OC, EC, OM and functional group measurements for IMPROVE and CSN using FT-IR

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Grand Canyon National Park
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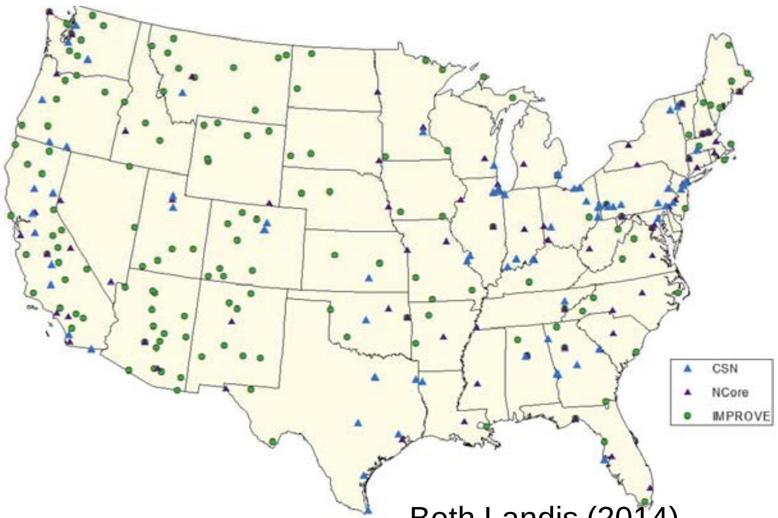
Carbonaceous Aerosol Characterization in IMPROVE and CSN – current status

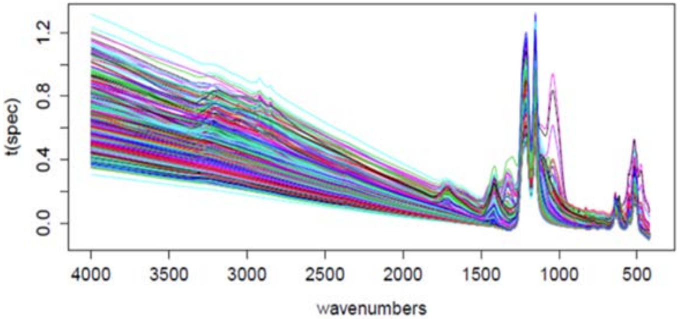
- Networks use same approach
  - IMPROVE/URG sampler
  - TOR
    - Organic carbon (OC)
      - Monthly median blank corrected
    - Elemental carbon (EC)
- Long-time series of data
  - Beginning 2007-10 for CSN
  - 1989/2005 for IMPROVE
- Organic matter (OM = carbon + associated oxygen, hydrogen, sulfur, nitrogen)
  - Estimated using OM/OC = 1.8 in IMPROVE network
  - OM/OC = 1.4, common for urban sites like CSN sites



Beth Landis (2014)

Alternate approach for carbon characterization: Fourier Transform Infrared (FT-IR) Spectroscopy

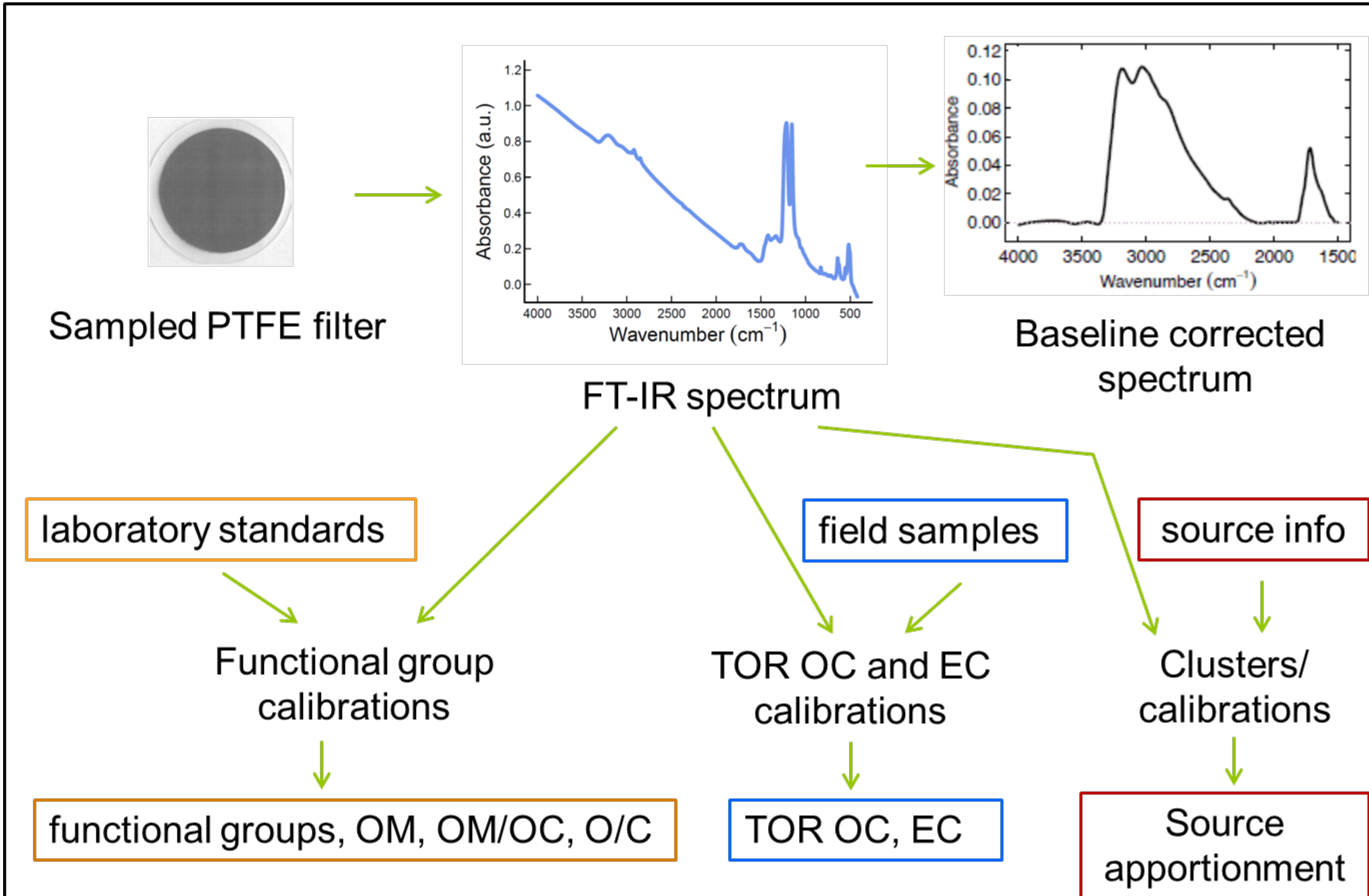
- Non-destructive analysis of routinely collected teflon filters
  - IMPROVE
  - CSN
  - FRM (mass only network)
- Fast and inexpensive method
- FT-IR can produce:
  - TOR-equivalent OC, EC – maintain time-series
  - Functional groups (C-H, C=O, C-NH2)
    - OM/OC
    - atmospheric chemistry
    - source apportionment of OM

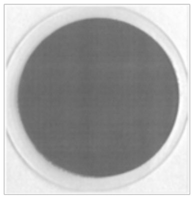


800 FT-IR spectra

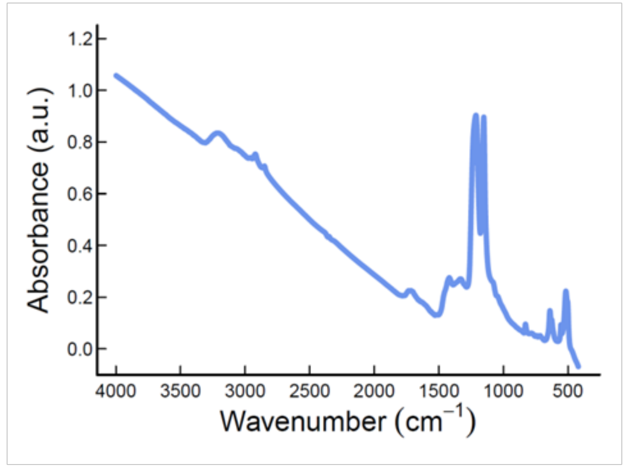
Leveraging EPA and NPS funding

- EPA and NPS
  - Me
  - Post-doctoral scholar Andy Weakley
  - Undergraduate students to collect FT-IR spectra
  - FT-IR instruments
- Satoshi Takahama, assistant professor at EPFL in Switzerland
  - Post-doctoral scholar Matteo Reggente
  - Staff Researcher Adele Kuzmiakova
  - Graduate student Giulia Ruggeri (part-time)
- EPRI
  - Post-doc Mohammed Kamruzzaman to add new functional groups
  - Pending projects
    - Add complex mixtures of standards to functional group calibrations
    - Compare functional group measurements to AMS
    - Measure functional groups in the SEARCH network current and archived filters


Sampled PTFE filter
Absorbance (a.u.)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})
FT-IR spectrum
Absorbance
0.12
0.10
0.08
0.06
0.04
0.02
0.00
4000
3500
3000
2500
2000
1500
Wavenumber (cm^{-1})
Baseline corrected spectrum
laboratory standards
field samples
source info
Functional group calibrations
TOR OC and EC calibrations
Clusters/ calibrations
functional groups, OM, OM/OC, O/C
TOR OC, EC
Source apportionment



Sampled PTFE filter



FT-IR spectrum

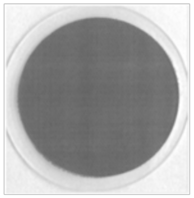
field samples

TOR OC and EC calibrations

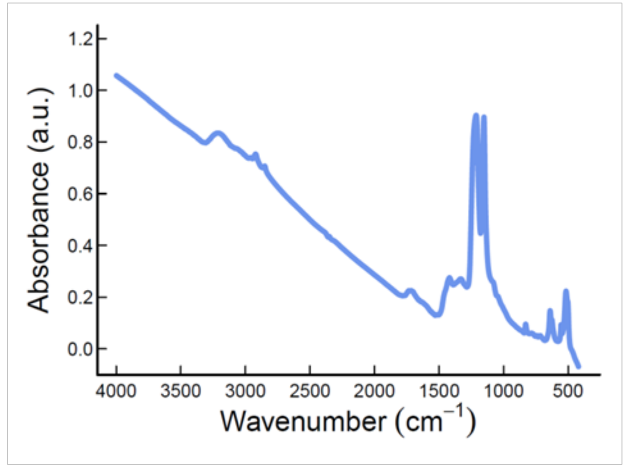
TOR OC, EC

IMPROVE

CSN (FRM)



Sampled PTFE filter



FT-IR spectrum

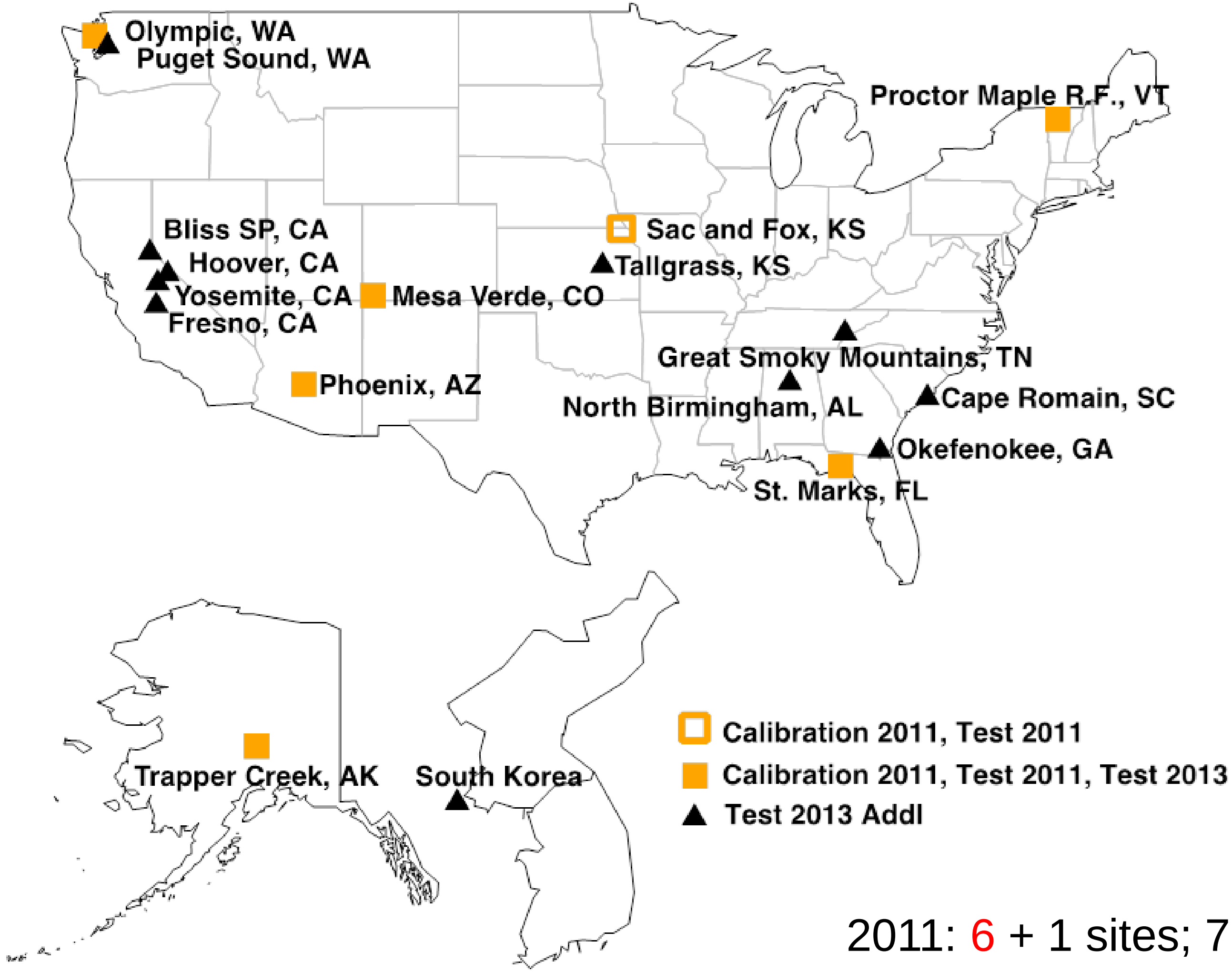
field samples

TOR OC and EC calibrations

TOR OC, EC

IMPROVE

IMPROVE 2011 and 2013



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

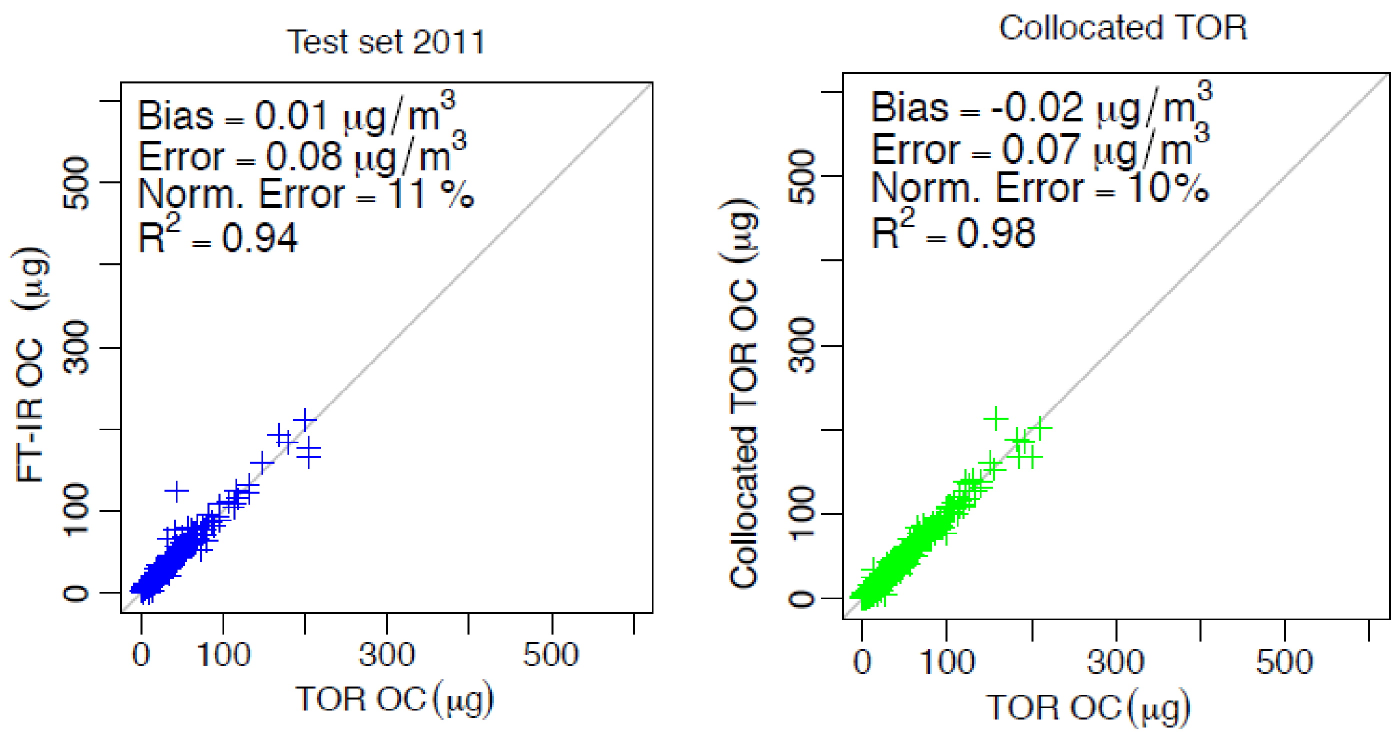
Methods

- FT-IR spectra
  - Teflon filter samples
  - 5 minutes for one spectrum
  - No pre-processing of spectra
- TOR OC and EC data (FED)
  - OC is monthly median blank corrected
- 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

IMPROVE FT-IR OC

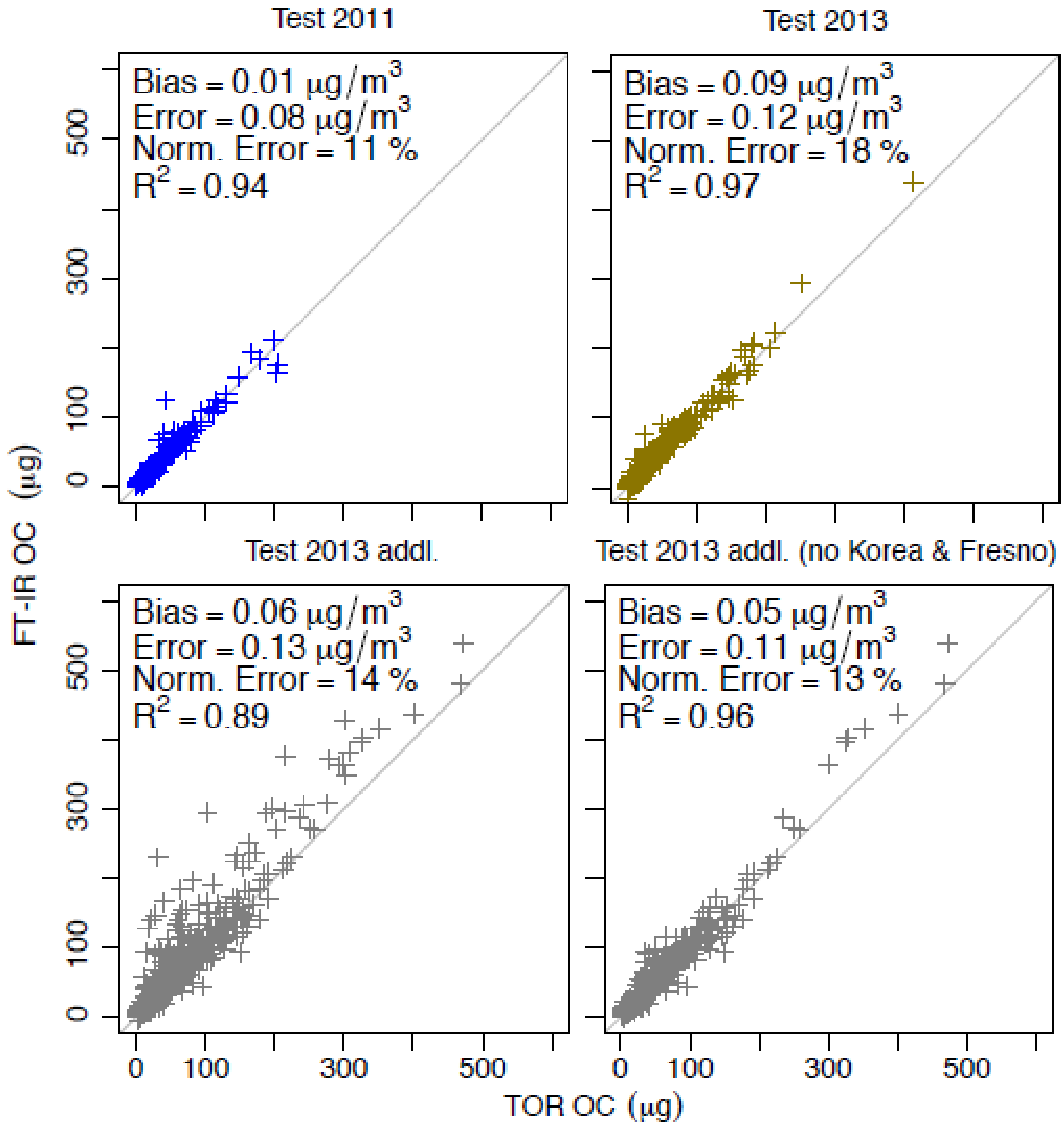


	FT-IR OC
MDL (μg/m³)	0.14
% below MDL	3
precision (μg/m³)	0.12

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

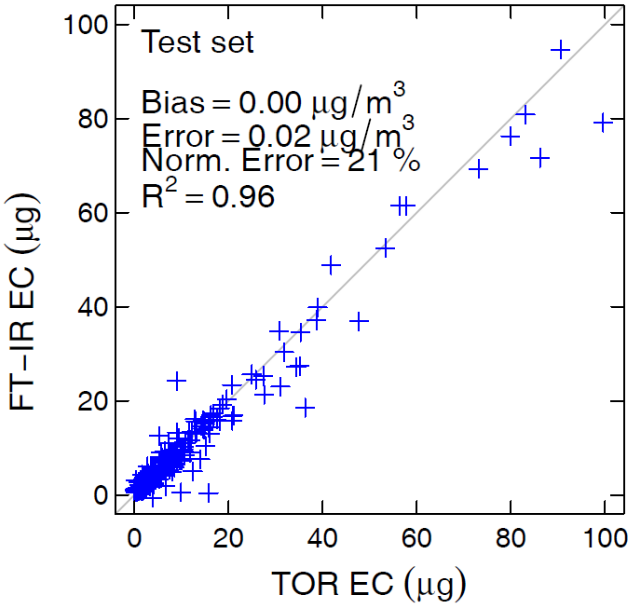
Dillner and Takahama, 2015a

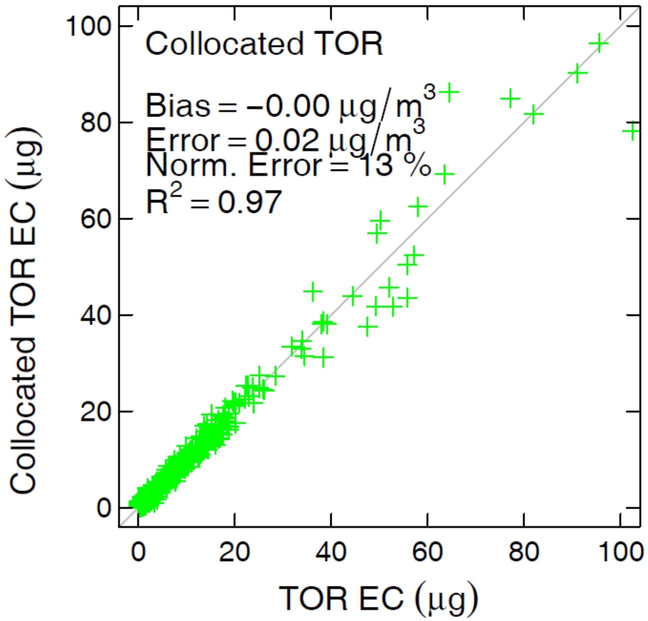
IMPROVE FT-IR OC- different time and sites



Reggente, Dillner and Takahama, 2015

IMPROVE FT-IR EC



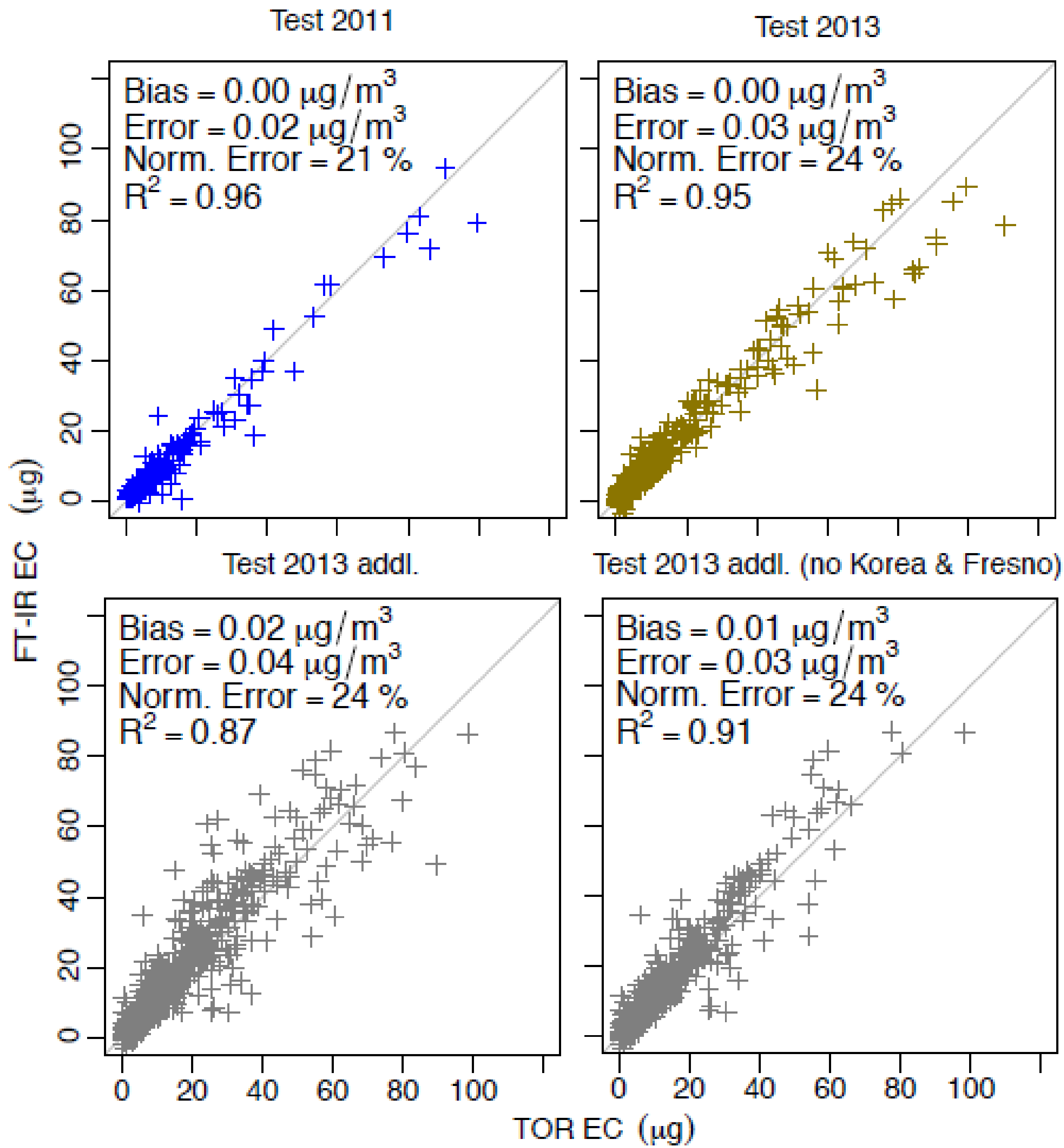


	FT-IR EC
MDL (μg/m^3)	0.01
% below MDL	1
precision (μg/m^3)	0.04

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

Dillner and Takahama, 2015b

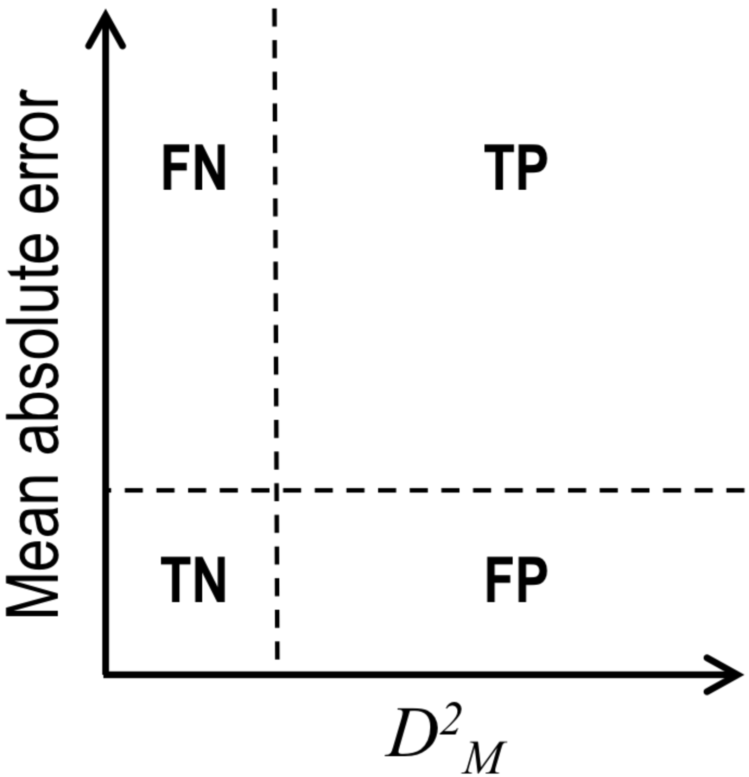
IMPROVE FT-IR EC - different time and sites



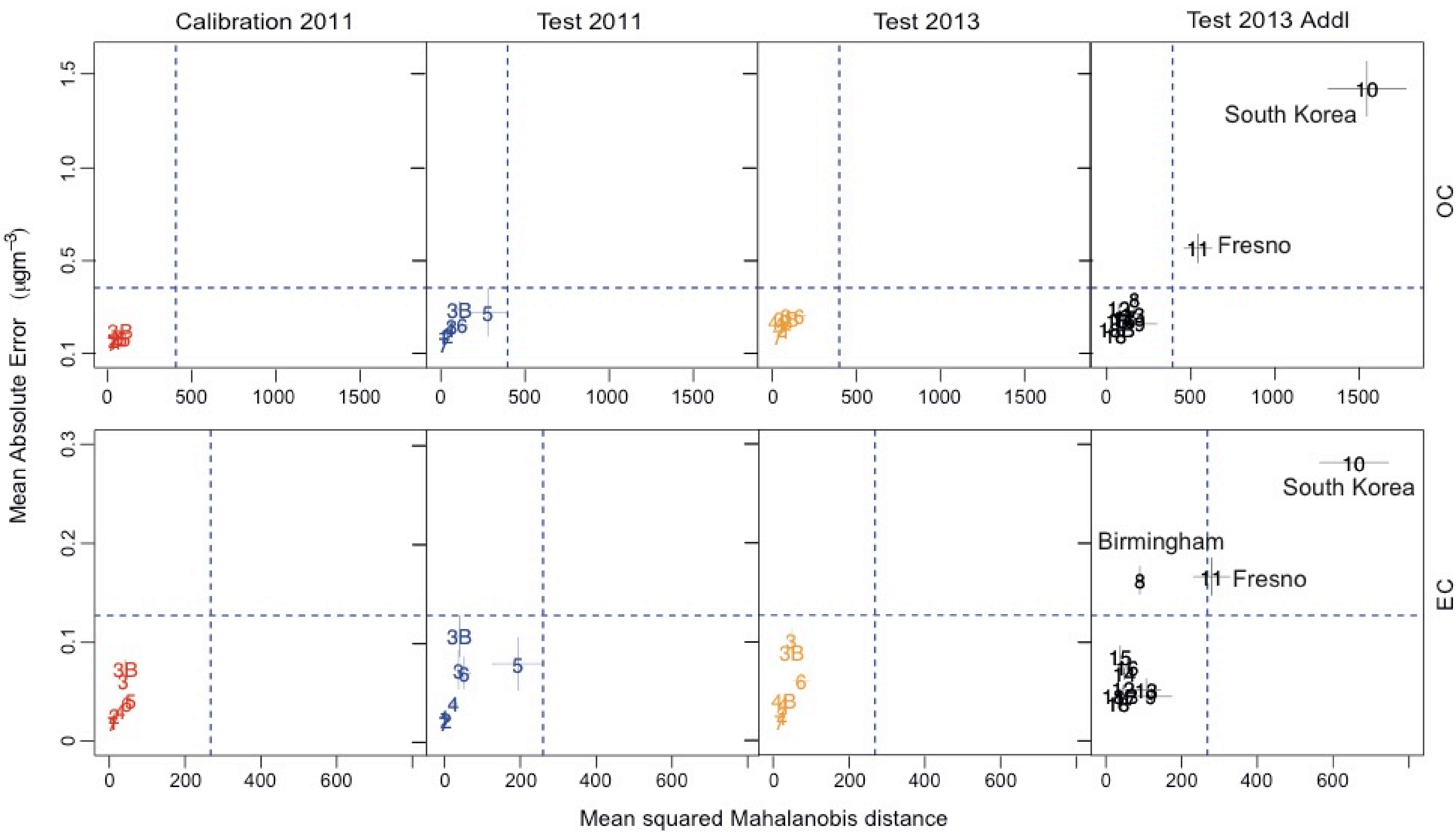
Reggente, Dillner and Takahama, 2015

Anticipating prediction error by Mahalanobis distance

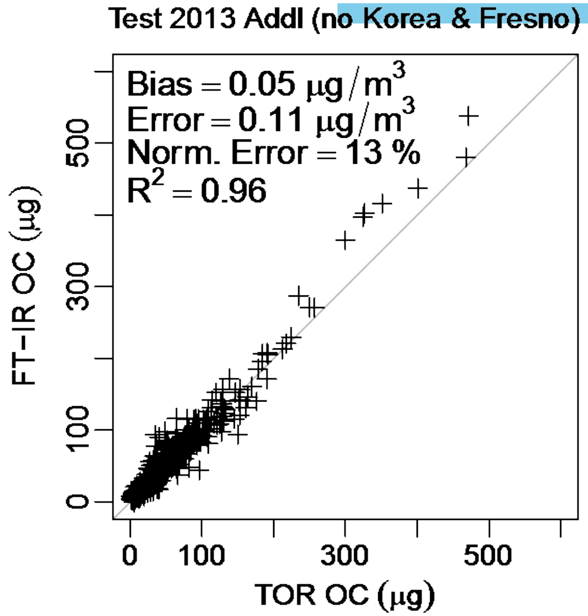
- Mahalanobis distance (D_M) is a way to measure similarity between spectra.
- The D^2_M is calculated between a new spectra or set of spectra and the calibration spectra **without knowledge** of OC, EC concentrations
- We evaluate our ability to anticipate prediction errors of OC, EC in 4 quadrants:
  - TP – true positive
  - TN – true negative
  - FP – false positive
  - FN – false negative



Distances and prediction errors

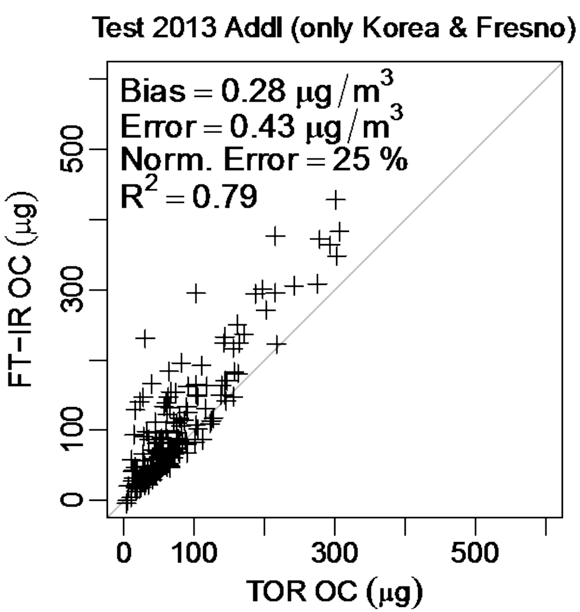


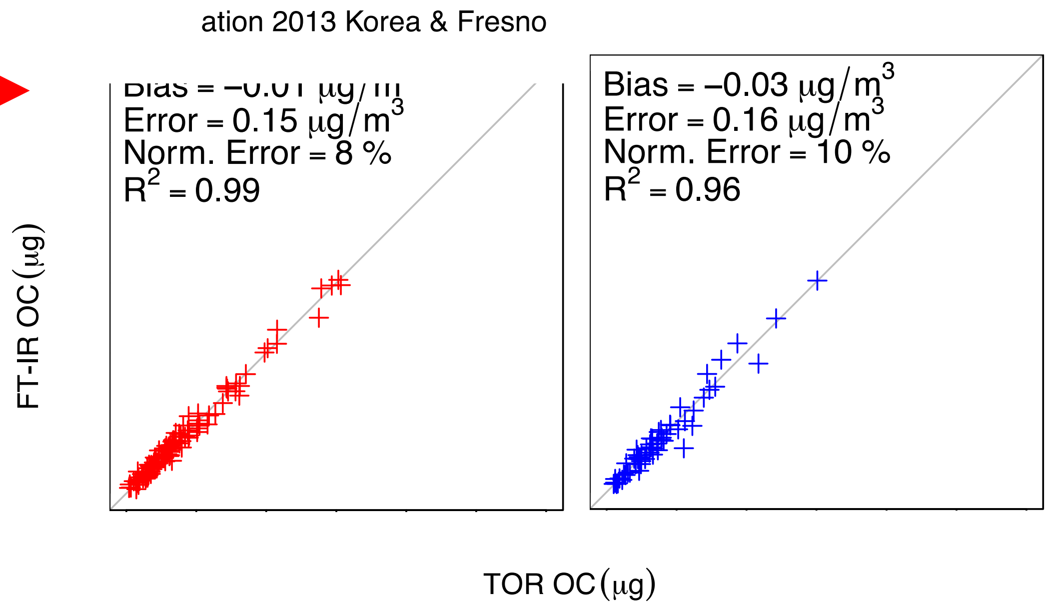
Reducing prediction error (OC)



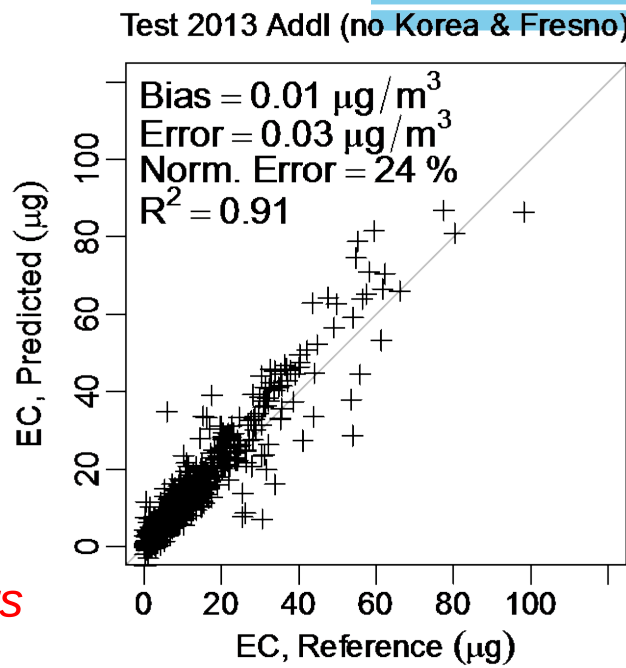
High Mahalanobis distance sites removed

Recalibration leads to lower errors



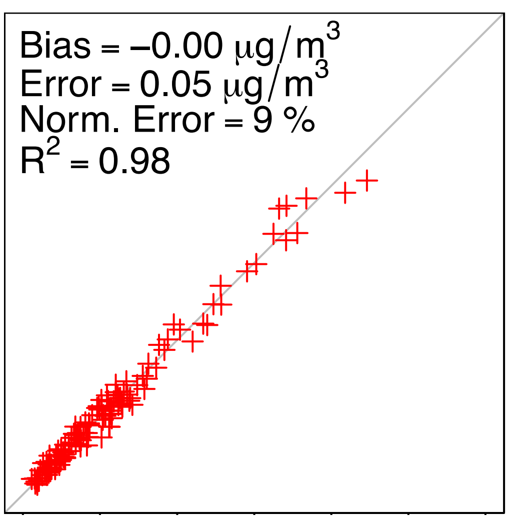


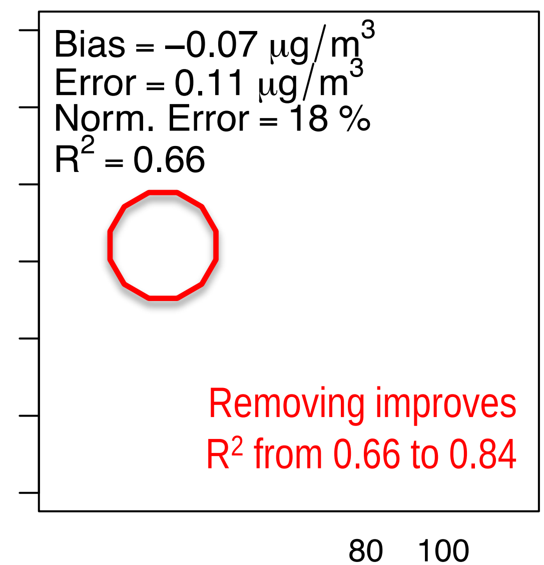
Reducing prediction error (EC)



High Mahalanobis distance sites removed

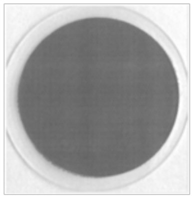
Recalibration leads to lower errors



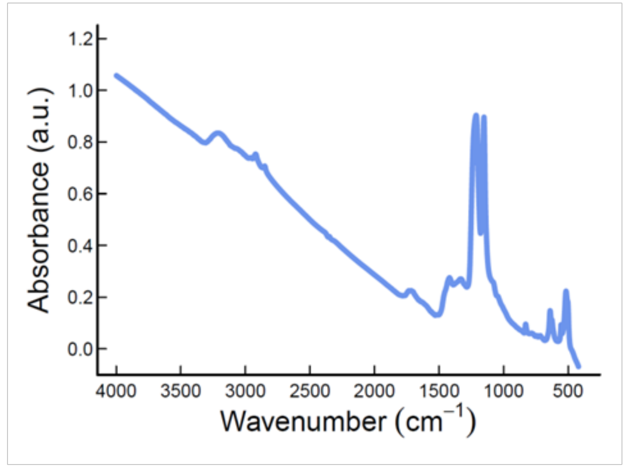


Spectra collection for IMPROVE 2015 samples

- Analyzed more than 10,000 teflon (module A) IMPROVE samples (sample year 2015)
  - Post-weigh -> FT-IR -> XRF - > Laser
- Weekly QC – for each FT-IR instrument
  - Collect duplicate spectra twice per day
  - Analyze laboratory standards
  - Analyze 10 filters on the other FT-IR instrument
  - Visual inspection of background and sample spectra
  - Weekly report
- Will be used for network-wide OC and EC calibrations and predictions



Sampled PTFE filter



FT-IR spectrum

field samples

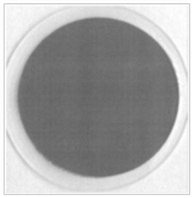
TOR OC and EC calibrations

TOR OC, EC

IMPROVE

IMPROVE OC and EC summary

- Good predictions in future year
  - same sites
  - most other sites
- Metric to anticipate poorly predicted sites
  - Model using sites works well
- Analyzed over 10,000 IMPROVE samples from 2015



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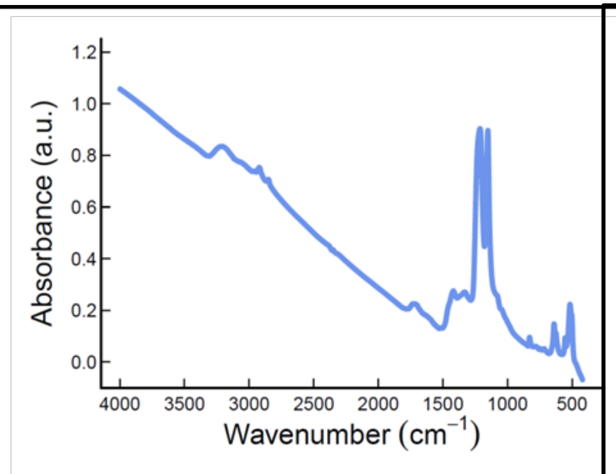


FT-IR spectrum

Network-wide calibration

- Analyze remaining 2015 samples
- Develop IMPROVE calibrations
  - Site or sample specific calibration
- New site protocol

IMPROVE OC and EC summary

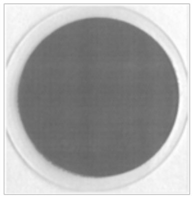
- Good predictions in future year
  - same sites
  - most other sites
- Metric to anticipate poorly predicted sites
  - Model using sites works well
- Analyzed over 10,000 IMPROVE samples from 2015

field samples

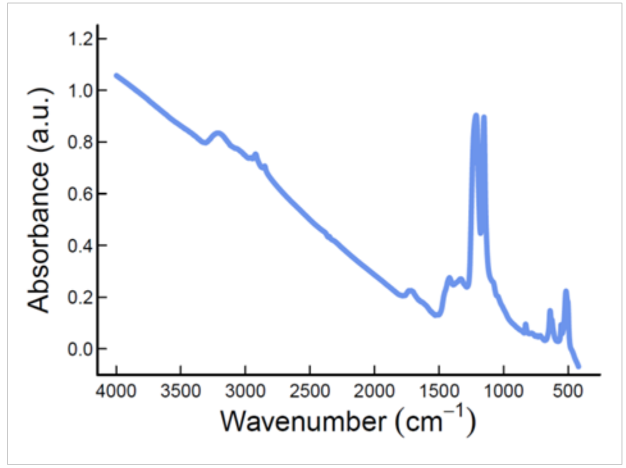
TOR OC and EC calibrations

TOR OC, EC

IMPROVE



Sampled PTFE filter



FT-IR spectrum

field samples

TOR OC and EC calibrations

TOR OC, EC

CSN (FRM)

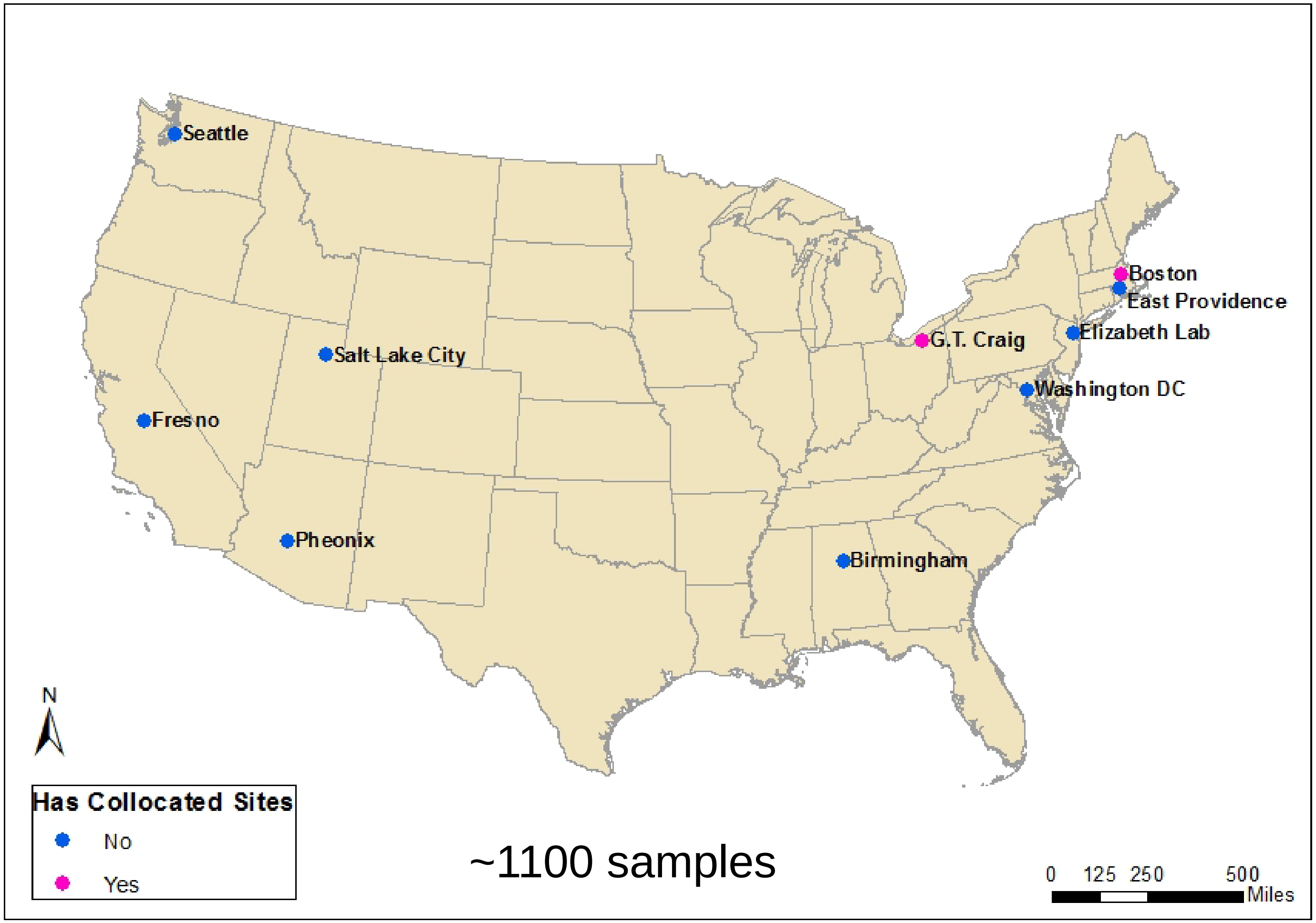
Why a separate calibration for CSN?

1. Aerial density differences ($\mu g/cm^2$)
   - CSN 6.7 lpm flowrate, 47 mm filter
   - IMPROVE 22.8 lpm flowrate, 25 mm filter
   - IMPROVE aerial density = 12 X CSN aerial density
2. PM composition differences
   - urban v. rural
   - lower flowrate CSN sampler may lead to less volatilization of VOC and SVOCs
3. Spectral methods “see” filter material
   - CSN – Whatman
   - IMPROVE – Pall

Methods for CSN

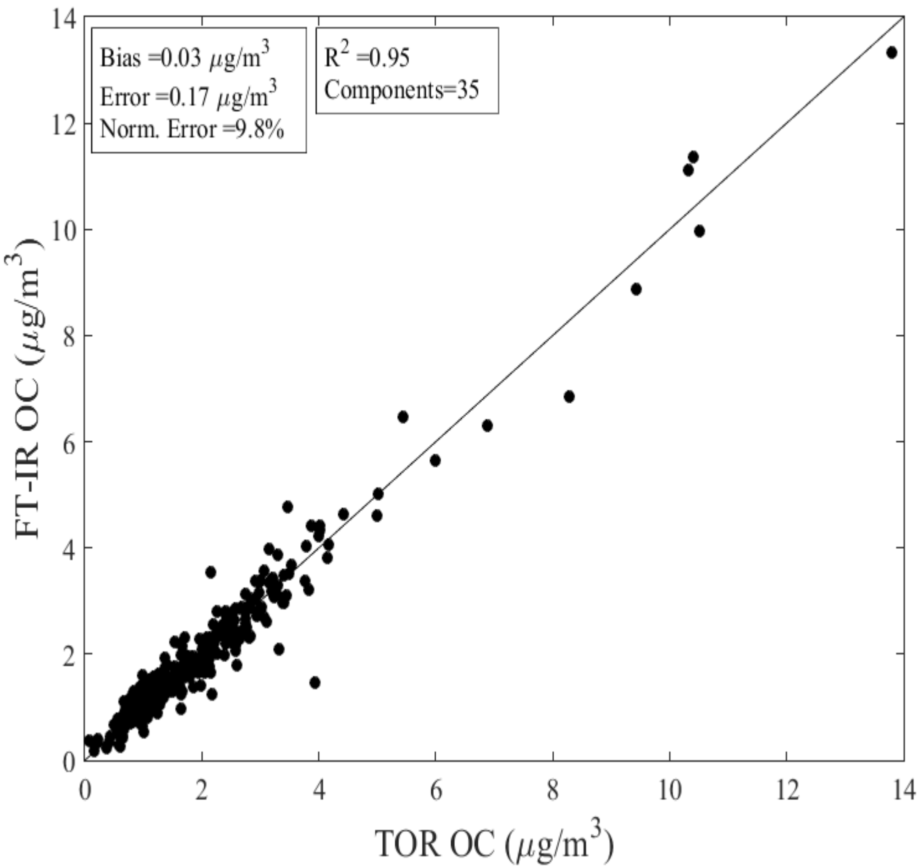
- Ten 1 in 3 CSN sites (+2 collocated) from 2013
- FT-IR spectra from teflon filters
  - Raw spectra (used for IMPROVE)
  - Preprocessed spectra
    - Second derivative of spectra
    - Selected wavenumbers
- Artifact corrected TOR OC data
  - monthly median blanks (blank data from AQS)
- PLS Regression (same method used for IMPROVE) to correlate FT-IR spectra to TOR EC and artifact-corrected TOR OC

CSN sites analyzed in 2013



~1100 samples

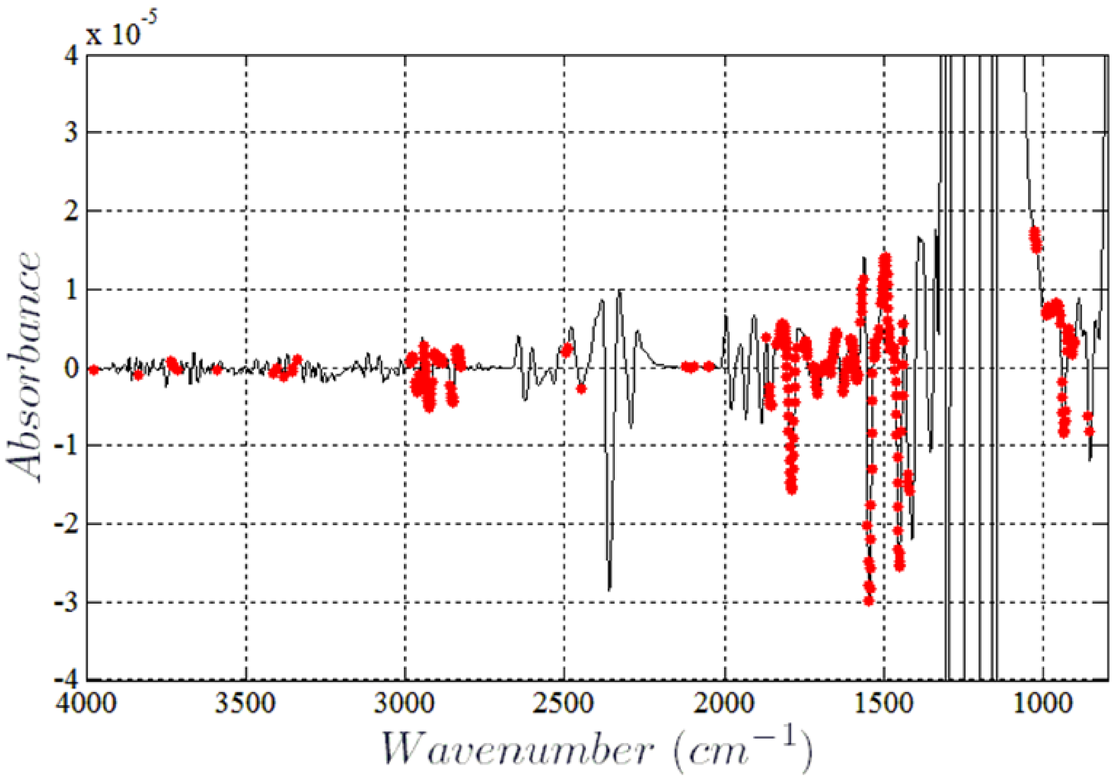
Prediction of TOR OC in CSN



<u>IMPROVE OC</u>

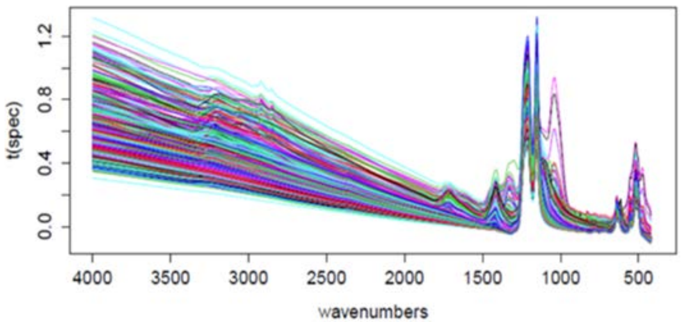
Bias = 0.02 μg/m^3
Error 0.08 μg/m^3
Norm. Error = 11%
R^2 = 0.96

Preprocessed spectrum



- 2nd derivative
- Important wavenumbers (in red)

Raw spectrum



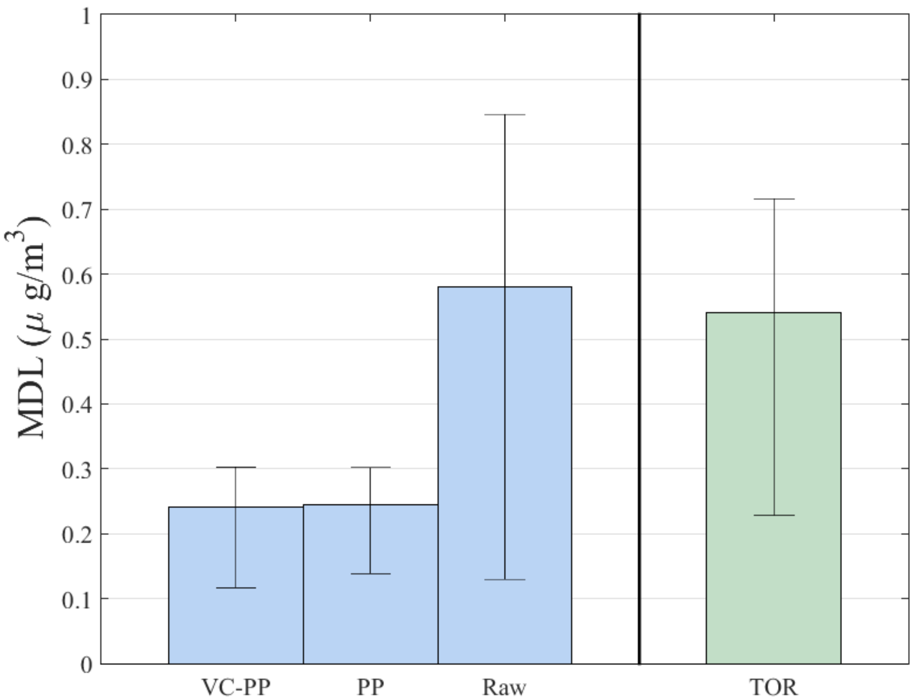
Prediction of TOR OC in CSN using preprocessed spectra

Spectra type	LV#	R^2	Bias ($\mu g/m^3$)	Error ($\mu g/m^3$)	Norm. Error (%)	MDL* ($\mu g/m^3$)	Below MDL	Precision ($\mu g/m^3$)
Raw	35	0.95	0.03	0.17	9.8	0.58	5.3%	0.15
Preprocessed (PP)	4	0.96	0.04	0.15	8.8	0.24	0.0%	0.09
Preprocessed – vapor corrected (VC-PP)	3	0.96	0.03	0.14	9.4	0.24	0.7%	0.13
	TOR†	0.95	-0.01	0.08	8.4	0.54	2.6%	0.37

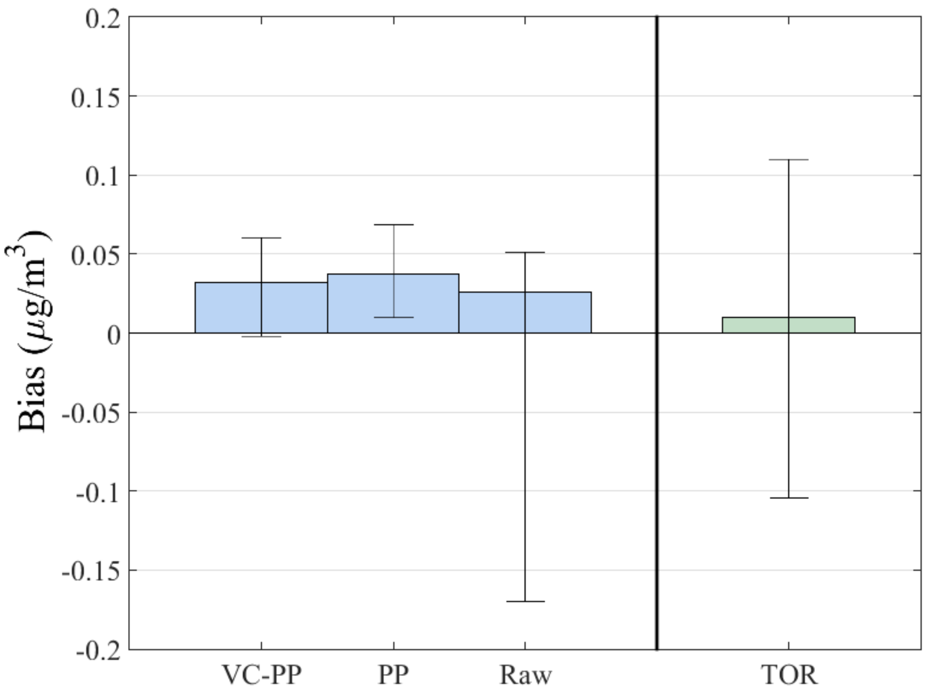
*MDLs estimated from field blanks

MDL and Bias uncertainties

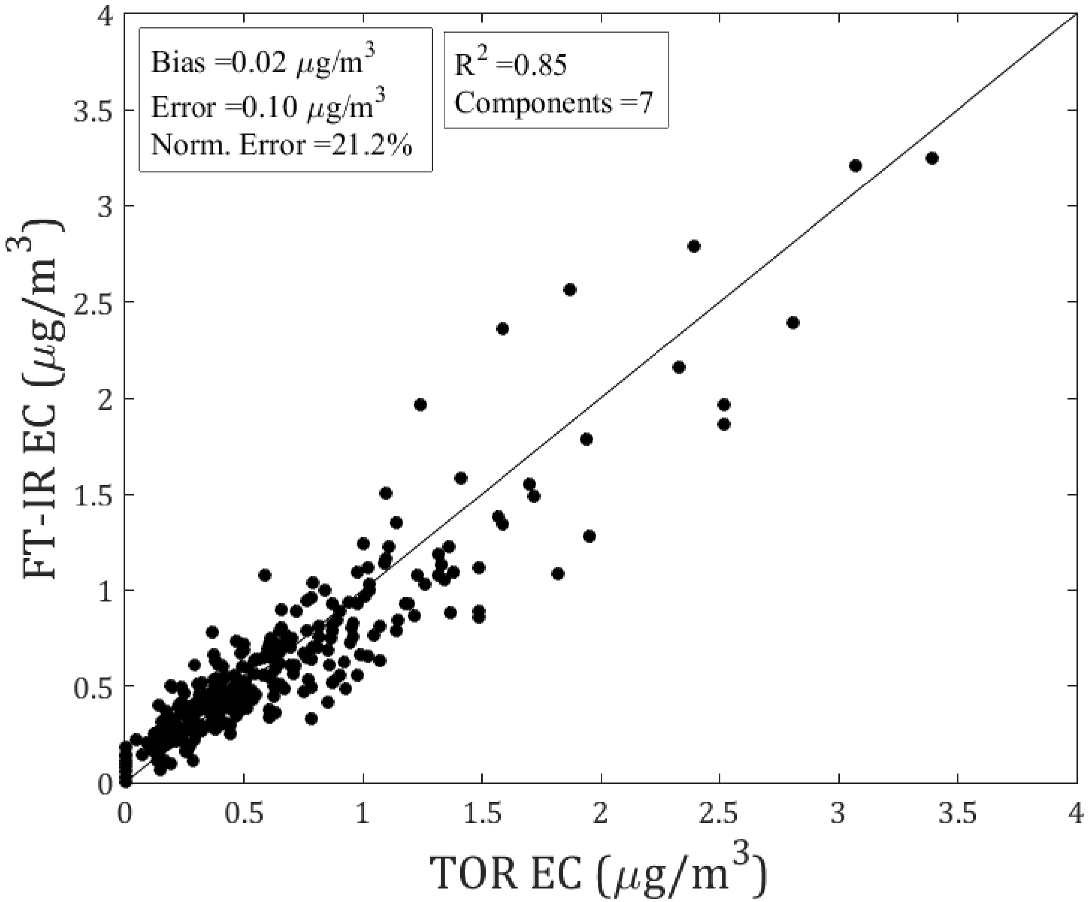
MDL



Bias



EC prediction for CSN using preprocessed spectra



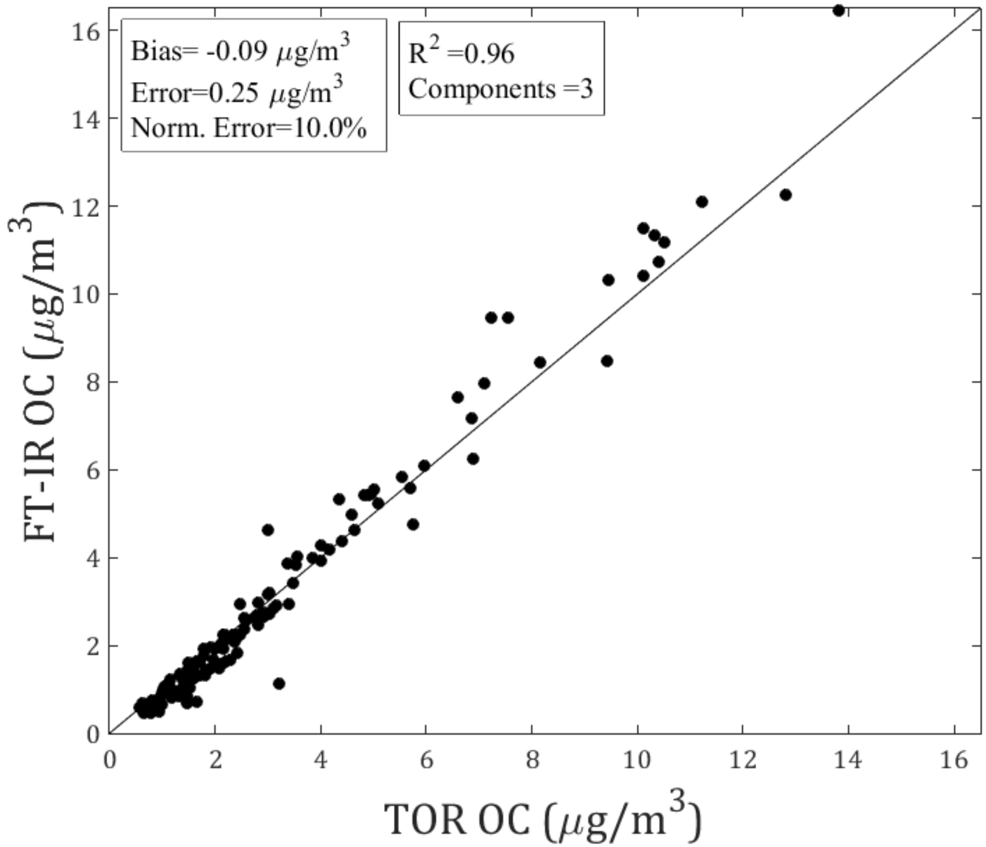
<u>IMPROVE EC</u>

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

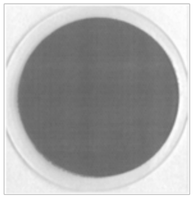
Calibration transfer to FRM

- Predict TOR OC and EC in FRM samples from the CSN calibration
- FRM teflon filters from the same 10 sites
  - Mostly MTL filters
  - Fresno samples and half of Phoenix samples were collected on the same filter type as CSN (Whatman)
- FRM samplers - 16.7 lpm flowrate
  - FRM aerial density ~ 2 X CSN aerial density
- Used CSN vapor-corrected preprocessed spectra calibration to predict OC on FRM-Whatman samples

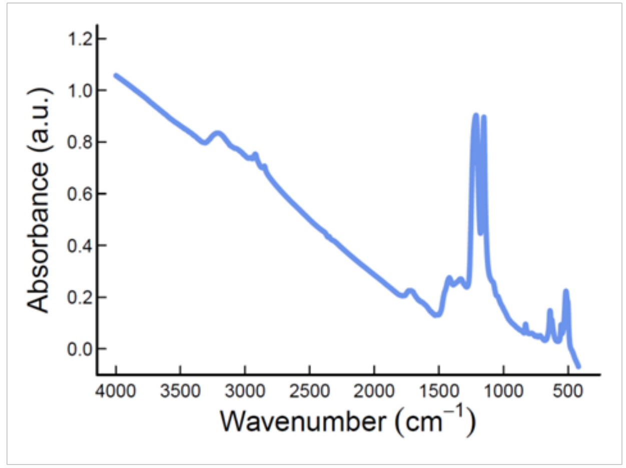
Predicting TOR OC on FRM (Whatman) samples from CSN calibration



- FT-IR OC corrected for difference in aerial density
- Same R^2 and normalized error as CSN predictions
- Slightly higher bias and error



Sampled PTFE filter



FT-IR spectrum

field samples

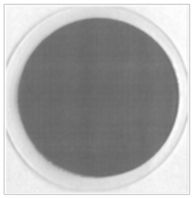
TOR OC and EC calibrations

TOR OC, EC

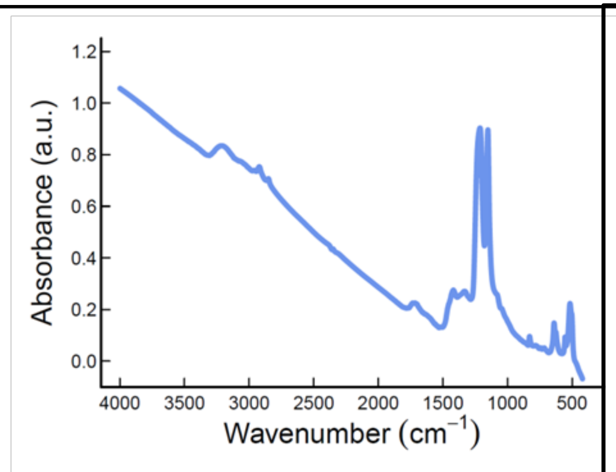
CSN (FRM)

Summary CSN (FRM)

- CSN same predictive capability as IMPROVE
- Preprocessed spectra
  - Lower MDL and better precision
  - Decrease uncertainty in MDL and other metrics
  - Predict FRM samples with same filter type



Sampled PTFE filter



FT-IR spectrum

Next Steps

- FRM and IMPROVE predictions
- Scale-up to network-wide CSN calibration
  - Analyze one year of CSN filters

field samples

TOR OC and EC calibrations

TOR OC, EC

CSN (FRM)

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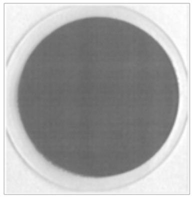
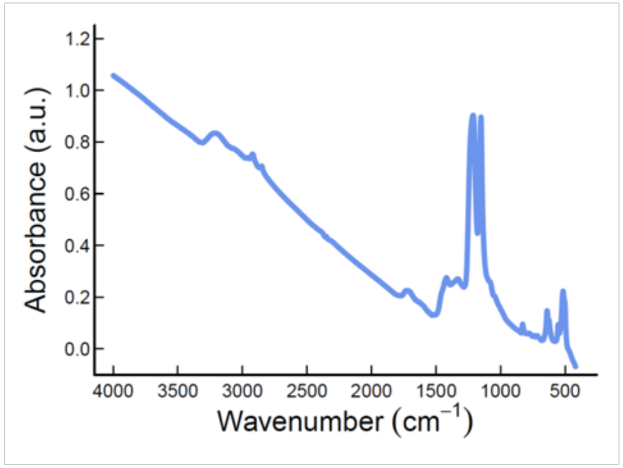


Sampled PTFE filter



FT-IR spectrum

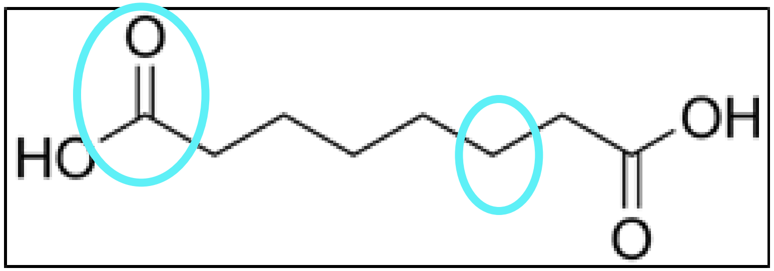
laboratory standards

Functional group calibrations

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

Organic Functional Groups and OM/OC

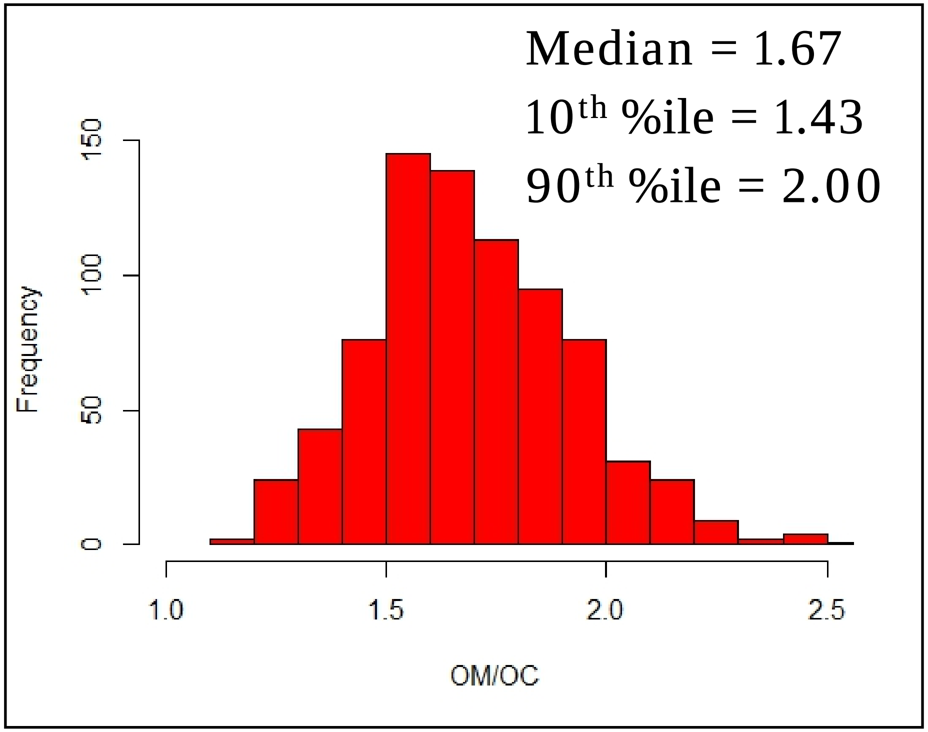
- FT-IR absorbances correspond to organic functional groups

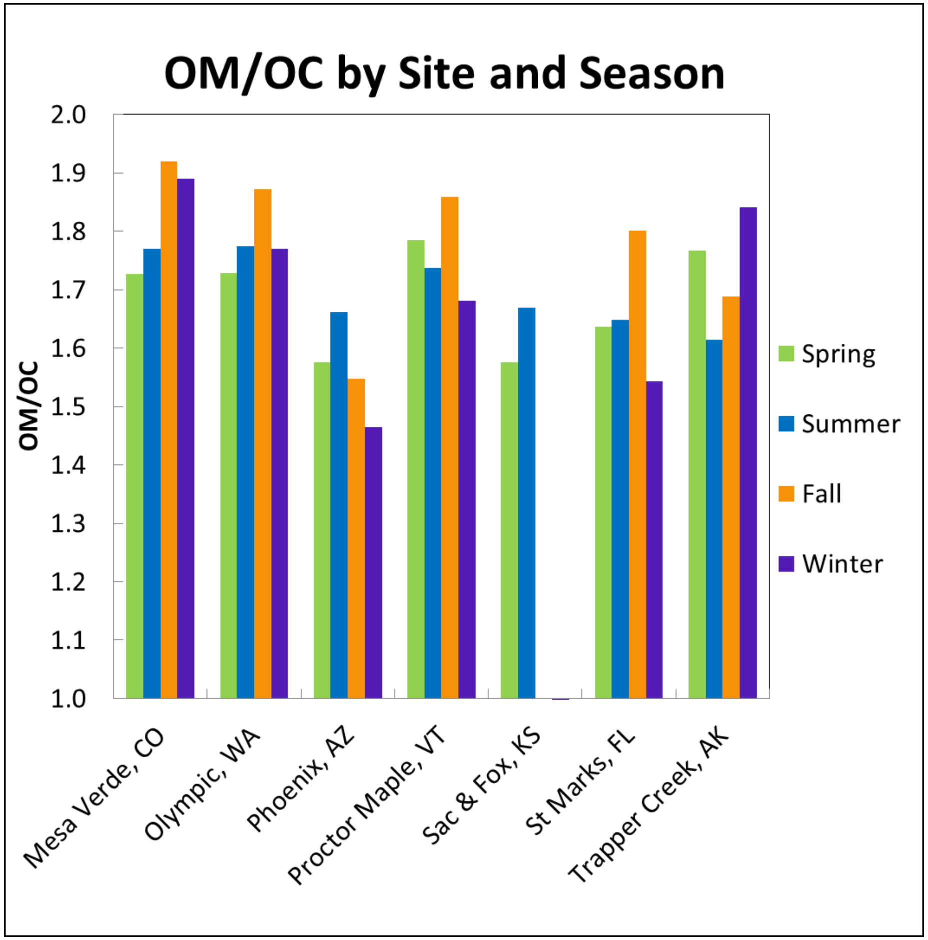


Aliphatic C-H
Carbonyl (C=O)
Acid O-H
Alcohol O-H
Organonitrates
Amines
Organosulfates
Aromatic C-H

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

OM/OC in ~800 samples in 2011





- IMPROVE OM/OC = 1.8
- Sample, site and seasonal variability

Ruthenburg et al., 2014

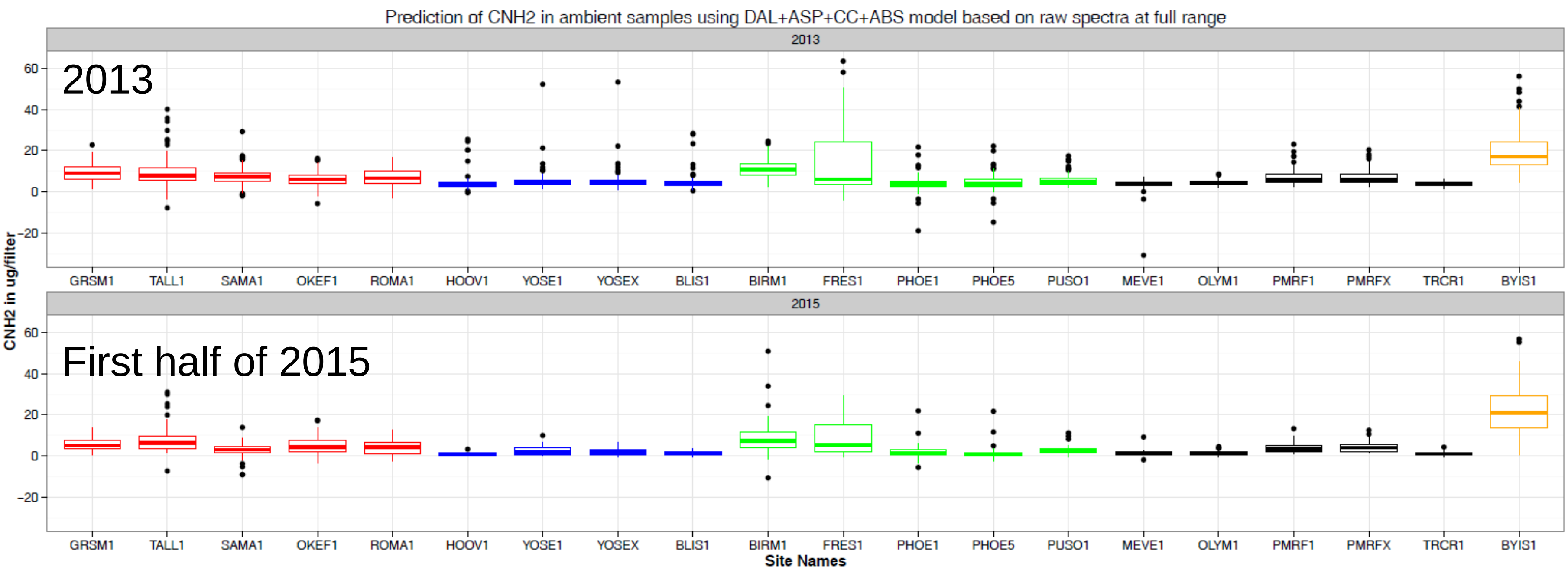
Improving OM/OC

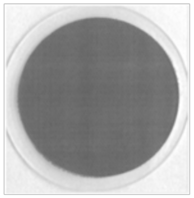
- Model selection
  - Systematically decreasing number of factors in PLS model improves functional group prediction (Takahama and Dillner, 2015)
- Wavenumber selection
  - Minimizes noise, provide interpretability (also useful for OC and EC measurements, Takahama, Ruggeri and Dillner, to be submitted in 2015)
- Add additional functional groups

Organic Nitrogen and Sulfur

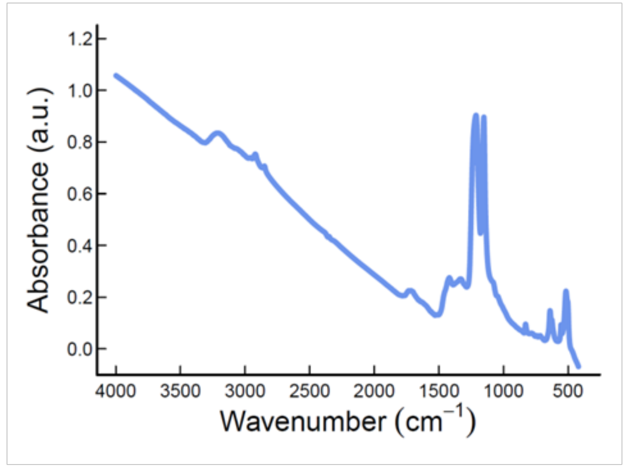
- Minor constituents can impact OM/OC
  - OM/OC for O-N and O–S 1.7 up to 3 or higher
- Minor constituents can provide source information
  - Organosulfates (C-OSO3) – biogenic SOA
  - Amines (C-NH2) - associated agriculture-related SOA and biomass burning
  - Organonitrates (C-ONO_2) – anthropogenic SOA associated with combustion (NO_x)

Predicted amines





Sampled PTFE filter



FT-IR spectrum

laboratory standards

Functional group calibrations

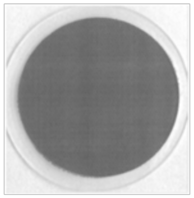
functional groups, OM, OM/OC, O/C

Summary Functional groups and OM/OC

- Improving OM/OC
  - Model and wavenumber selection
  - Adding new functional groups
    - Source tracers

Next Steps

- Impact of new groups on OM/OC
- Comparing PLS to peak fitting



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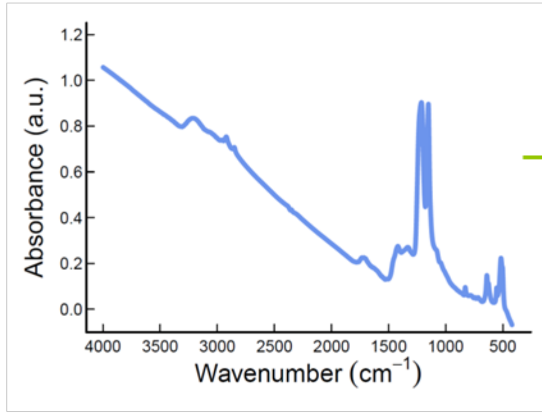
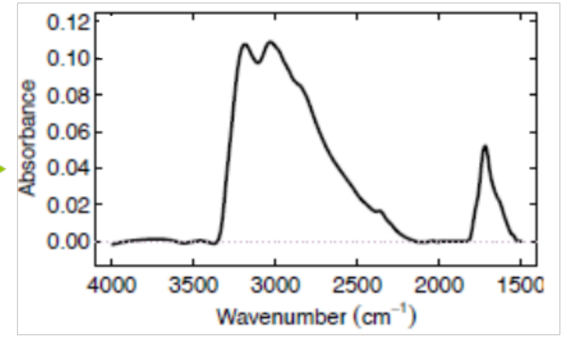
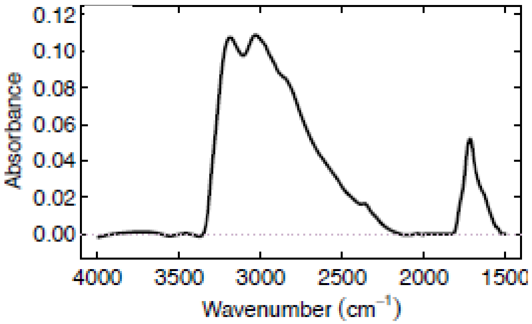


FT-IR spectrum



Baseline corrected spectrum



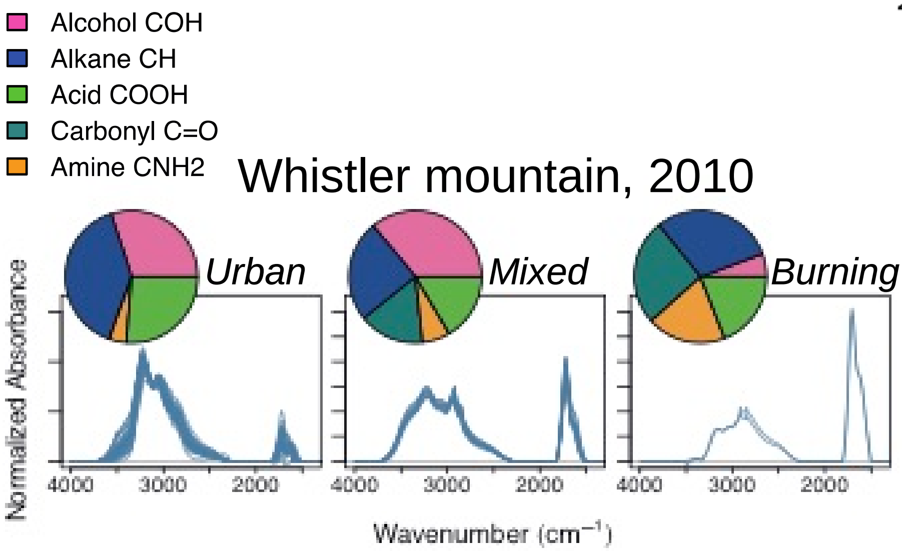
Baseline correction

- Removing teflon absorbance from spectra
- Motivation
  - Calibration transfer (CSN->FRM)
    - Aerial density – factor of 2 – can scale
    - Same ambient composition, maybe somewhat different SVOCs
    - Different filter media
  - Source apportionment
- Current baseline method
  - Polynomial fits
  - Individual processing
  - Subjective judgement
- New automated baseline method
  - Smoothing splines
  - Large datasets
  - Consistent and repeatable

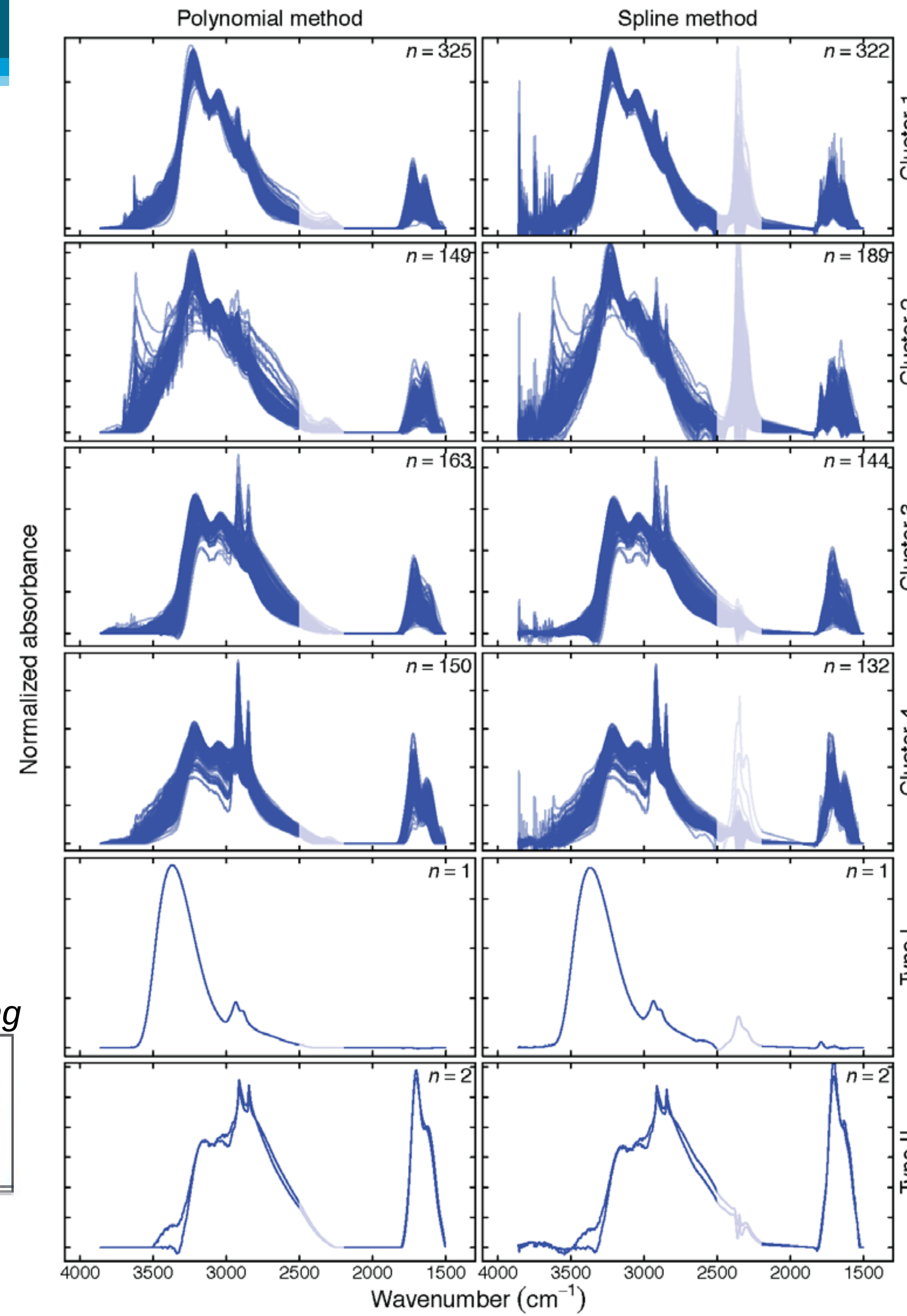
Source apportionment

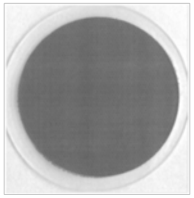
Baseline correction is the first step to spectra clustering, classification, and source apportionment.

Clustering of 787 spectra with 10% discrepancy.

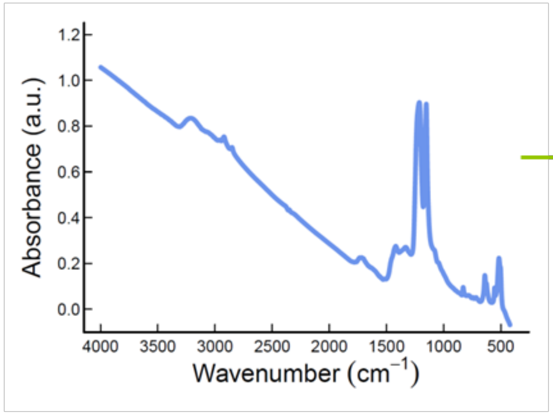


Takahama et al., *Atmos. Chem. Phys.*, 2011

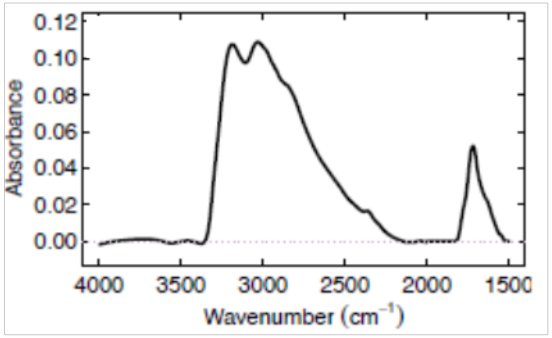




Sampled PTFE filter



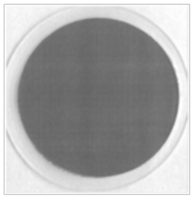
FT-IR spectrum



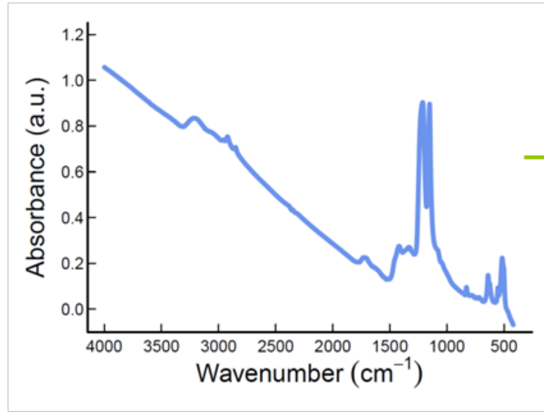
Baseline corrected spectrum

<u>Summary and Future work</u>

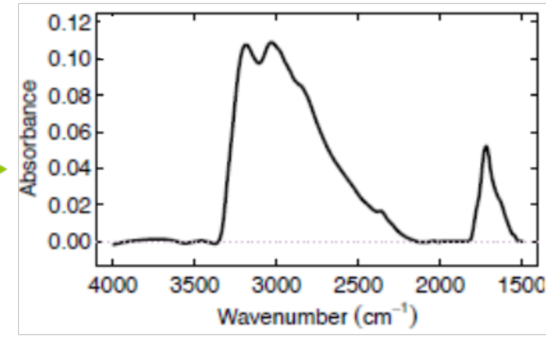
- Promising method for network data sets
    - calibration transfer
    - source apportionment



Sampled PTFE filter



FT-IR spectrum



Baseline corrected spectrum

laboratory standards

field samples

source info

Functional group calibrations

TOR OC and EC calibrations

Clusters/ calibrations

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

TOR OC, EC

Source apportionment

Recent Publications

EPA/NPS funded
Takahama funded
EPRI funded

- OC and EC
  1. Predicting OC for IMPROVE, Dillner and Takahama, 2015 a
  2. Predicting EC for IMPROVE, Dillner and Takahama, 2015 b
  3. Predicting OC and EC at different sites/years, Reggente et al., 2015, submitted
- Functional groups
  4. Improving OM/OC estimates from lab standards by improving PLS model selection, Takahama and Dillner, 2015

Publications – in process

EPA/NPS funded
Takahama funded
EPRI funded

- OC and EC for CSN and FRM
  1. Predicting OC for CSN, Weakley, Takahama, and Dillner, submit in 2015
  2. Predicting EC for CSN, Weakley, Takahama, and Dillner, submit early 2016
  3. Determining and removing outliers in calibration set, Weakley, Takahama, and Dillner, submit 2016
  4. Predicting OC and EC for FRM from CSN calibrations, Weakley, Takahama, and Dillner, submit 2016
- Functional groups
  5. Including organic-sulfur and organic-nitrogen in OM/OC estimates, Kamruzzaman and Dillner, 2016
  6. Interpretation of important wavenumbers, Takahama, Ruggeri and Dillner, submit 2015
  7. Comparison of PLS and peak fitting methods, Takahama and Dillner, 2016
- Baseline correction
  8. Automating baseline correction to allow for OC, EC and functional group measurements on different teflon filters, Kuzmiakova, Dillner and Takahama, submit in 2015

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  - IMPROVE program and EPA (National Park Service Cooperative Agreement P11AC91045),
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