CHARACTERIZING CARBONACEOUS AEROSOL IN NATIONAL AND REGIONAL MONITORING NETWORKS WITH FT-IR

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IMPROVE Steering Committee
Boundary Waters Canoe Area
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Collaborators, post-docs and students:

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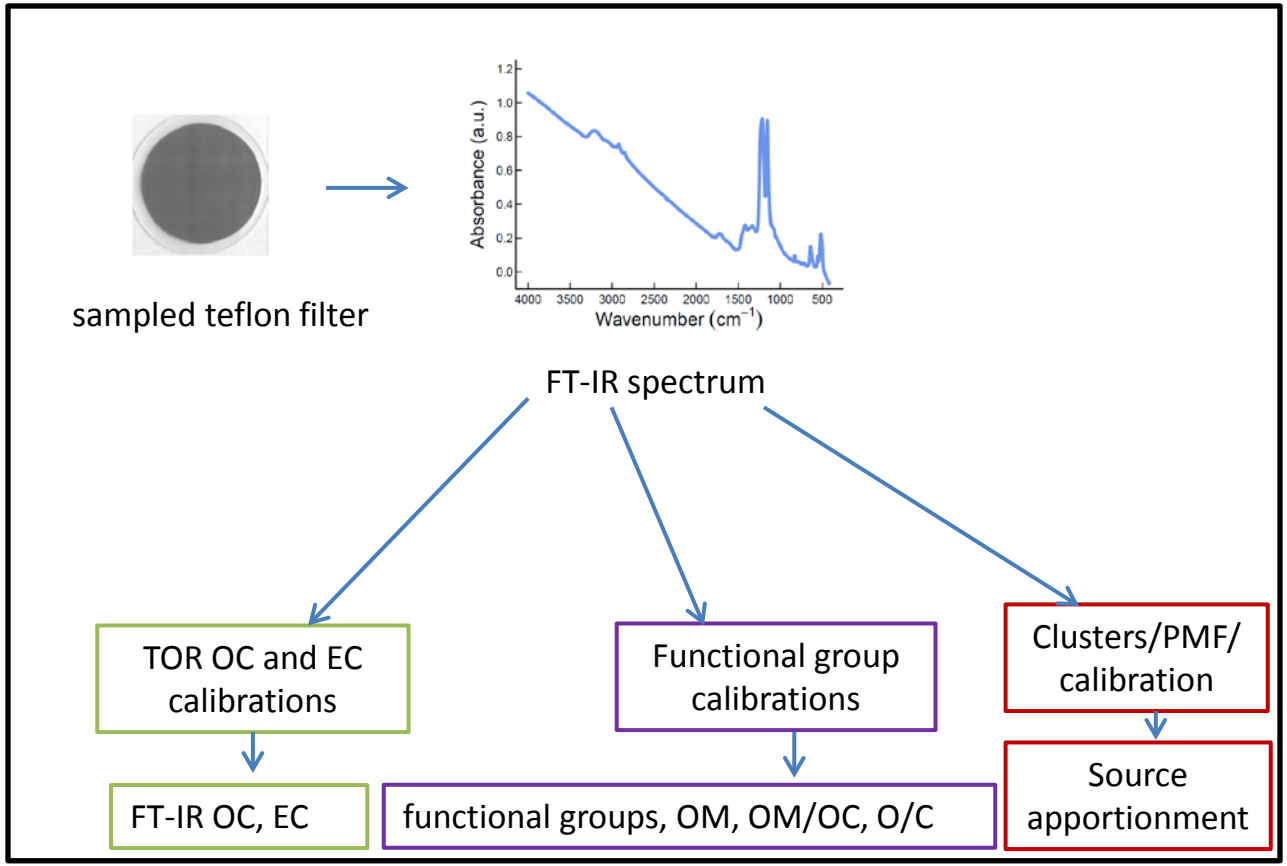
Fourier Transform – Infrared (FT-IR) Spectrometry

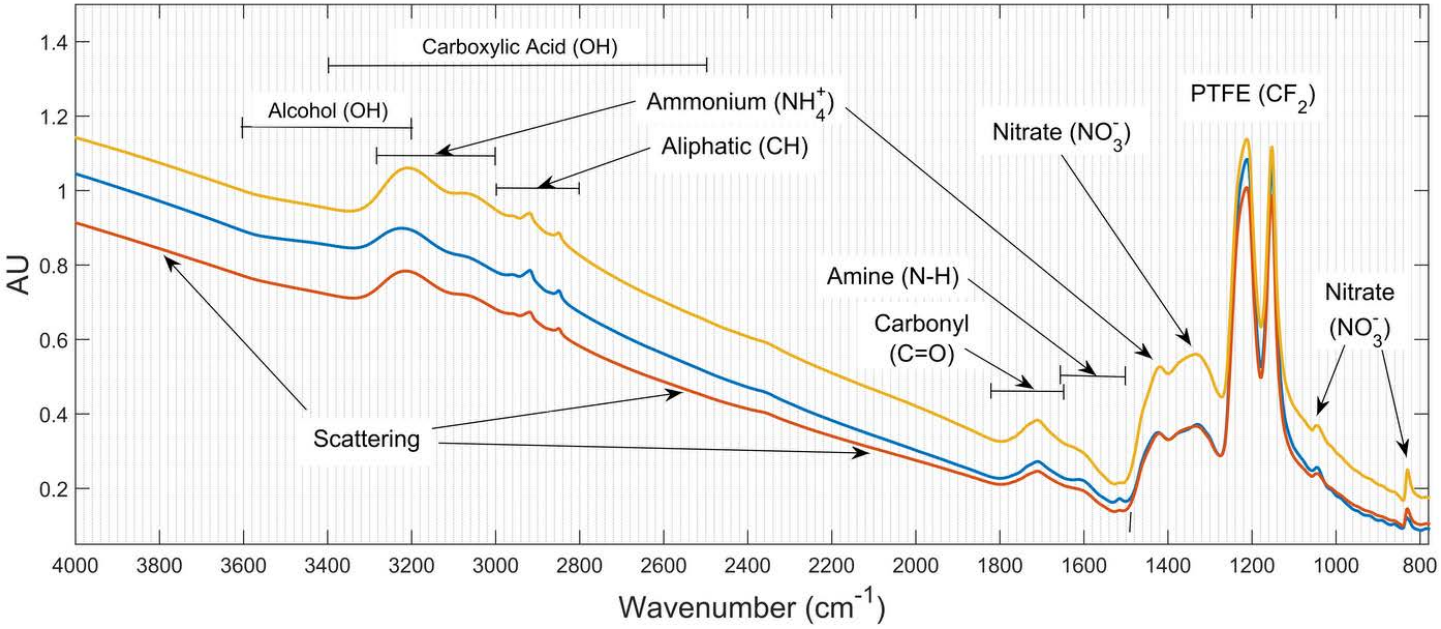
- Non-destructive, fast technique
- Probes particulate matter composition (organics and inorganic bonds)
- PM2.5 samples collected on Teflon (PTFE) filters
- Feature-rich vibrational spectra in the mid-IR range
- For monitoring networks
    - Routinely collected Teflon samples
    - Analysis by other techniques (XRF) and archived
    - Reproduce existing OC and EC data
    - Provides additional characterization including functional groups, organic matter (OM), and source apportionment (and inorganics)

Objective: Characterize Carbonaceous PM



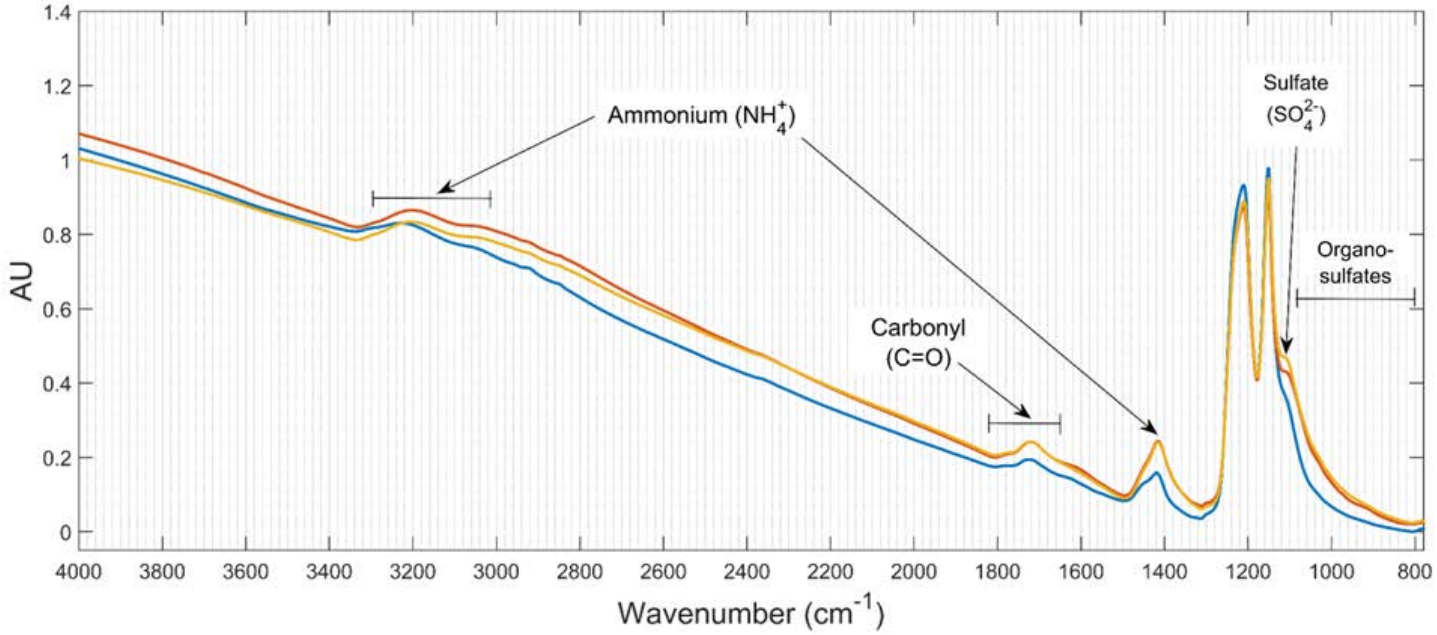
FT-IR spectra of IMPROVE filters

Fresno, CA, January, 2013

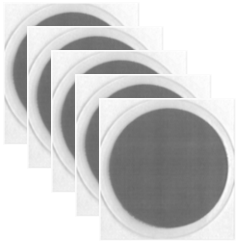


FT-IR spectra of IMPROVE samples

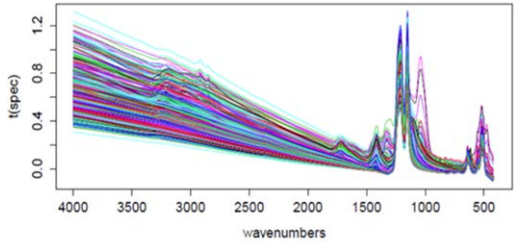
Birmingham, AL, August and September, 2013



Methods: Calibration Development



Ambient or laboratory sampled teflon filters



FT-IR spectra

TOR data

TOR OC and EC calibrations

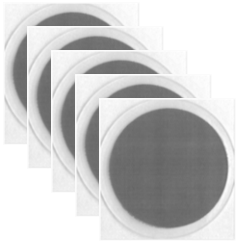
laboratory standards masses

Functional group and OM calibrations

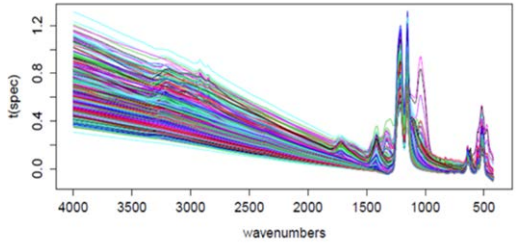
source info

Clusters/PMF/ calibration

Methods: Calibrations for FT-IR OC and EC



ambient sampled teflon filters



FT-IR spectra

TOR data

TOR OC and EC calibrations

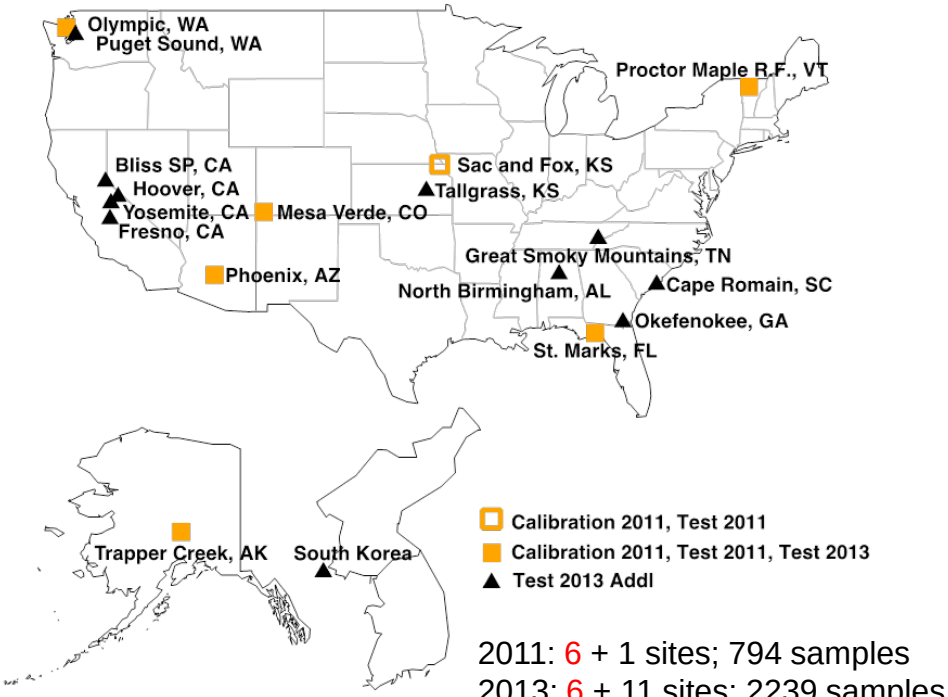
IMPROVE

CSN

FRM

IMPROVE 2011, 2013, 2015 to current

2011 and 2013



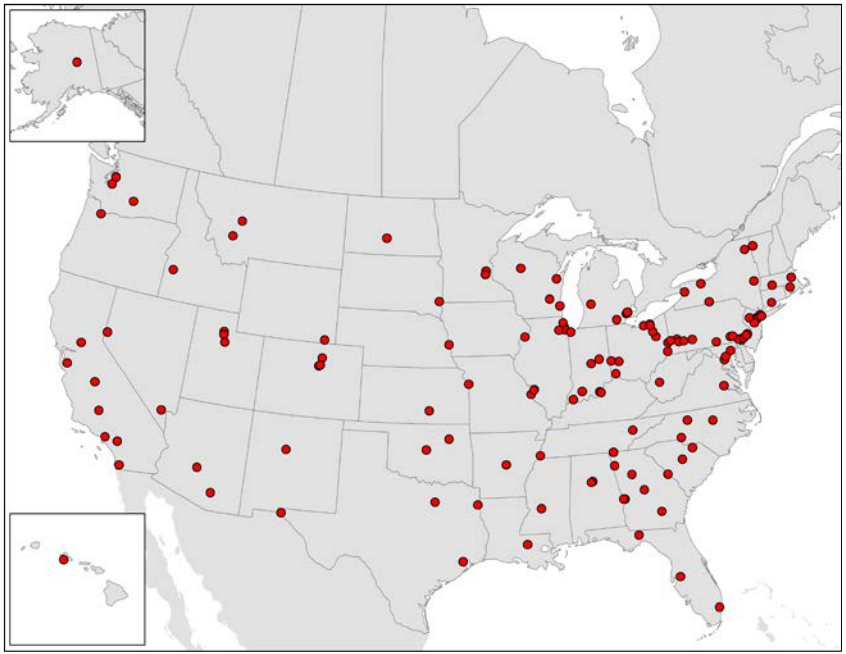
2011: 6 + 1 sites; 794 samples
2013: 6 + 11 sites; 2239 samples

2015 to current

CSN and FRM 2013 and CSN 2017

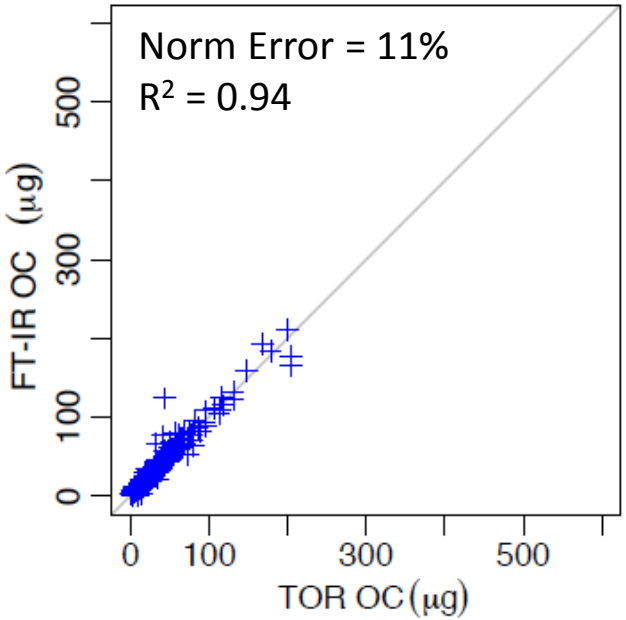
CSN and FRM in 2013

CSN 2017

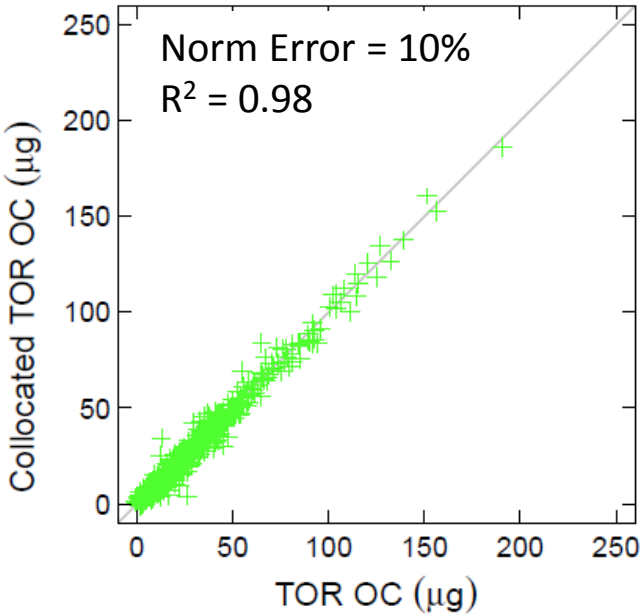


FT-IR OC: TOR-equivalent OC in IMPROVE

IMPROVE 2011 – 7 sites

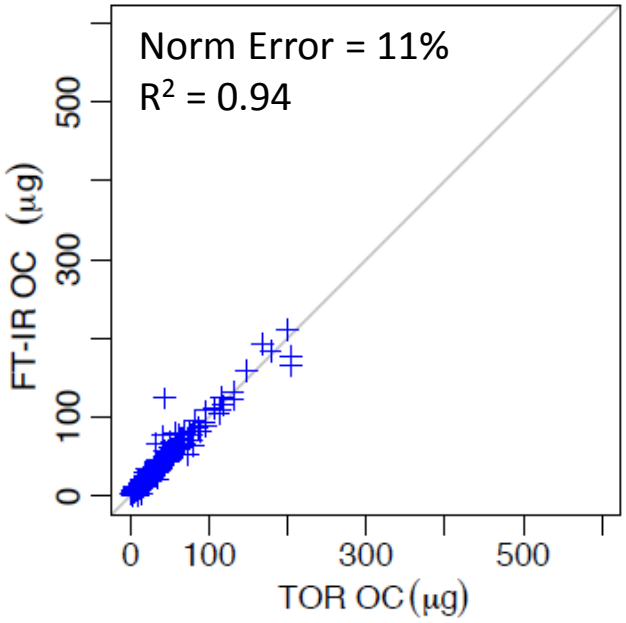


IMPROVE 2011 – 7 collocated TOR sites



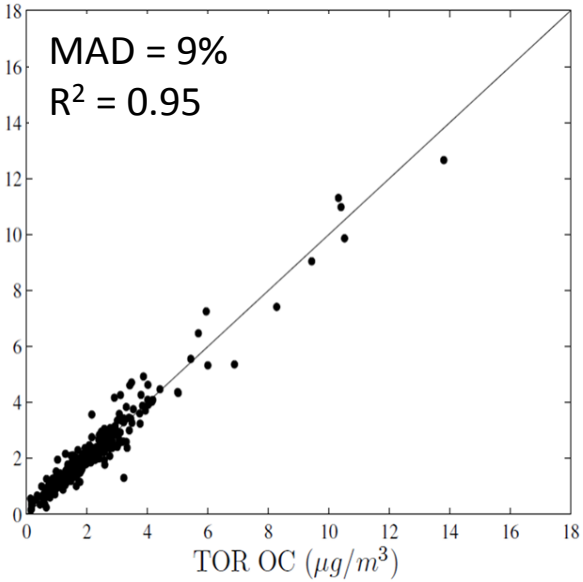
FT-IR OC: TOR – equivalent OC

IMPROVE 2011 – 7 sites



Dillner and Takahama, 2015a

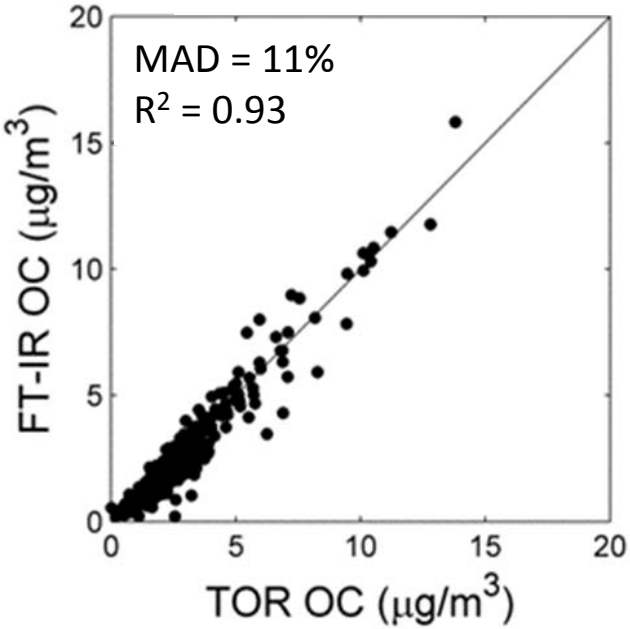
CSN 2013 – 9 sites



CSN collocated TOR similar to IMPROVE

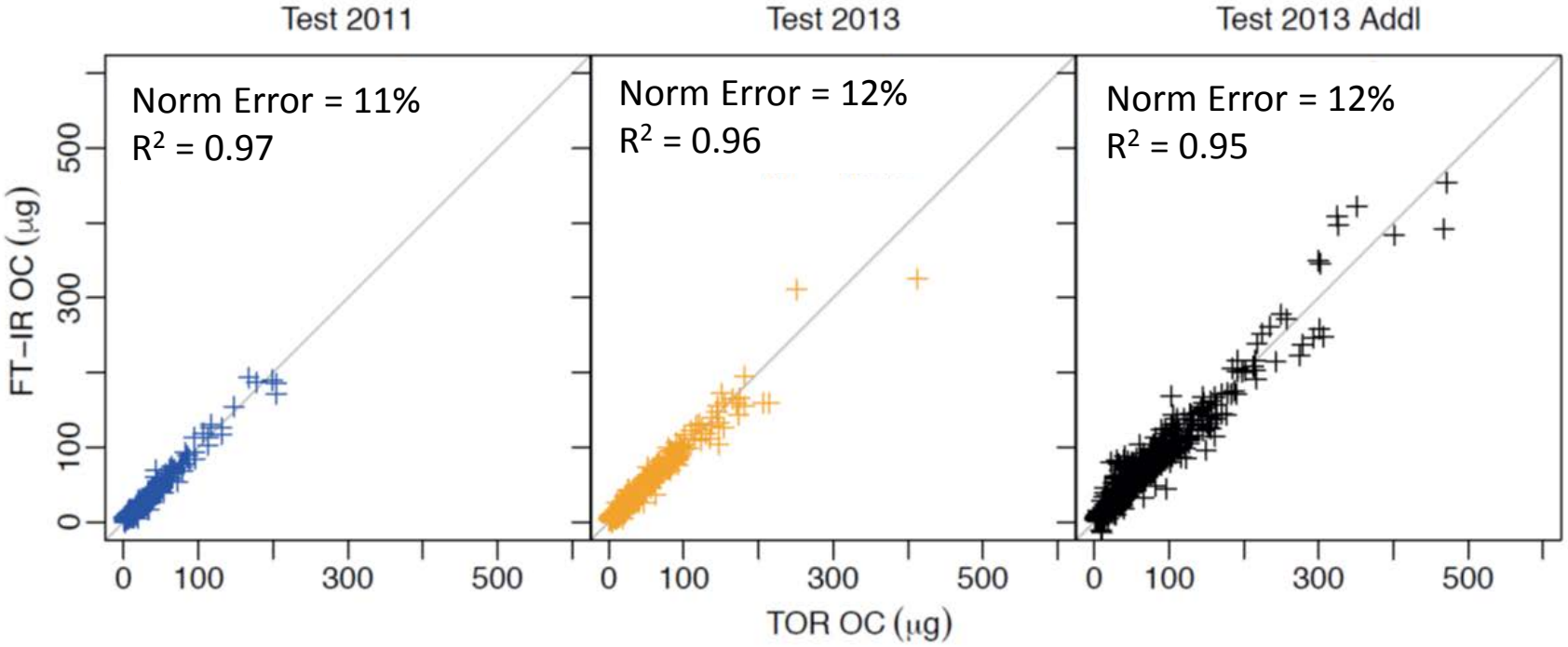
Weakley, Takahama, Dillner, 2016

FRM 2013 – 9 sites



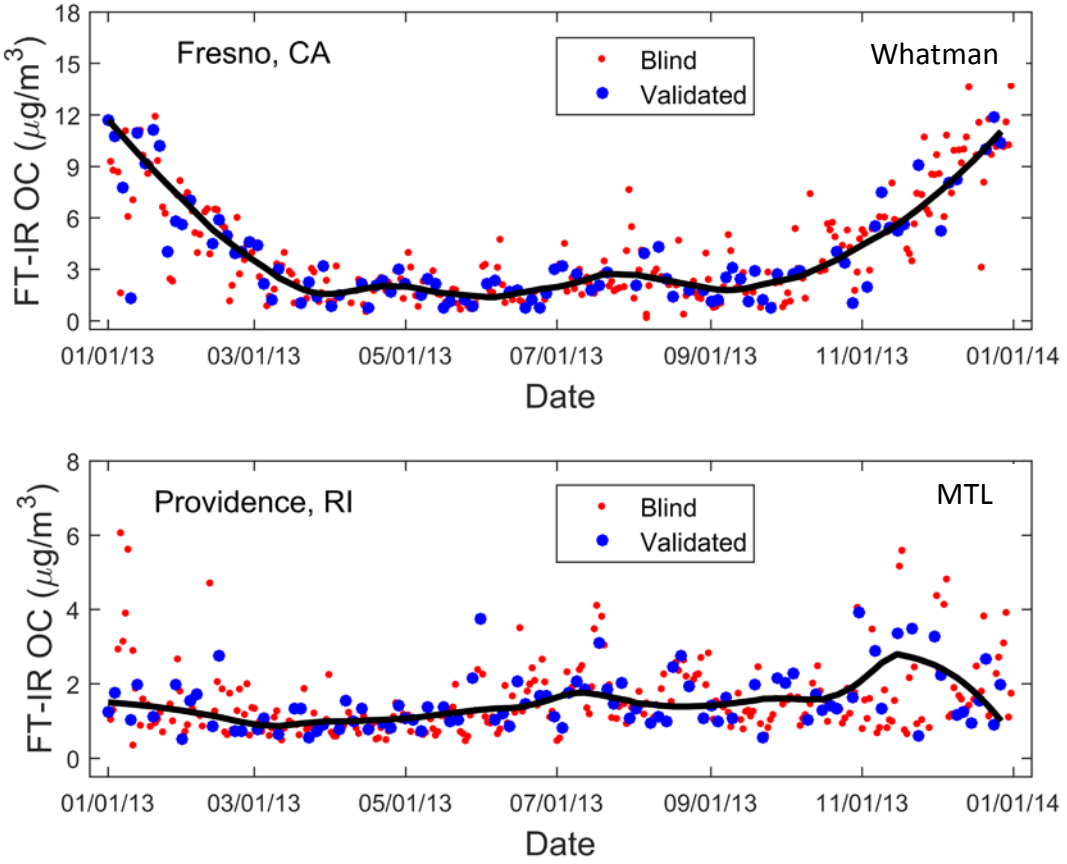
Weakley, Takahama, Dillner, in preparation

IMPROVE FT-IR OC
extending predictions to different years and sites with spectral processing



Updated from Reggente, Dillner and Takahama, 2016

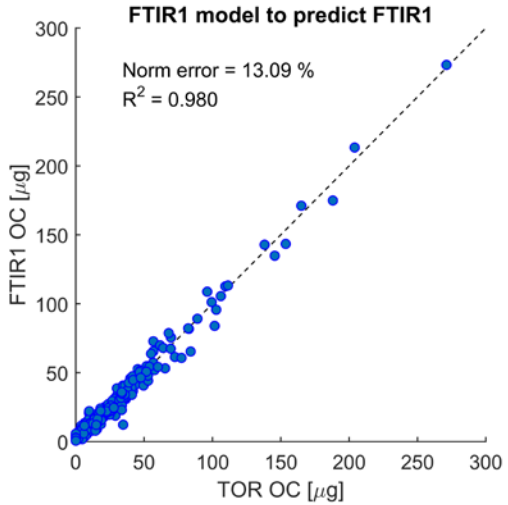
FT-IR OC in FRM network - new data

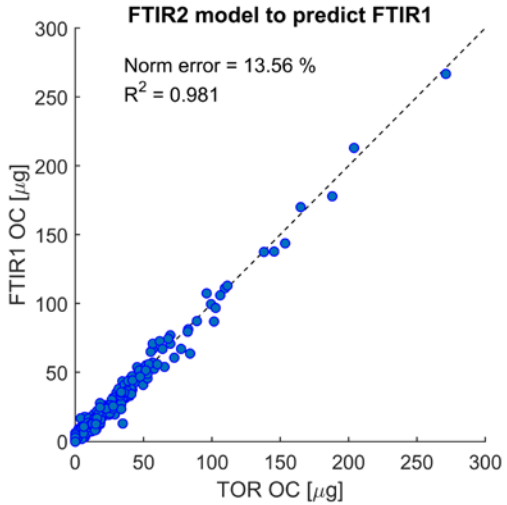


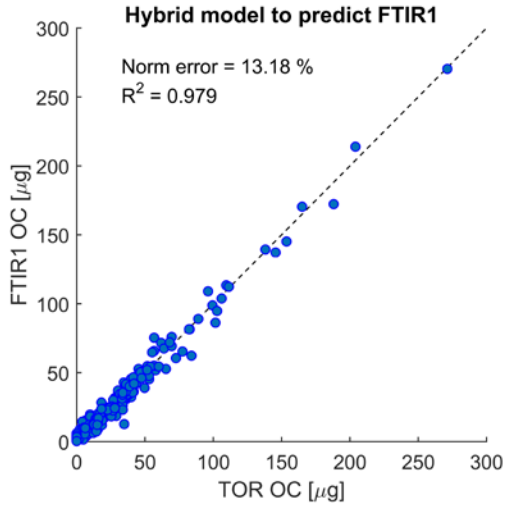
Weakley, Takahama, Dillner, in preparation

Calibration for two FT-IR instruments

- Subset of 2015 IMPROVE samples analyzed on FTIR1 and FTIR2
- Developed model for each instrument separately and one jointly, apply to test set
- Models perform equally well – similar results for EC

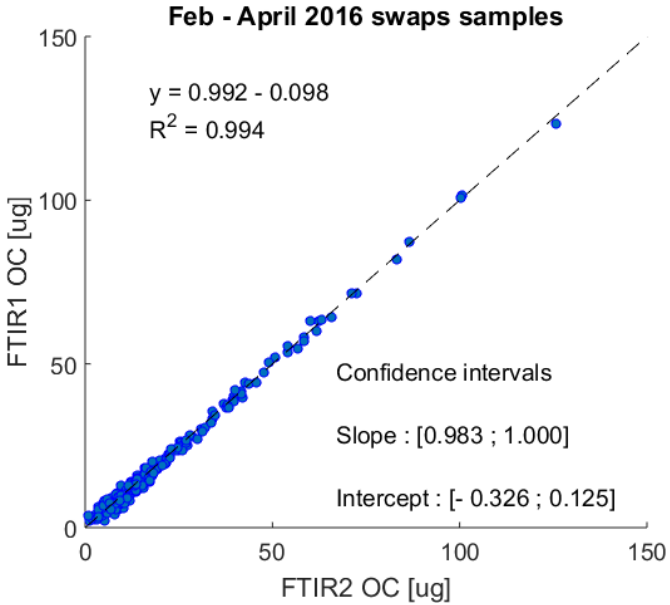


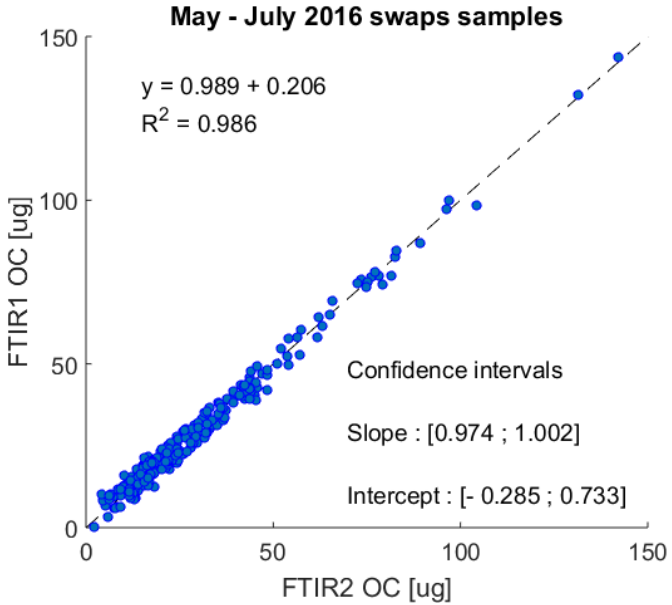




Debus, Weakley, Takahama, Dillner, in prep.

Instrument stability – moved instrument in May, 2016

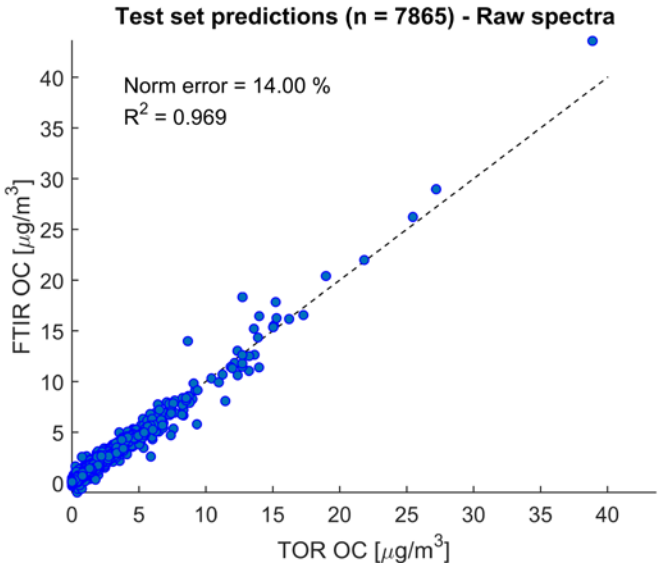


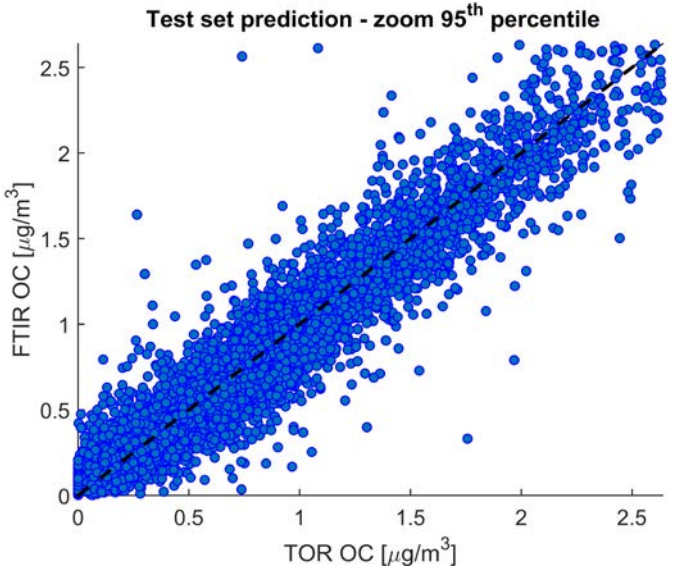


- Previous analysis using lab standards showed bias after move
- Analysis using ambient samples shows no statistical difference in the relationship between instruments
- Began using ambient samples in weekly QC to better assess instrument stability

2015 IMPROVE FT-IR OC preliminary results

- All sites
- 1 FT-IR
- Calibration:
  - ~1000 samples
- Predictions
  - ~8000 samples



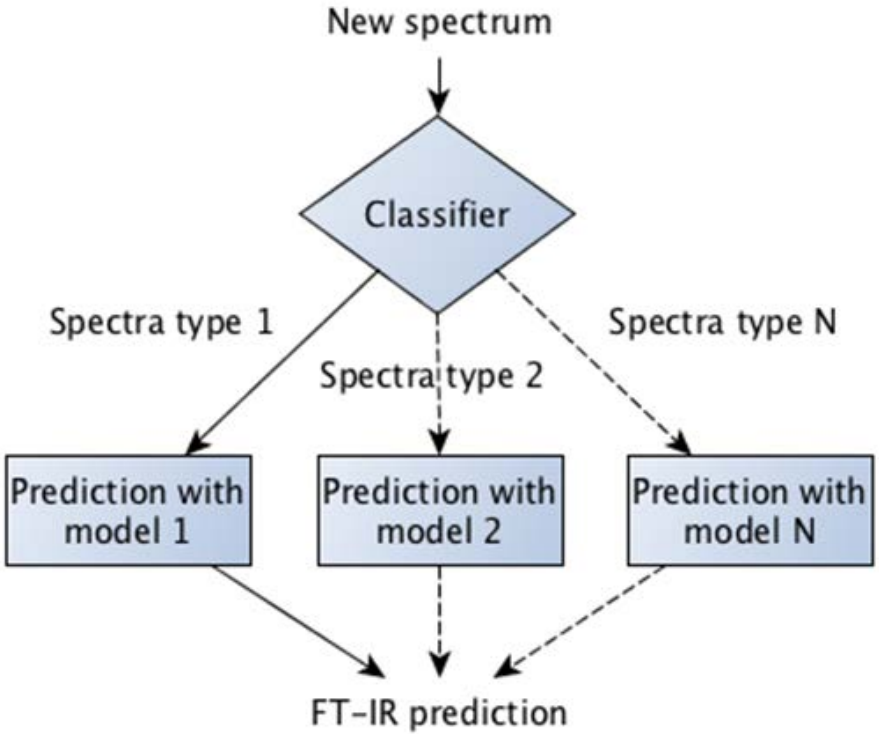


EC

- Lower mass than OC
- Less IR active than OC
- Functional group composition of EC changes with source and atmospheric processing

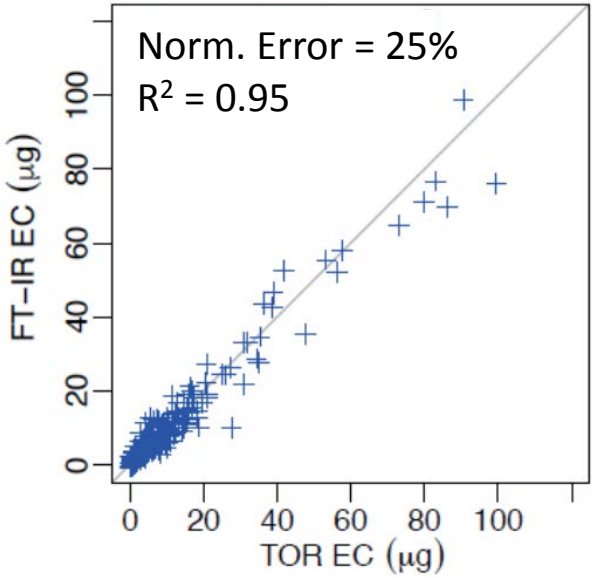
➡ Requires additional methods to produced high quality FT-IR EC data

Multi-level modeling

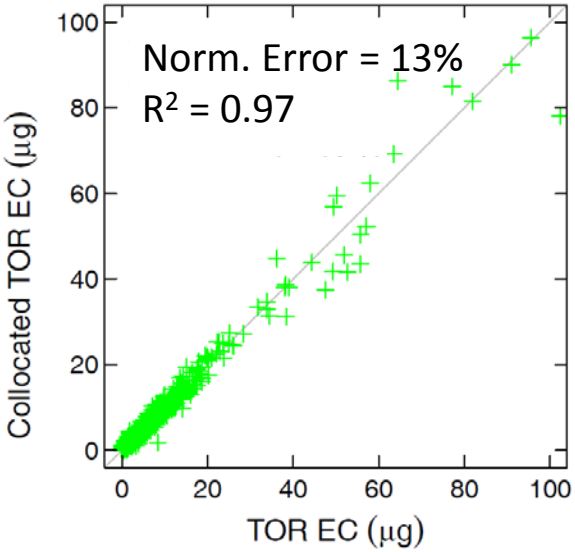


FT-IR EC in IMPROVE and CSN

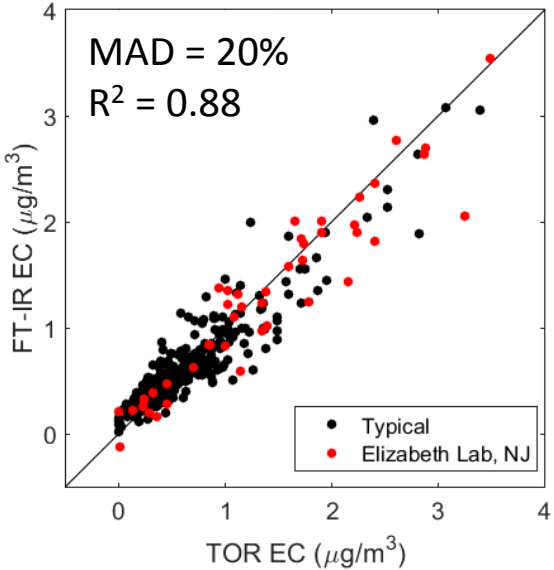
IMPROVE



IMPROVE collocated TOR



CSN

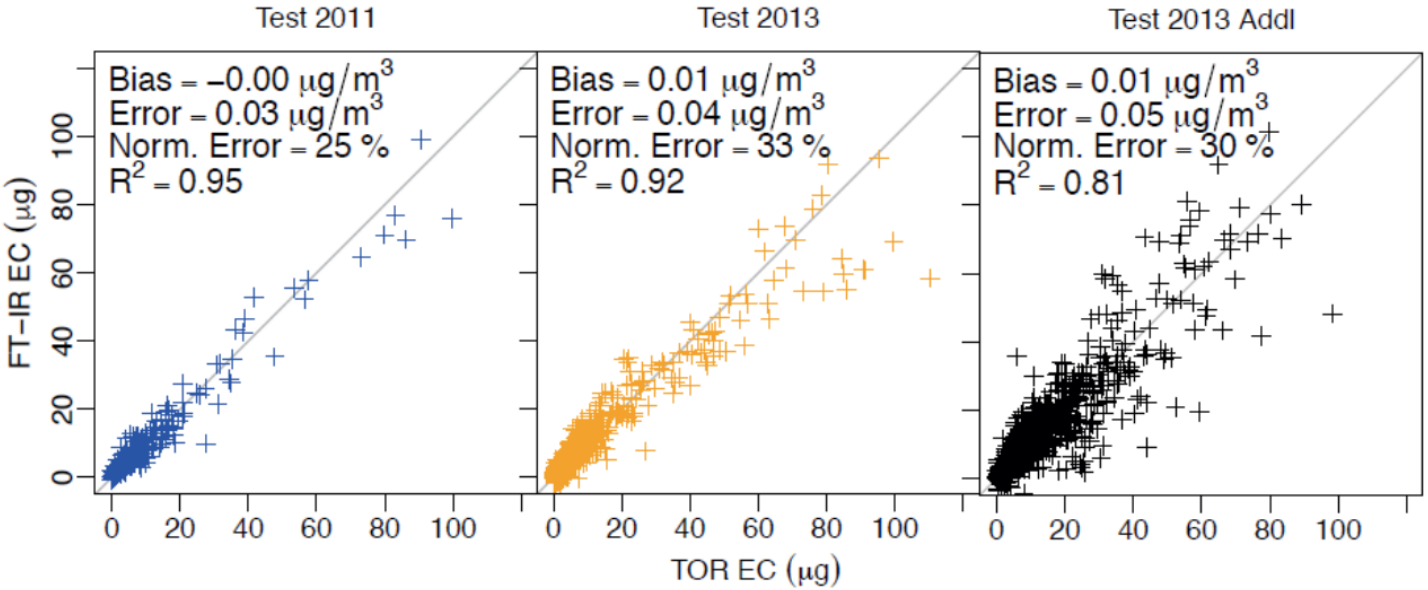


CSN collocated TOR similar to IMPROVE

Dillner and Takahama, 2015b

Adapted from Weakley, Takahama, Dillner, submitted

IMPROVE EC
Extending to different year and sites with spectral processing

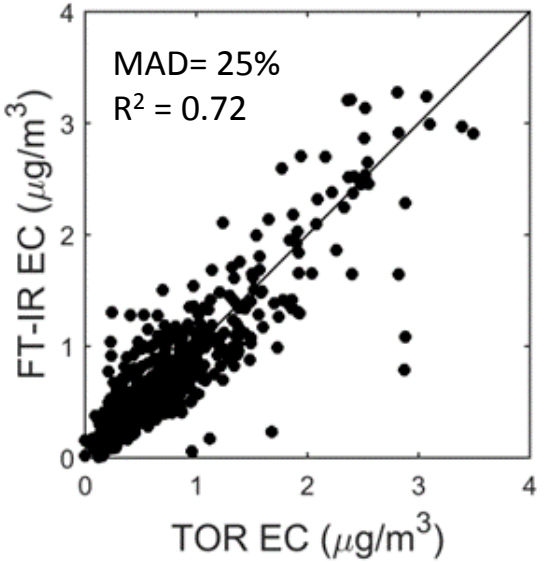


Updated from Reggente, Dillner and Takahama, 2016

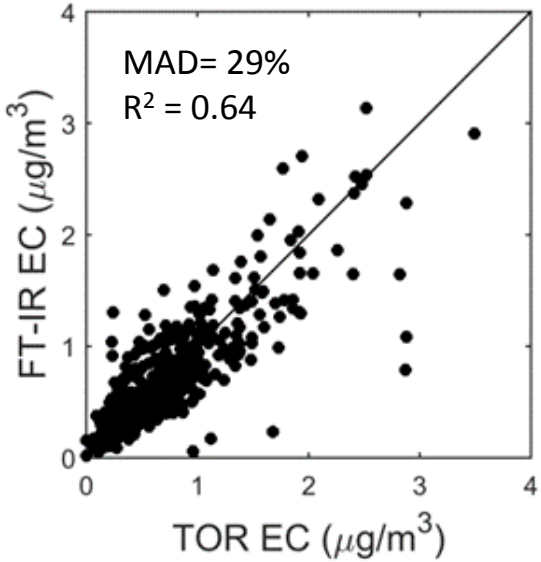
FT-IR EC in FRM

- Use spectra of CSN filters and CSN TOR data to develop calibration for FRM
- Baseline correct to minimize filter type
- Account for flow differences

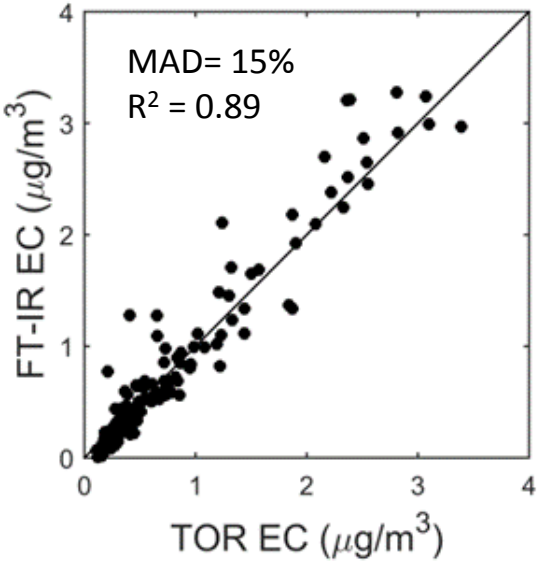
All samples



Filter type different from calibration

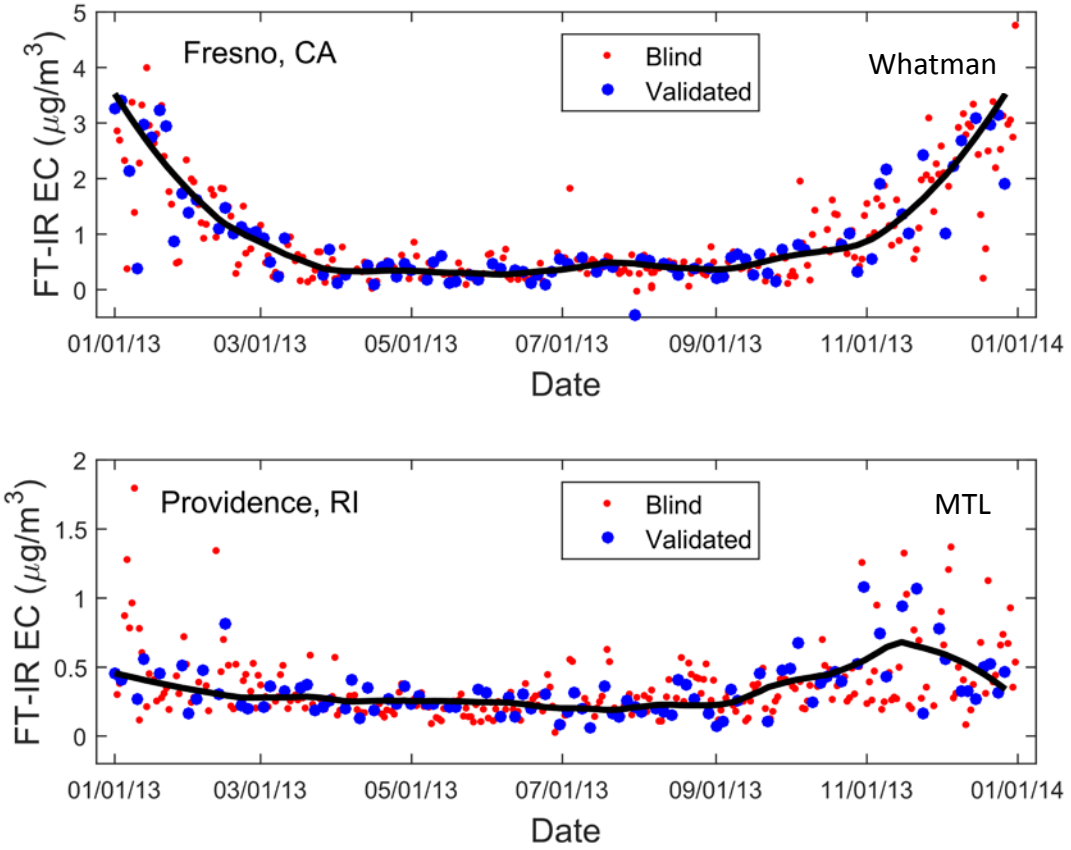


Filter type same as calibration

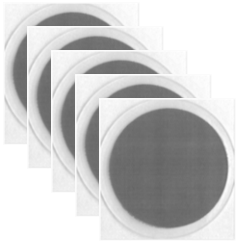


Weakley, Takahama, Dillner, in preparation

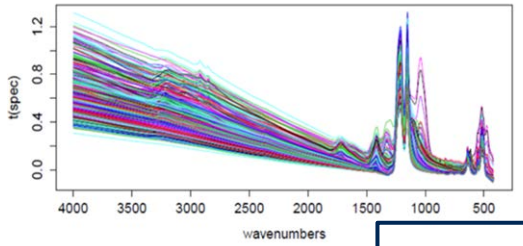
FT-IR EC in FRM network - new data



Calibration Development for FT-IR OC and EC



ambient sampled teflon filters



FT-IR spectra

TOR data

TOR OC and EC calibrations

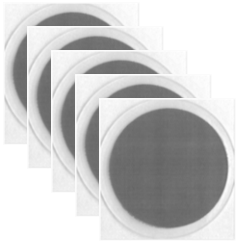
IMPROVE

CSN

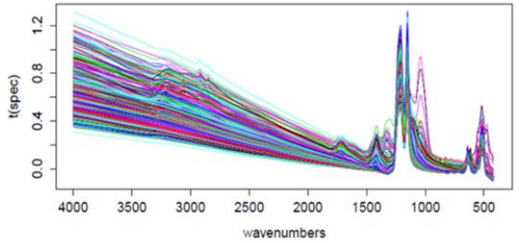
FRM

- Predict FT-IR OC EC in IMPROVE, CSN, FRM
- Calibration useful for multiple years
- One calibration for multiple FTIRs
- Instrument stab.
- Network wide calibration begun

Calibration Development for functional groups



laboratory sampled teflon filters

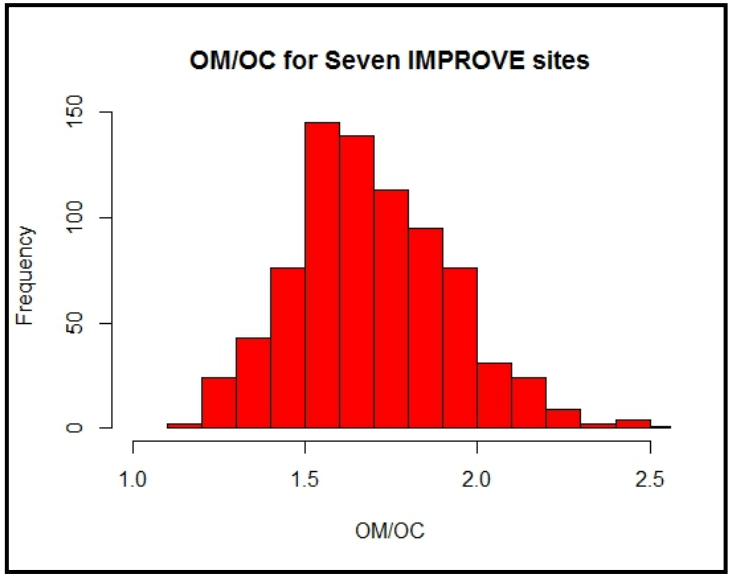


FT-IR spectra

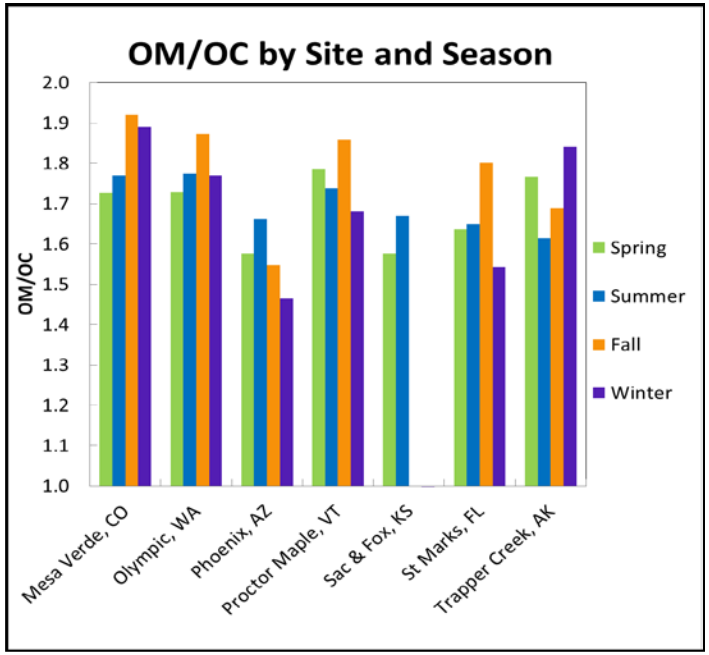
laboratory standards masses

Functional group and OM calibrations

OM/OC in 2011 IMPROVE samples



- 4 dominate functional group standards
  - CH, C=O, cOH, aOH
  - $(NH_4)_2SO_4$ - interferent with OH
  - 1 or 2 compounds per standard

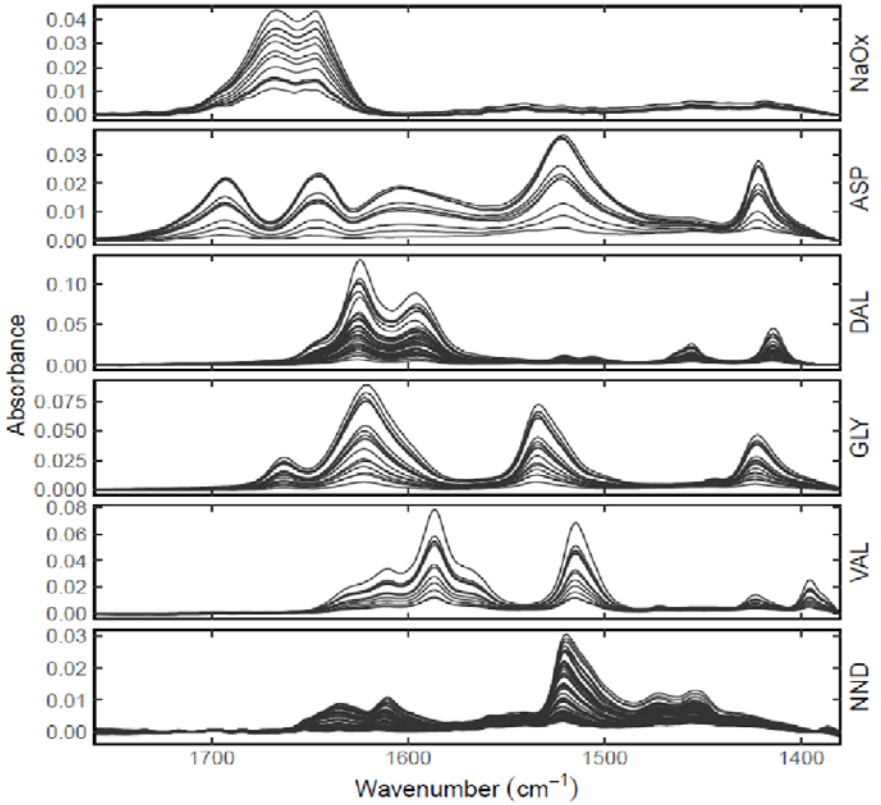


- Median OM/OC = 1.67
- Site variability – urban site lowest
- Seasonal variability

Ruthenburg et al., 2014

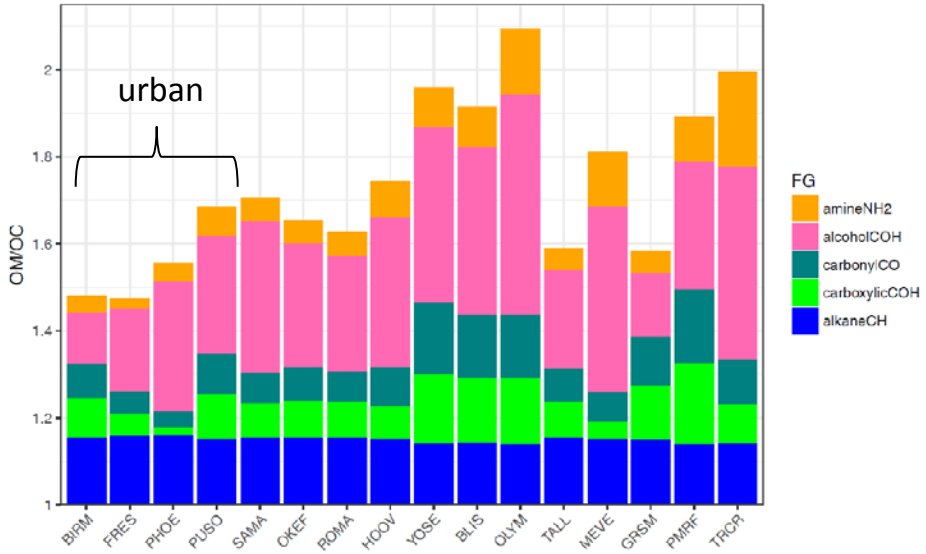
Amine (NH_2) standard selection

- Standards
  - 1 interferent (carboxylate)
  - 4 amino acids
  - 1 amine
- Peak height vary by compound
- Selected wavenumber region and standards
  - robust predictions
  - not over predict



Kamruzzaman, Takahama and Dillner, accepted

Annual mean OM/OC at 16 IMPROVE sites in 2013 from five functional groups



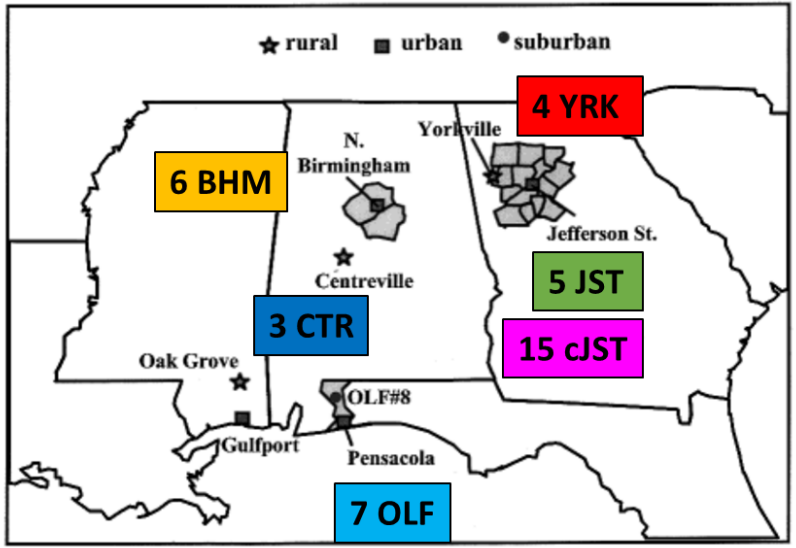
Contribution of each functional group to OM/OC

Urban sites – lower OM/OC

Kamruzzaman, Takahama and Dillner, accepted

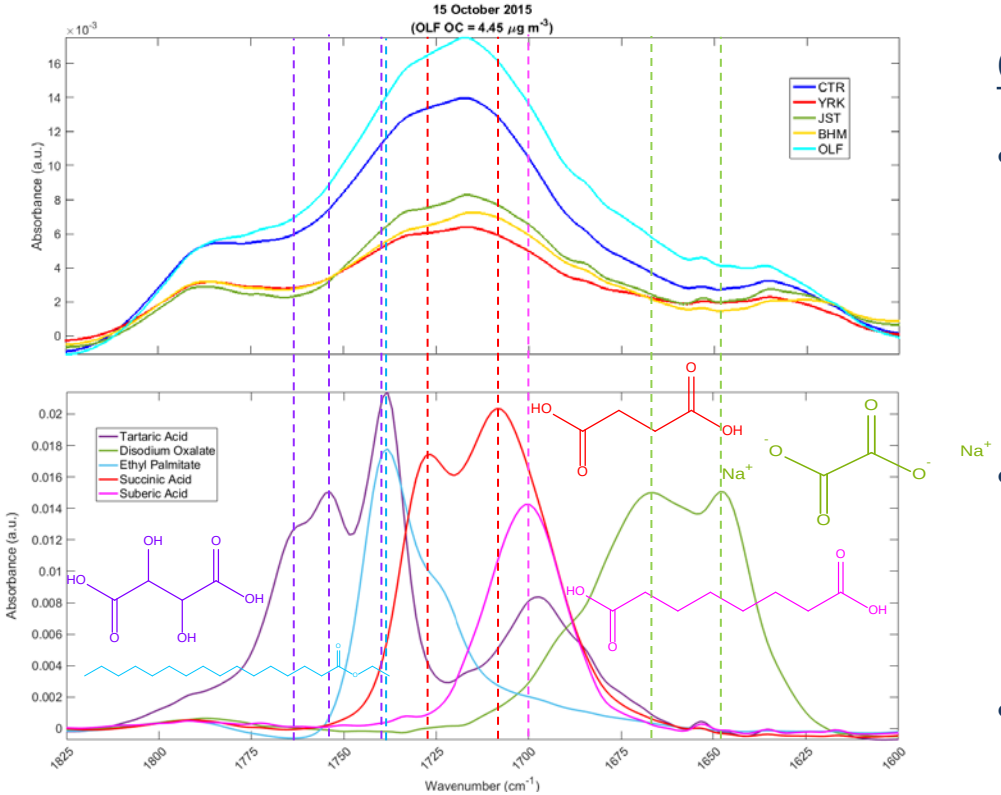
Functional groups and OM in the SEARCH network

- Southeastern Aerosol Research and Characterization Network
  - regional speciation network
  - 2 urban/rural pairs
  - 1 suburban site
- Sampling
  - Filter based
  - Continuous
- More extensive analysis than IMPROVE or CSN
- Network discontinued as of 12/31/2016



FT-IR analysis
- 2016 – daily samples
- 2008-2015 – 1 month/season (1 in 3 days)

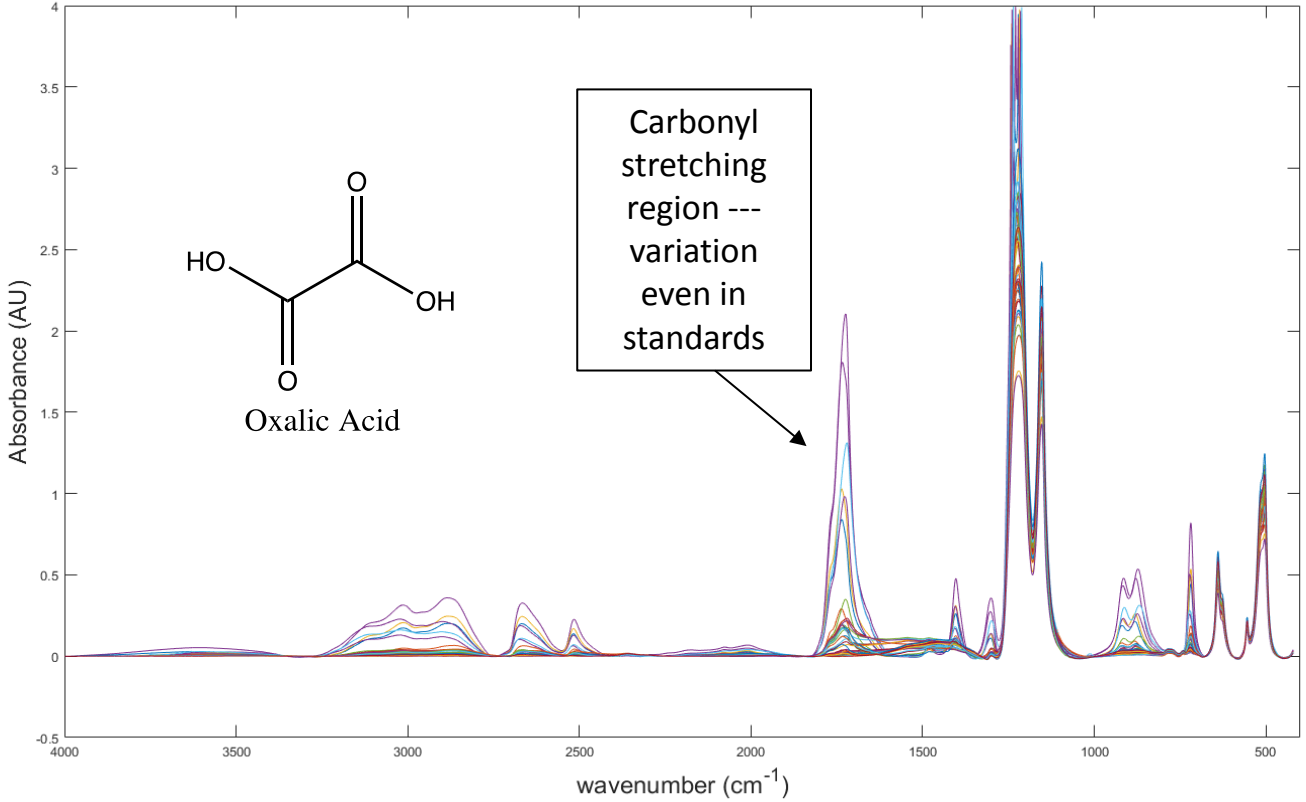
Selecting appropriate standards for calibration



Objectives:

- Atmospherically relevant and representative of classes of compounds (literature)
- Peaks observed in ambient spectrum (figure at left)
- Favorable properties for laboratory use

Oxalic Acid – most abundant dicarboxylic acid



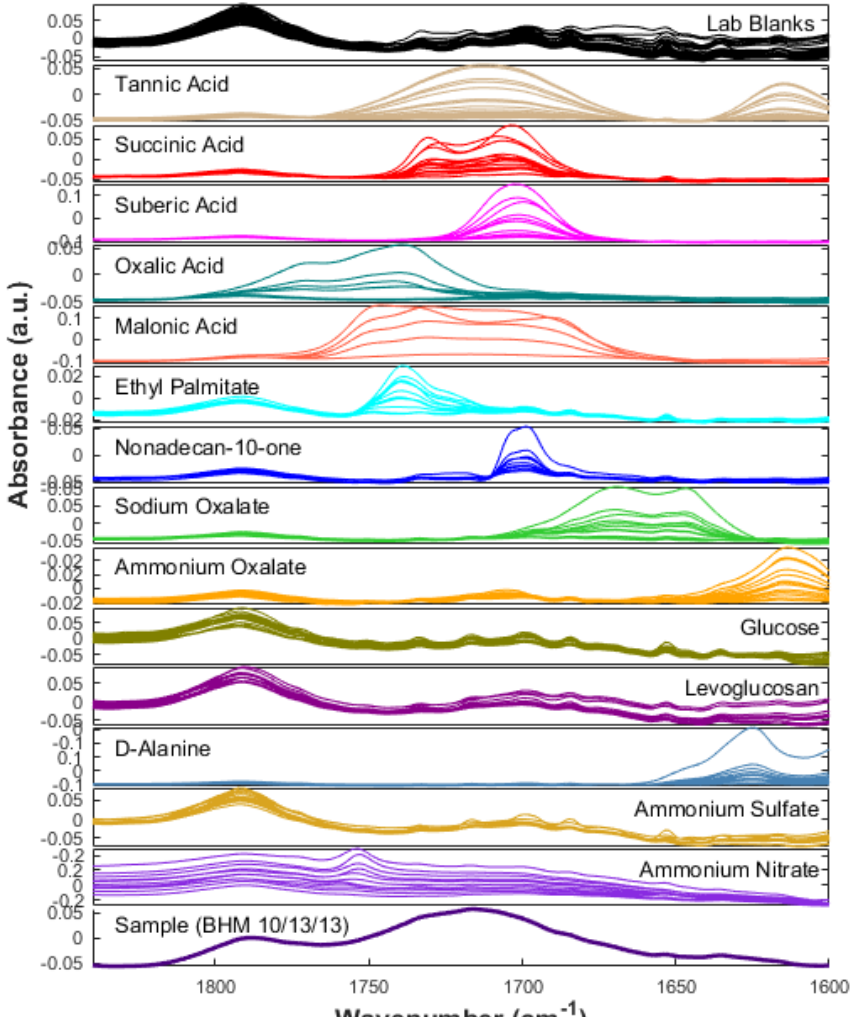
Carbonyl compounds

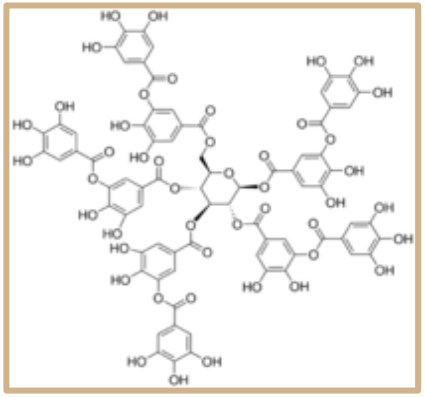
- Tannic acid
  - Represents "HULIS" here
- Carboxylic acids:
  - Short, long-chain di-carboxylic acids
- Non-acid carbonyls:
  - Ester
  - Ketone
- Carboxylate salts
- Carbohydrates
- Amino acid

Interfering compounds

- Inorganic salts

Carbonyl Stretching Region



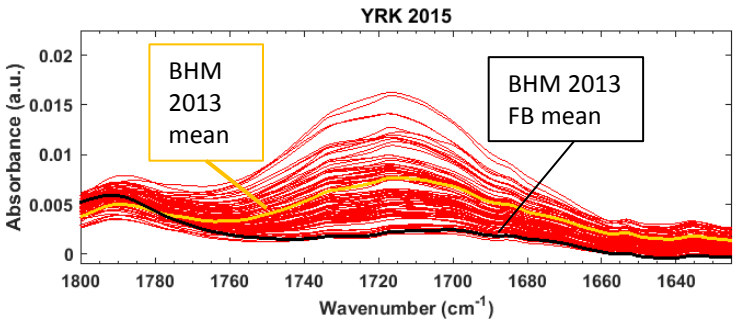


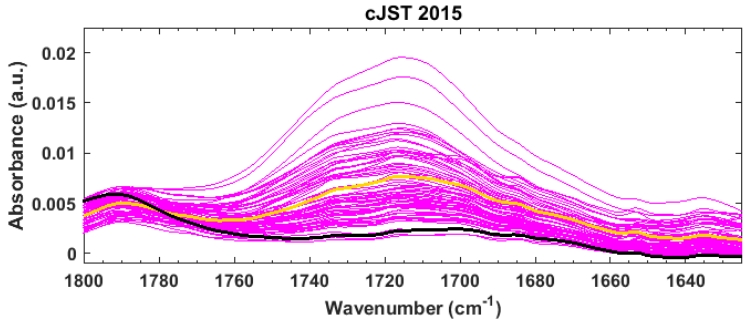
Carbonyl region by site for 2015

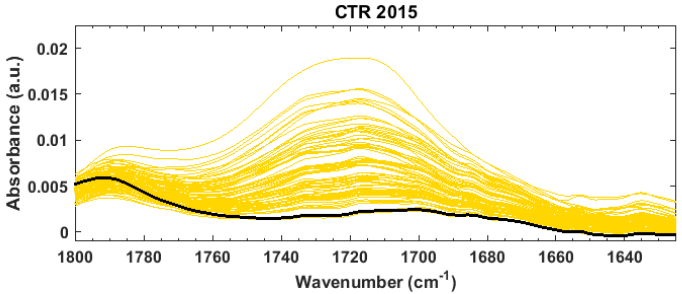
- Variability in peak height (amount)
- Common shape
- Could point to a common, oxidized carbonyl character

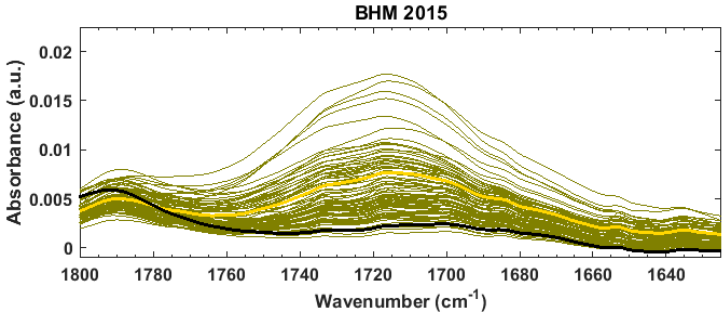
Rural

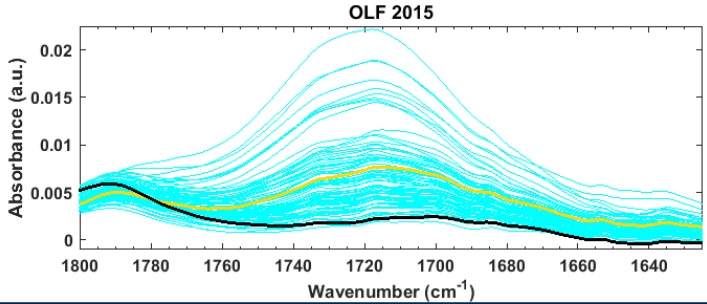
Urban





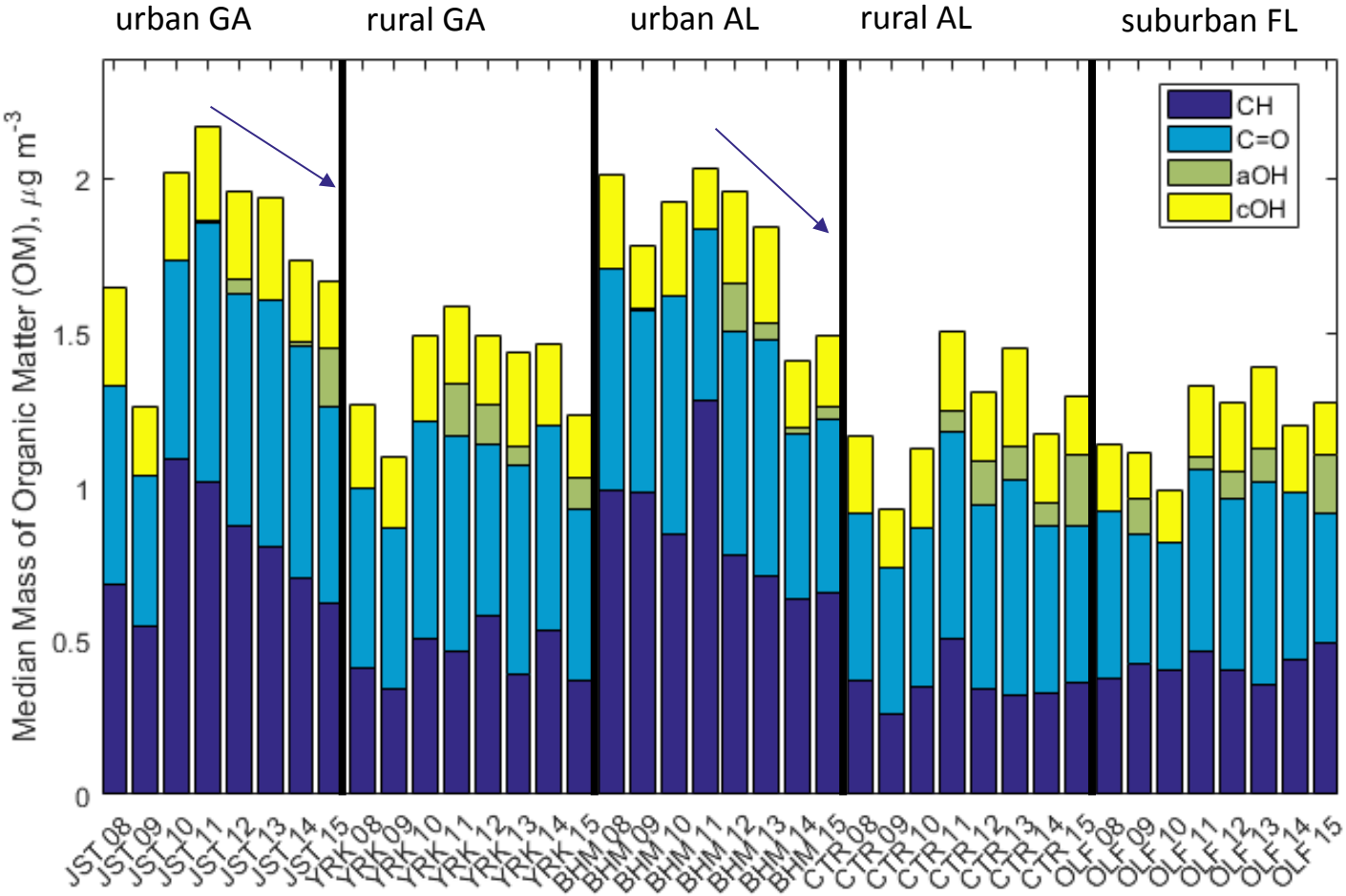




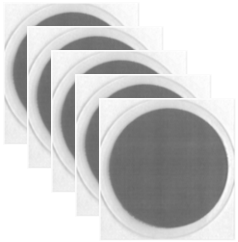


Trends in OM

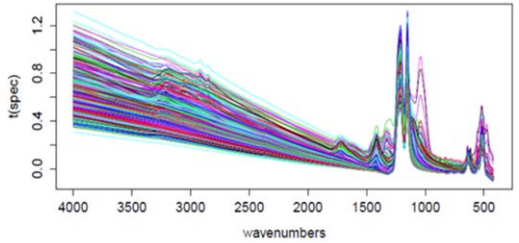
Urban sites (JST, BHM)
highest OM
Decreasing OM and CH
urban sites
2010-2015



Calibration Development for functional groups



laboratory sampled teflon filters



FT-IR spectra

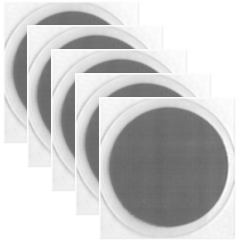
laboratory standards masses

Functional group calibrations

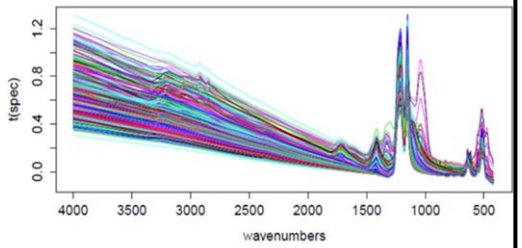
Summary

- 5 functional groups measured for IMPROVE
- Variability in OM/OC
- Developing functional group and OM/OC for SEARCH (CSN and others)

Calibration Development for functional groups



laboratory sampled teflon filters



FT-IR spectra

laboratory standards masses

Functional group calibrations

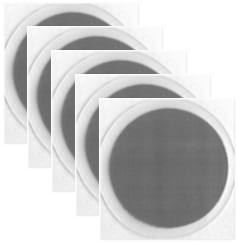
Summary

- 5 functional groups measured for IMPROVE
- Variability in OM/OC
- Developing functional group and OM/OC for SEARCH (CSN and others)

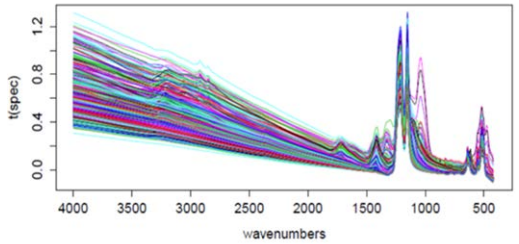
Next Steps

- Finalize functional groups and OM in SEARCH (EPRI)
- Apply new modeling approaches (classical constraint satisfaction, ANN) to constrain OM (EPRI)
- Possible implementation in IMPROVE and CSN

Calibration Development for source apportionment



Ambient or laboratory sampled teflon filters

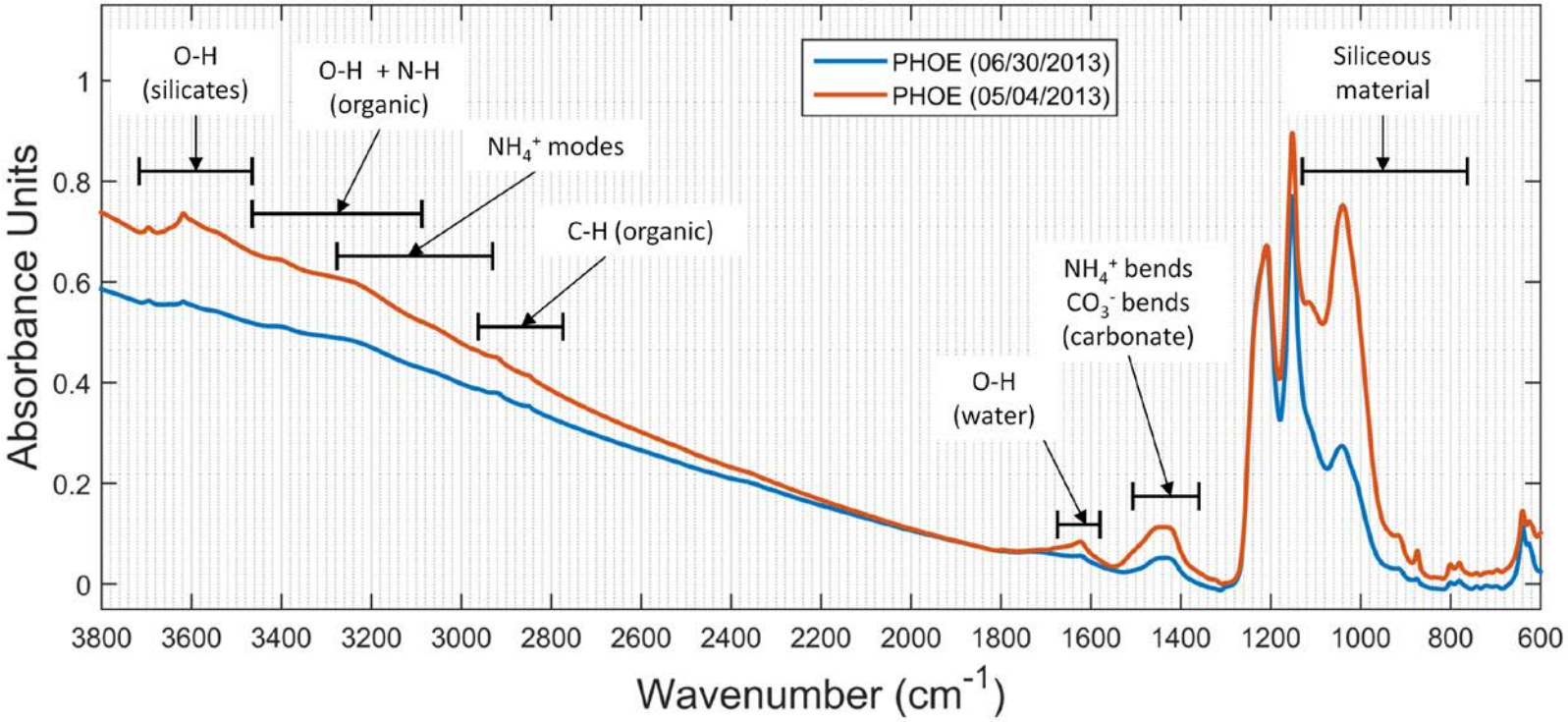


FT-IR spectra

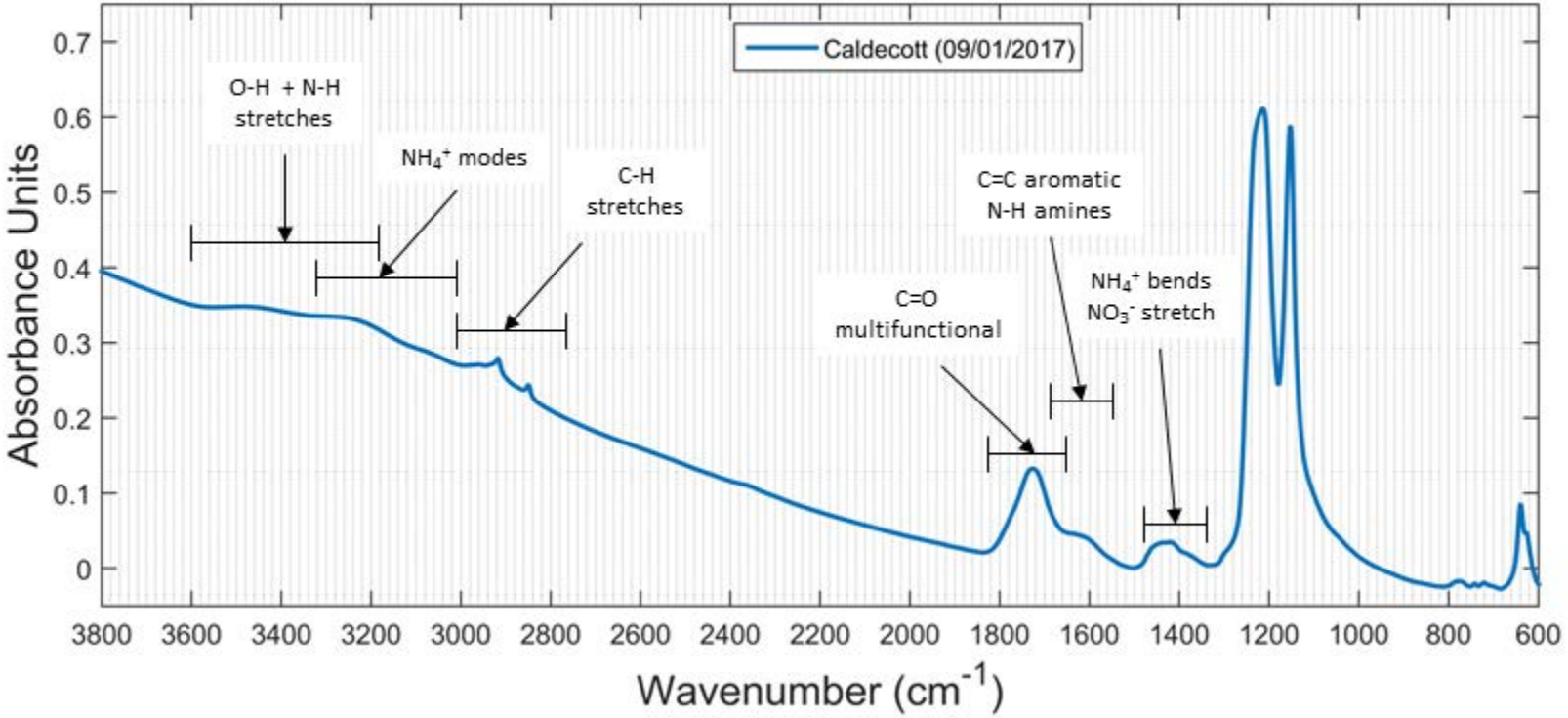
source info

Clusters/PMF/ calibration

Soil (IMPROVE Phoenix samples in spring)

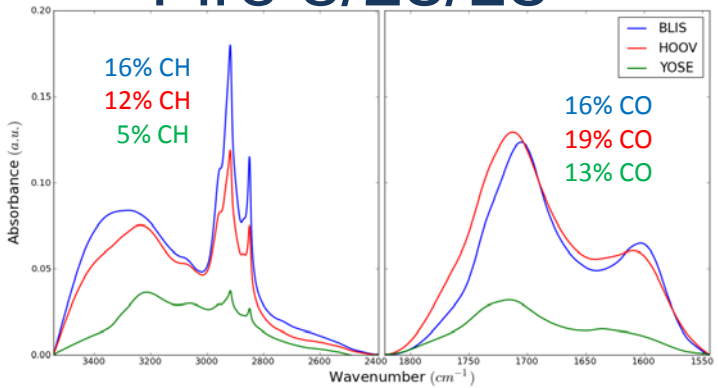


Fresh vehicle emissions (Caldecott Tunnel sample)

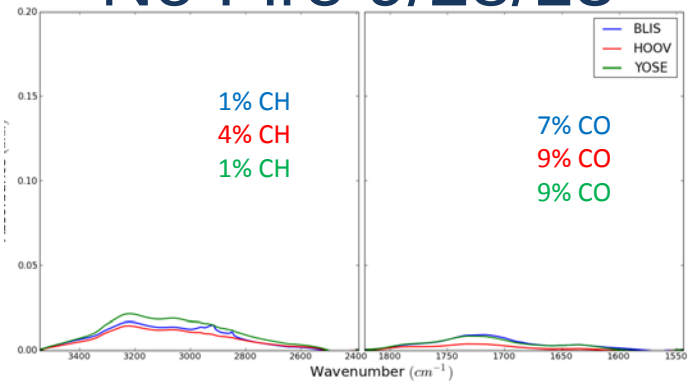


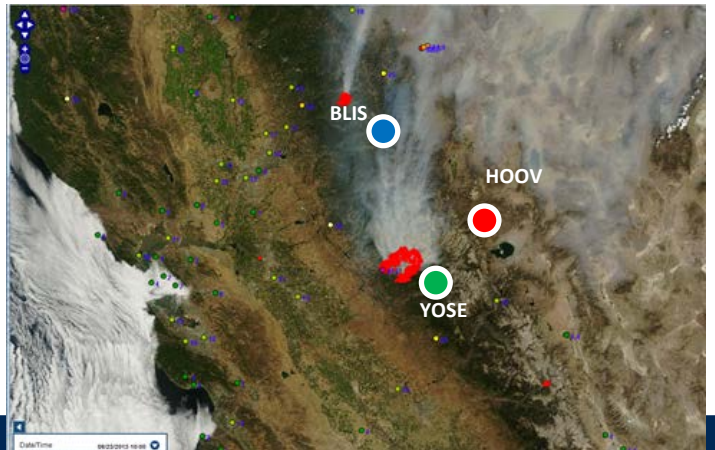
Rim Fire

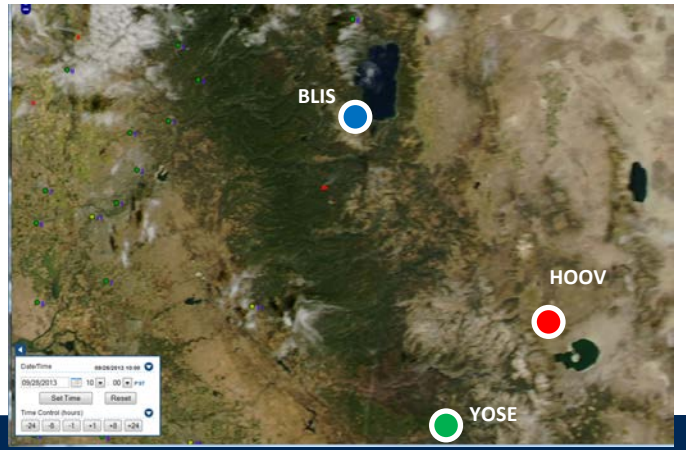
Fire 8/23/13



No Fire 9/28/13

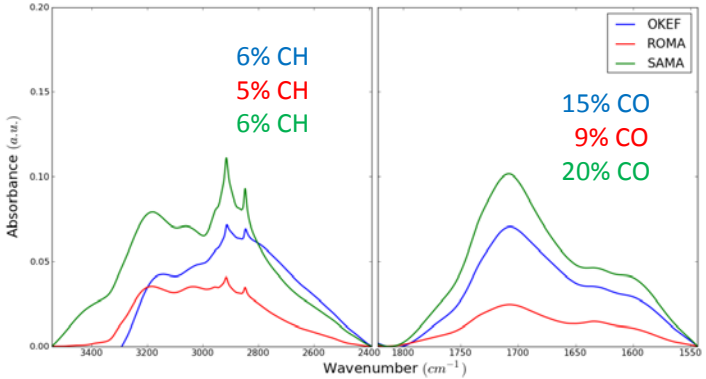


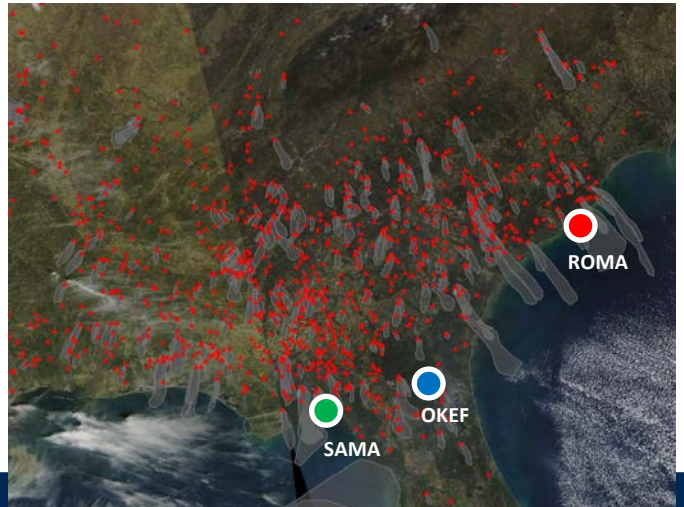




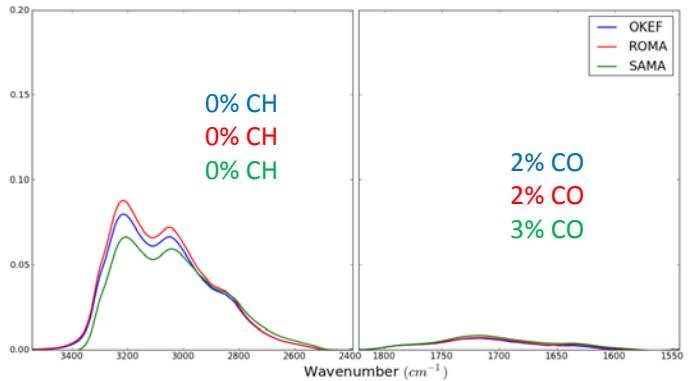
Prescribed Fires

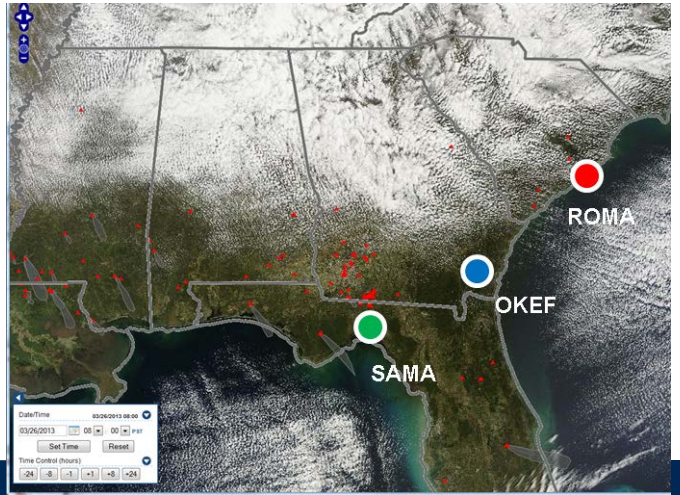
Fire 3/8/13





No Fire 3/26/13





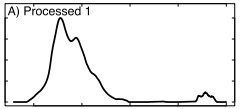
Organic matter source apportionment

IMPROVE 2011
Urban: Phoenix, AZ
Rural: 6 sites

Ambient sample spectra

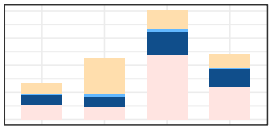
Spectral Decomposition (PMF)

Source profiles (e.g., PMF factor profiles)



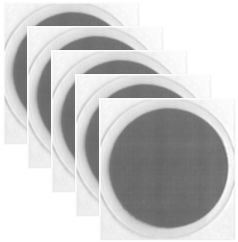
Source association

Source-apportioned OM

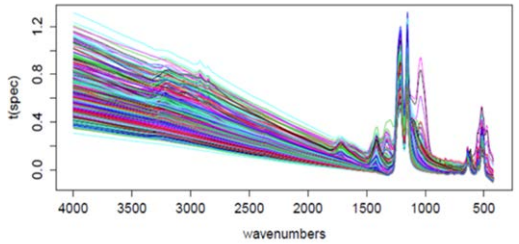


Kuzmiakova, Dillner and Takahama, *in prep.*

Calibration Development for source apportionment



ambient sampled teflon filters



FT-IR spectra

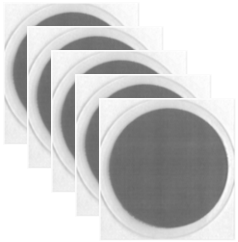
source info

Clusters/PMF/ calibration

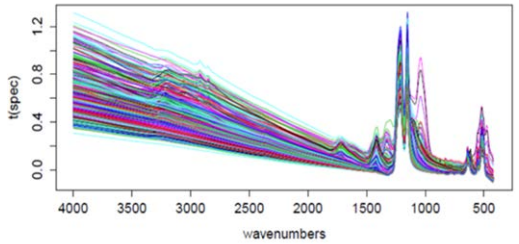
Summary

- Promising methods for network data sets for source apportionment

Calibration Development for source apportionment



ambient sampled teflon filters



FT-IR spectra

source info

Clusters/PMF/ calibration

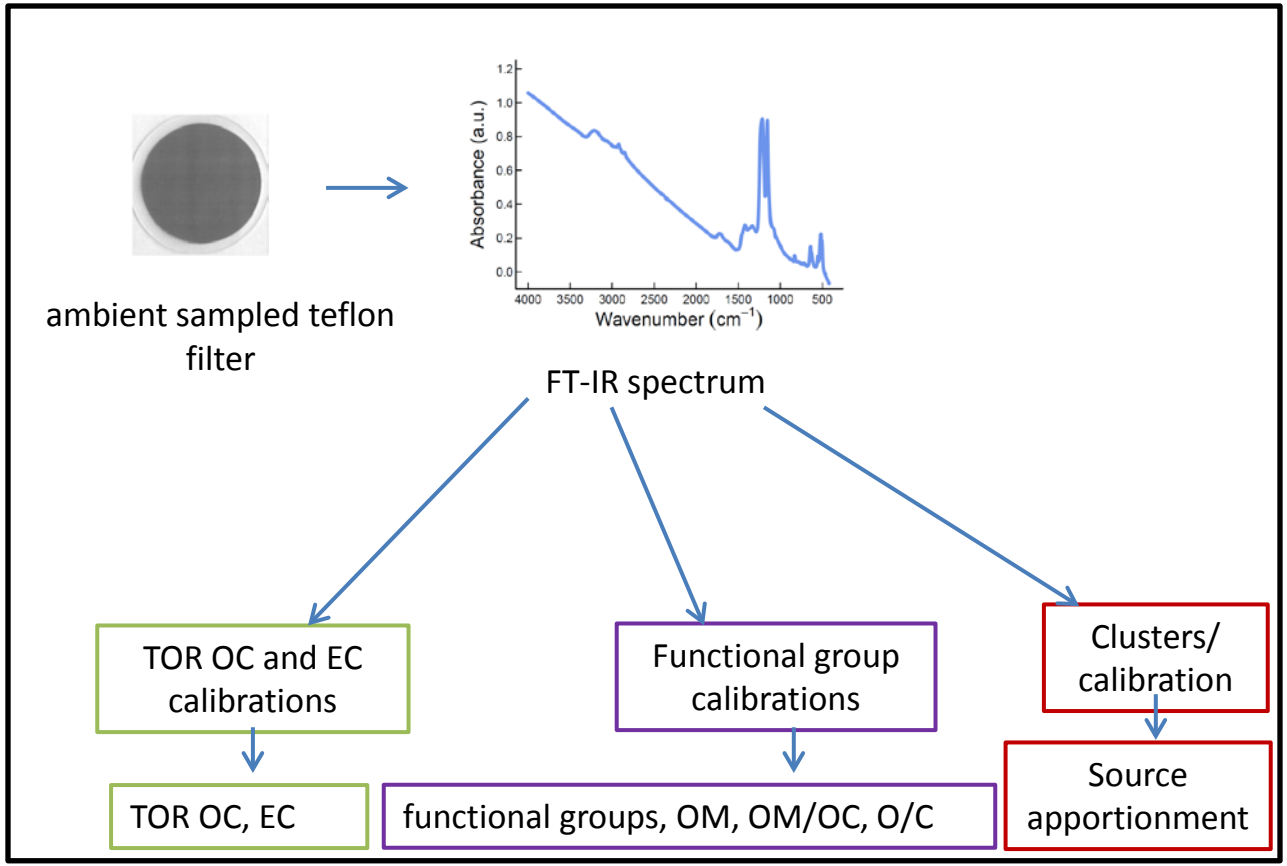
Potential Future Work

- Use levoglucosan data to estimate smoke impact on IMPROVE and FRM samples
- Use source samples to constrain PMF type modeling or do Chemical Mass Balance modeling

Summary

- Promising methods for network data sets for source apportionment

Characterizing PM in monitoring networks with FT-IR



Summary

FT-IR is a non-destructive, fast method

Uses teflon filters routinely collected in networks

Shown proof of concept for:

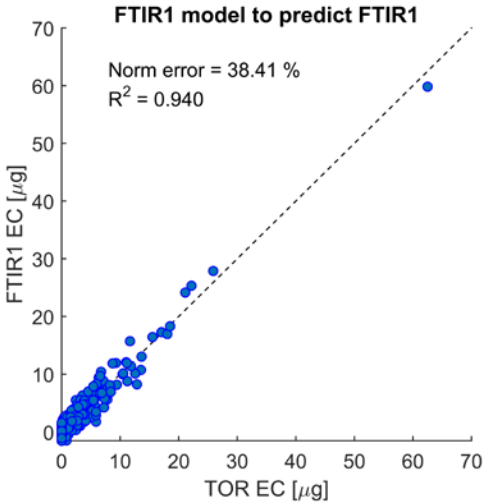
- TOR OC and EC in IMPROVE, CSN and FRM
- Calibrations across multiple instruments, instrument stability
- Network wide calibrations
- OM/OC and functional groups
  - Functional group contribution to OM (or OM/OC)
  - Additional functional groups
- Source apportionment
  - Promising but more development needed

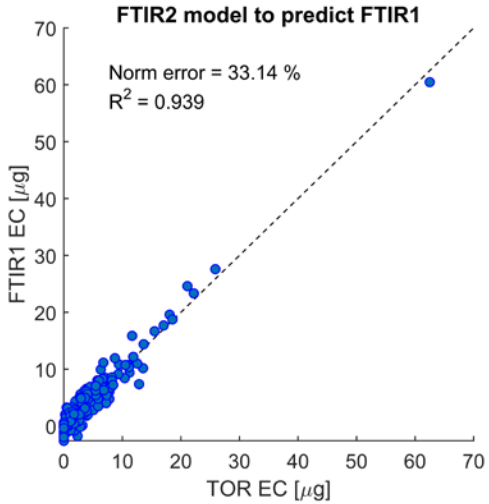
FT-IR is non-destructive, fast method for characterizing carbonaceous particulate matter in monitoring networks

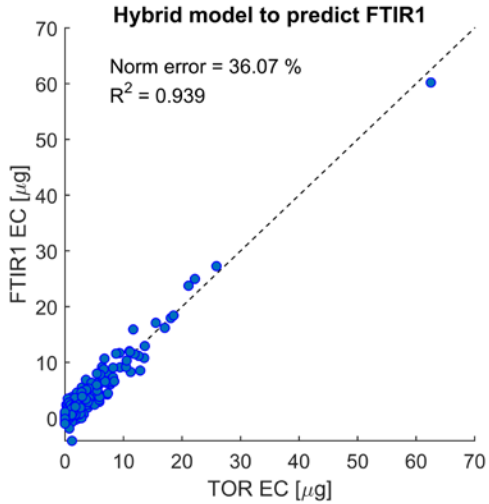
Publications cited in this talk and related

- **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 and FRM**
  - Predicting TOR OC for CSN, Weakley, Takahama and Dillner, 2016
  - Predicting TOR EC for CSN, Weakley, Takahama, and Dillner, submitted
  - 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
  - OM/OC with improved model selection, Takahama and Dillner, 2015
  - Amines and their impact on OM/OC in IMPROVE, Kamruzzaman, Takahama and Dillner, in revision
- **Automated Baseline correction**
  - Automated baseline correction method, Kuzmiakova, Dillner and Takahama, 2016
- **Source Apportionment**
  - Source Apportionment in IMPROVE, Kuzmiakova, Dillner and Takahama, in prep

Subset of IMPROVE 2015 samples analyzed on two FT-IR instruments – FT-IR EC







Debus, Weakley, Takahama, Dillner, in prep.

Time series of FTIR OC - TOR OC