Measuring OM/OC on individual IMPROVE Teflon filters using FT-IR analysis

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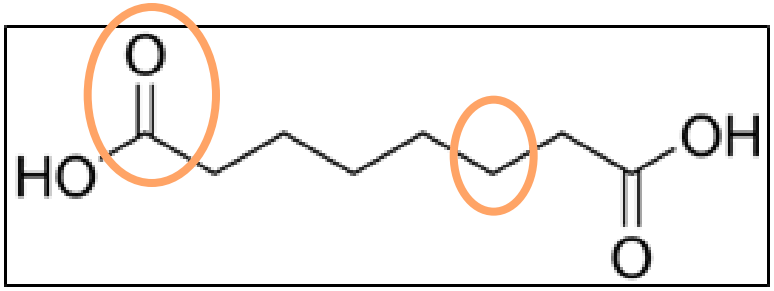
OM on IMPROVE samples

- Organic mass (OM) includes carbon, oxygen, hydrogen, nitrogen and sulfur
- OM used in Regional Haze Rule
- Current method for estimating OM
  - OM = (Measured OC) X (OM/OC)
    - IMPROVE currently using 1.8
    - CSN proposing to use 1.4
    - OM/OC may vary from 1.4 to 2.0 or more
- Prefer method that measures OM or OM/OC on each filter

Fourier Transform Infrared (FT-IR) Spectroscopy

- Non-destructive analysis of Teflon filters
- IR absorbances correspond to organic functional groups



Aliphatic C-H
Carbonyl (C=O)
Acid O-H
Alcohol O-H
Organonitrites
Amines
Organosulfate

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

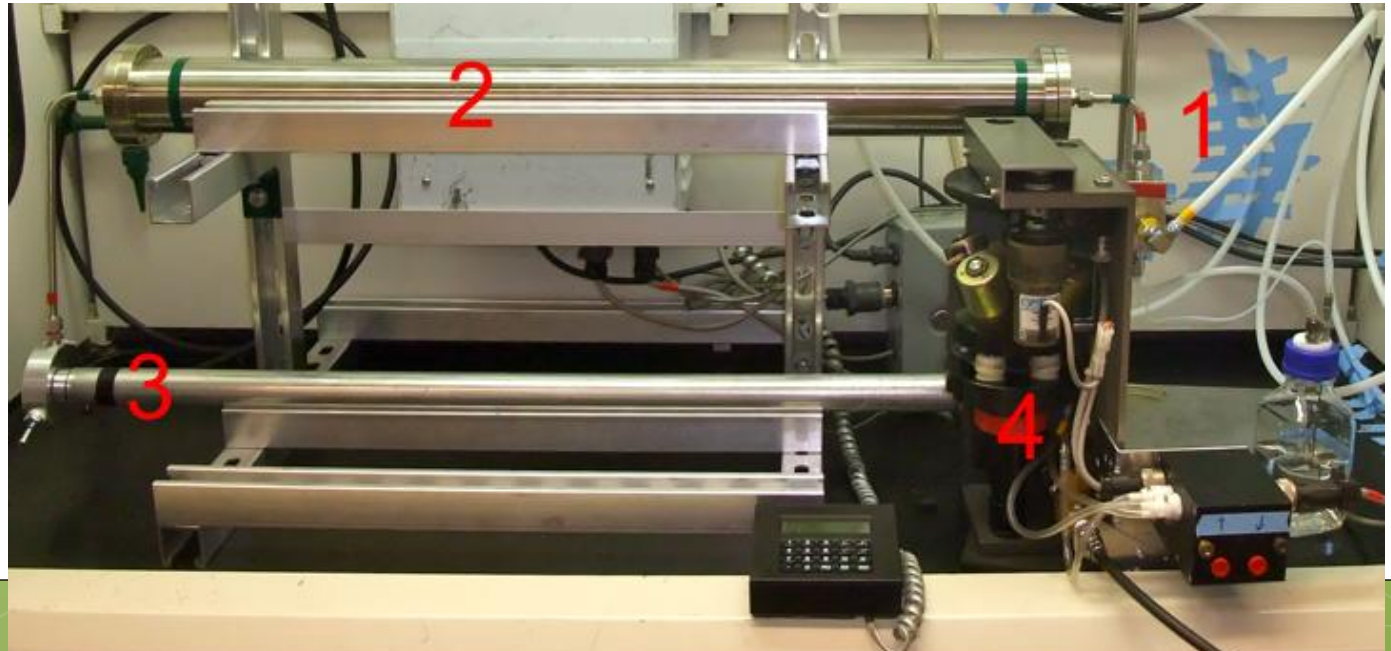
FT-IR - limitations

- Not organic compound specific (i.e., levoglucosan)
- No one has quantified graphitic carbon in particulate matter
- Interferants
  - Teflon filter material
  - Ammonium

Organic Laboratory Standards

Lab standards are generated and used to calibrate infrared absorbance to functional group mass

1. Single component solutions are atomized
2. Droplets pass through a diffusion dryer
3. Particles are mixed with particle-free dry air
4. Collect on Teflon filters using IMPROVE sampler



FT-IR Spectra of standards

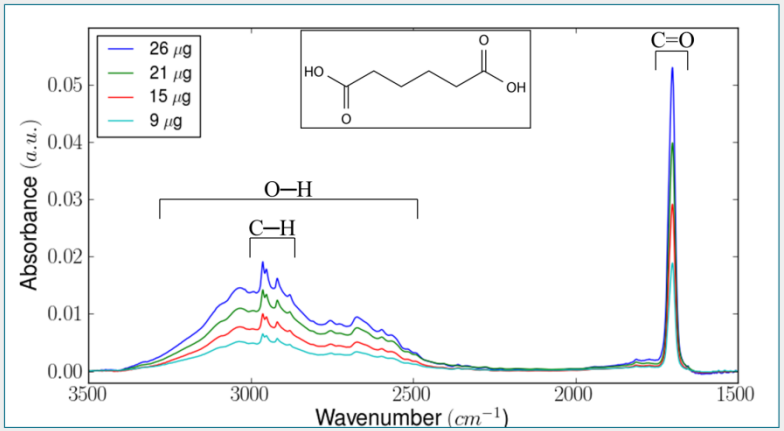


Figure 1. Adipic acid molecular structure and spectra with labeled functional group bands: C-H stretch, 3000-2840 cm^{-1}; C=O stretch, 1720-1706 cm^{-1}; and broad O-H stretch, 3300-2500 cm^{-1}. [4]

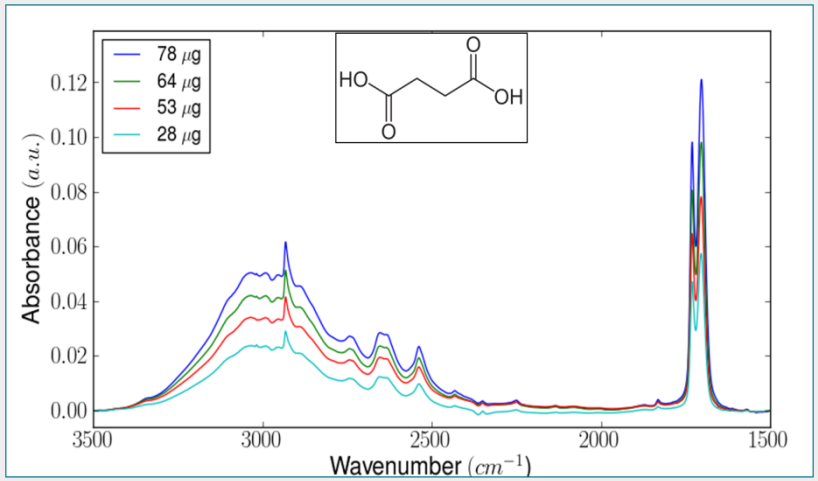
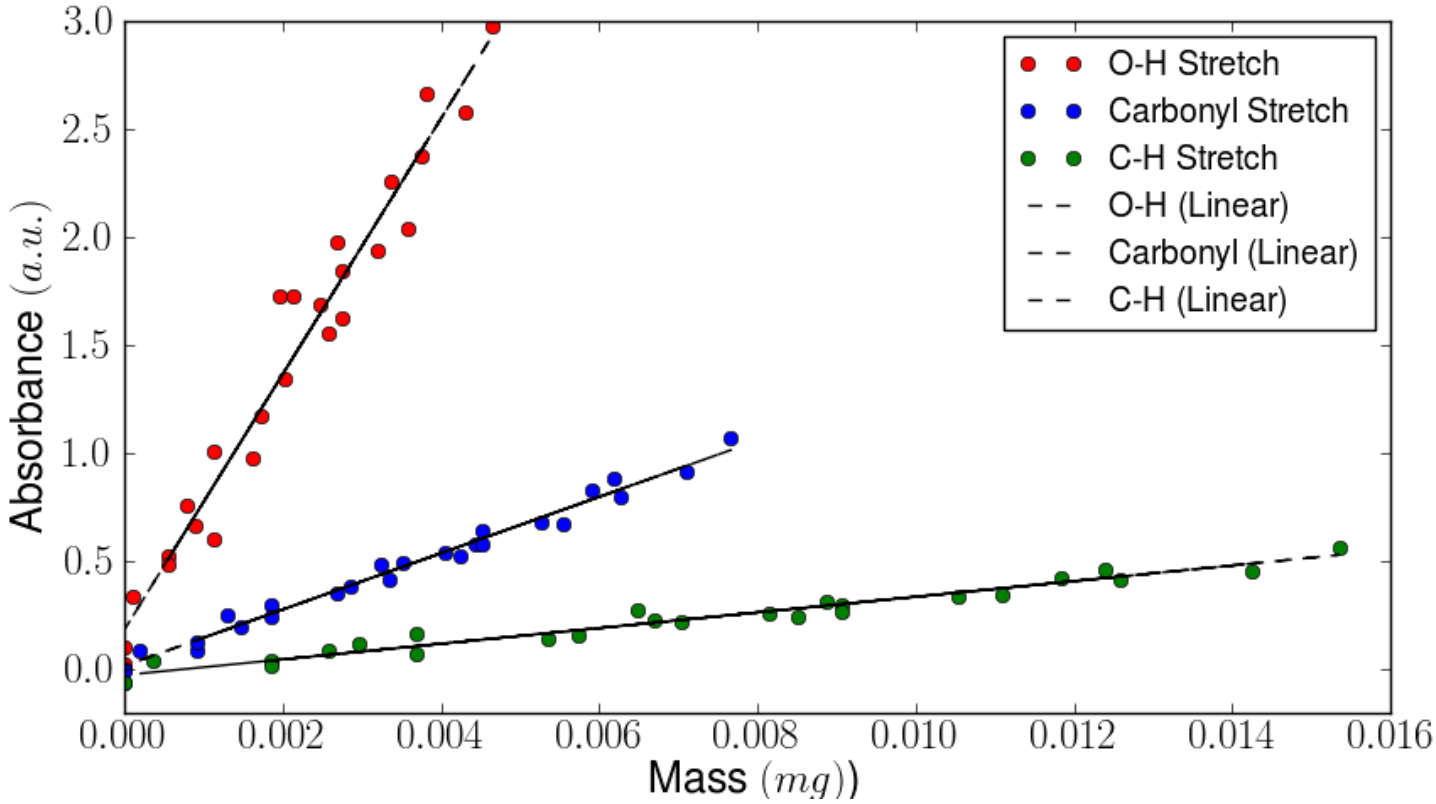


Figure 3. Spectra from a range of succinic acid masses.

Infrared Spectroscopy of Organic Particles on Teflon



Absorbance is directly proportional to functional group mass on filter.

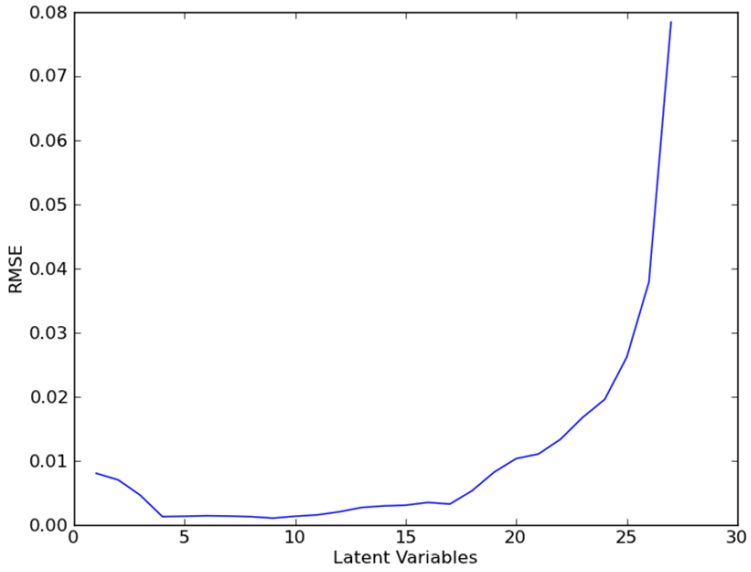
Multivariate Calibration

- Standards: 1, 2 or 3 compounds in layers.
- Separate calibrations for each functional group: Alcohol O-H, Carboxylic Acid O-H, Alkane C-H and Carbonyl C=O
- Functional group mass is

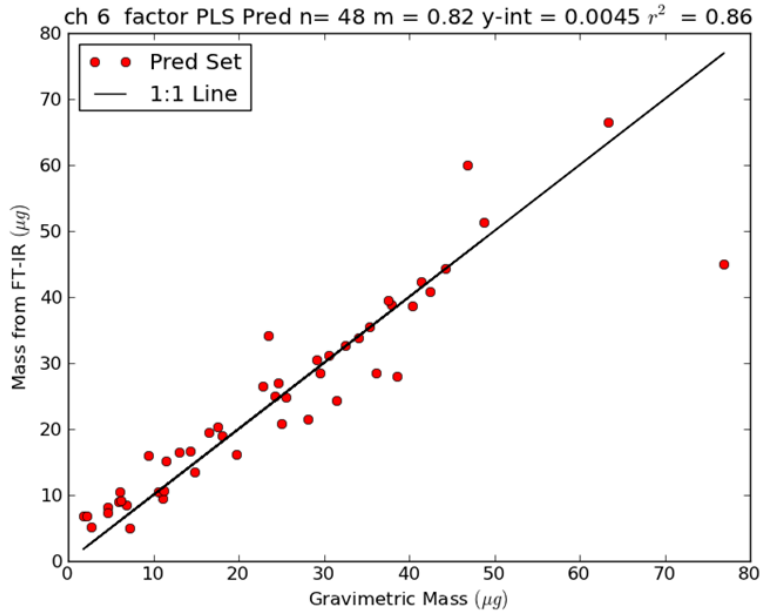
  (functional group molecular mass) / (standard compound molecular mass) * mass on filter
- Partial Least Squares Regression (PLSR) used to regress absorbing region of the infrared spectrum against functional group mass.
- Remove 1/3 of standards as test set. Remaining 2/3 used for calibration.

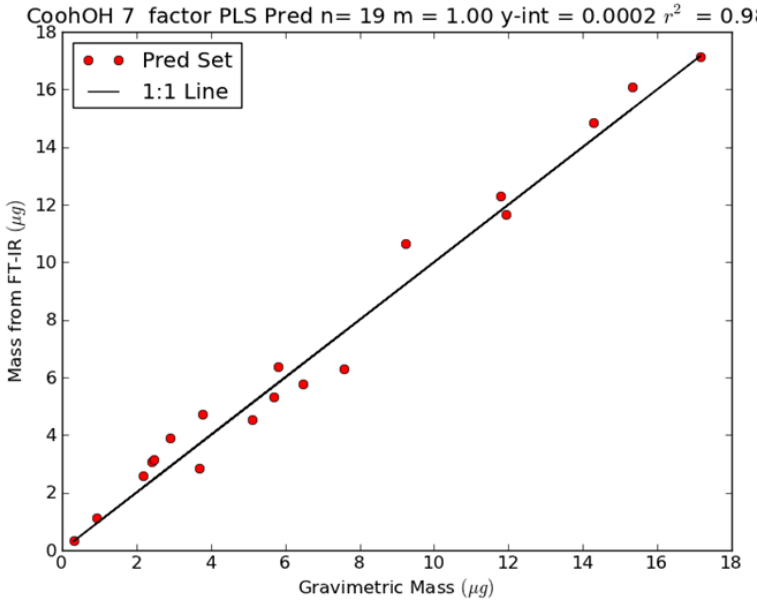
Partial Least Squares Regression (PLSR)

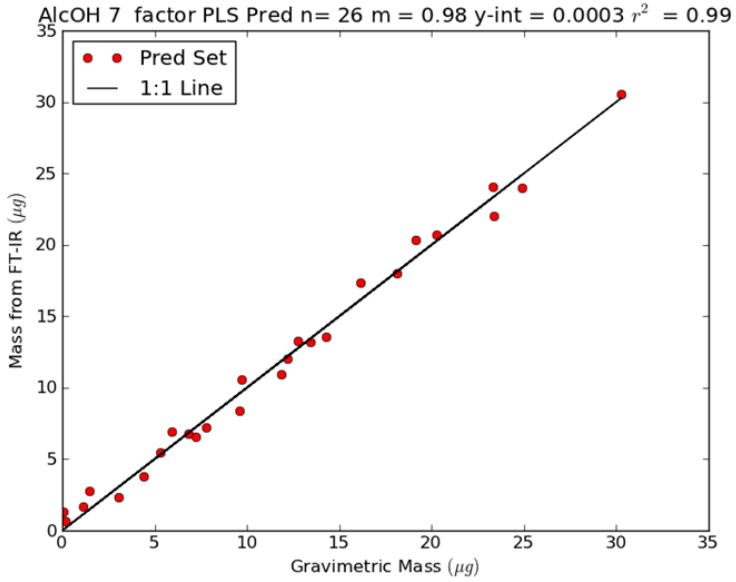
- Many spectral data points are reduced to a few factors or principal components
- Appropriate number of factors are determined by minimizing the root mean squared error of prediction for the test set

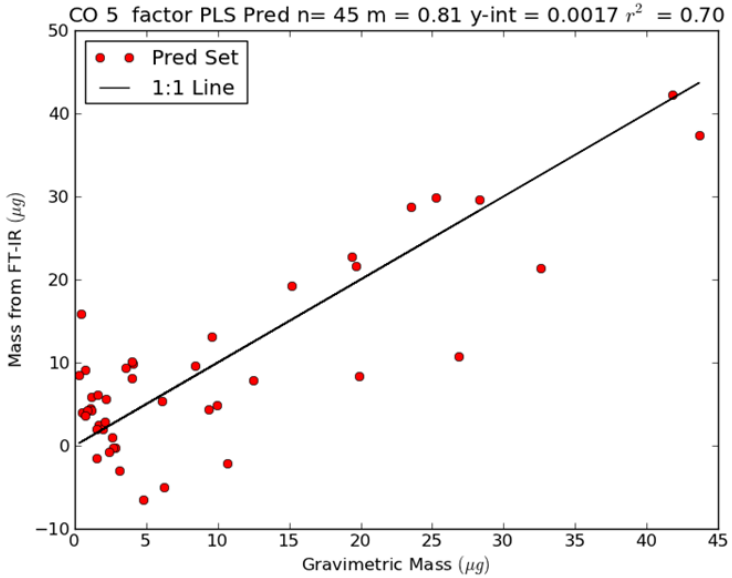


Results for test filters



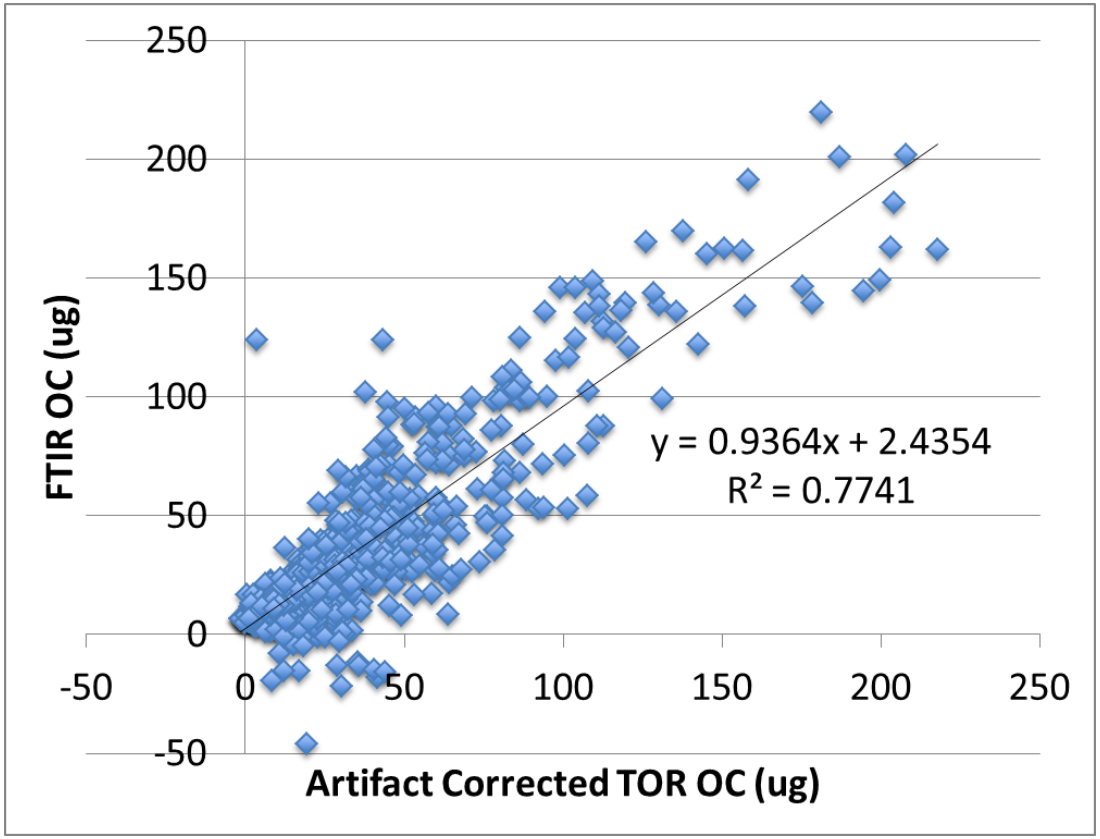






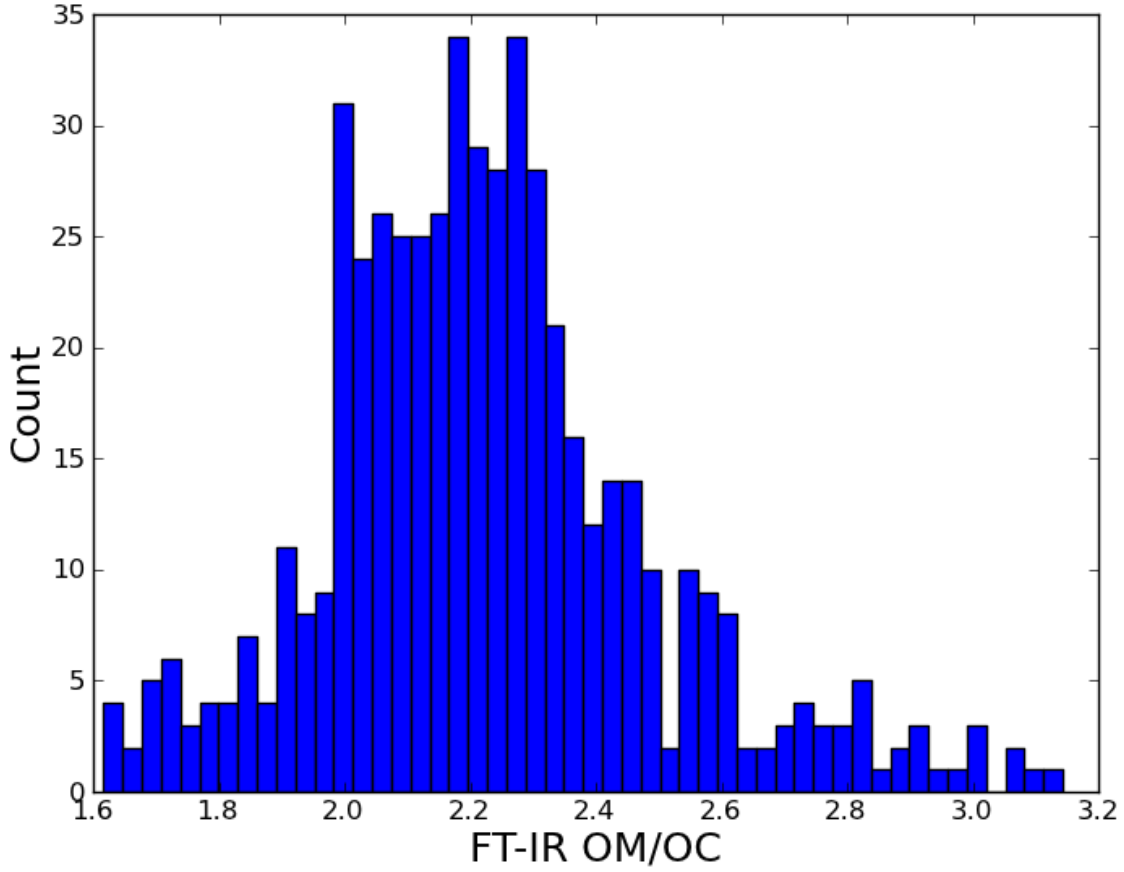
IMPROVE Sites analyzed by FT-IR

Results for IMPROVE Filters
8 Sites January 2011 – August 2011

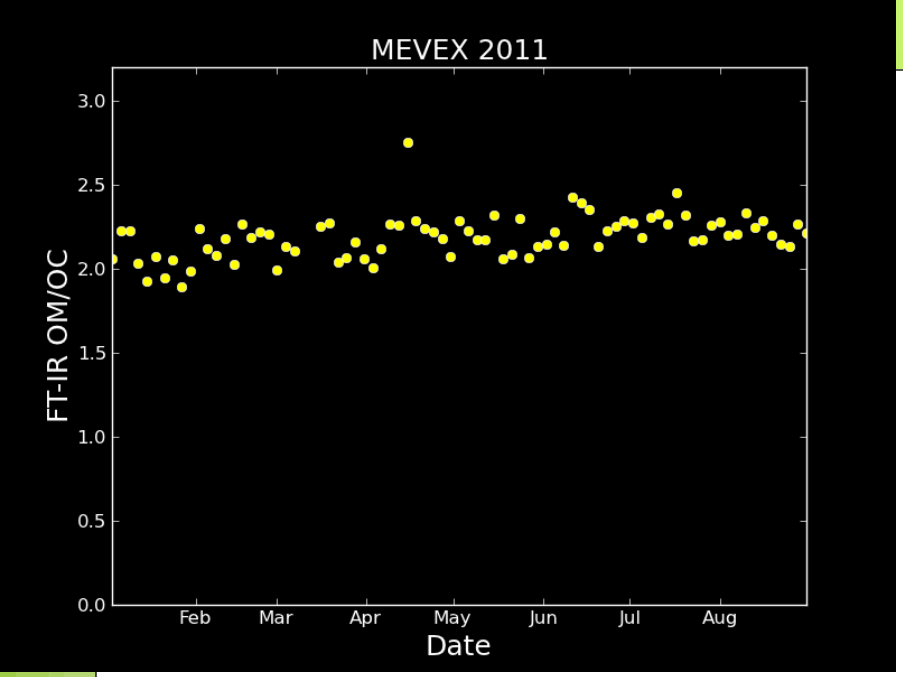


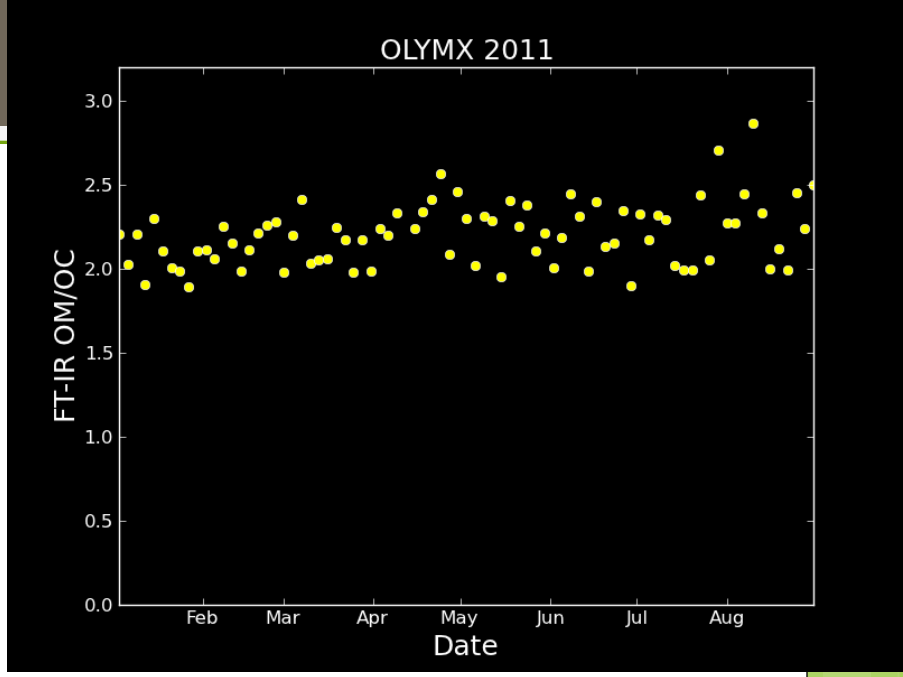
- OC reasonably correlated between methods
- IR OC < TOR OC

Eight IMPROVE Sites Jan-August 2011



OM/OC from FT-IR for individual filters – mainly > 1.8


MEVEX 2011
FT-IR OM/OC
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Feb
Mar
Apr
May
Jun
Jul
Aug
Date


OLYMX 2011
FT-IR OM/OC
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Feb
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Jul
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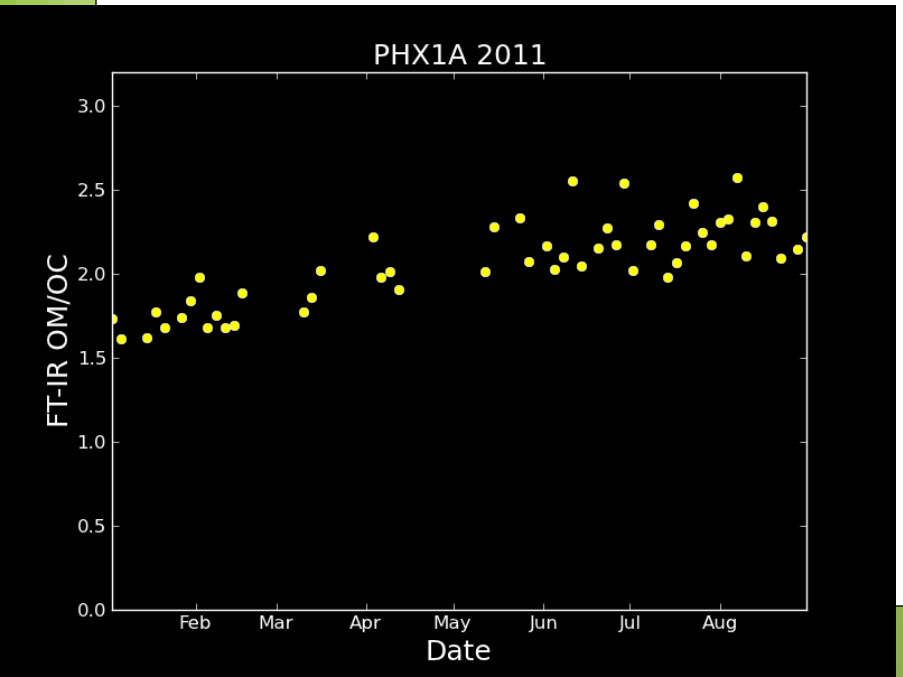
Date


PHX1A 2011
FT-IR OM/OC
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Feb
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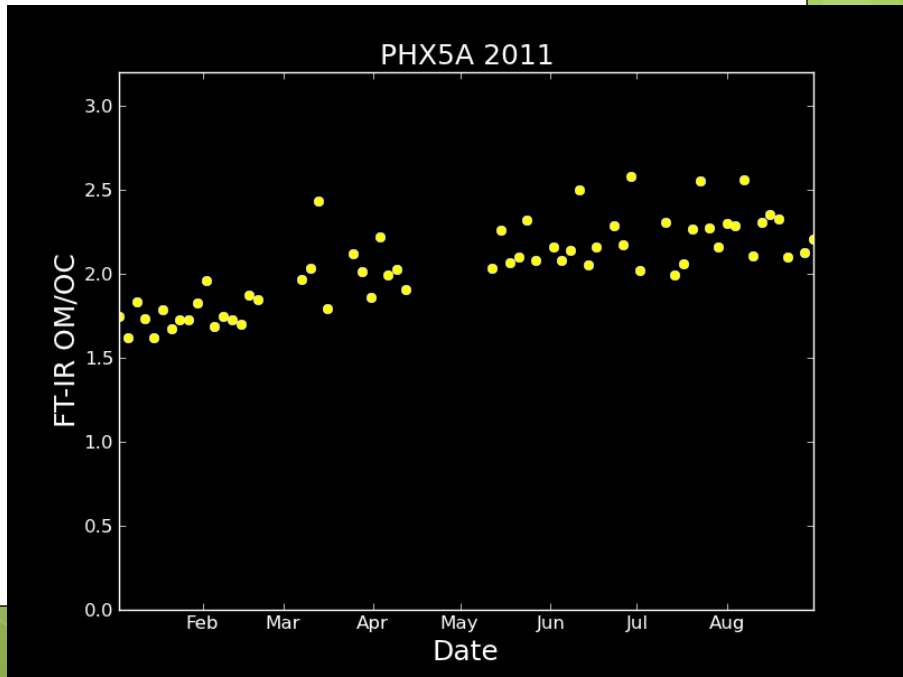
Date


PHX5A 2011
FT-IR OM/OC
3.0
2.5
2.0
1.5
1.0
0.5
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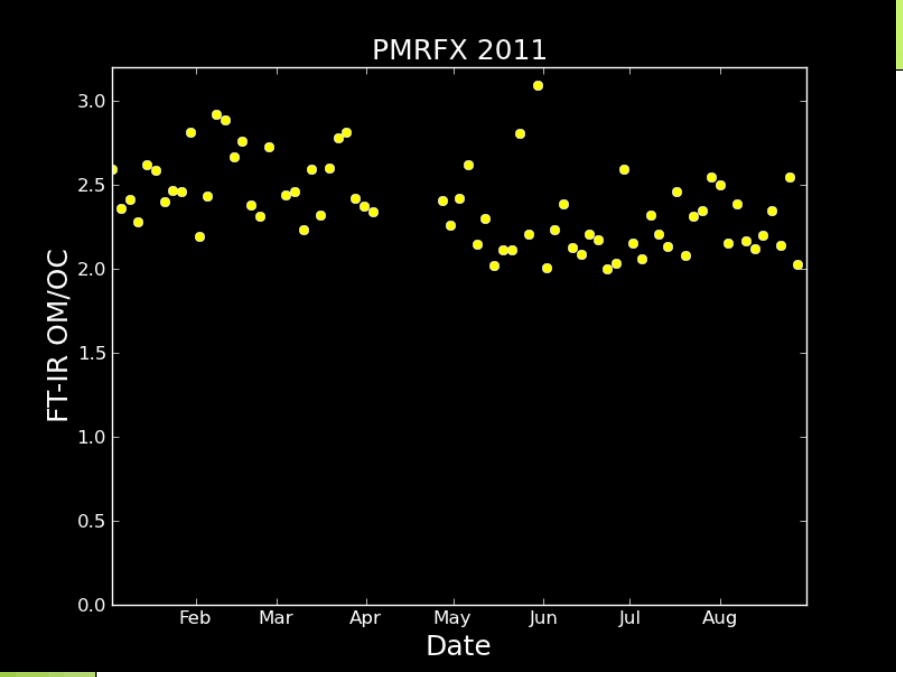
Date


PMRFX 2011
FT-IR OM/OC
3.0
2.5
2.0
1.5
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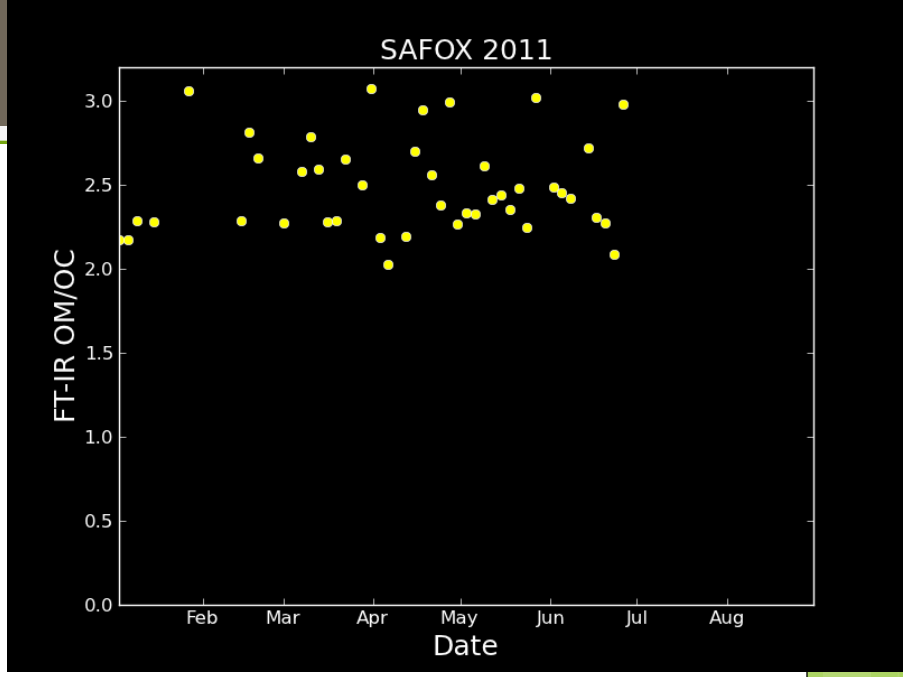
Date


SAFOX 2011
FT-IR OM/OC
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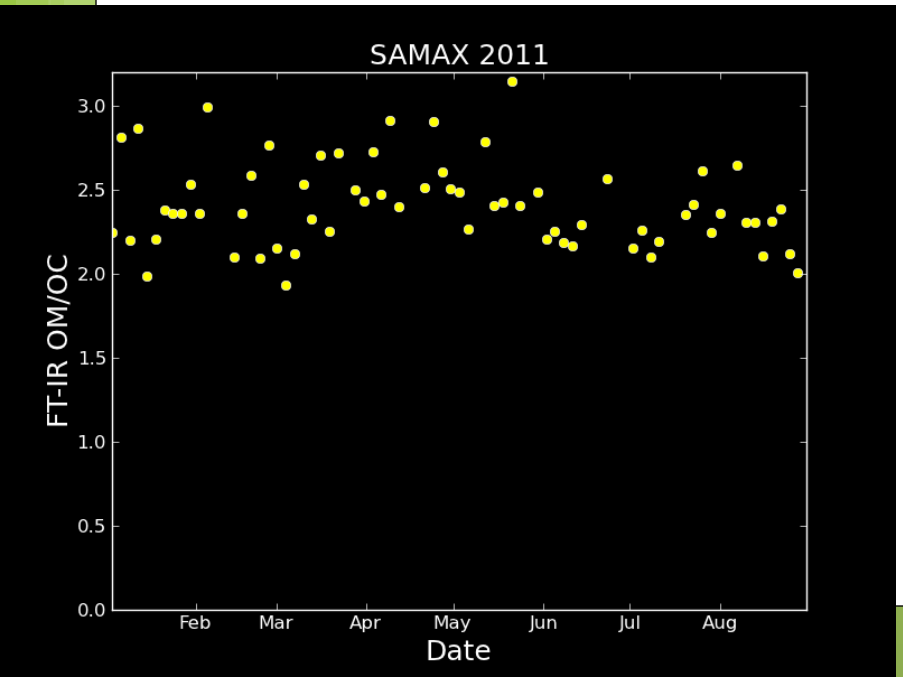
SAMAX 2011
FT-IR OM/OC
3.0
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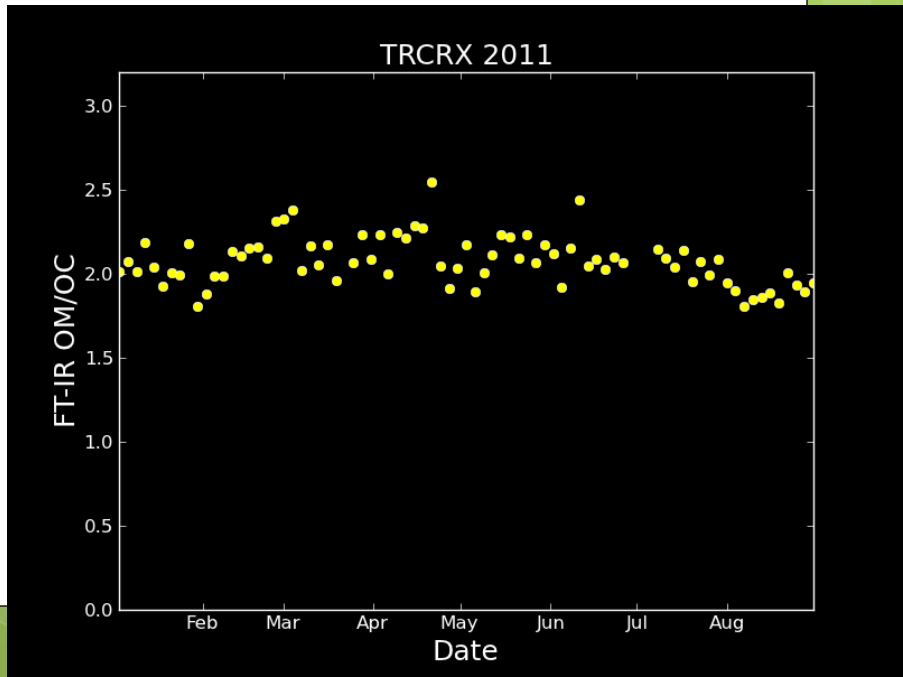
TRCRX 2011
FT-IR OM/OC
3.0
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2.0
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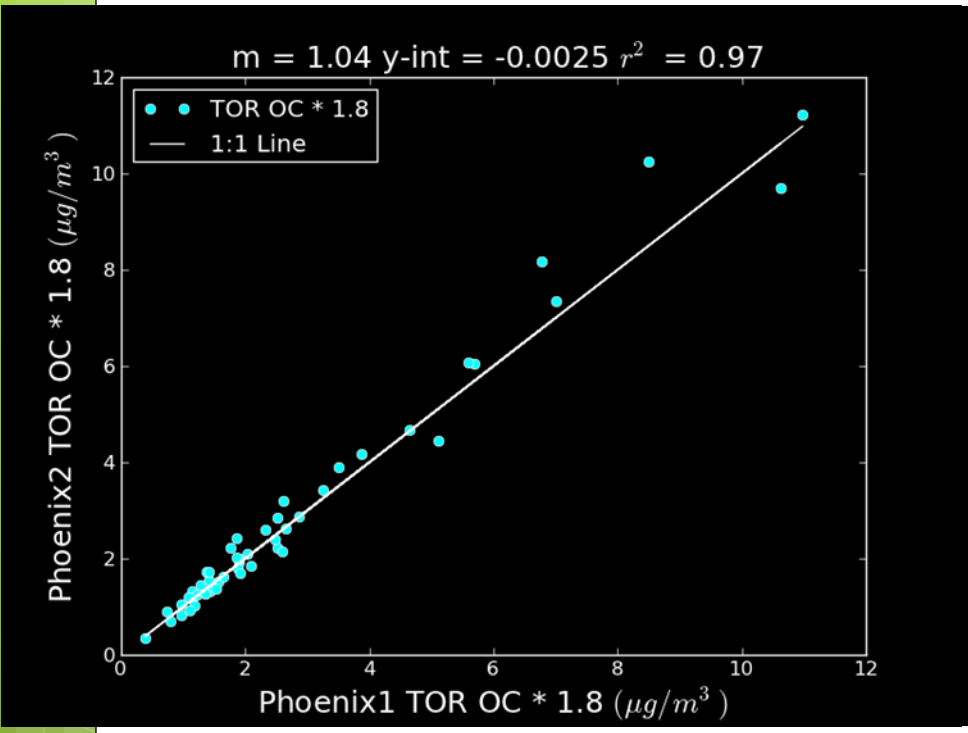
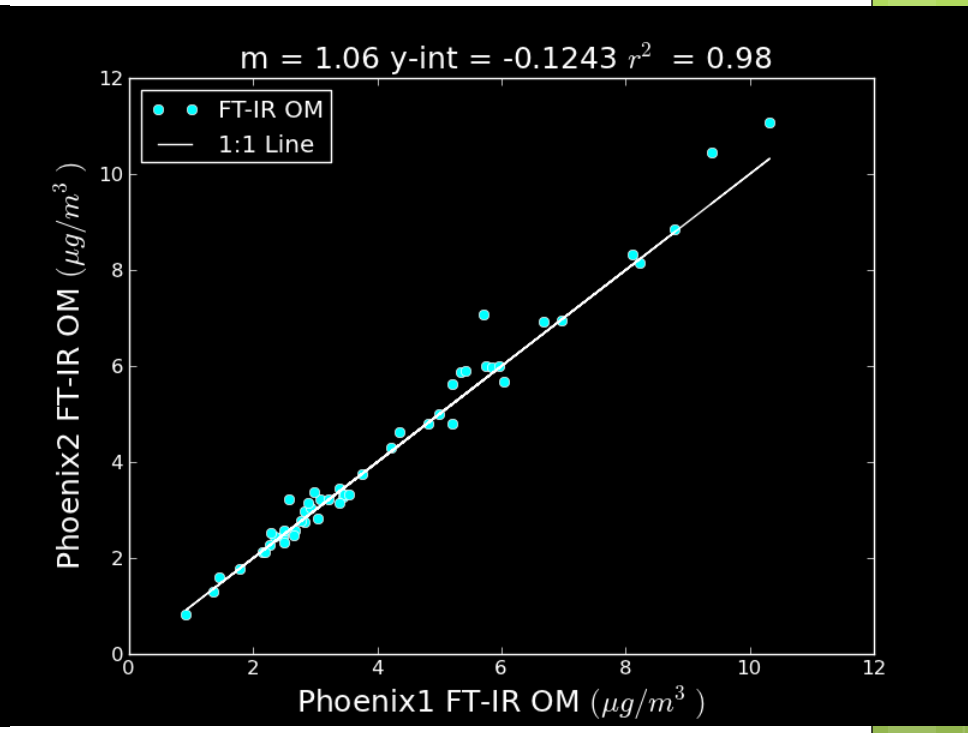
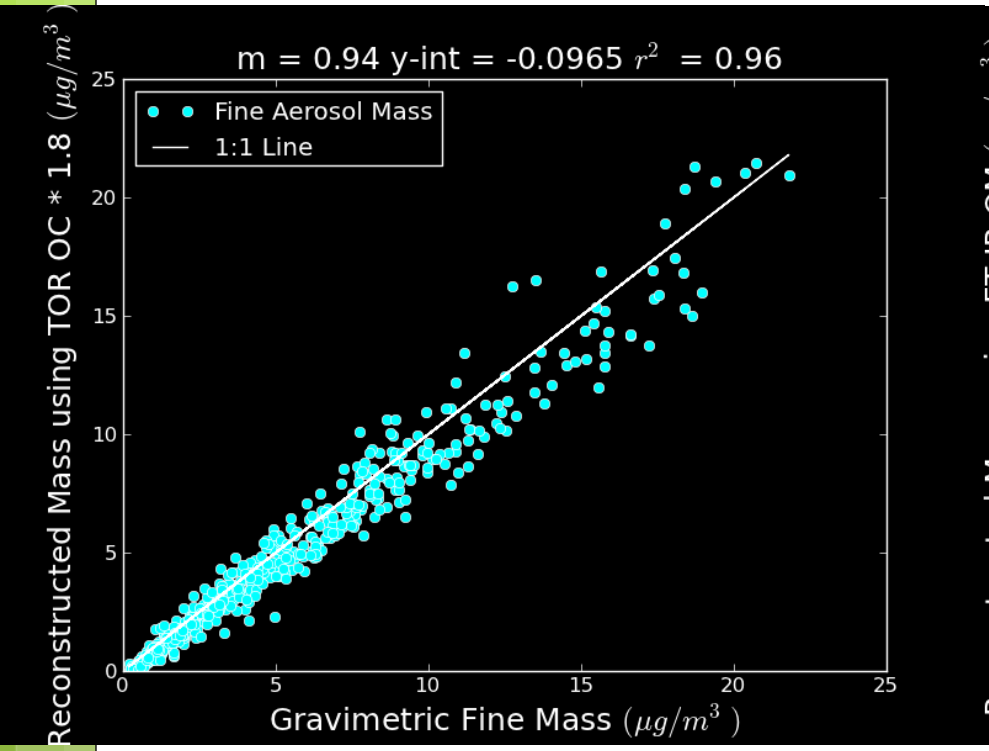
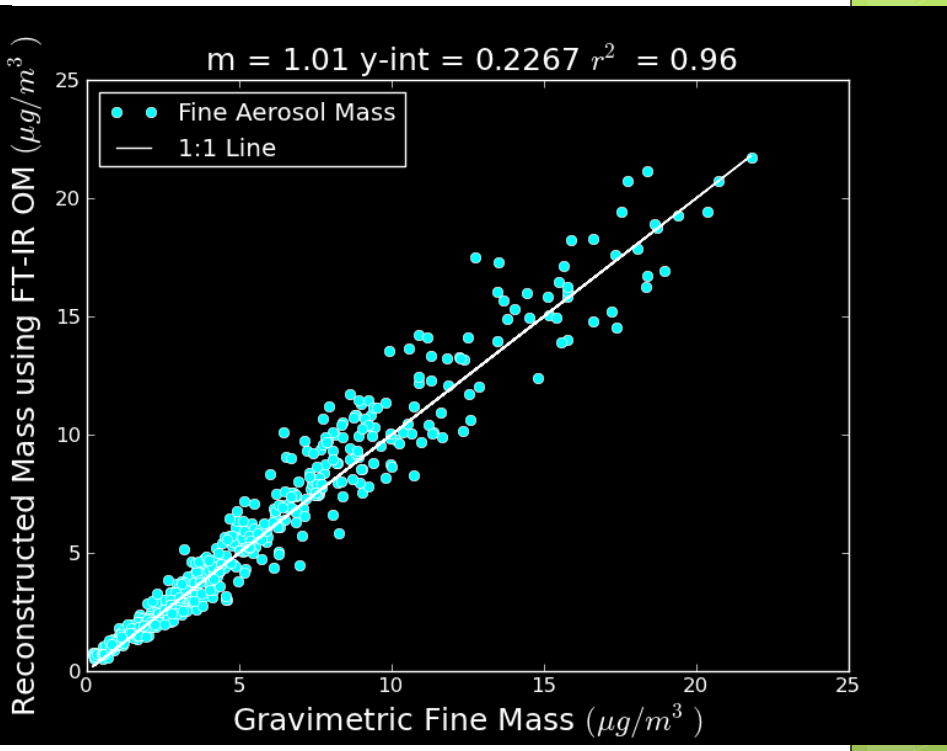
First look at measurement precision using collocated Phoenix Samplers





Reconstructed Mass





- Reconstructed mass with FTIR matches gravimetric mass more closely
- Correlations for two techniques are the same.

Accomplishments to date:

- Developed 1, 2 and 3 layer standards containing four functional groups:
  - Carbonyl, Acid OH, Alcohol OH, CH
- Developed PLSR calibrations
  - Show good precision
- Applied to 8 sites for 2011 samples
  - Values look reasonable, bit high
  - Improves agreement with gravimetric mass
  - OM/OC vary by day, site, season

Feasibility of applying FT-IR analysis to network

- All PM2.5 Teflon filters in the network can be analyzed using one FTIR instrument
- Automation of IMPROVE filter analysis
  - Modify IR and use similar automation system to HIPS
- Full calibration method
  - Requires more standards/method evaluation
  - Evaluations for precision and MDLs
- Automation/QC of data analysis
  - Can be developed after calibration established

Preparing for end of funding

- Developed SOPs for weighing standards, creating laboratory standards, and analyzing standards and samples on FT-IR
- In short-term, FTIR and system for making standards will be maintained by another staff member.
- Balance will be maintained by others who use it
- SOP for using computer code to analyze spectra and predict functional group mass will be developed
- Code, spectra, data files and figures will be loaded onto my computer and backed-up by IT personnel
- A paper describing methods and results will be published

Future goals if funding is available

- Analyze one year of IMPROVE samples to create a robust data set for analysis
- Make additional standards and further develop the calibration method to measure OM, OC and functional groups from Teflon filters
- Evaluate accuracy, precision and MDLs of OM, OC and functional groups,
- Further evaluate the viability of using this method in the network.

Summary

- FT-IR analysis of Teflon filters useful for IMPROVE
  - OM/OC per filter
  - Functional group information – sources
- Non-destructive to Teflon filters
- Fast and reasonably cheap (<PESA)
- Feasible to physically integrate into existing filter analyses at CNL
- Preparing SOPs and documentation to be able to restart project sometime in the future