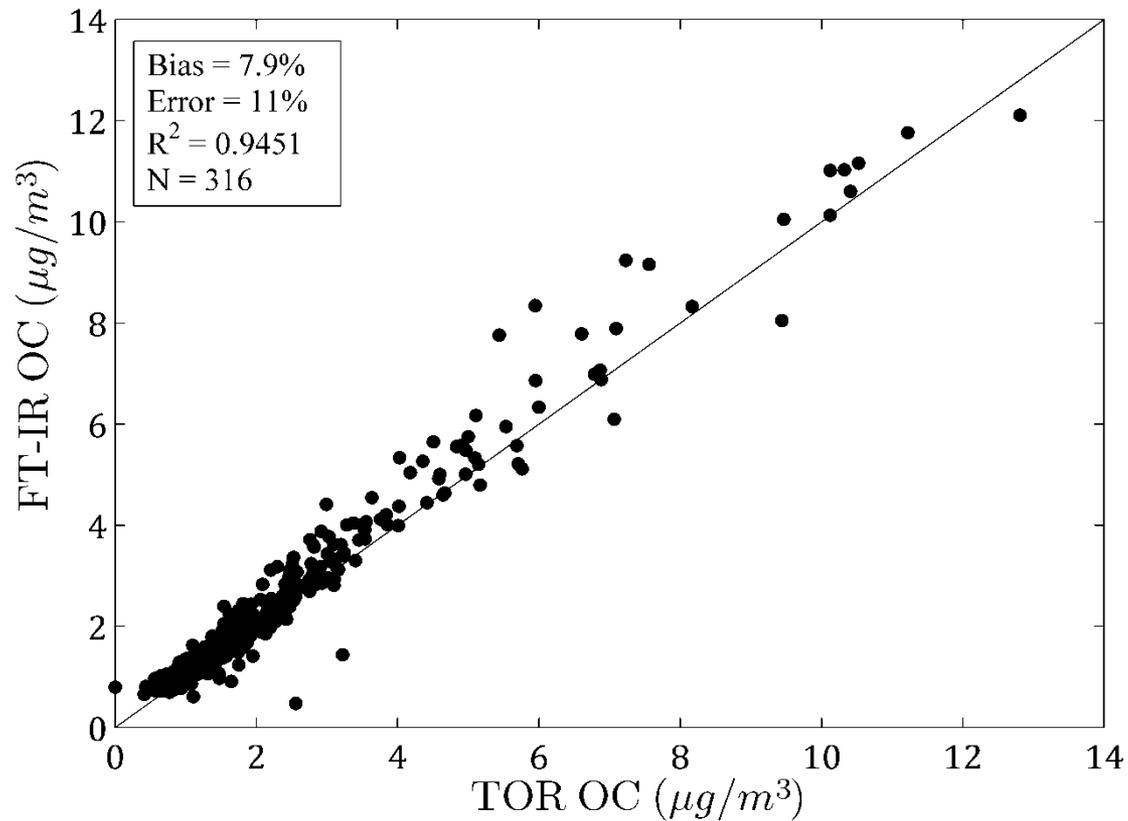
Bias =  $0.02 \mu\text{g}/\text{m}^3$   
Error =  $0.08 \mu\text{g}/\text{m}^3$   
Norm. Error = 11%  
 $R^2 = 0.96$

# Functional groups used to predict OC

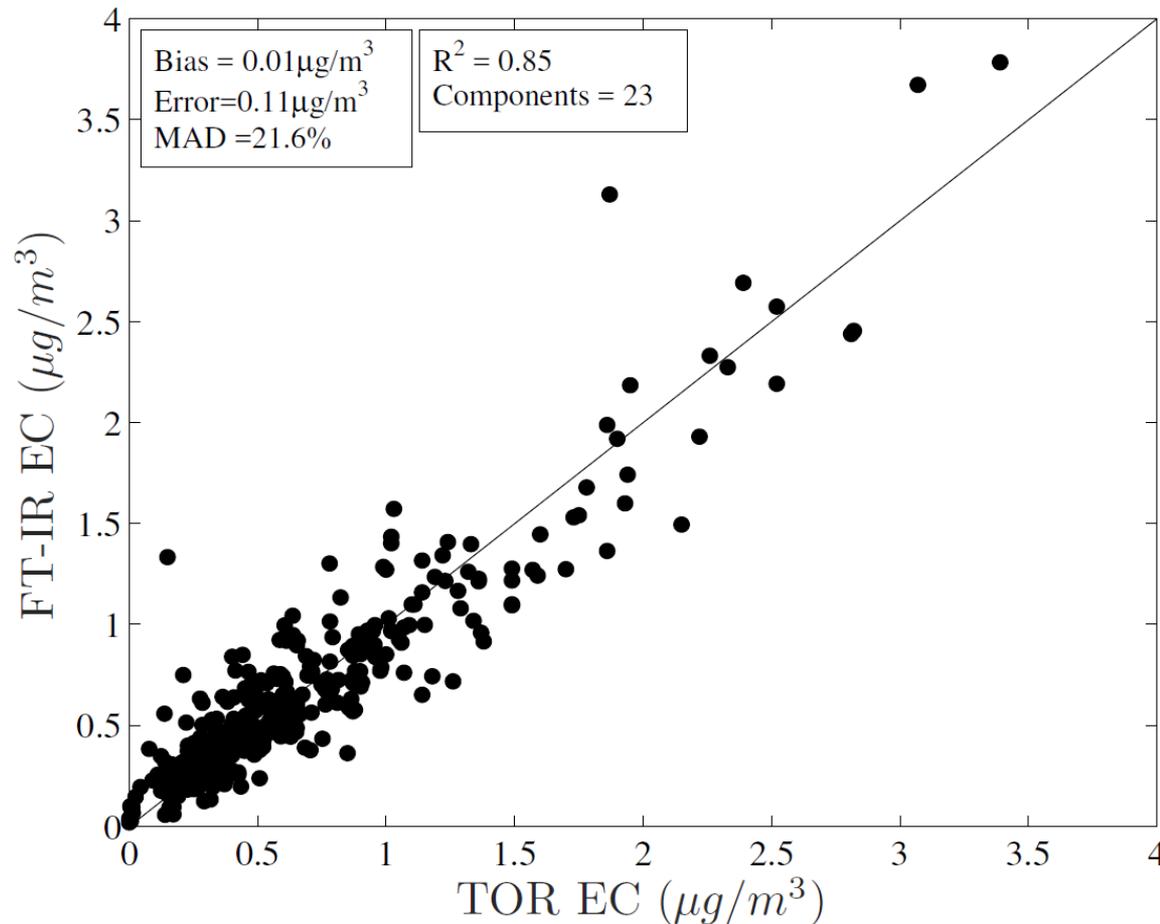


2<sup>nd</sup> Derivative spectrum with important wavenumbers used to predict OC in red

# Predicting TOR OC on FRM samples



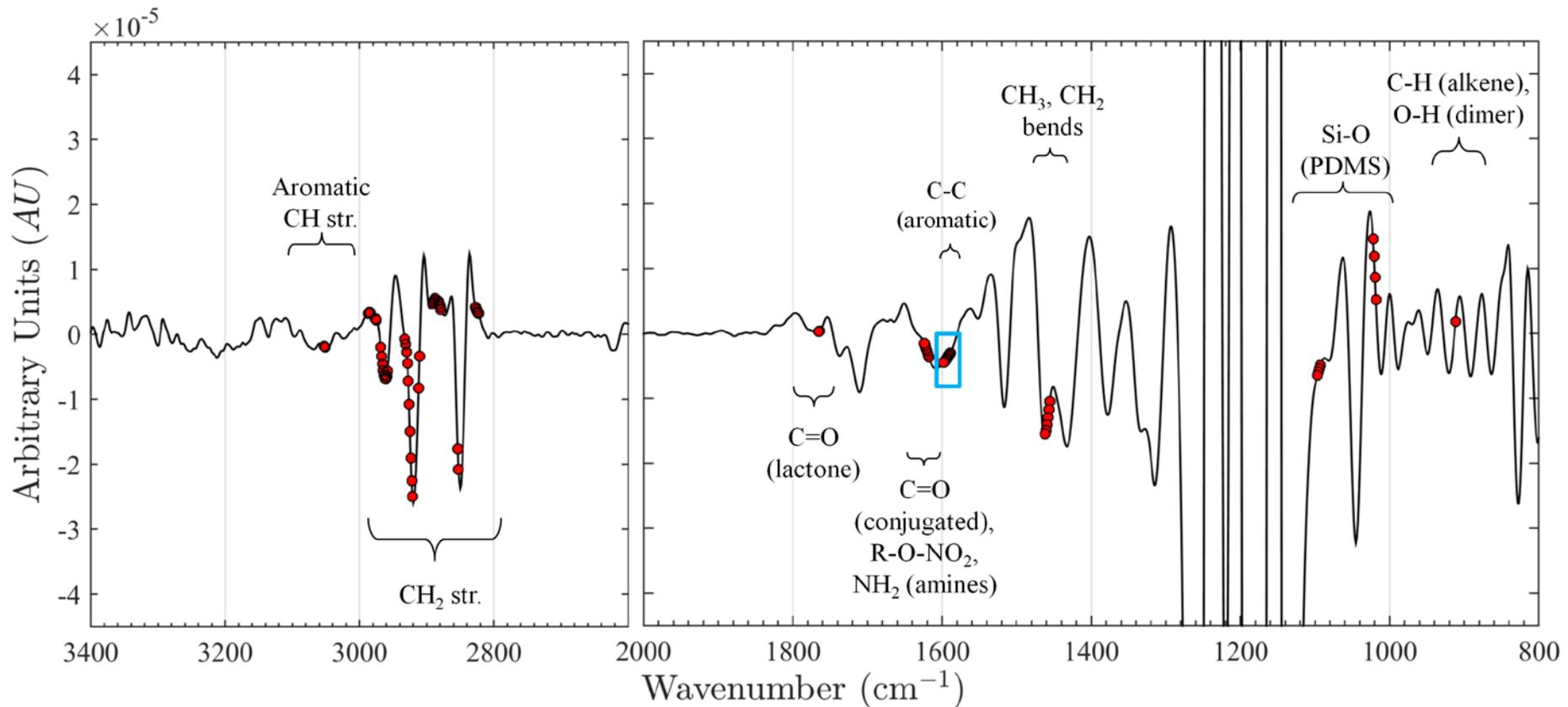
# EC prediction for CSN using 2<sup>nd</sup> Derivative spectra



## IMPROVE EC

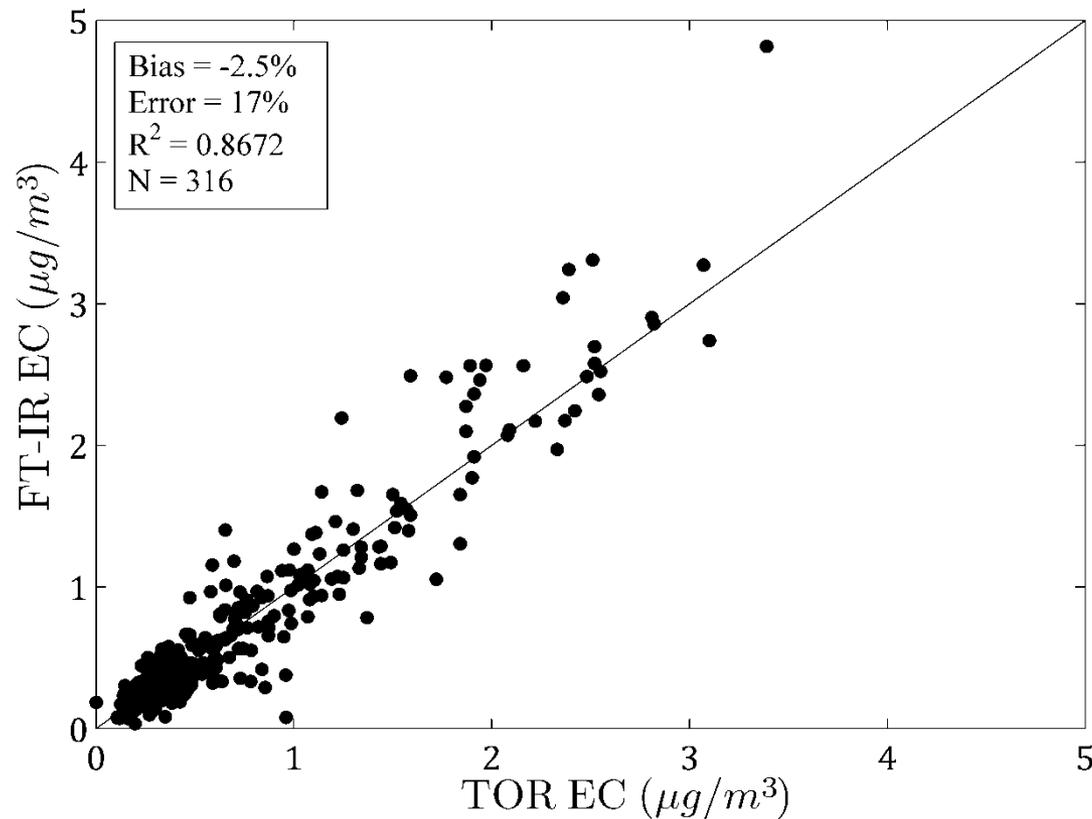
Bias =  $0.00\mu\text{g}/\text{m}^3$   
Error =  $0.02\mu\text{g}/\text{m}^3$   
Norm. Error = 21%  
 $R^2 = 0.96$

# Functional groups used to predict EC



2<sup>nd</sup> Derivative spectrum with important wavenumbers used to predict EC in red

# Predicting TOR EC on FRM samples



# Conclusions

- FT-IR can reproduce TOR OC and EC in IMPROVE and CSN with good accuracy and precision
- Predictions based on appropriate functional groups
- Can predict TOR OC and EC on FRM samples which have no speciated data

# Acknowledgements

- Funding for this project:
  - EPA and IMPROVE program an (National Park Service Cooperative Agreement P11AC91045),
  - Swiss Polytechnic University-Lausanne (EPFL) funding
  - EPRI
- Collaborators, post-docs and students:

Sean Raffuse	Adele Kuzmiakova
Katie George	Travis Ruthenburg
Mohammed Kamruzzaman	Charity Coury
- CSN and IMPROVE program and state personnel
- Bret Schichtel and Bill Malm, National Park Service
- Beth Landis, Joann Rice and Neil Frank, EPA
- Tony Wexler, UC Davis