Using a Non-destructive, Inexpensive Method to Measure Carbonaceous Particulate Matter in CSN and IMPROVE

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- Collaborators, post-docs and students:

Satoshi Takahama	Sean Raffuse
Andy Weakley	Katie George
Mohammed Kamruzzaman	Adele Kuzmiakova
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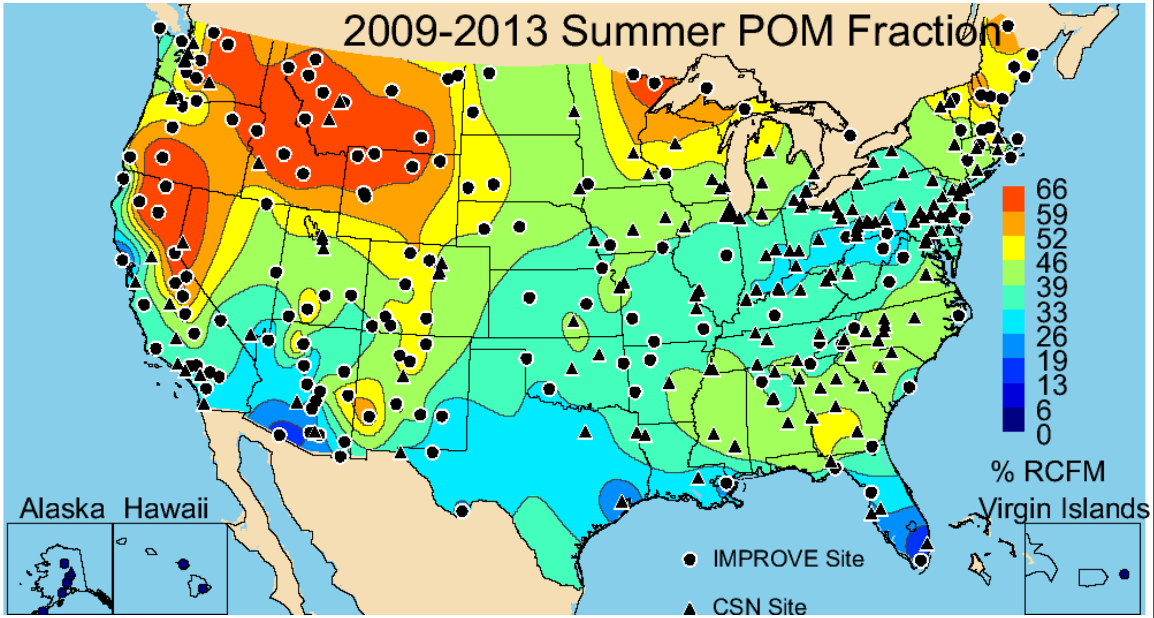
Outline

- Motivation for developing alternate method for carbon characterization
- Alternative method: Fourier transform-infrared (FT-IR) spectroscopy
- FT-IR in CSN and IMPROVE
  - Reproduce TOR OC and EC
  - Quantify OM/OC and functional groups
  - Attribute sources
- Conclusions

Organic Particulate Matter

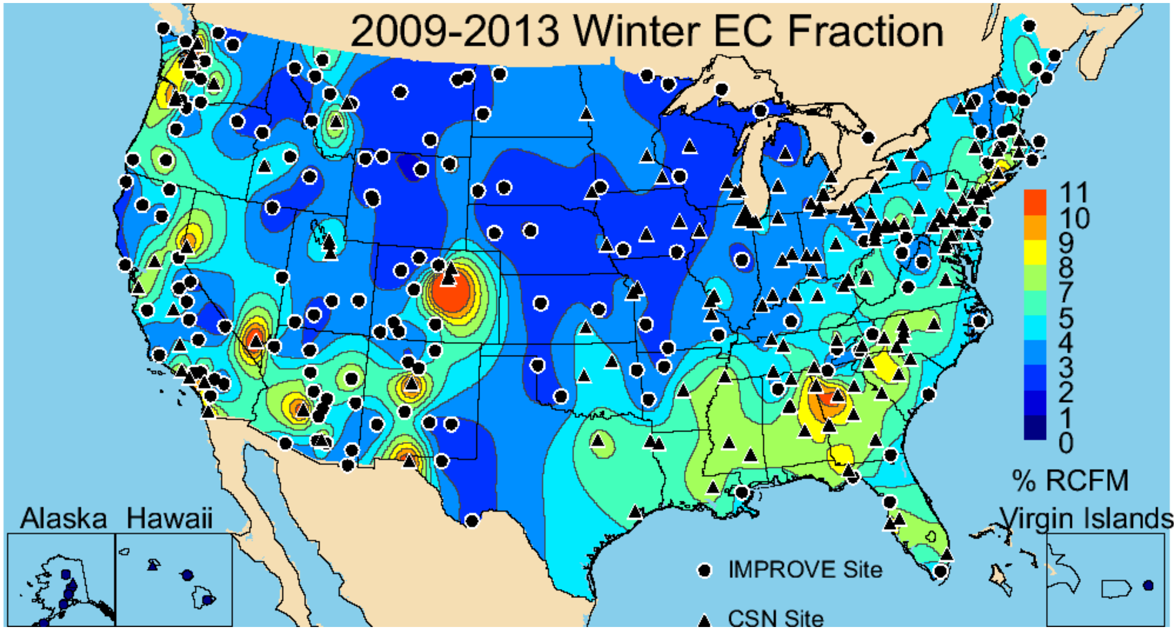
- Large % of PM
- Complex mixture
- Directly emitted and formed in atmosphere
- Climate
- Visibility
- Health



Courtesy of J. Hand, after Hand et al., Spatial and Temporal Trends in OC and EC across the US, 2013

Elemental Carbon PM

- Smaller fraction of PM
- Visibility
- Radiative forcing
  - Solar absorption
  - Snow albedo
  - Clouds



Courtesy of J. Hand, after Hand et al., Spatial and Temporal Trends in OC and EC across the US, 2013

IMPROVE and CSN Carbonaceous Aerosol Characterization

- Same sampler and filter
- Thermal optical reflectance (TOR)
  - Organic carbon (OC)
  - Elemental carbon (EC)
- Long-time series of data
  - Beginning 2007-10 for CSN
  - Beginning 1988 for IMPROVE

CSN carbon sampler

Limitations of TOR method

- Expensive
- Destructive to sample
- Prone to sampling artifacts
- Organic matter (OM) estimated
  - Rural OM/OC = 1.8
  - Urban OM/OC = 1.4
- Operational definitions of OC and EC

Wish list for carbon measurements in monitoring networks

- Measurements
  - Maintain long time record of TOR OC and EC
  - Measure OM and OM/OC
  - Atmospherically relevant chemical properties
  - Source-related chemical properties
- Mechanics of the method
  - Inexpensive and fast
  - Non-destructive (no pyrolysis)
  - No sampling artifact
  - Use filters routinely collected in monitoring networks

Outline

- Motivation for developing alternate method for carbon characterization
- **Alternative method: Fourier transform-infrared (FT-IR) spectroscopy**
- FT-IR in CSN and IMPROVE
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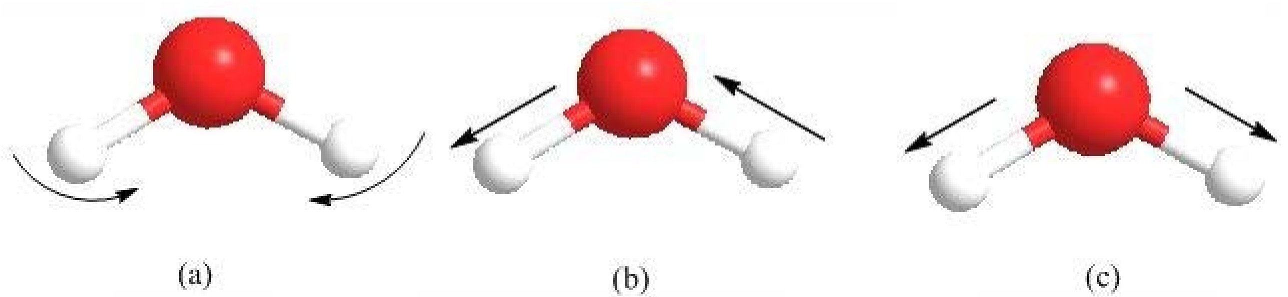
Alternate approach – Fourier Transform Infrared (FT-IR) spectroscopy

- Simple analytical technique that many of us learned about (and forgot) in college chemistry
- Chemical bonds absorb Infrared light
- Identify/quantify functional groups (C-H, C=O)
- For example, H_2O



bending | antisymmetric stretching | symmetric stretching

Applications of FT-IR

Identification of explosives and controlled substances (functional groups)

www,channel3000.com

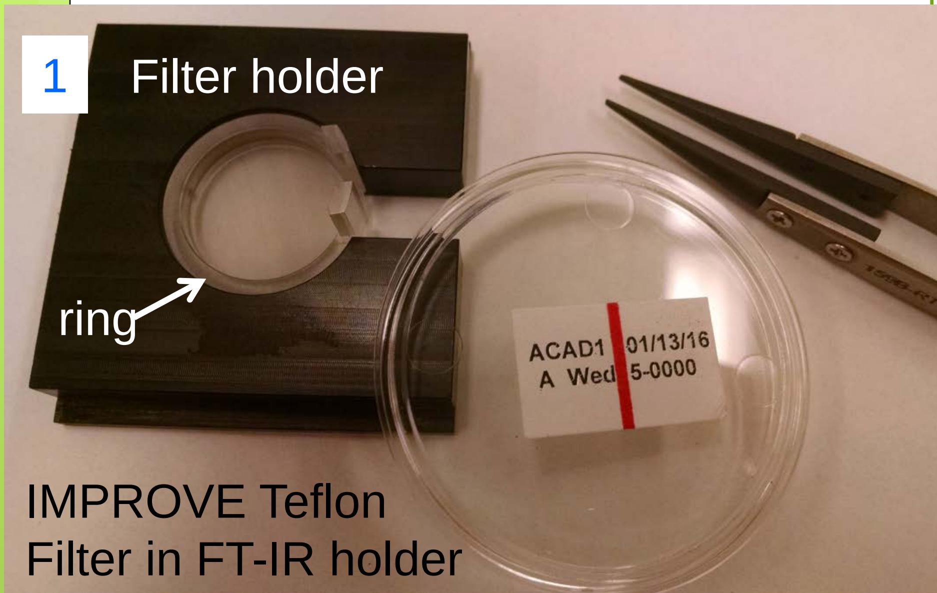
Clover or eucalyptus honey (**source**), **composition** of extra virgin olive oil, **rapid, routine** detection of impurities in food

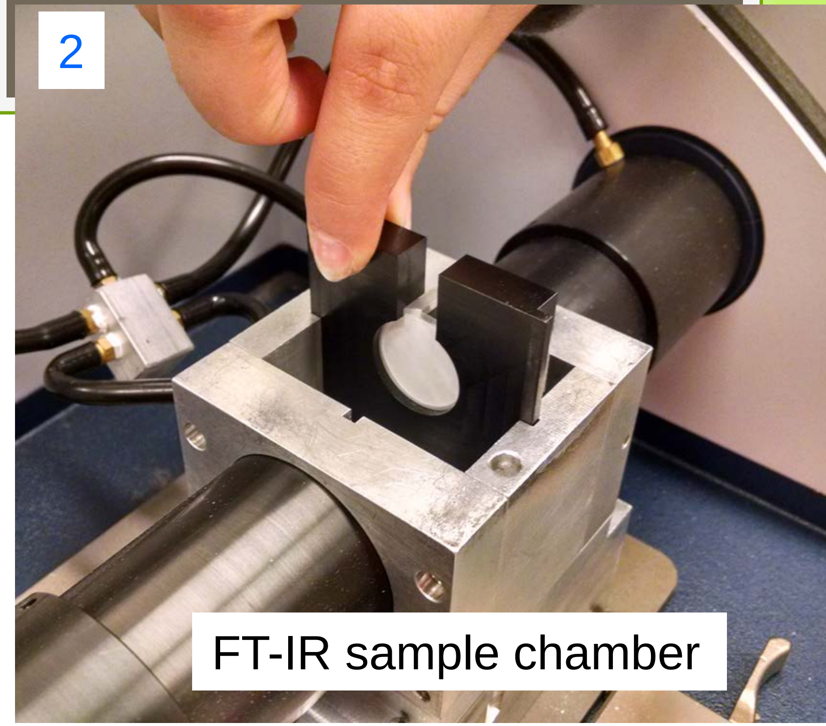
Forgery, methods and deterioration of art. **Non-destructively** identify and quantify **organic** materials such as varnishes, paint media, adhesives, and plastics, and changes in the composition as the result of **aging**

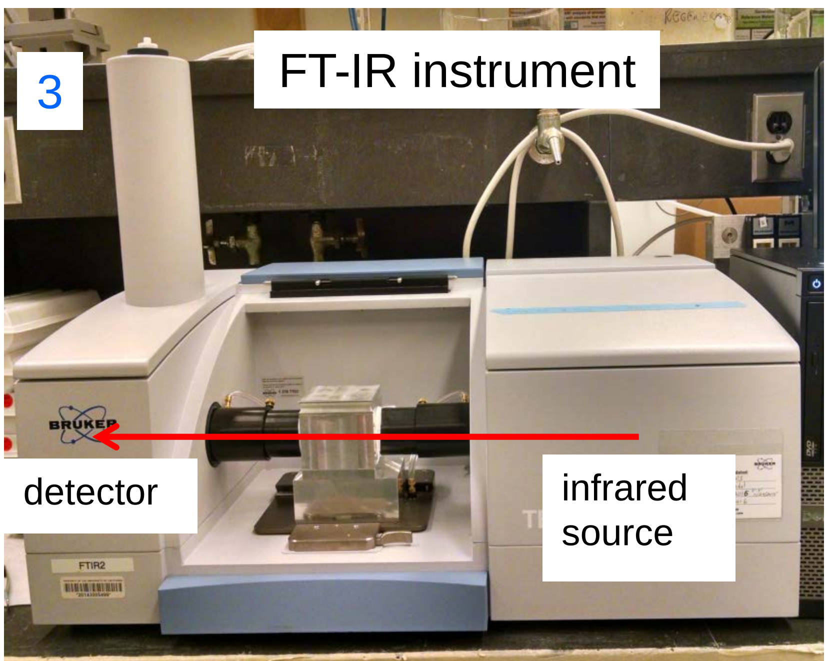
M. S. Lesney, Analyzing Artistry, Todays Chemist at Work, 2002.
W.I. Atkinson, Spectroscopy Ranges Far Afield, Todays Chemist at Work, 9 (12), 19-22, 2000.

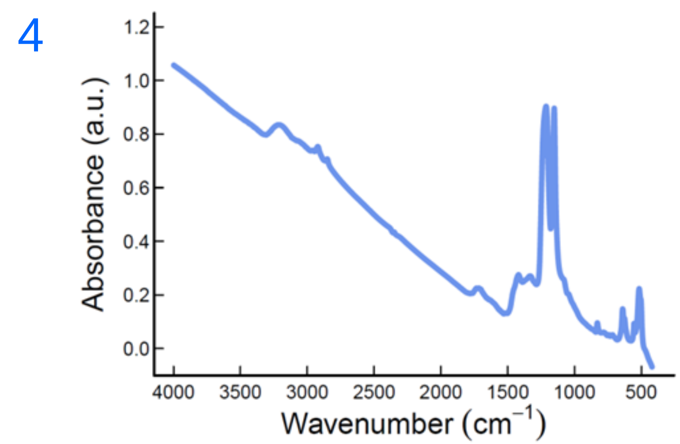
FT-IR in PM monitoring networks

- FT-IR can measure:
  - TOR-equivalent OC, EC – maintain time-series
  - Functional groups (C-H, C=O, C-NH_2)
    - Organic matter (OM), OM/OC
    - Atmospherically relevant chemical properties
  - Source information for OM
- Inexpensive and fast method
- Non-destructive
- Teflon filter samples
  - No organic sampling artifact
  - FRM (PM2.5 NAAQS), CSN, IMPROVE
  - No need for additional sampler









FT-IR spectrum from one Teflon filter sample

FT-IR on particles collected on Teflon filters

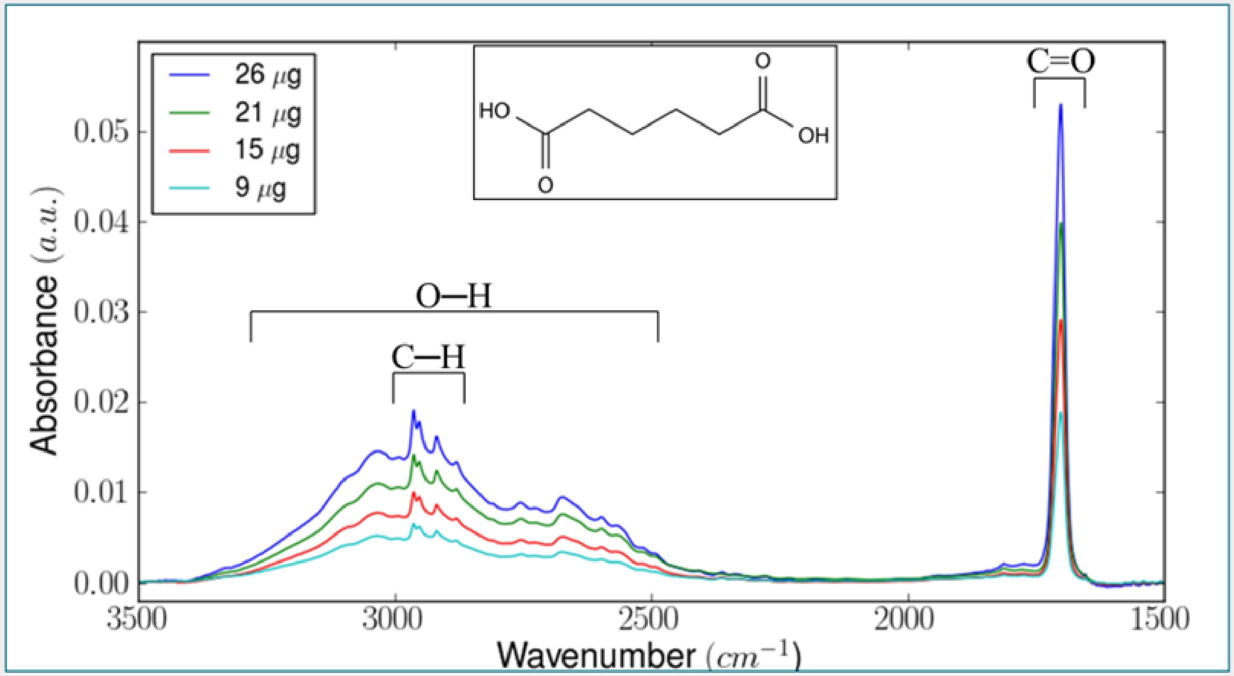


Figure 1. Adipic acid molecular structure and spectra with labeled functional group bands: C-H stretch, 3000-2840 cm^{-1}; C=O stretch, 1720-1706 cm^{-1}; and broad O-H stretch, 3300-2500 cm^{-1}. [4]

Outline

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  - **Attribute sources**
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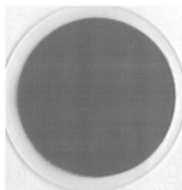
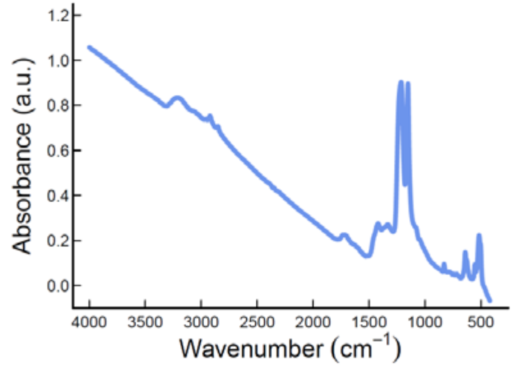
Characterizing Carbonaceous PM



ambient sampled teflon filter



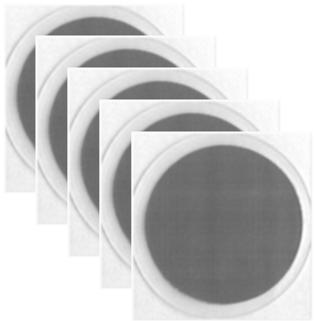
FT-IR spectrum

TOR OC and EC calibrations → TOR OC, EC

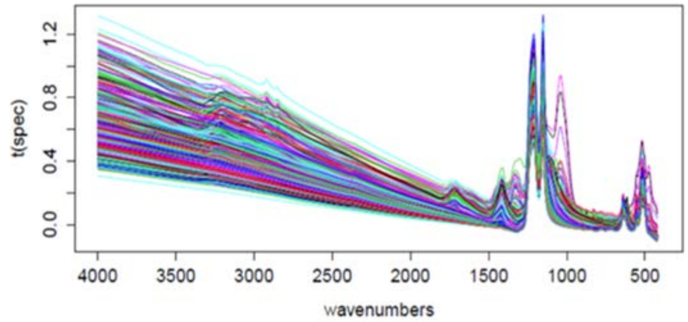
Functional group calibrations → functional groups, OM, OM/OC, O/C

Clusters/ calibration → Source apportionment

Calibration Development



ambient sampled teflon filters



FT-IR spectra

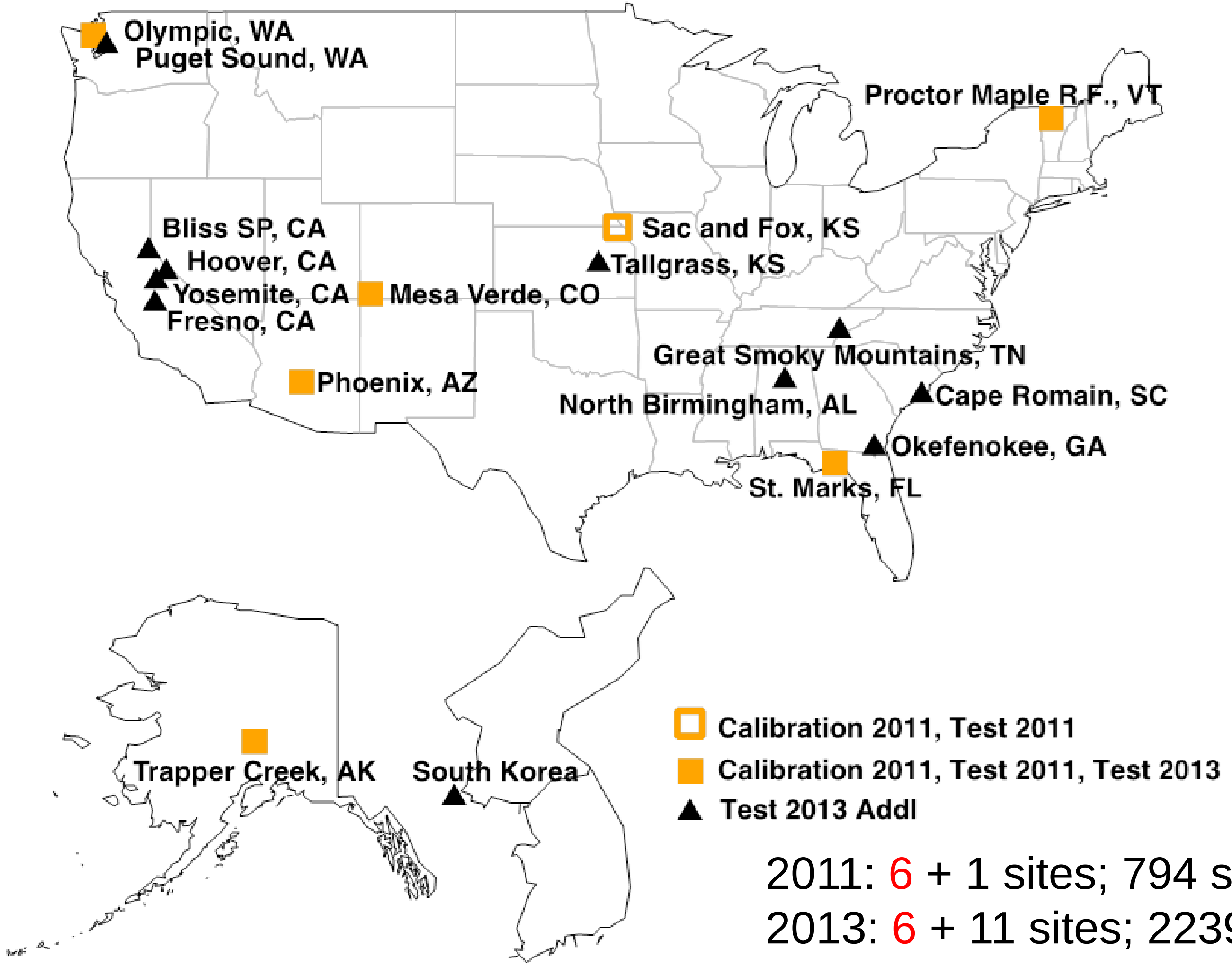
TOR data

TOR OC and EC calibrations

IMPROVE

CSN (FRM)

IMPROVE 2011 and 2013



2011: 6 + 1 sites; 794 samples
2013: 6 + 11 sites; 2239 samples

Methods

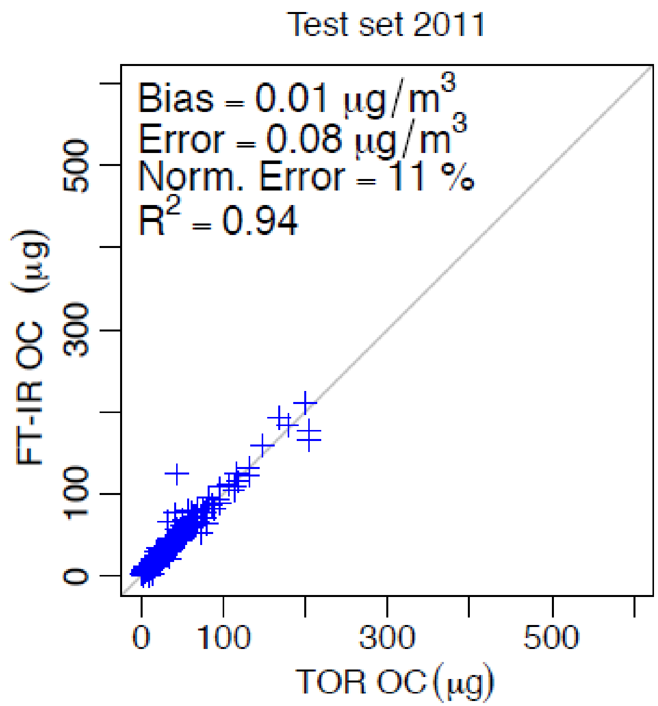
- FT-IR spectra of Teflon samples
- TOR OC and EC data
- Calibration
  - Inputs: spectra from 2/3 of 2011 samples and parallel TOR data
  - Model: Partial least squares (PLS) regression
    - Correlates spectra to TOR OC and EC
- Evaluation of calibration
  - 1/3 of 2011 sample spectra
  - all of 2013 sample spectra

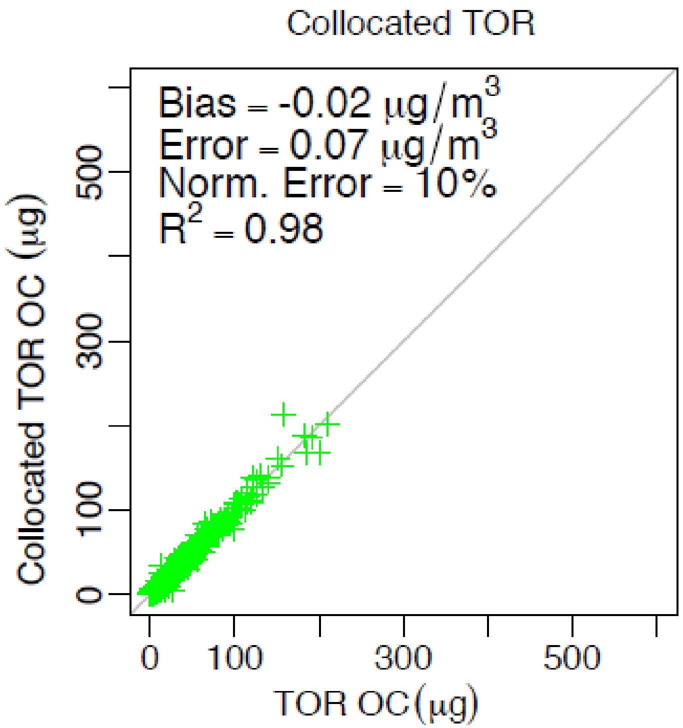
Performance Metrics

- Bias = FT-IR OC – TOR OC
- Error = |Bias|
- Normalized error = Error/TOR OC, %
- R^2

- Compare to collocated TOR data

IMPROVE FT-IR OC





	FT-IR OC
MDL (μg/m³)	0.14
% below MDL	3
precision (μg/m³)	0.12

	TOR OC
MDL (μg/m³)	0.05
% below MDL	2
precision (μg/m³)	0.14

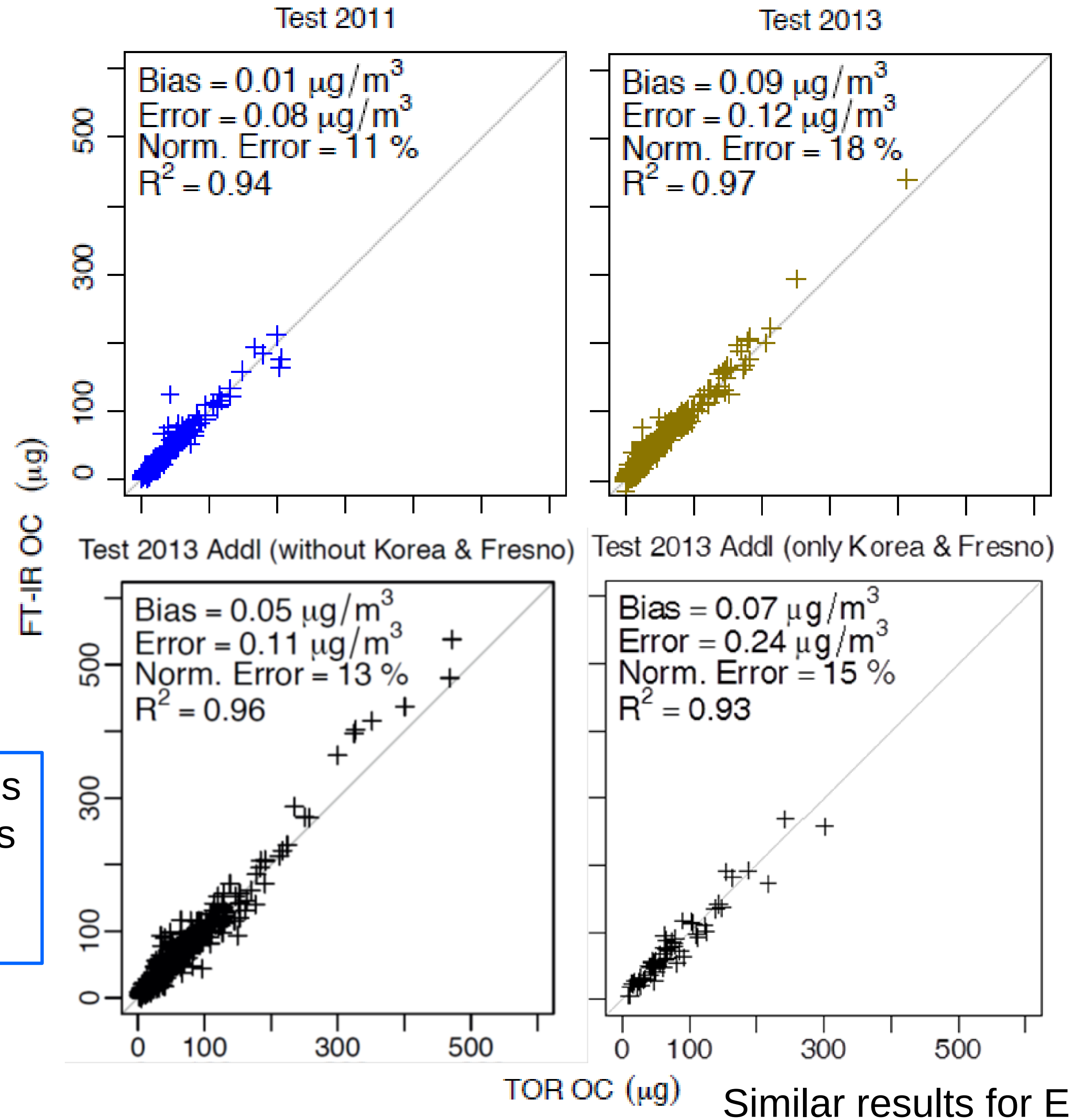
Dillner and Takahama, 2015a

IMPROVE FT-IR OC

extending predictions to different years and sites

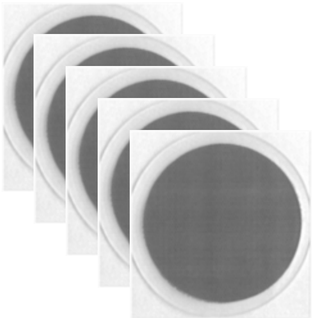
if Calibration samples ≅ Measured samples then, good measurements

Reggente, Dillner and Takahama, 2016

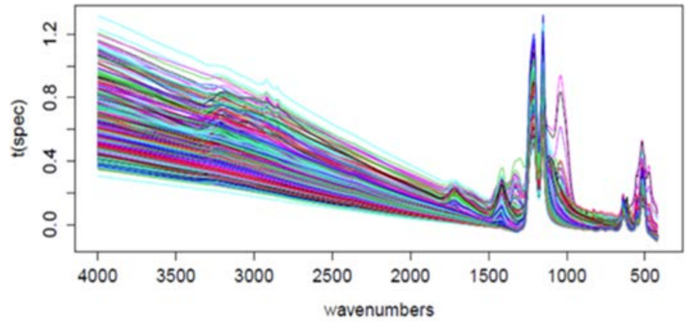


Similar results for EC

Calibration Development



ambient sampled teflon filters



FT-IR spectra

TOR data

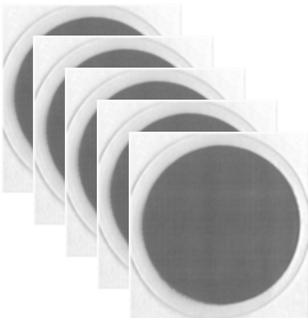
TOR OC and EC calibrations

IMPROVE

IMPROVE OC and EC summary

- High quality predictions
- Different sites and year

Calibration Development



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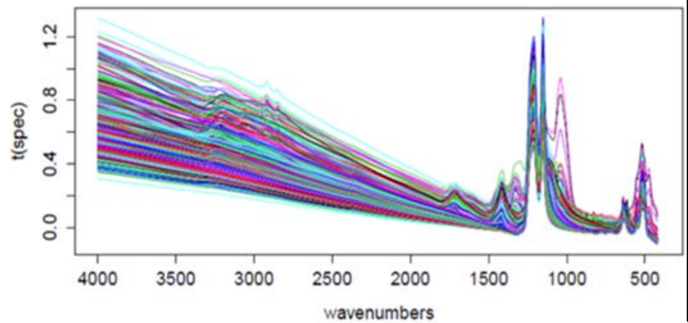


FT-IR spectra

TOR data

TOR OC and EC calibrations

IMPROVE

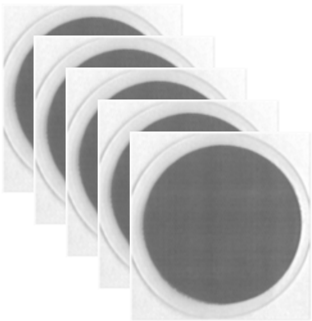
Next Step

- Extend calibrations network-wide

IMPROVE OC and EC summary

- High quality predictions
- Different sites and year

Calibration Development



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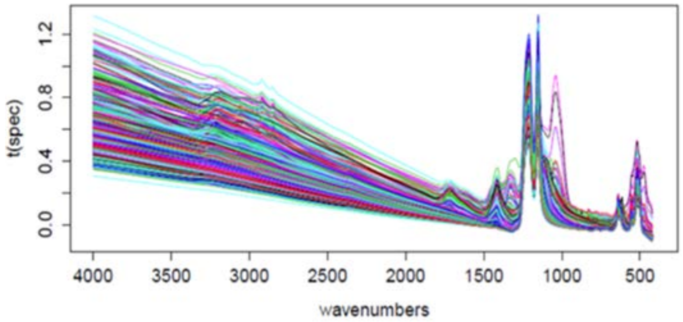


FT-IR spectra

TOR data

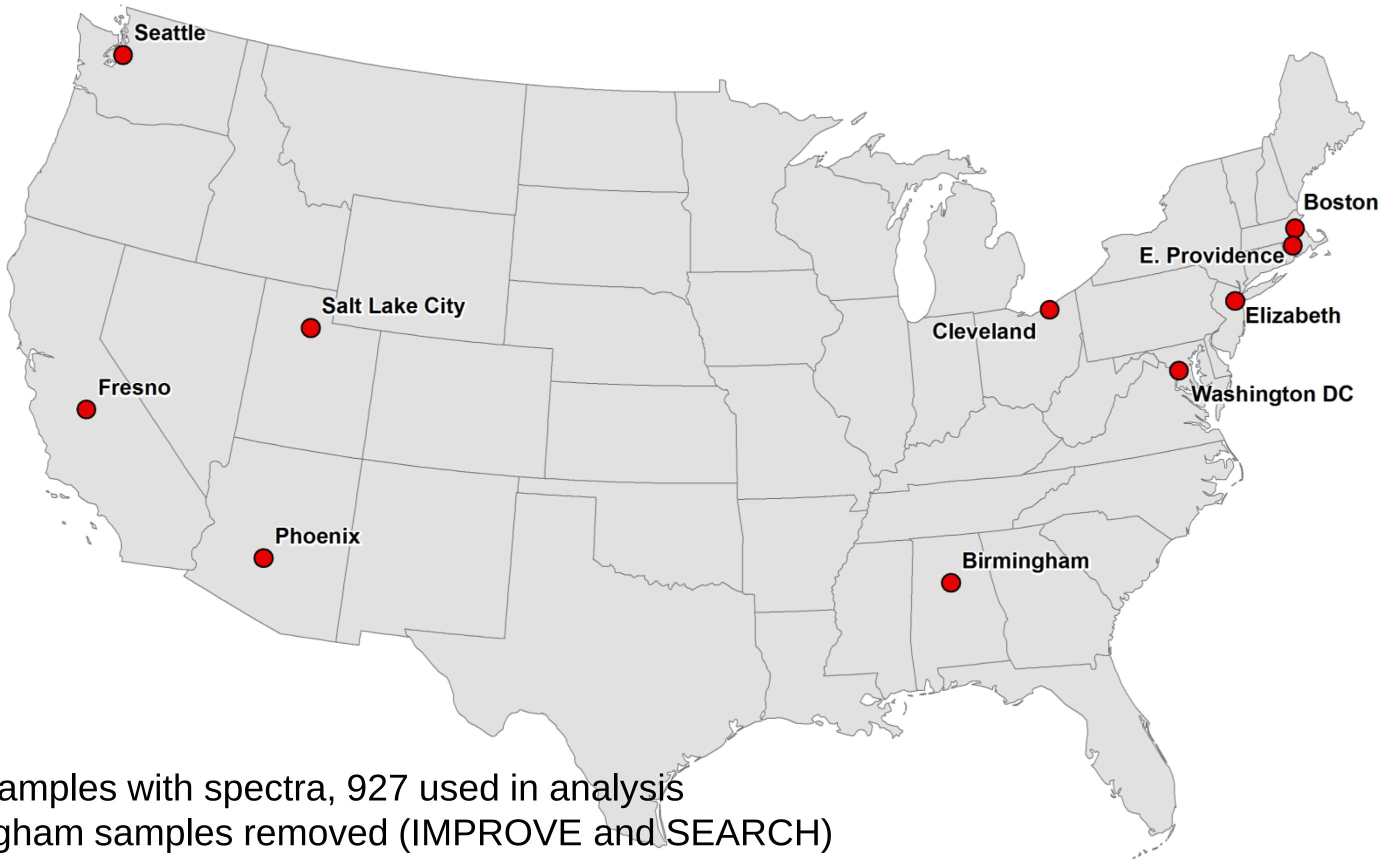
TOR OC and EC calibrations

CSN (FRM)

Why a separate calibration for CSN?

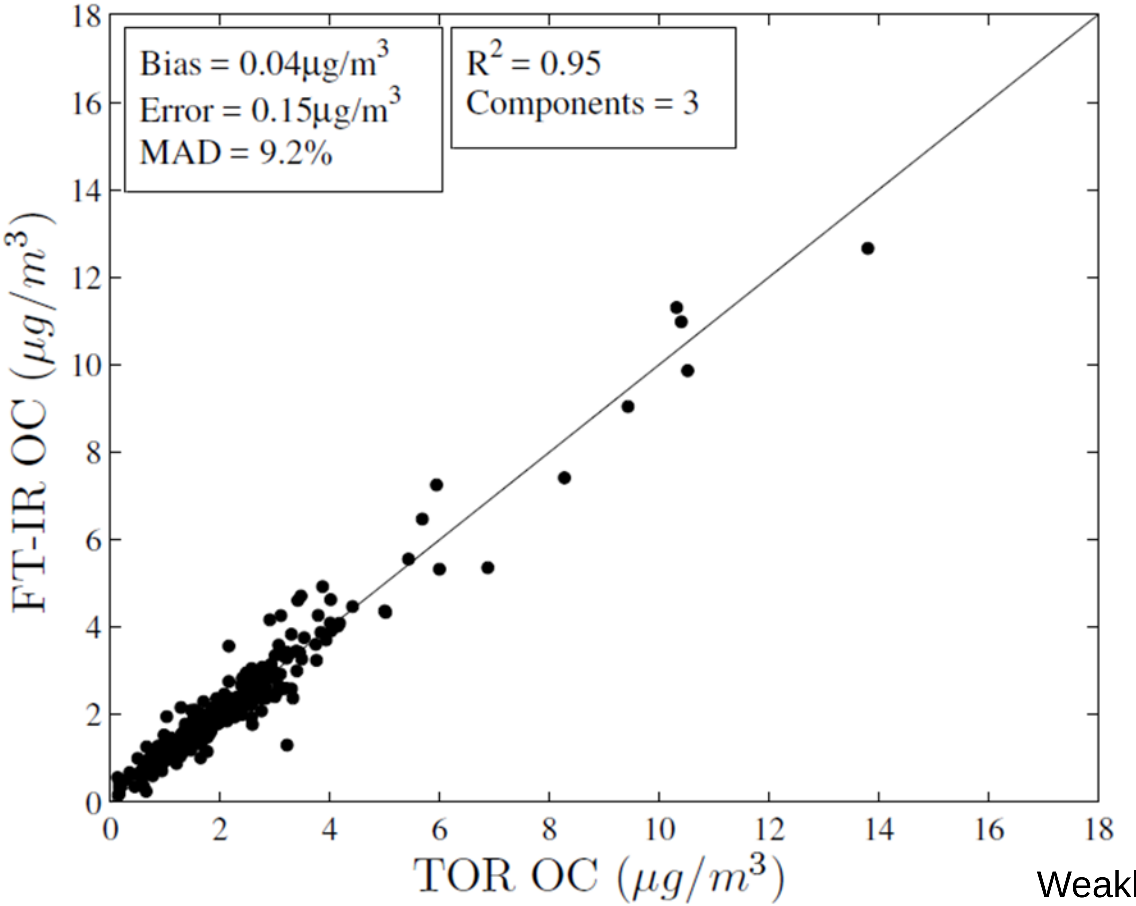
1. Aerial density differences ($\mu g/cm^2$)
   - CSN lower flowrate, larger filter than IMPROVE
   - CSN = IMPROVE/12 for collocated samples
2. PM composition differences
3. Filter type – spectroscopic methods “see” filter
   - IMPROVE (current) – Pall
   - CSN – Whatman (through 2015), MTL in 2016
   - FRM – some Whatman, some MTL, some other

CSN sites analyzed in 2013



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

Prediction of TOR OC in CSN



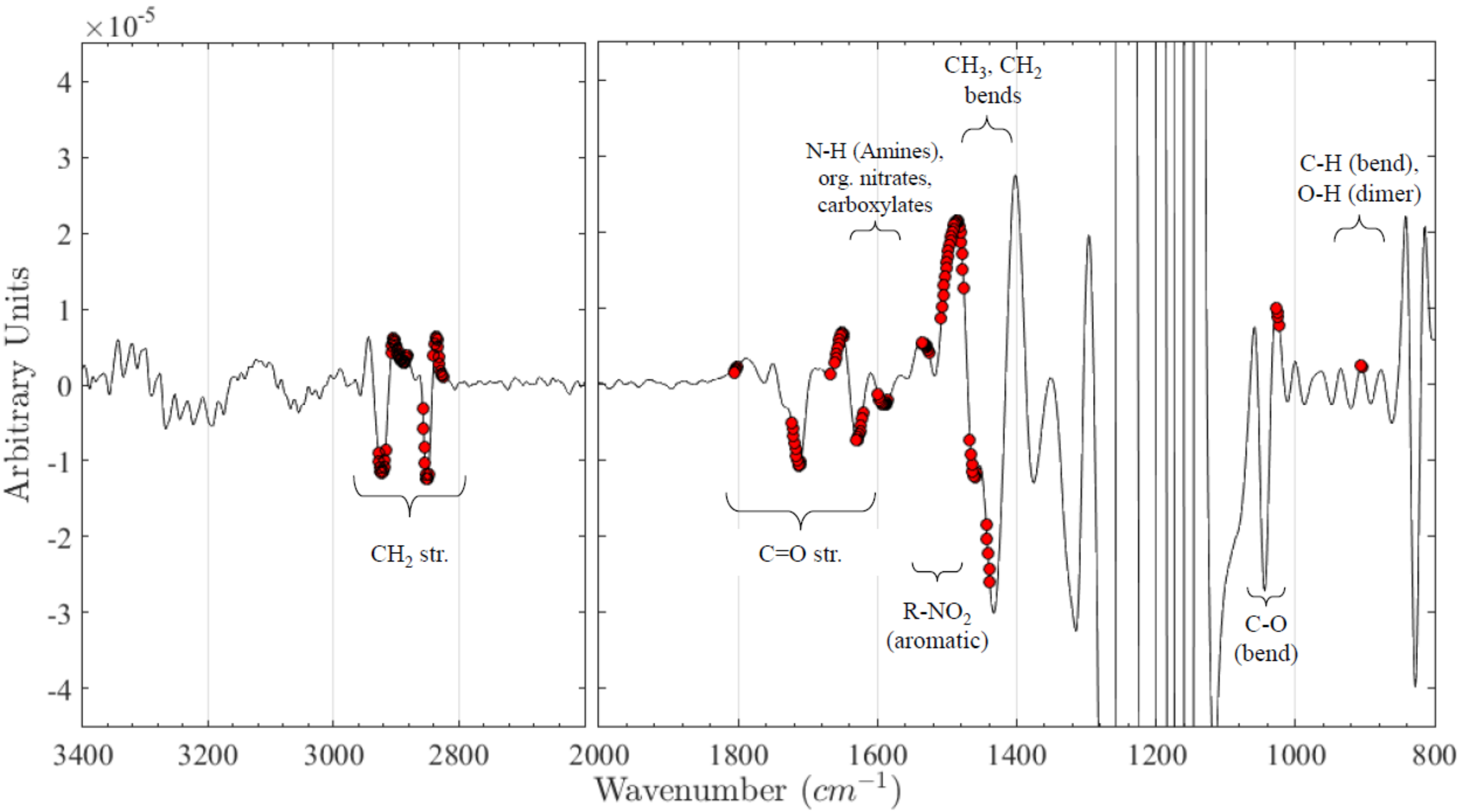
IMPROVE OC

Bias = 0.02 µg/m^3
Error 0.08 µg/m^3
Norm. Error = 11%
R^2 = 0.96

Similar results for EC

Weakley, Takahama, Dillner, 2016a

Functional groups used to predict OC

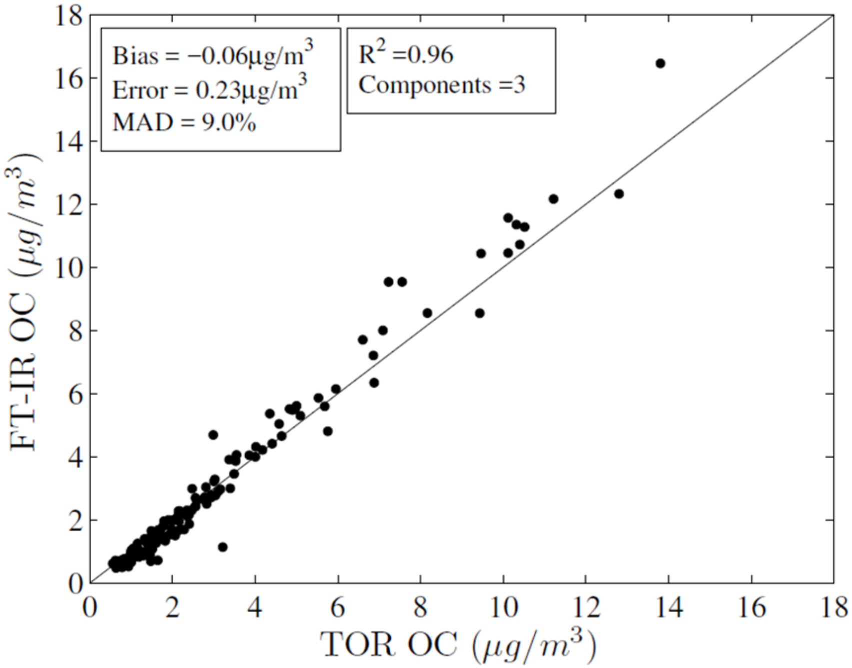


2nd Derivative spectrum with important wavenumbers used to predict OC in red

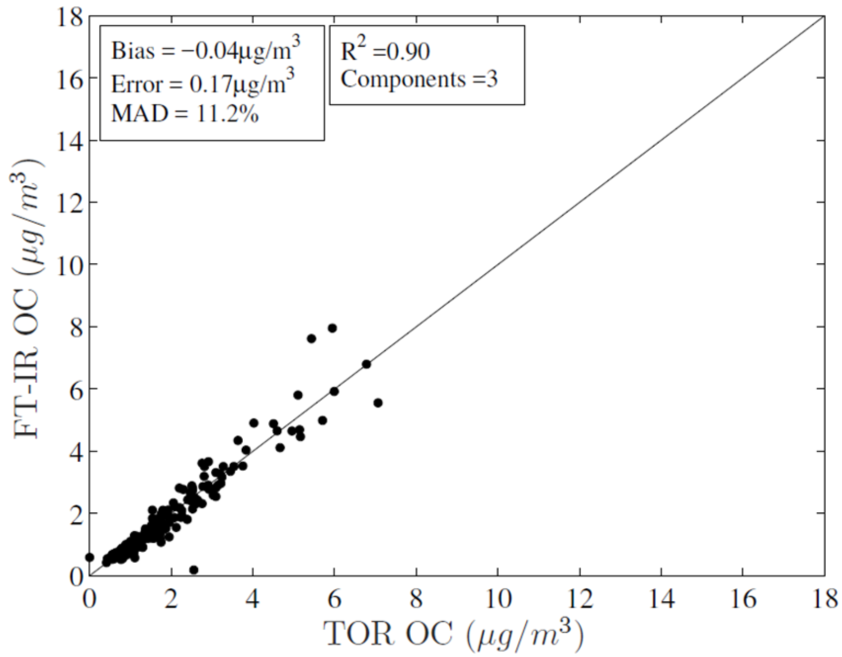
CSN calibration to predict OC and EC in FRM

TOR OC on FRM samples - high quality predictions

Different flowrate, same filter type

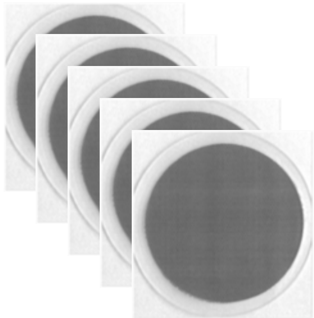


Different flowrate, different filter type

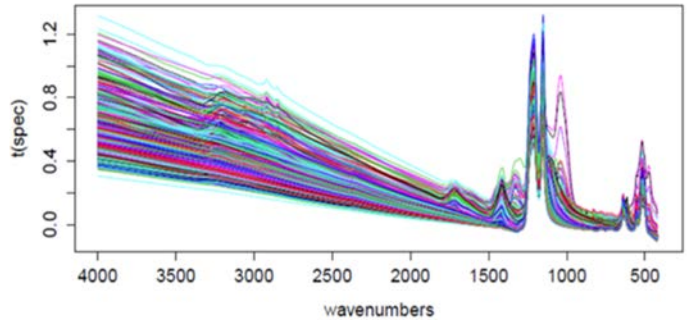


Weakley, Takahama, Dillner 2016c, in preparation

Calibration Development



ambient sampled teflon filters



FT-IR spectra

TOR data

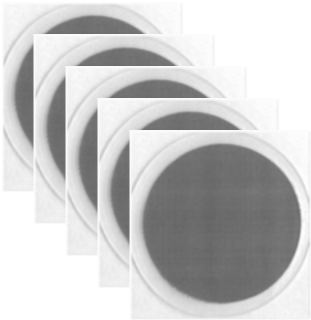
TOR OC and EC calibrations

CSN (FRM)

Summary CSN (FRM)

- Same OC predictive capability as IMPROVE
- Identification of functional groups
- Predict FRM samples

Calibration Development



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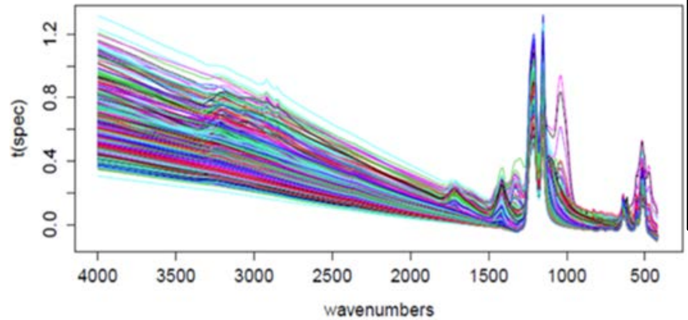


FT-IR spectra

TOR data

TOR OC and EC calibrations

CSN (FRM)

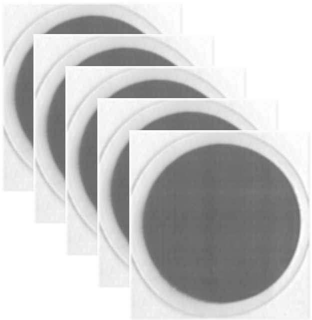
Next Step

- Network-wide CSN calibration

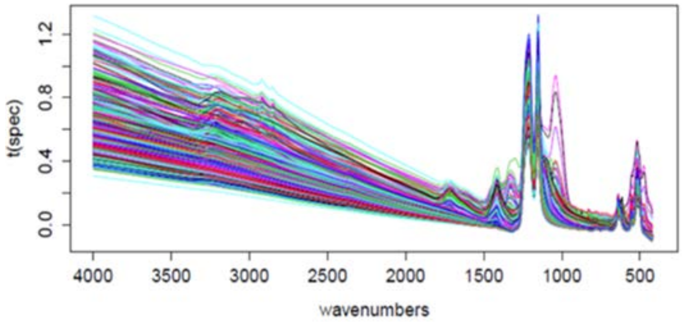
Summary CSN (FRM)

- Same OC predictive capability as IMPROVE
- Identification of functional groups
- Predict FRM samples

Calibration Development



laboratory sampled teflon filters

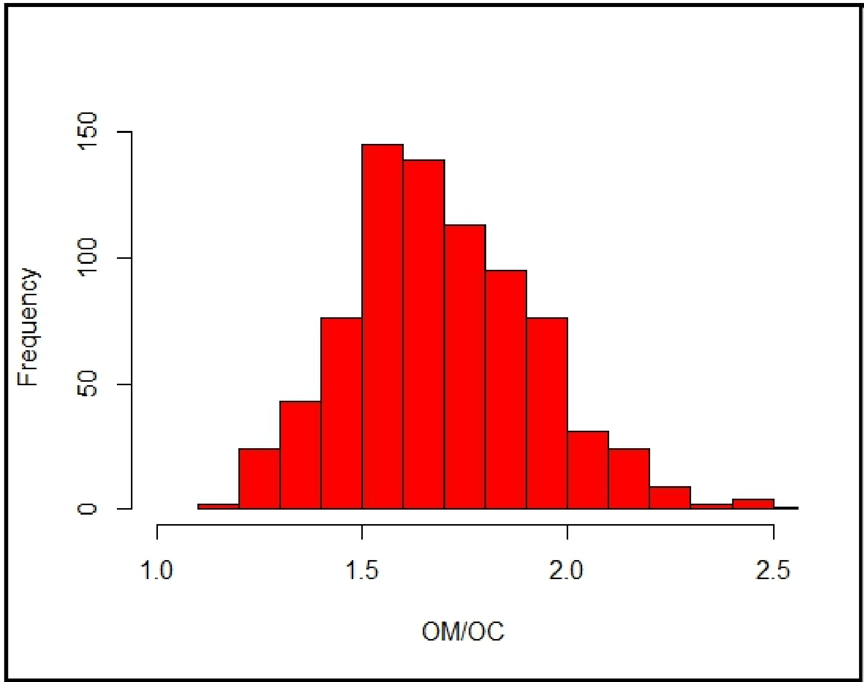


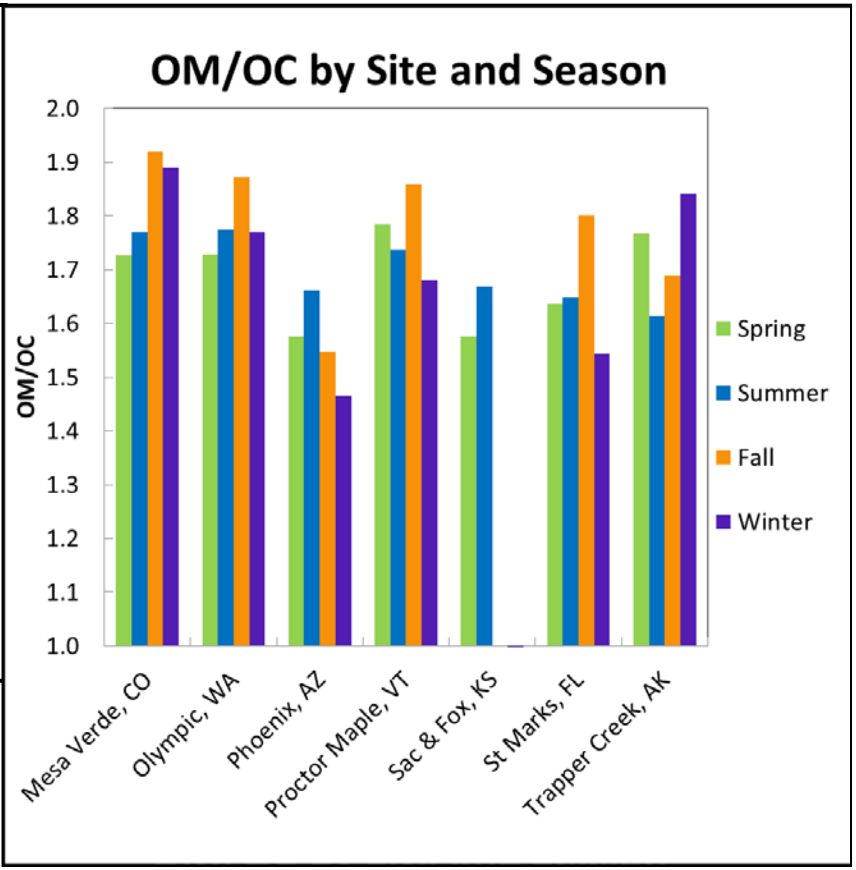
FT-IR spectra

laboratory standards masses

Functional group calibrations

OM/OC in 800 IMPROVE samples in 2011



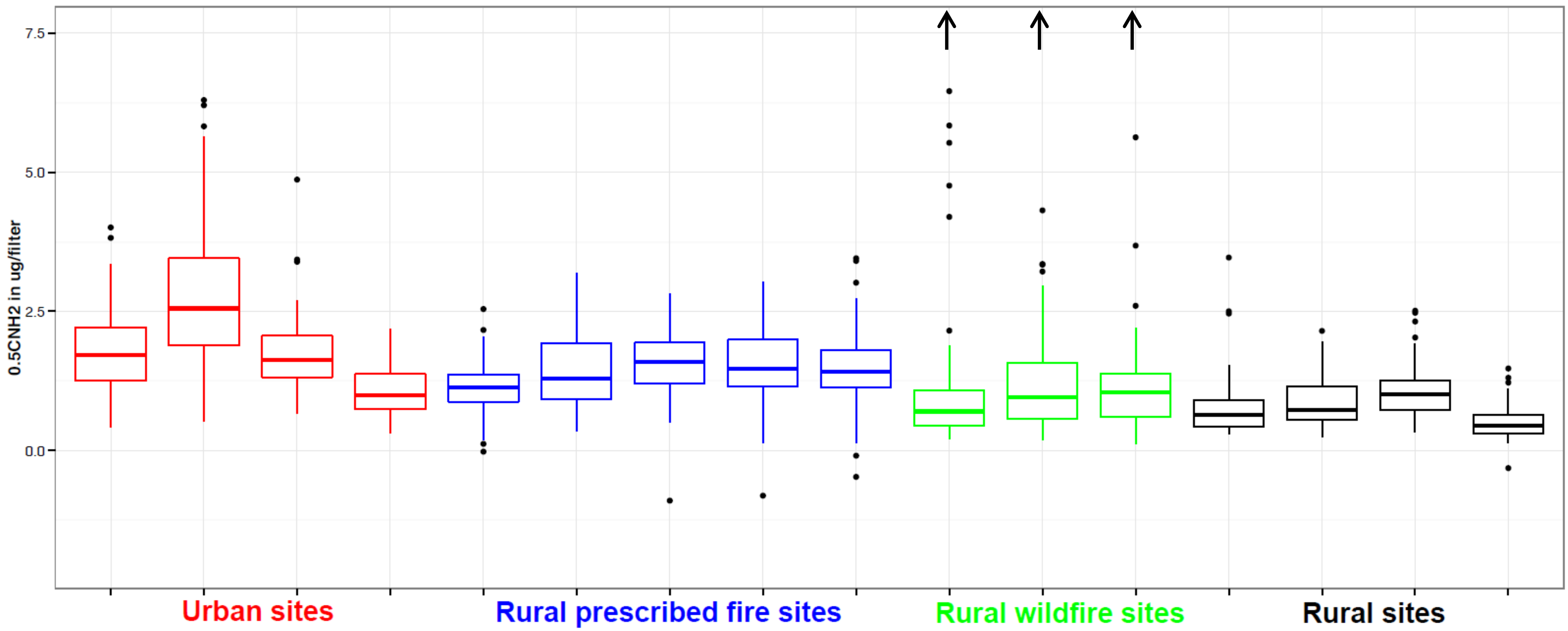


- Median OM/OC = 1.67
- IMPROVE OM/OC = 1.8
- Sample variability
  - 10^{th} %ile = 1.43
  - 90^{th} %ile = 2.00

- Site variability – urban site lowest
- Seasonal variability

Ruthenburg et al., 2014

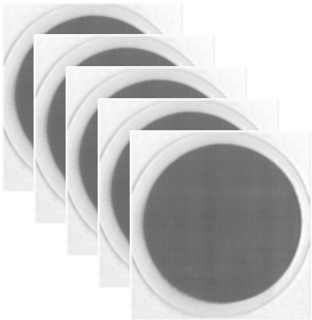
Amines (C-NH_2)



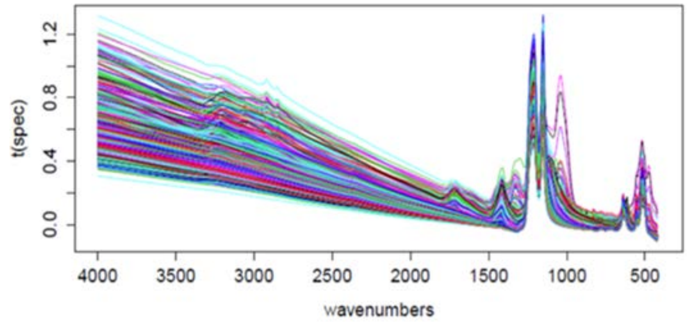
- Urban – vehicles
  - Fresno (highest median) – vehicles and cattle
- Wildfire – biomass burning

Kamruzzaman, Takahama and Dillner, in prep

Calibration Development



laboratory sampled teflon filters



FT-IR spectra

laboratory standards masses

Functional group calibrations

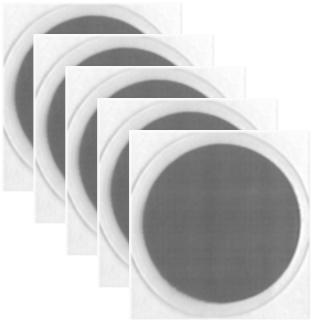
Summary

- OM/OC varies by site, season, sample
- Amines – tracer for sources

Next Step

- Additional functional groups

Calibration Development



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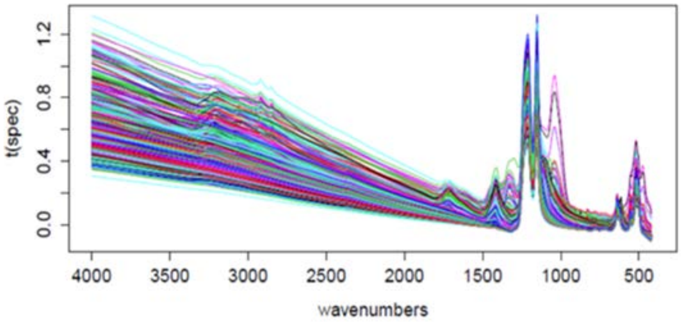


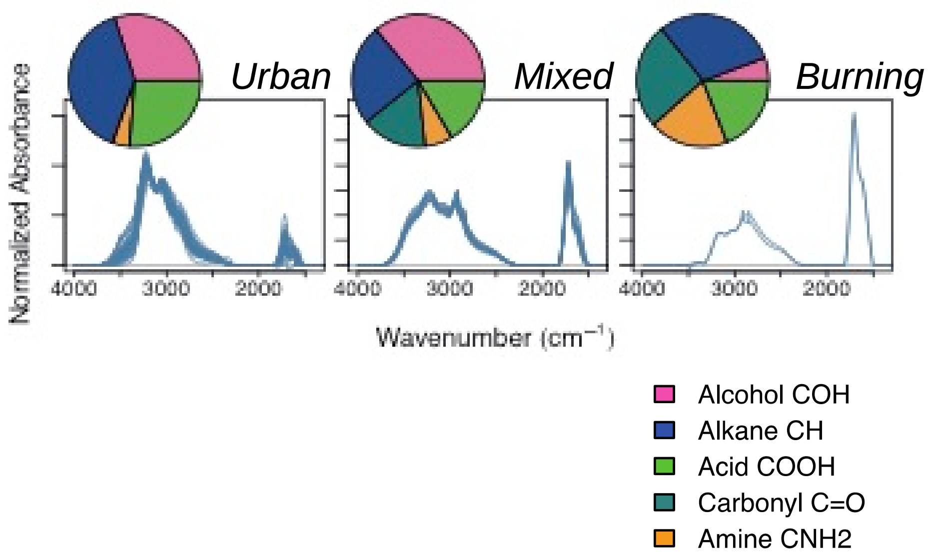
FT-IR spectra

source info

Clusters/ calibration

Source apportionment

Whistler mountain, 2010

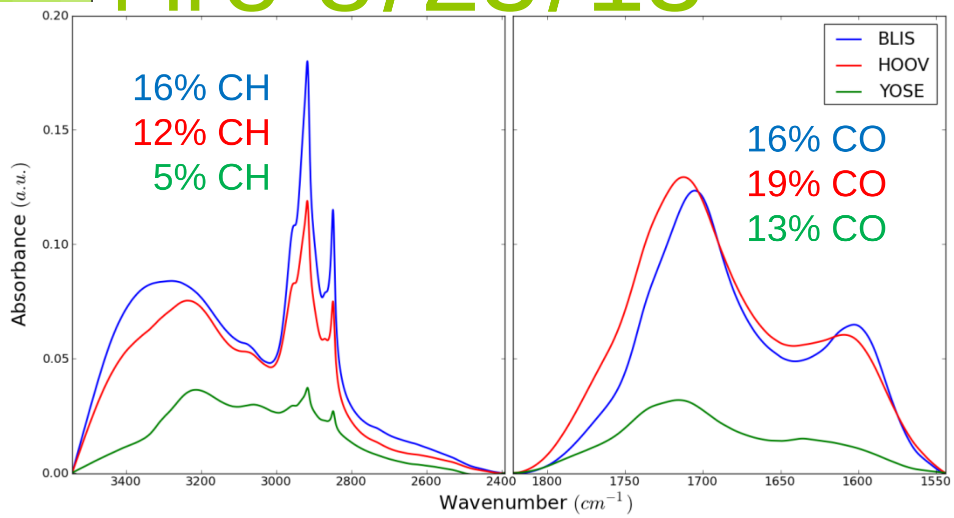


- Estimate sources
  - Clustering spectra
  - Functional group composition

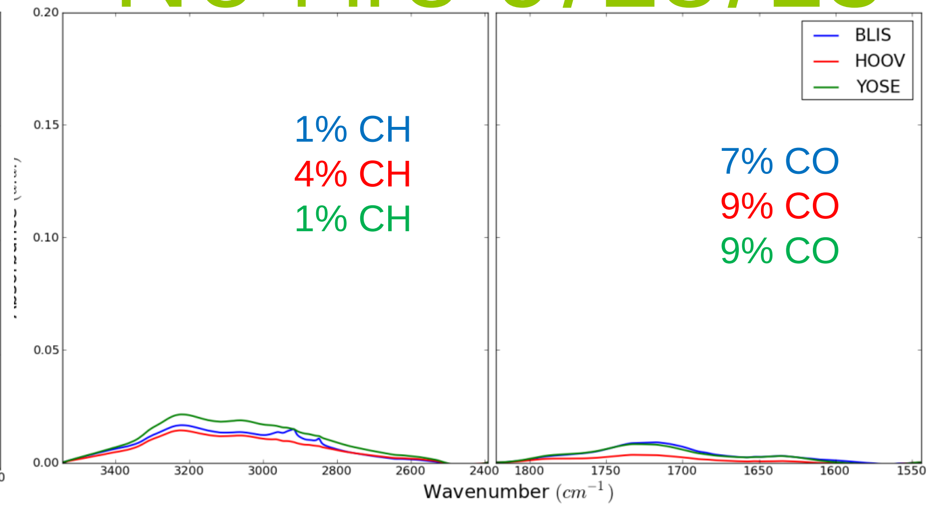
Takahama et al., *Atmos. Chem. Phys.*, 2011

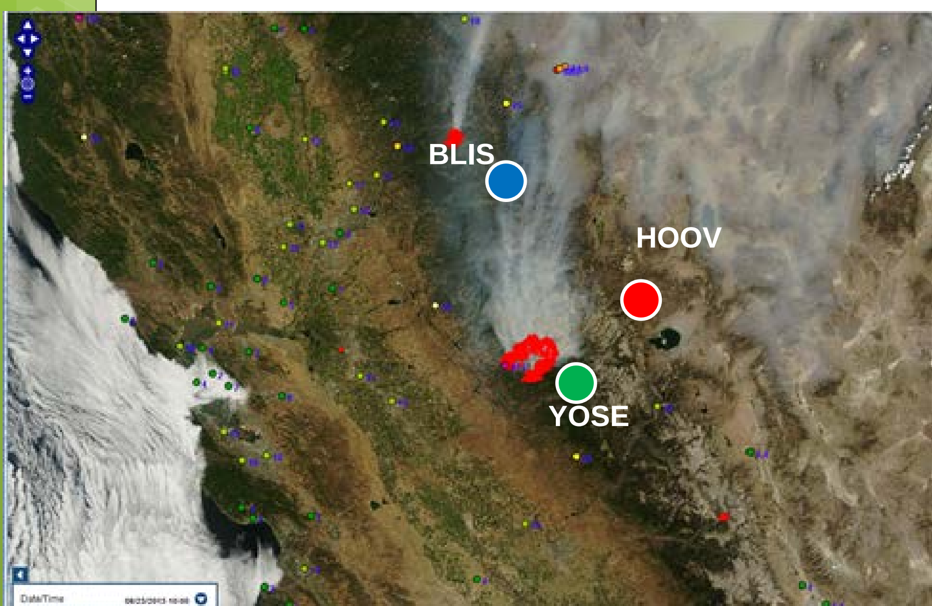
Rim Fire

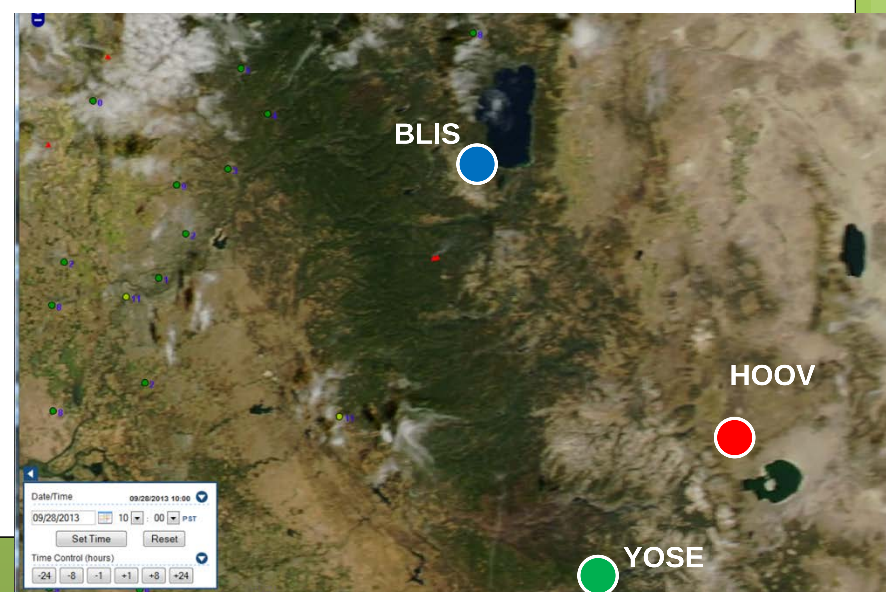
Fire 8/23/13



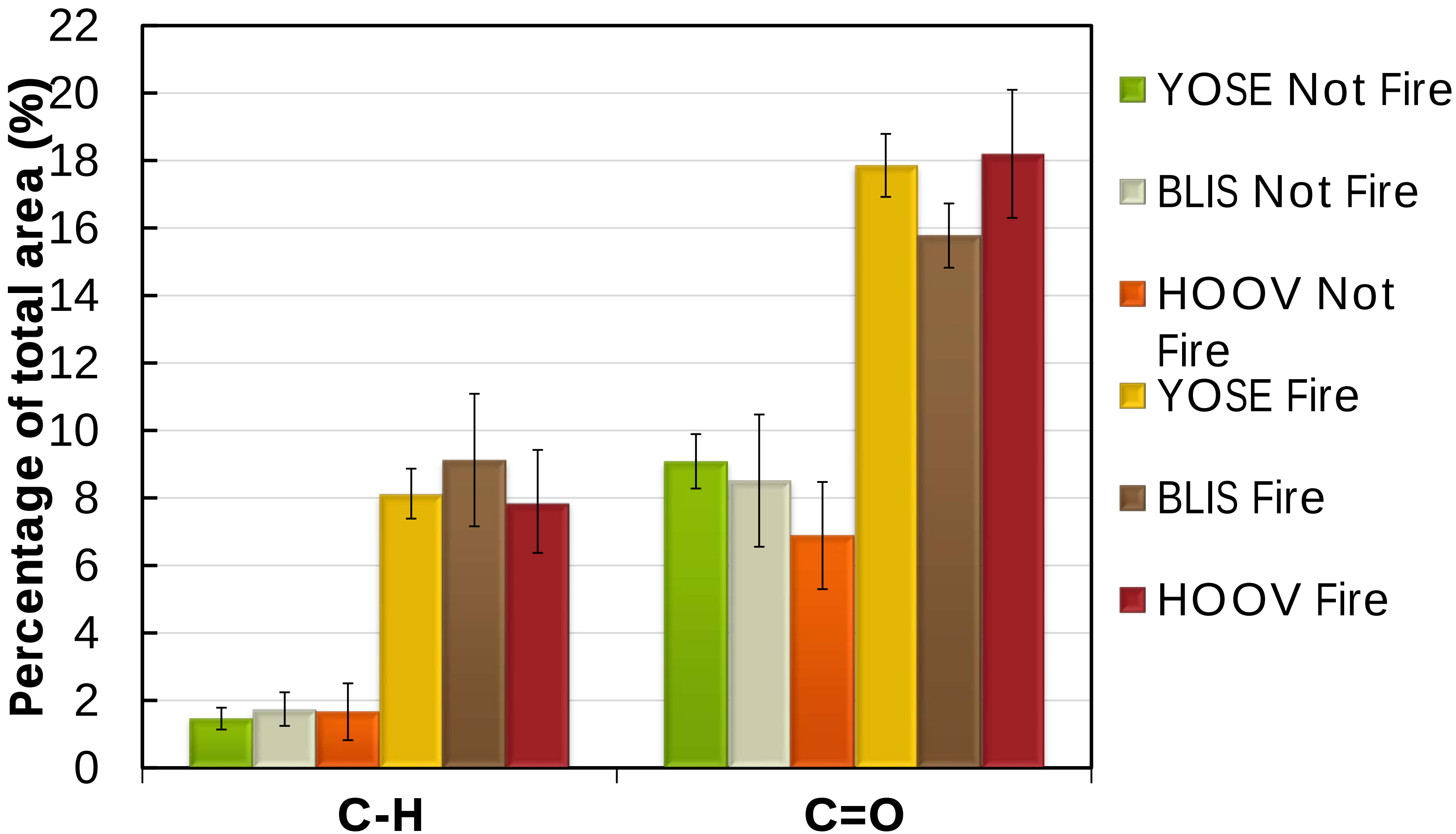
No Fire 9/28/13







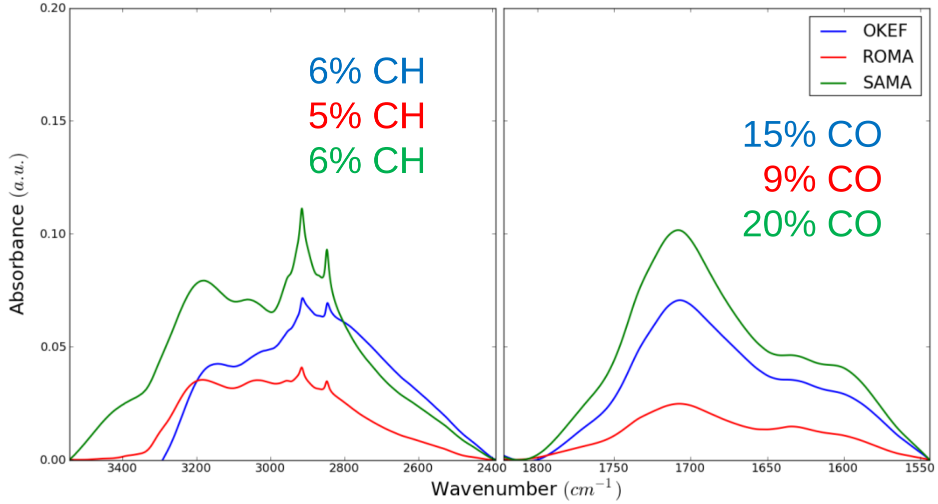
Rim fire (June 16 - Oct 31): %C-H and %C=O by area



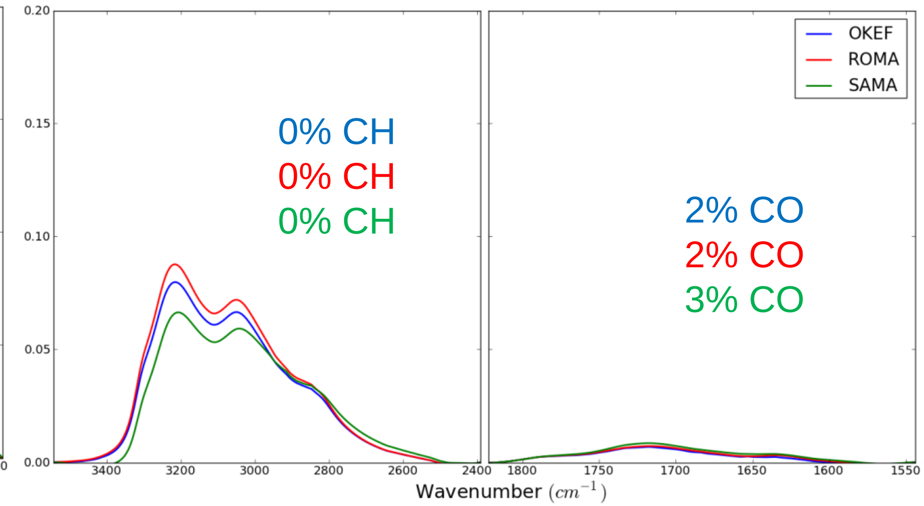
error bars = 95% confidence interval

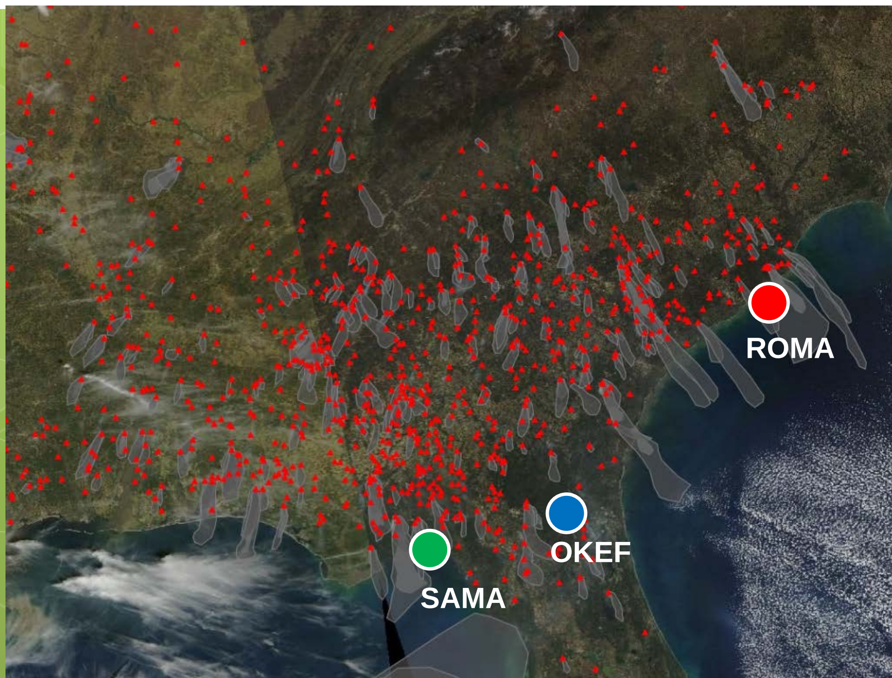
Prescribed Fires

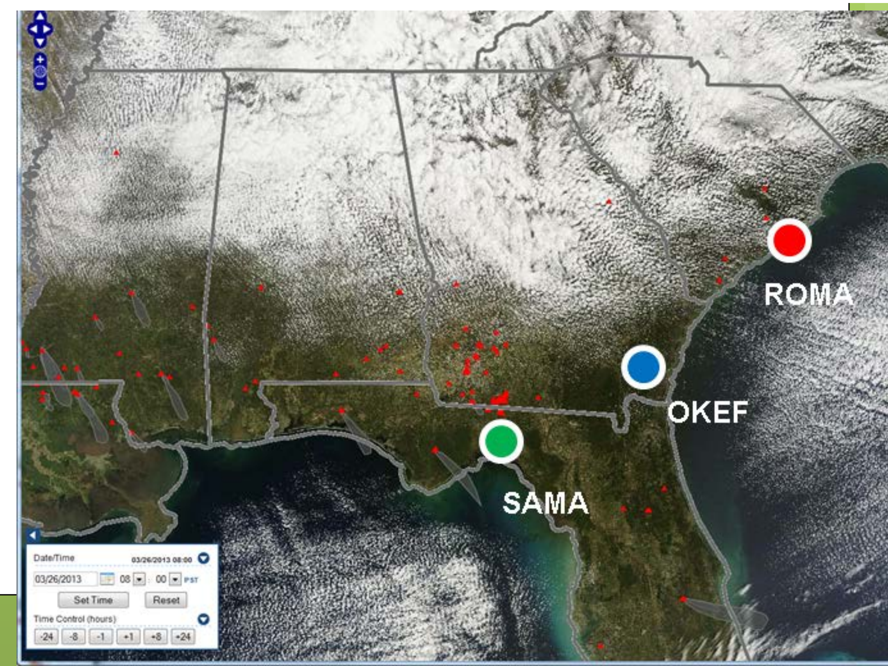
Fire 3/8/13



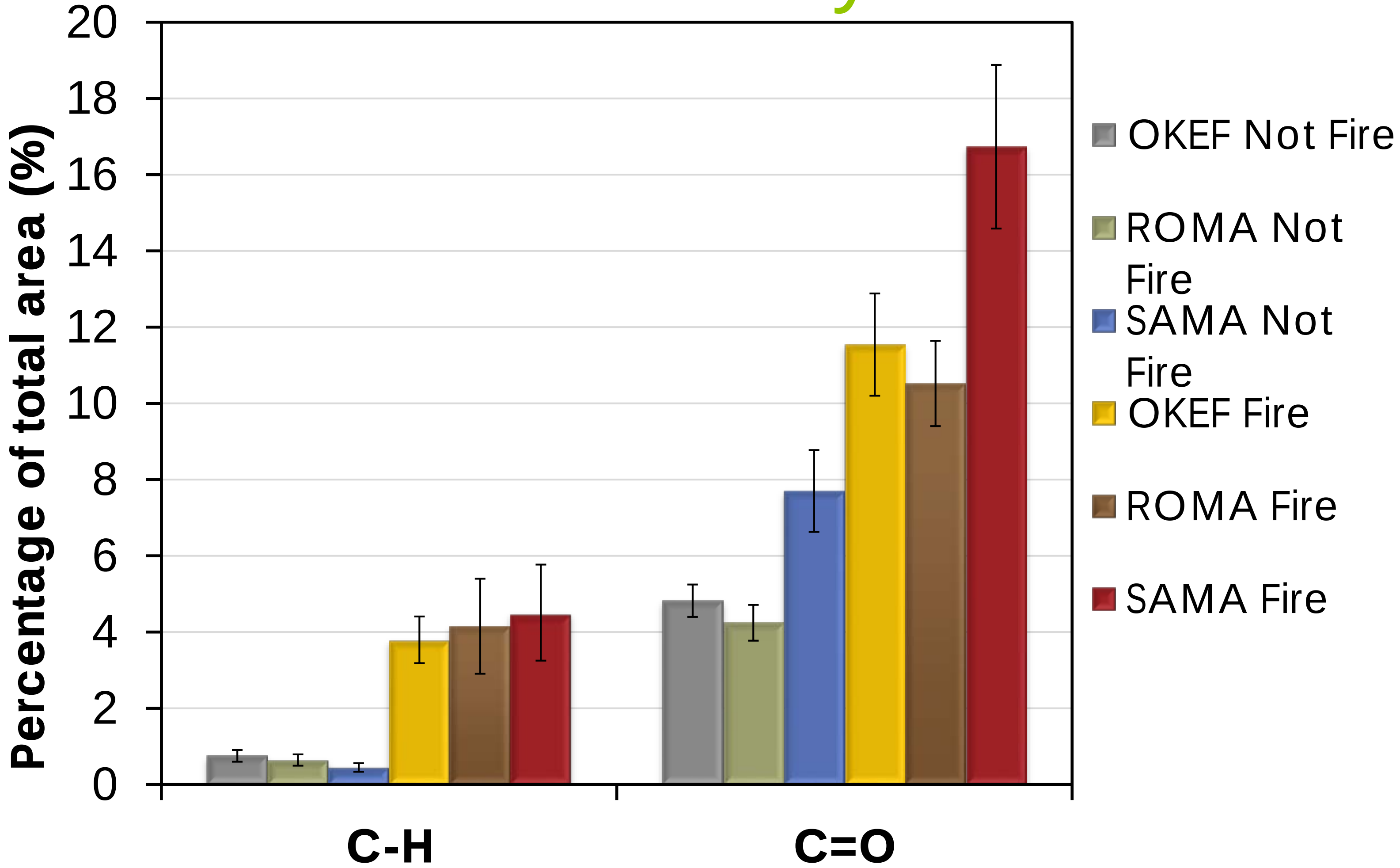
No Fire 3/26/13





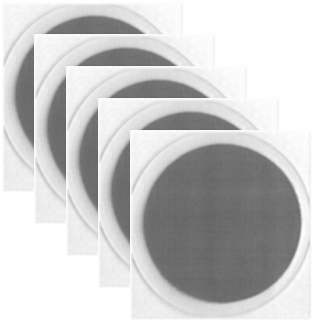


SE Sites (full year)
%C-H and %C=O by area

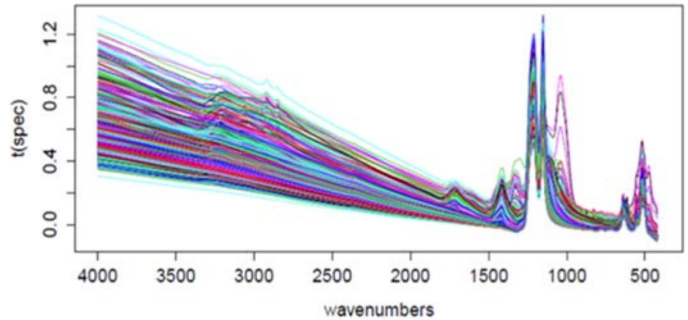


error bars = 95% confidence interval

Calibration Development



ambient sampled teflon filters



FT-IR spectra

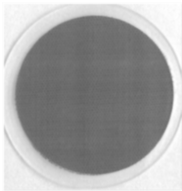
source info

Clusters/ calibration

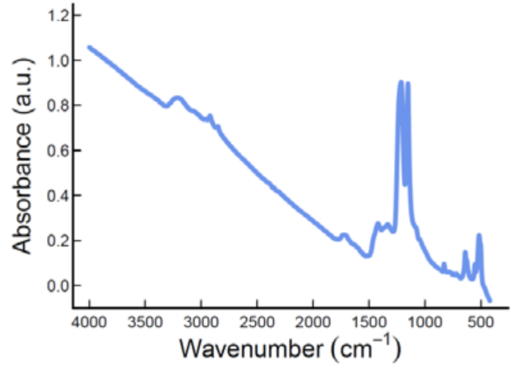
<u>Summary and Future work</u>

- Promising methods for network data sets for source apportionment
- Quantify fire impact with levoglucosan and FT-IR data in IMPROVE and FRM samples

Characterizing Carbonaceous PM



ambient sampled teflon filter



FT-IR spectrum

TOR OC and EC calibrations → TOR OC, EC

Functional group calibrations → functional groups, OM, OM/OC, O/C

Clusters/ calibration → Source apportionment

Conclusions

- FT-IR is a non-destructive, inexpensive method
  - No artifact or pyrolysis correction
- Uses teflon filters collected in CSN, FRM, IMPROVE
- Capabilities:
  - Reproduces TOR OC and EC
  - Quantifies OM/OC and functional groups
  - Identifies sources of carbon in PM

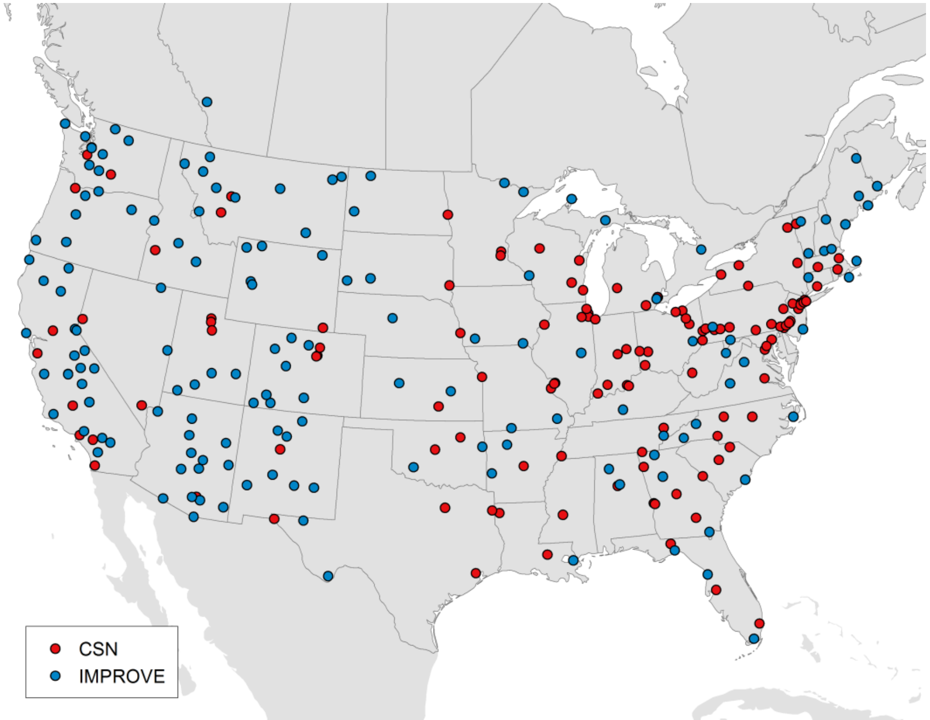
FT-IR is an inexpensive method for characterizing carbonaceous particulate matter in National Monitoring Networks

Recent and Upcoming Publications

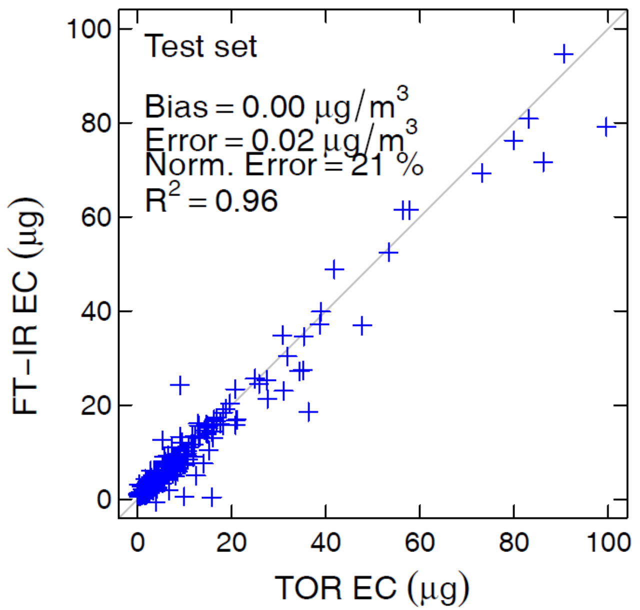
- **OC and EC - IMPROVE**
  - Predicting TOR OC for IMPROVE, Dillner and Takahama, 2015a
  - Predicting TOR EC for IMPROVE, Dillner and Takahama, 2015b
  - Predicting OC and EC for IMPROVE at different sites/years, Reggente et al., 2016
- **OC and EC - CSN**
  - Predicting TOR OC for CSN, Weakley, Takahama and Dillner, 2016
  - Predicting TOR EC for CSN, Weakley, Takahama, and Dillner, in prep
  - Predicting TOR OC and EC for FRM from CSN calibrations, Weakley, Takahama, and Dillner, in preparation
- **Functional groups and OM/OC**
  - Determination of OM and OM/OC by FT-IR, Ruthenburg et al., 2014
  - Quantification of carbonyl by FT-IR, Takahama et al., 2013
  - Improving OM/OC estimates by improving PLS model selection, Takahama and Dillner, 2015
  - Organosulfate, organonitrate and amines and their impact on OM/OC in IMPROVE, Kamruzzaman, Takahama and Dillner, in preparation
- **Automated Baseline correction**
  - Automating baseline, Kuzmiakova, Dillner and Takahama, 2016

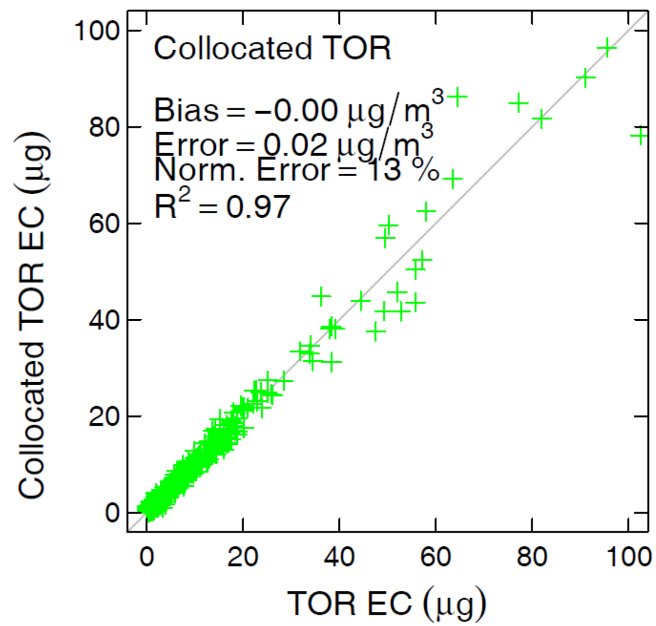
CSN and IMPROVE

- National particulate matter (PM) speciation networks
- CSN - urban
  - health effects
- IMPROVE - rural
  - visibility at National Parks
  - Regional Haze Rule
- Both networks
  - sources
  - atmospheric chemistry
  - long-term trends
  - ground-truth for modeling



IMPROVE FT-IR EC





	FT-IR EC
MDL (µg/m³)	0.01
% below MDL	1
precision (µg/m³)	0.04

	TOR EC
MDL (µg/m³)	0.01
% below MDL	3
precision (µg/m³)	0.11

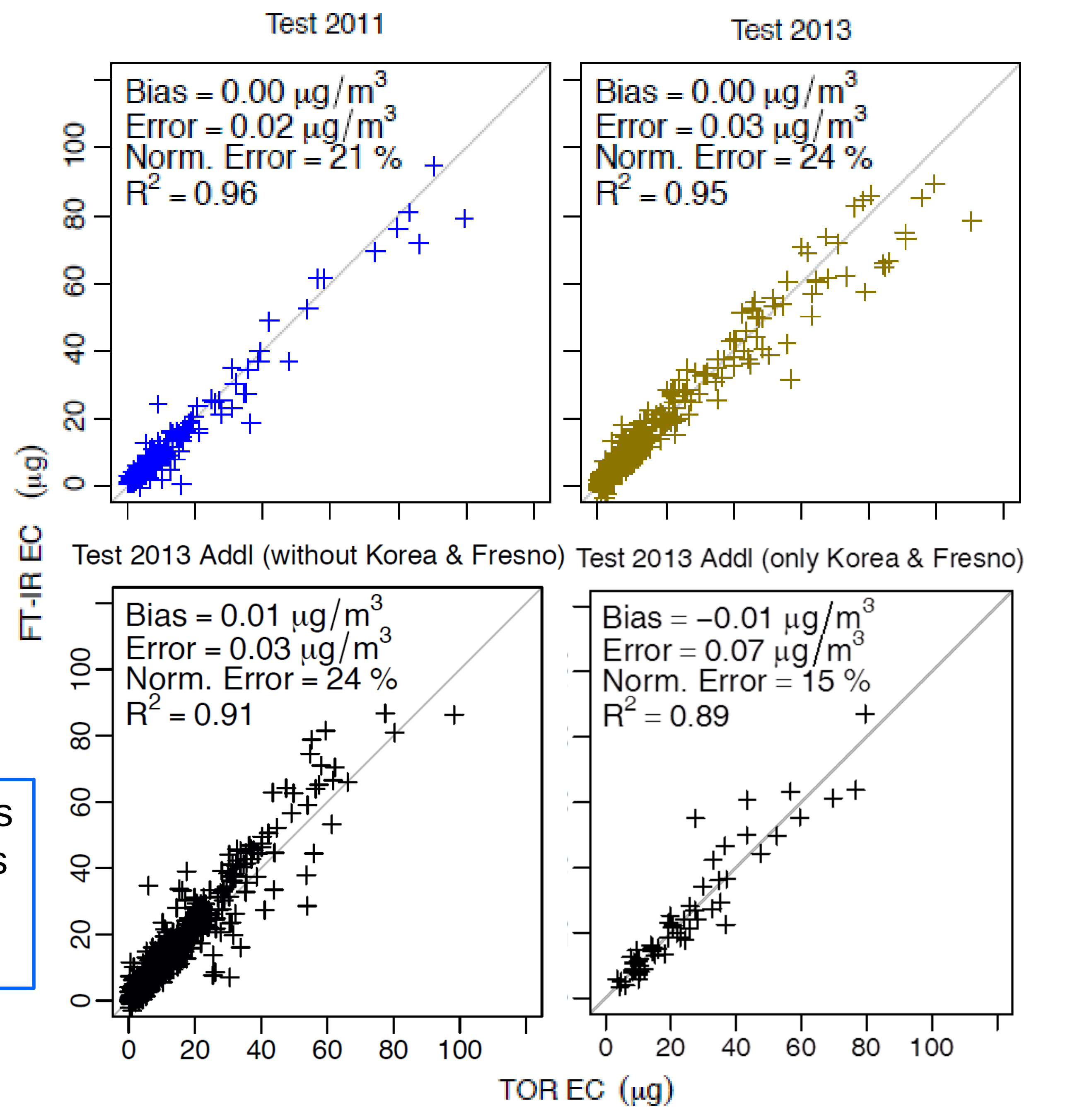
Dillner and Takahama, 2015b

IMPROVE FT-IR EC

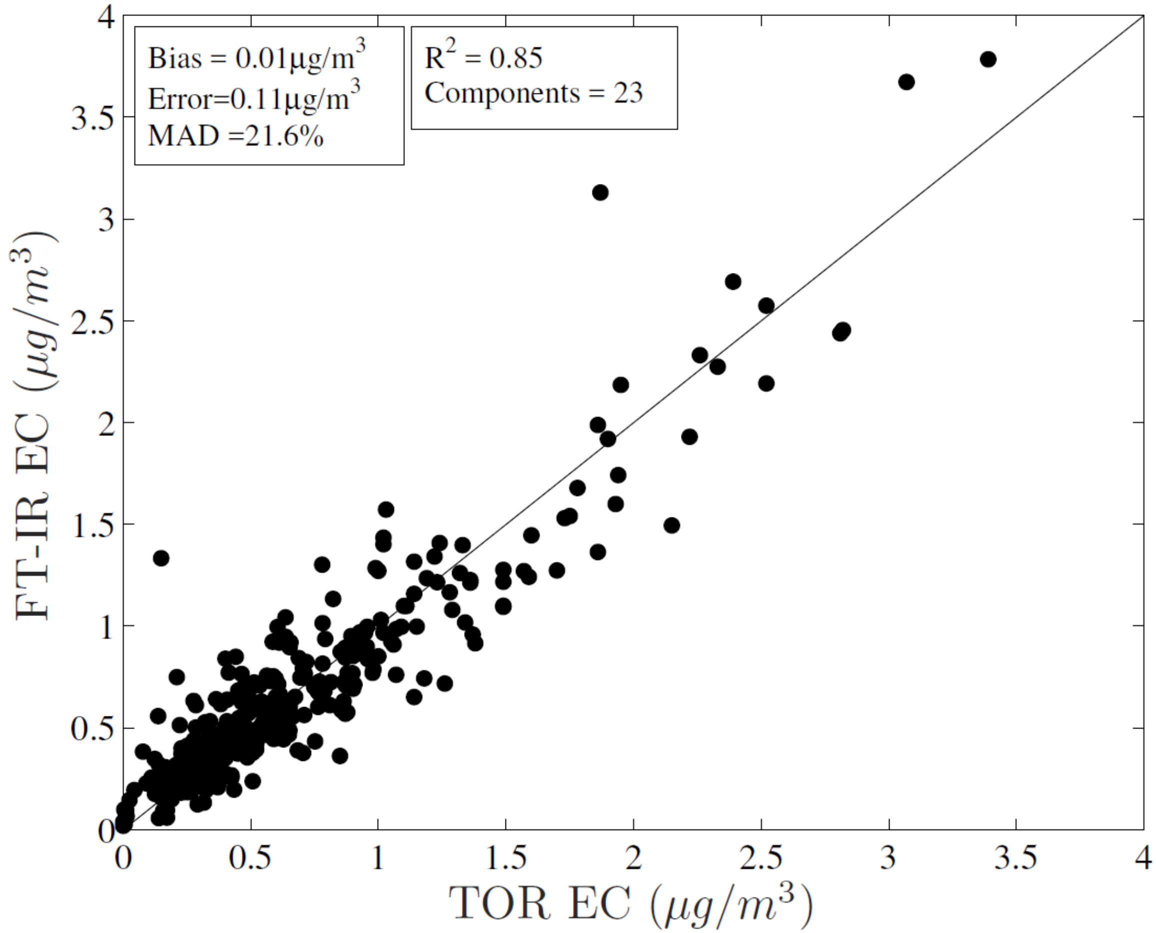
extending predictions to different years and sites

if Calibration samples ≅ Measured samples then, good measurements

Reggente, Dillner and Takahama, 2016



EC prediction for CSN using 2nd Derivative spectra



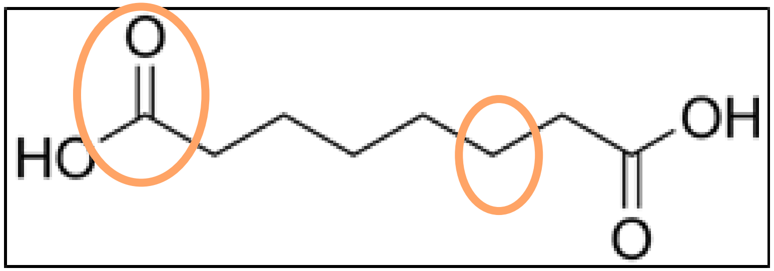
IMPROVE EC

Bias = 0.00 μg/m^3
Error = 0.02 μg/m^3
Norm. Error = 21%
R^2 = 0.96

Weakley, Takahama, Dillner 2016b, in preparation

Organic Functional Groups and OM/OC

- FT-IR absorbances correspond to organic functional groups



- Sum of functional groups = OM
- Calculate OM/OC per sample

Aliphatic C-H
Carbonyl (C=O)
Acid O-H
Alcohol O-H
Organonitrates
Amines
Organosulfates
Aromatic C-H