ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Estimation of OC and EC concentrations and OM/OC ratios in monitoring networks with infrared spectroscopy

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Atmospheric Particle Research Laboratory (APRL)
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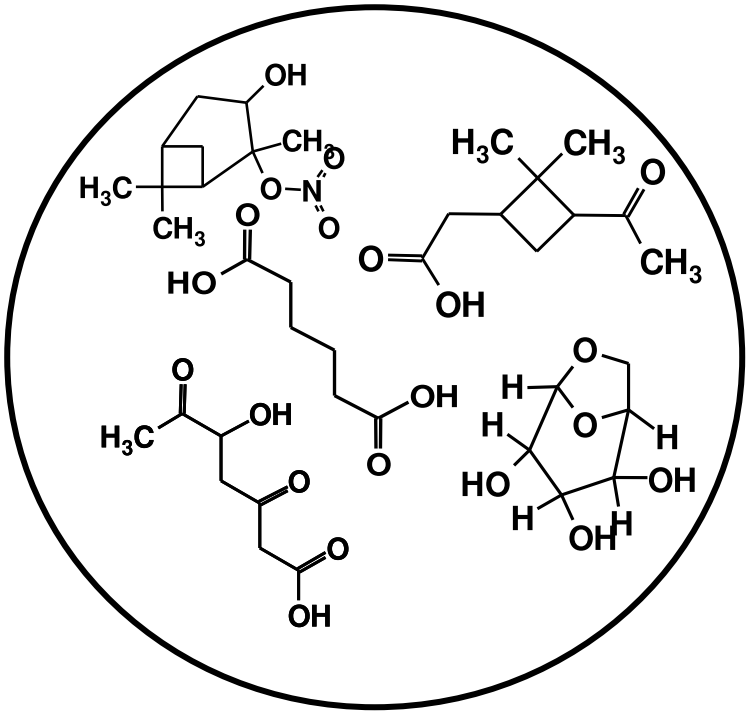
TFMM meeting
19 May 2016



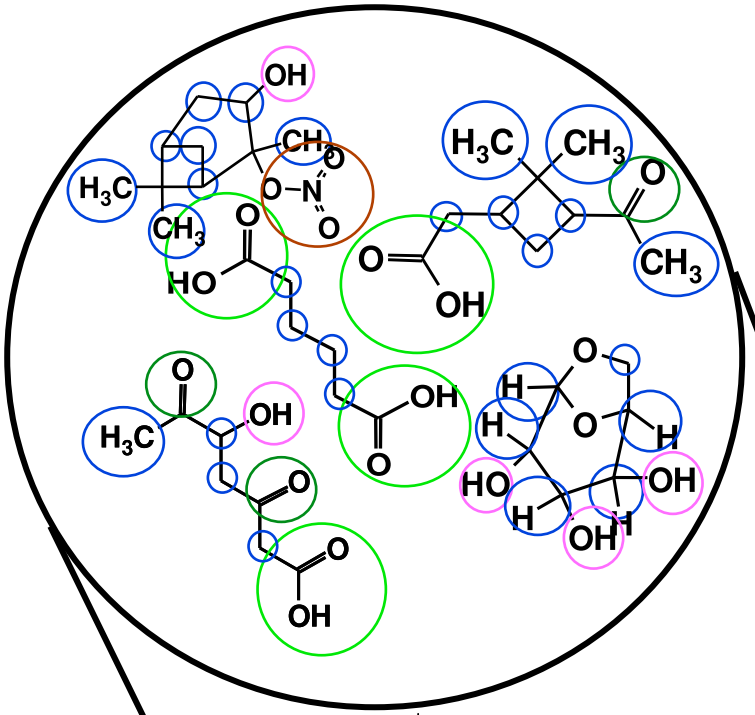
- Organic aerosols have many different sources
- Complex mixtures of 10,000+ compounds
- Carbon content commonly analyzed by thermal optical methods

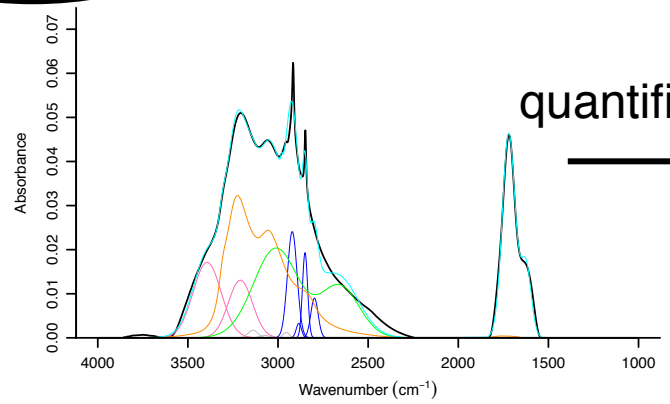
Infrared spectroscopy

- Measures absorption due to net change in dipole moment of vibrating/rotating molecules
- Absorption is linearly related to abundance of a substance
- Relatively inexpensive to own and operate, but requires advanced algorithms to process spectral information

FTIR spectrometer

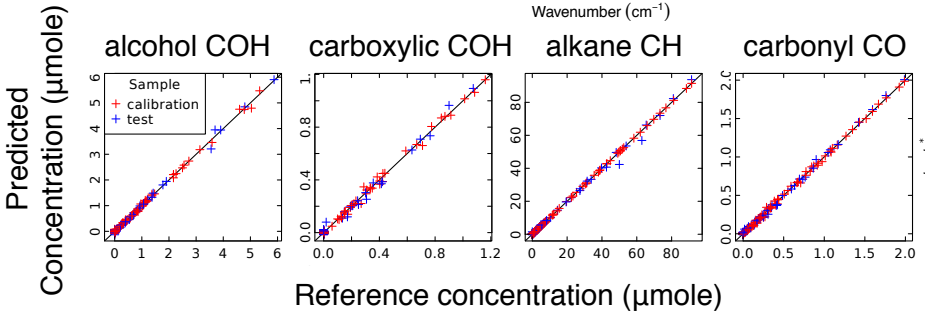
Infrared spectroscopy

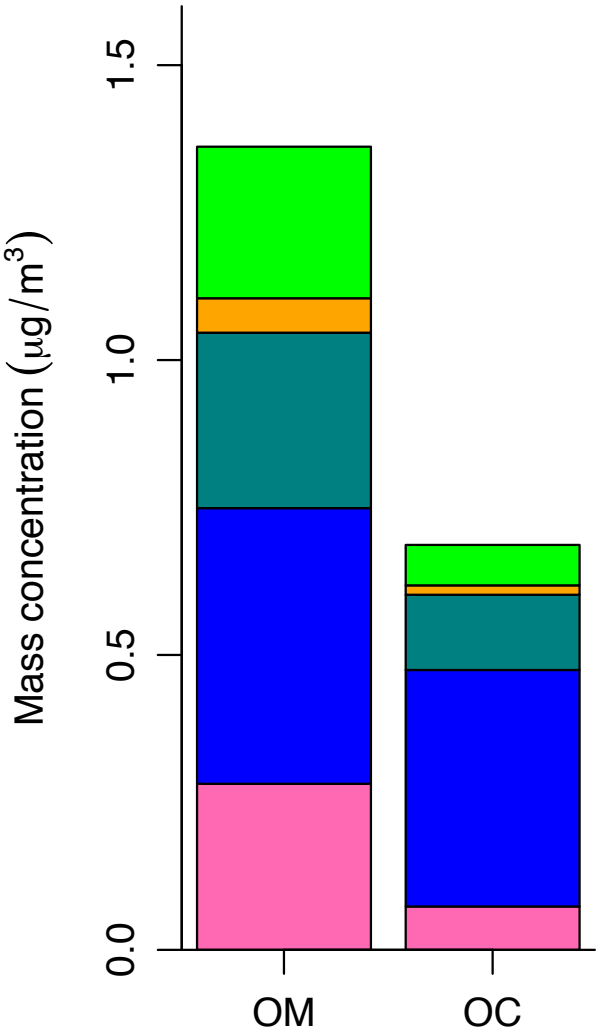




quantification

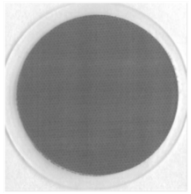
calibration





Analysis of samples collected on Teflon (PTFE) filters

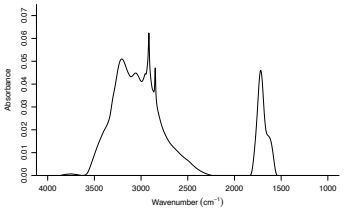
- Standard substrate for gravimetric mass measurements in regulatory monitoring in the US
- Widely used for other types of chemical analyses



gravimetric mass

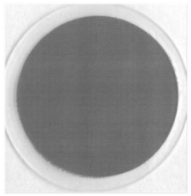
elemental composition (e.g., X-ray Fluorescence)

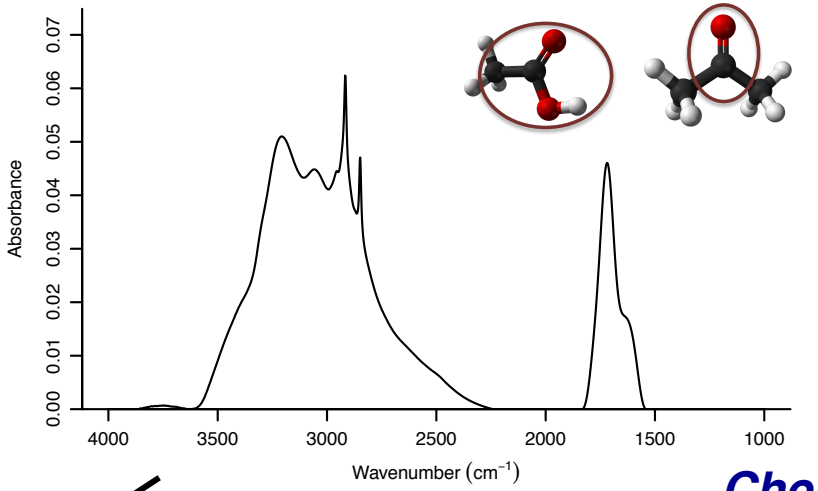
FTIR spectrum

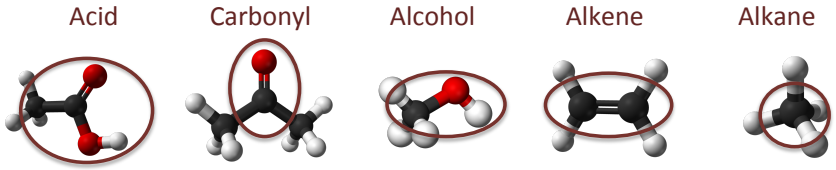


other (ions)

- No sample prep
- Non-destructive
- Rapid (few minutes per sample)
- Inexpensive
- *Integrate into PM analysis chain*





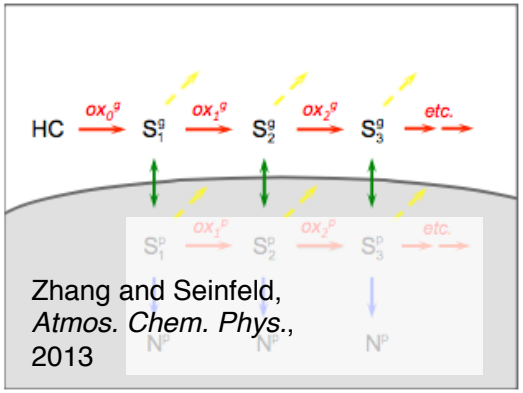


Chemometric algorithms

Functional groups
OM, OM/OC

Source contributions
to OM

TOR OC, EC

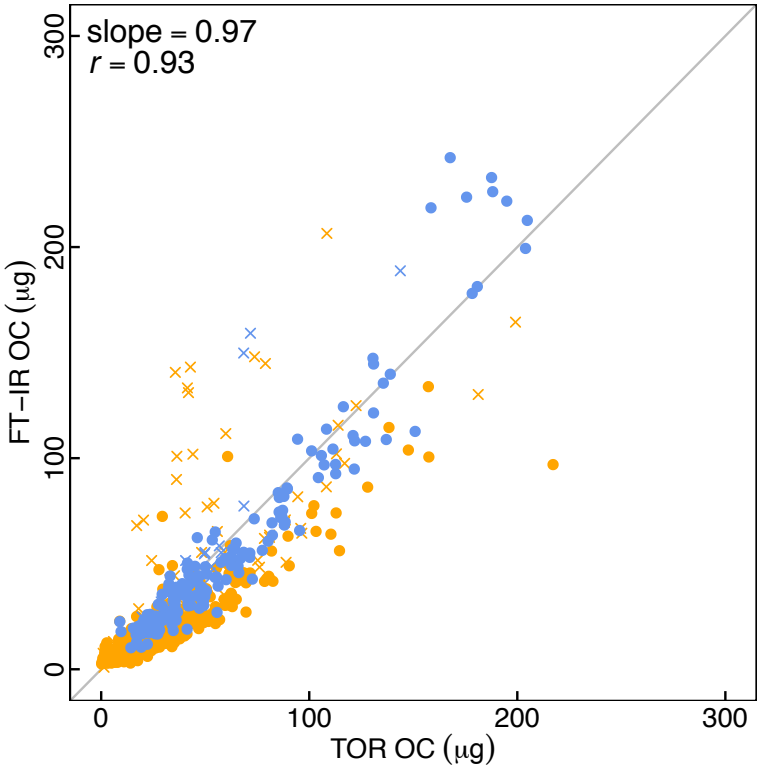


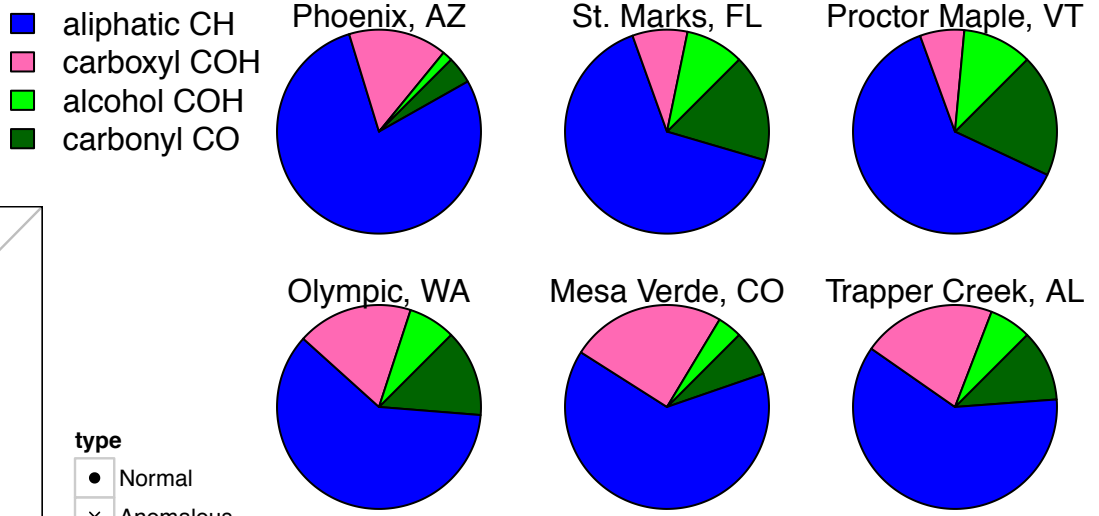
Zhang and Seinfeld,
Atmos. Chem. Phys.,
2013

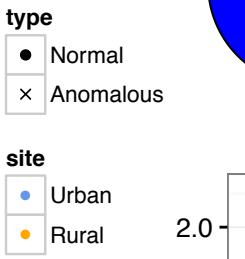
Numerical simulation + chemoinformatic algorithms

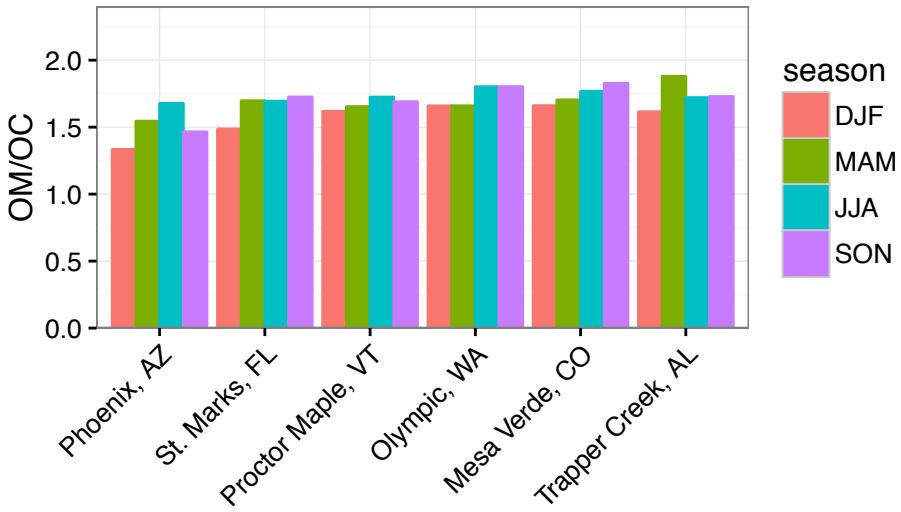
$PM_{2.5}$ OM in US IMPROVE network (2011)

Comparison with TOR OC ($PM_{2.5}$)





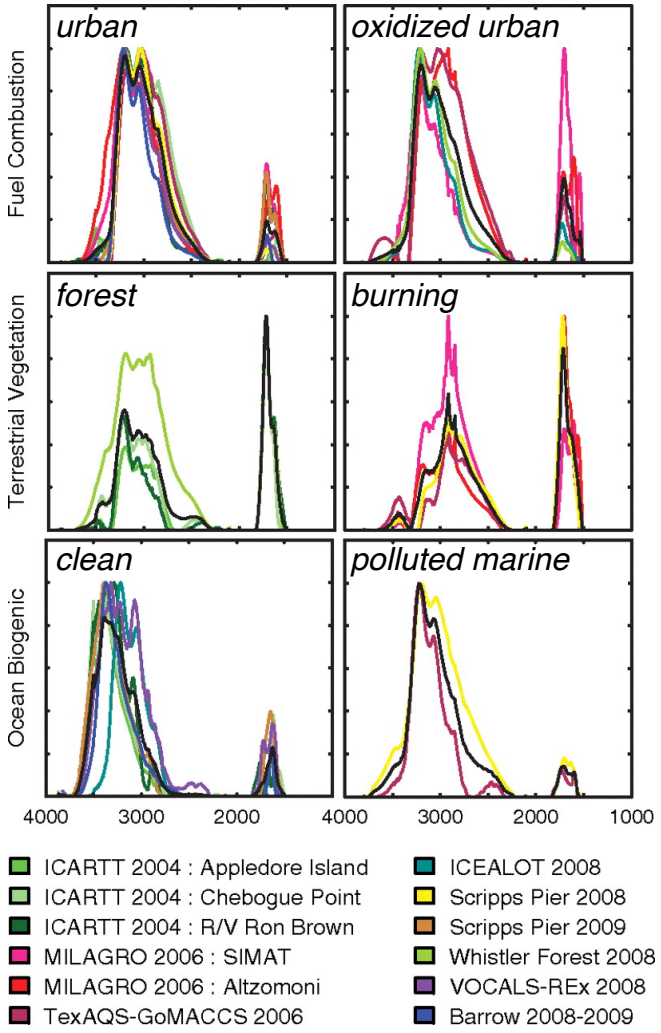




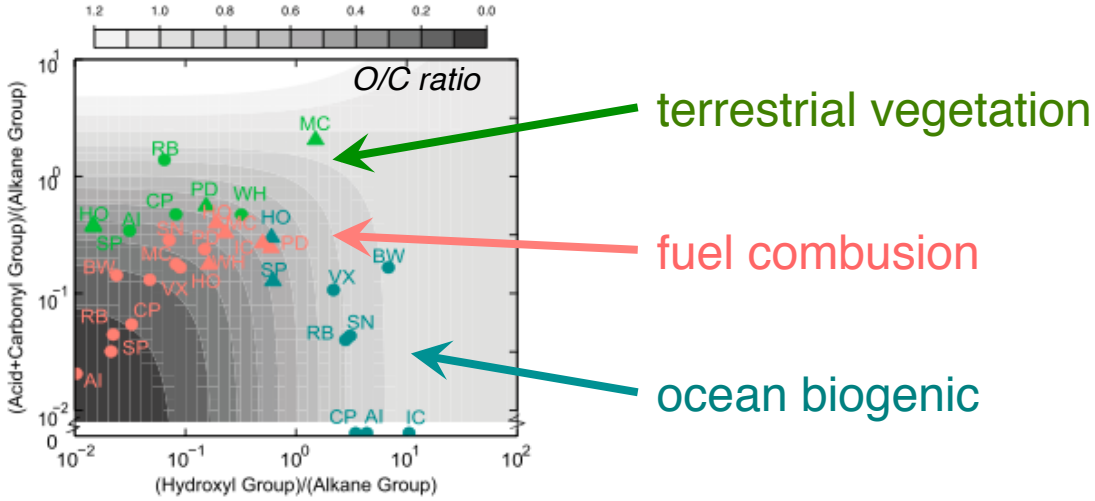
Ruthenburg et al., *Atmos. Environ.*, 2014
Takahama and Dillner, *J. Chemometrics*, 2015

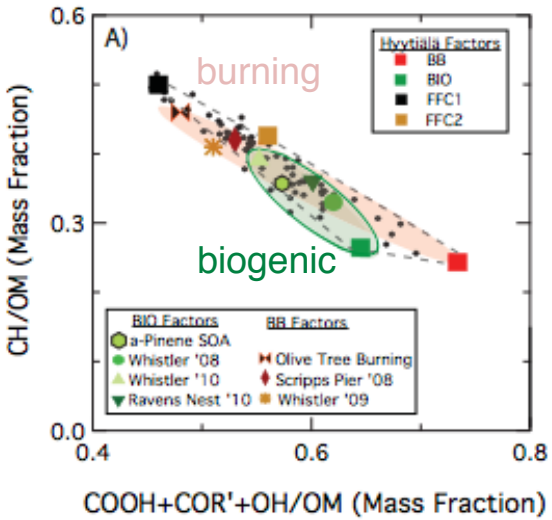
Source apportionment
with IR spectra and functional groups

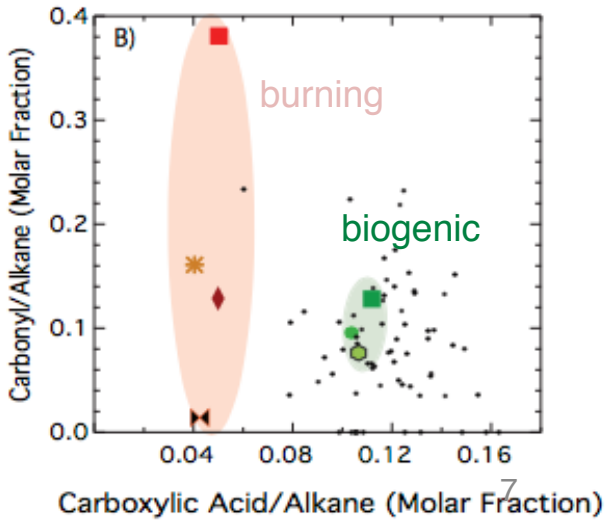
Spectroscopic similarity



Separation in composition space



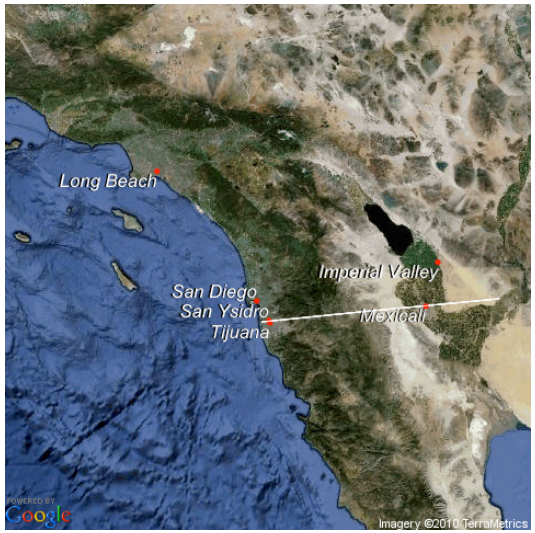




Russell et al., *PNAS*, 2011; Corrigan et al., *Atmos. Chem. Phys.*, 2013

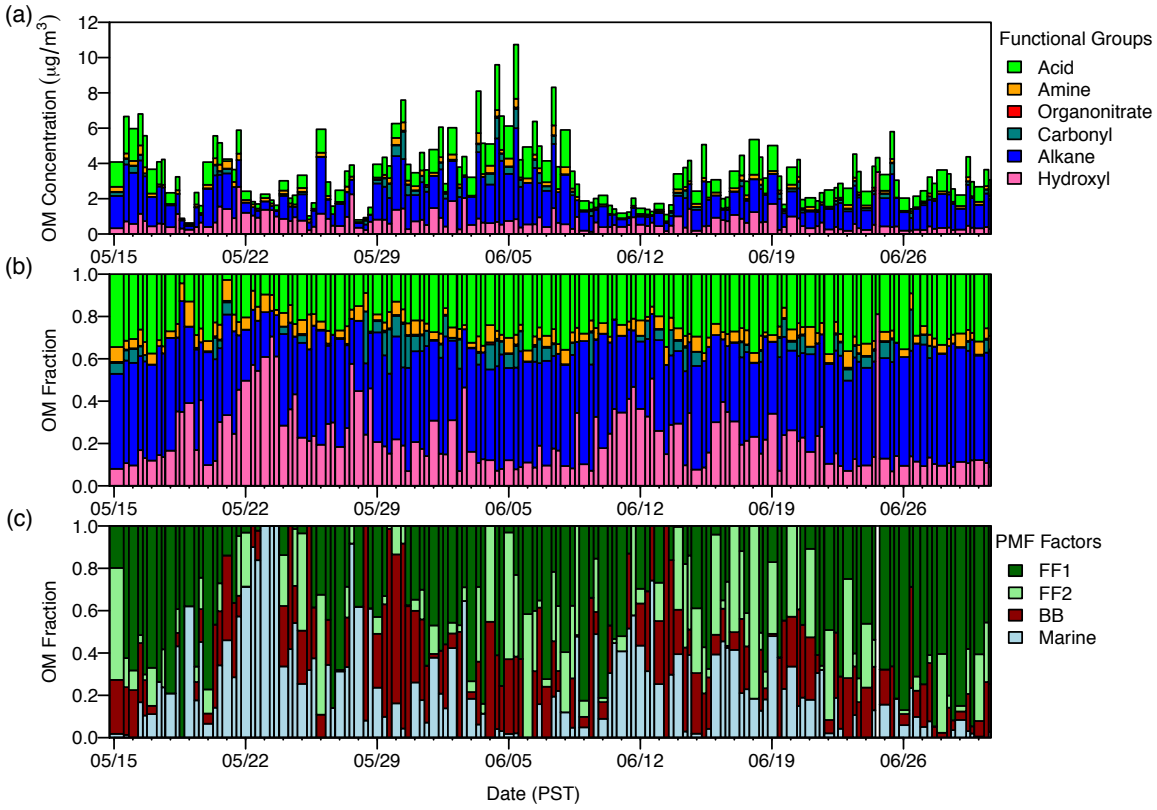
Source apportionment
Example: CalMex 2010

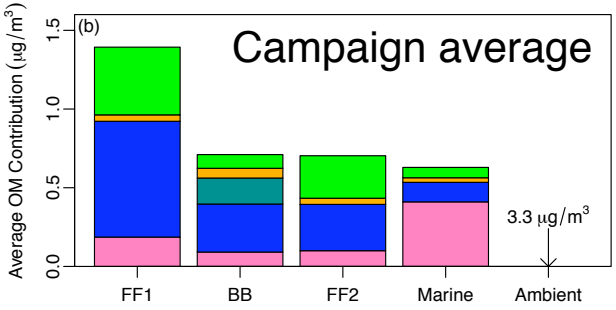
Takahama et al., *Atmos. Environ.*, 2013



Tijuana, Mexico
June – July 2010

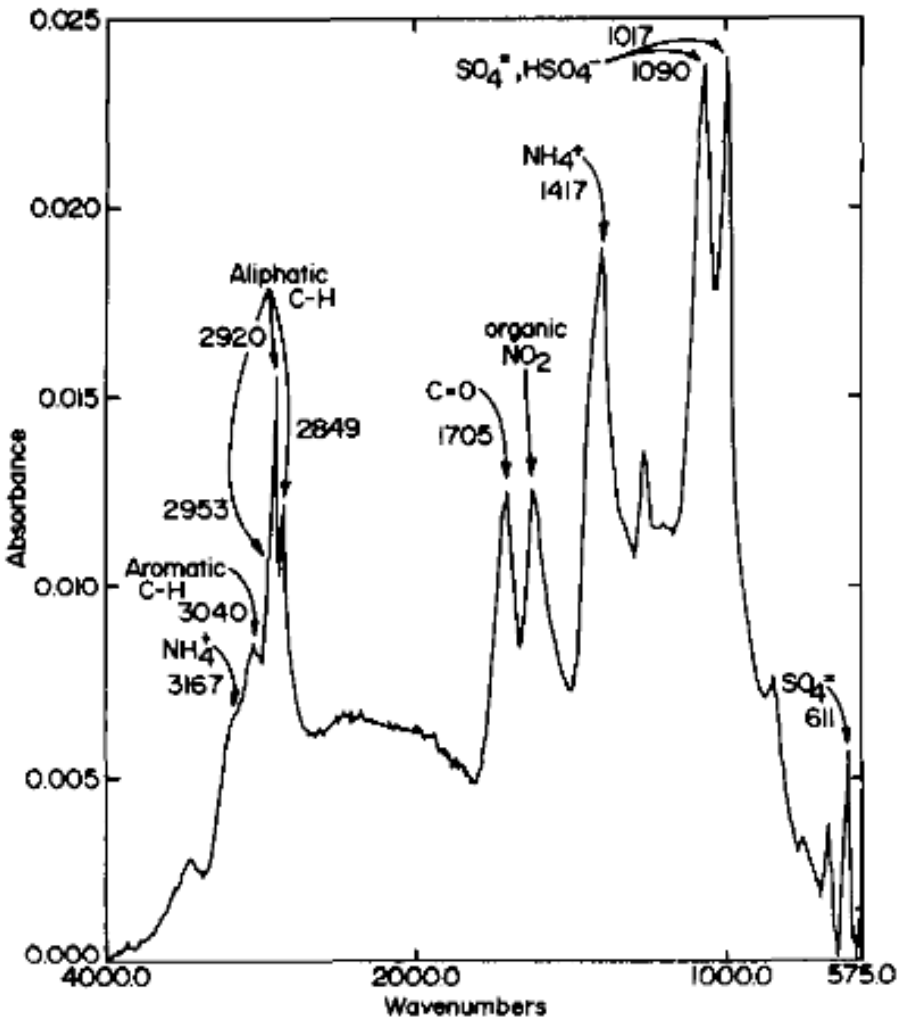
Factor analysis by
Positive Matrix Factorization





FT-IR for PM analysis

used since 1980s

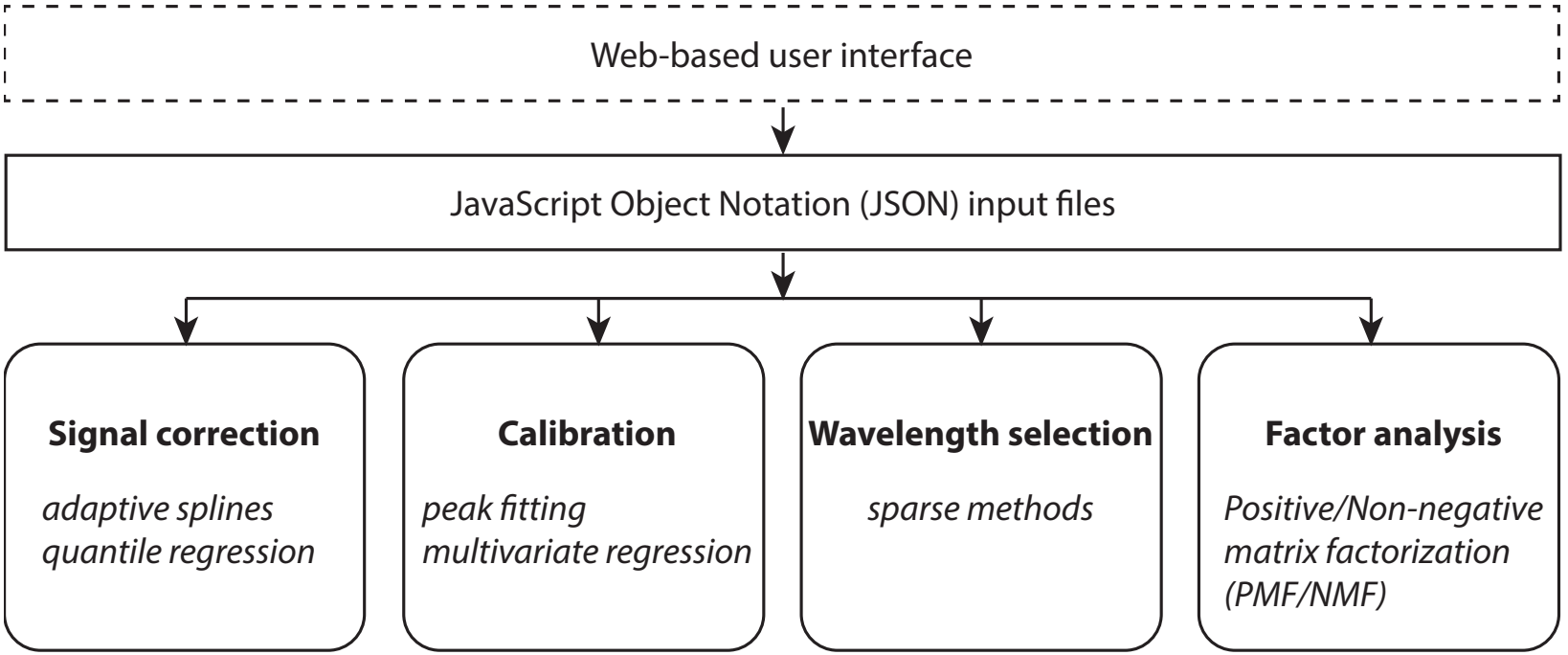


Los Angeles aerosol
Pickle and Allen, *Atmos. Environ.*, 1990

- Inorganic salts
  (e.g., ammonium sulfate)
- Mineral dust
- Water, ice
- Organic PM
  - Allen (UCLA, U. Texas)
  - Turpin (Rutgers U.)
  - Russell (Princeton, Scripps)
  - Dillner (UC Davis)
  - Others (PSI, Carnegie Mellon)

Challenge*: interpretion of complex spectra*

Algorithms and software



Implemented in R
(free and open source statistical environment)

Takahama et al., *Atmos. Chem. Phys.*, 2011
Takahama et al., *Aerosol Sci. Tech.*, 2013
Takahama et al., *J. Chemometrics*, 2015
Kuzmiakova et al., *Atmos. Meas. Tech.*, 2016
Takahama et al., *Atmos. Meas. Tech. Discuss.*, 2016

Please see http://aprl.epfl.ch

Extension to other collection media

Quartz fiber filters?

- By solvent extraction
- Current project with Swiss Federal Office of the Environment and Empa

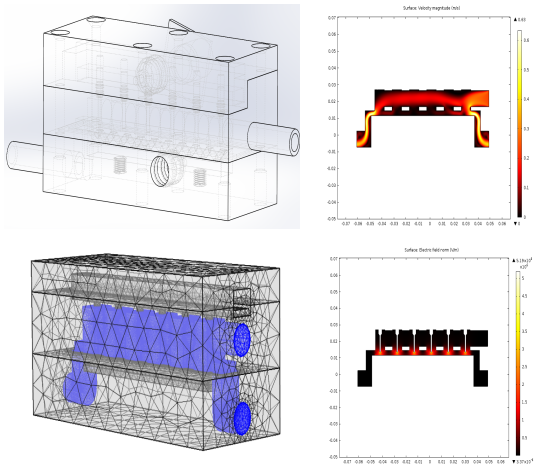
IR-transparent crystals:

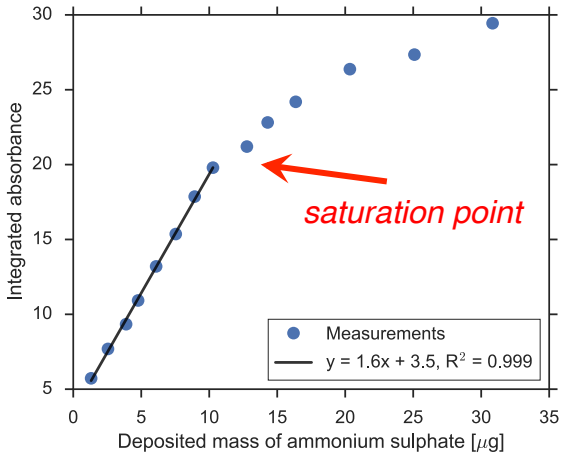
- Ensure high collection efficiency
- Linearity with mass
- *Semi-continuous*

European Research Council

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Empa
Materials Science and Technology





Modini and Takahama, *in prep.*, 2016

Estimating TOR OC, EC concentrations with infrared spectra

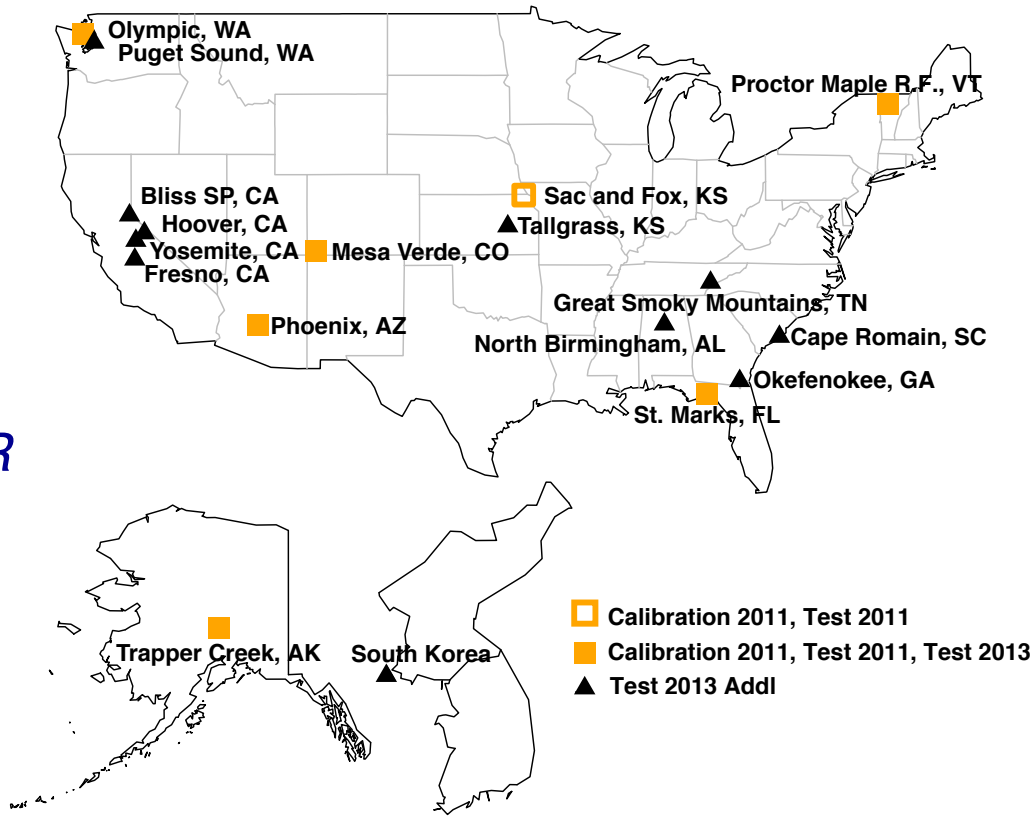
collocated OC or EC — *regression coefficients*

$$\mathbf{y} = \mathbf{Xb} + \mathbf{e}$$

spectra matrix — *residual*

- Is it feasible?
  prediction accuracy within TOR measurement precision
- How best to select samples to build a calibration model?
  composition and concentration range should be represented in calibration set

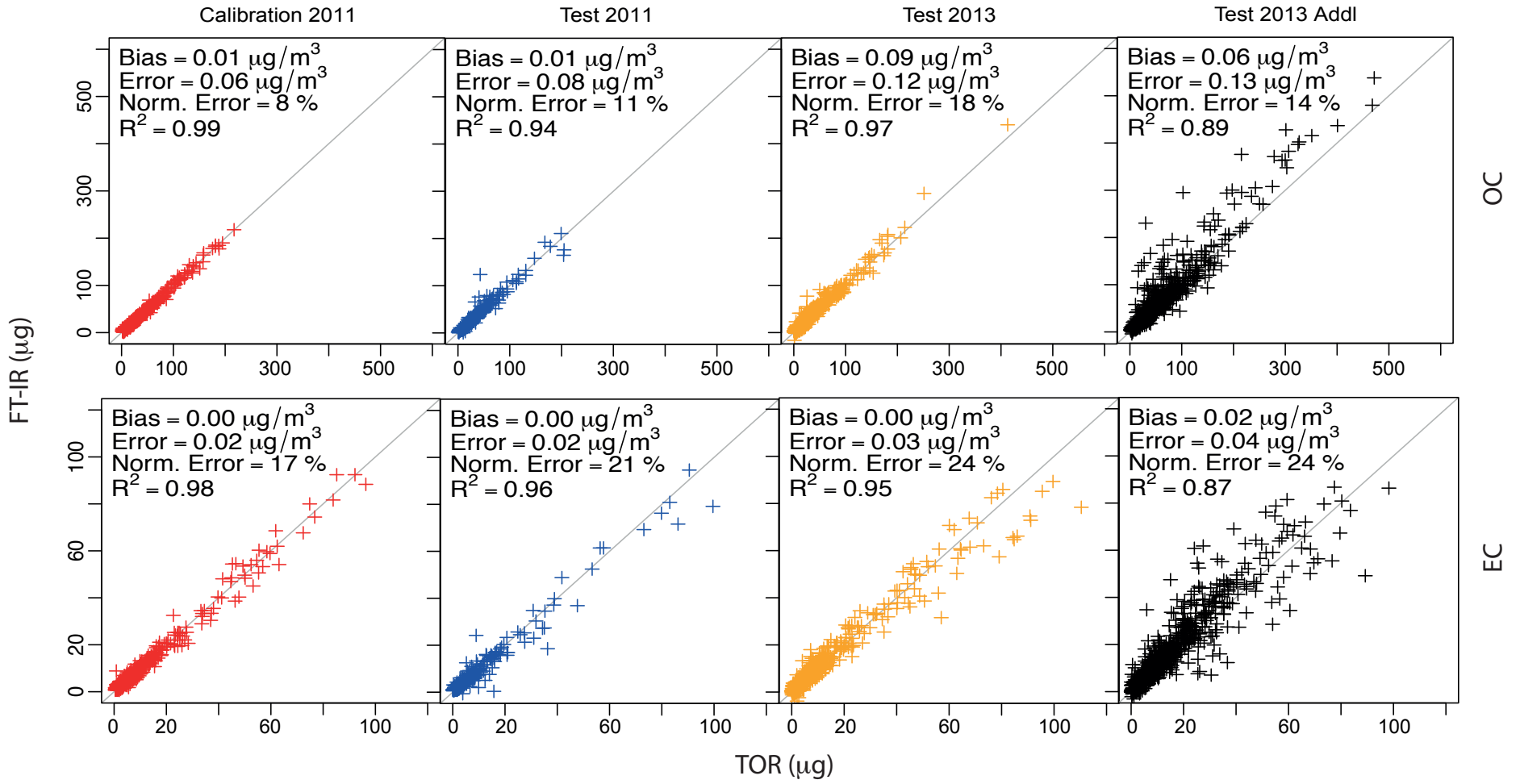
Dillner and Takahama, *Atmos. Meas. Tech.*, 2015 (OC)
Dillner and Takahama, *Atmos. Meas. Tech.*, 2015 (EC)



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

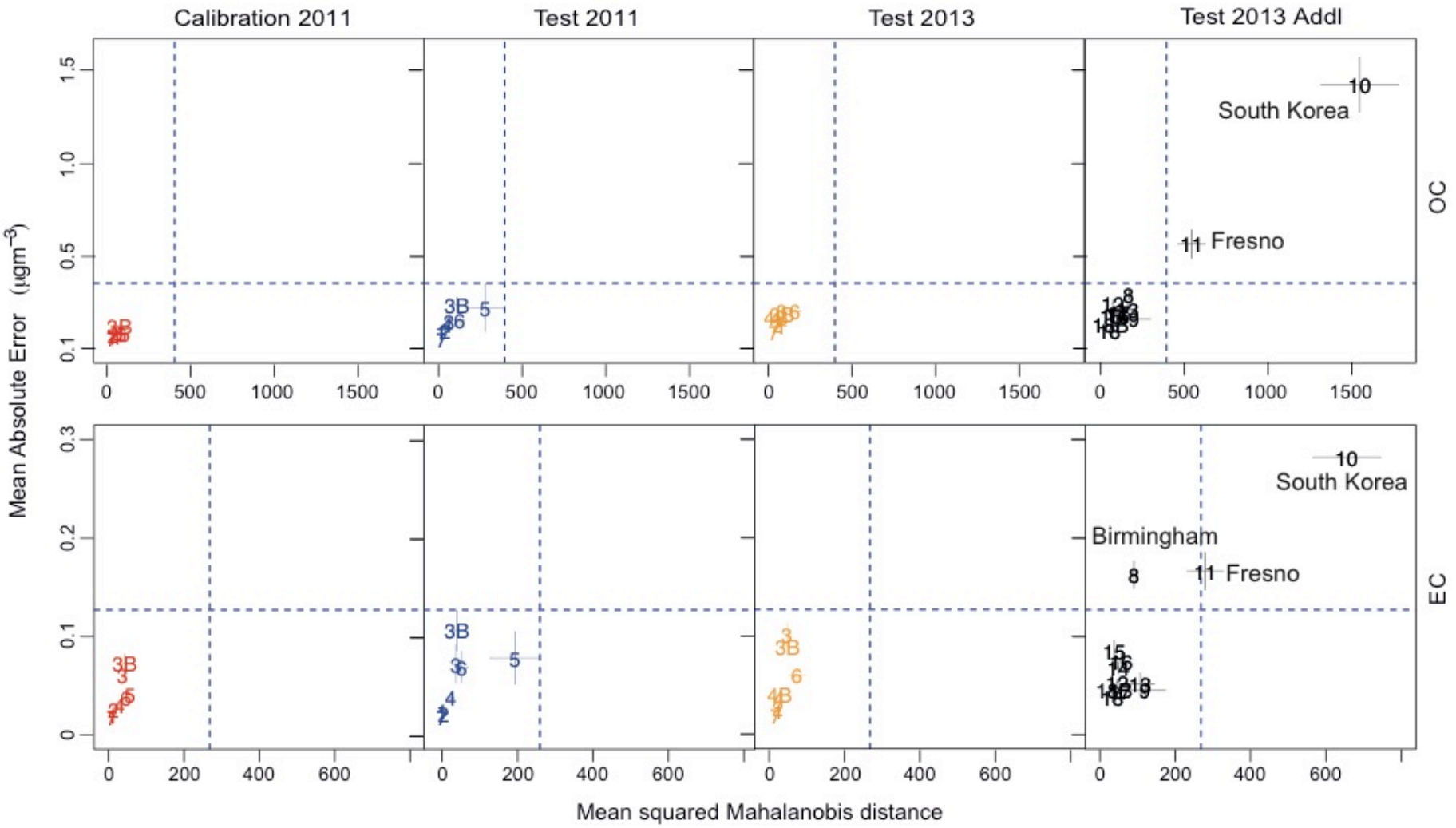
TOR-equivalent OC and EC predictions

Reggente, Dillner, and Takahama, *Atmos. Meas. Tech.*, 2016



Estimated obtained by FT-IR spectra calibrated to ambient collocated samples of TOR OC and EC

We can anticipate prediction error with only knowledge of spectral features in most cases

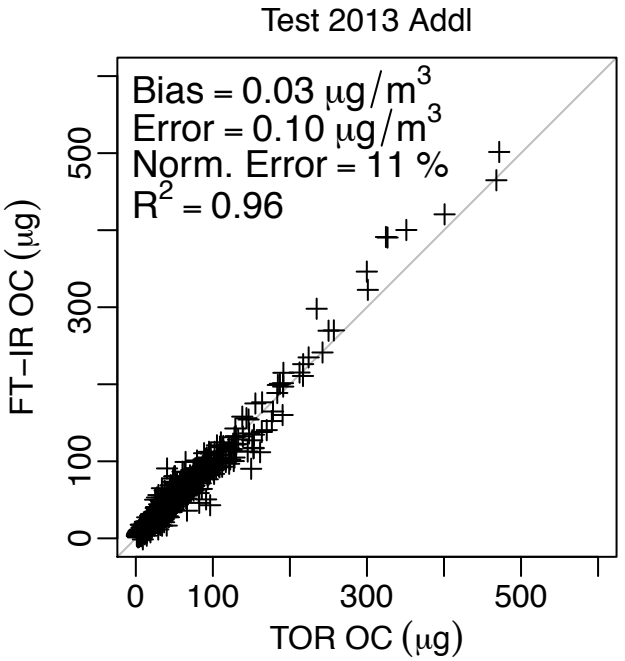


x-axis: spectral dissimilarity with respect to calibration set samples

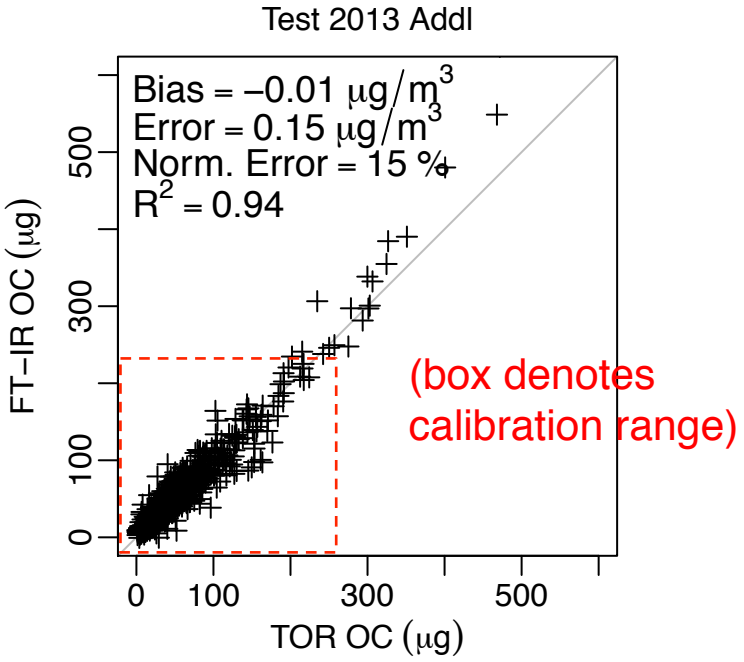
Reduction in prediction errors by re-calibration

Two strategies:

1) **Include samples from new sites** into the training set.

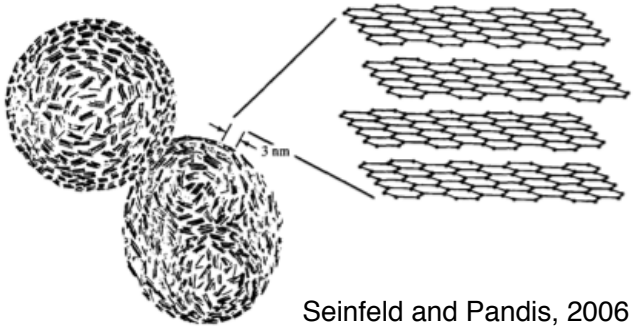


2) Using only the original set of samples, **eliminate uninformative wavelengths** that interfere with predictions.



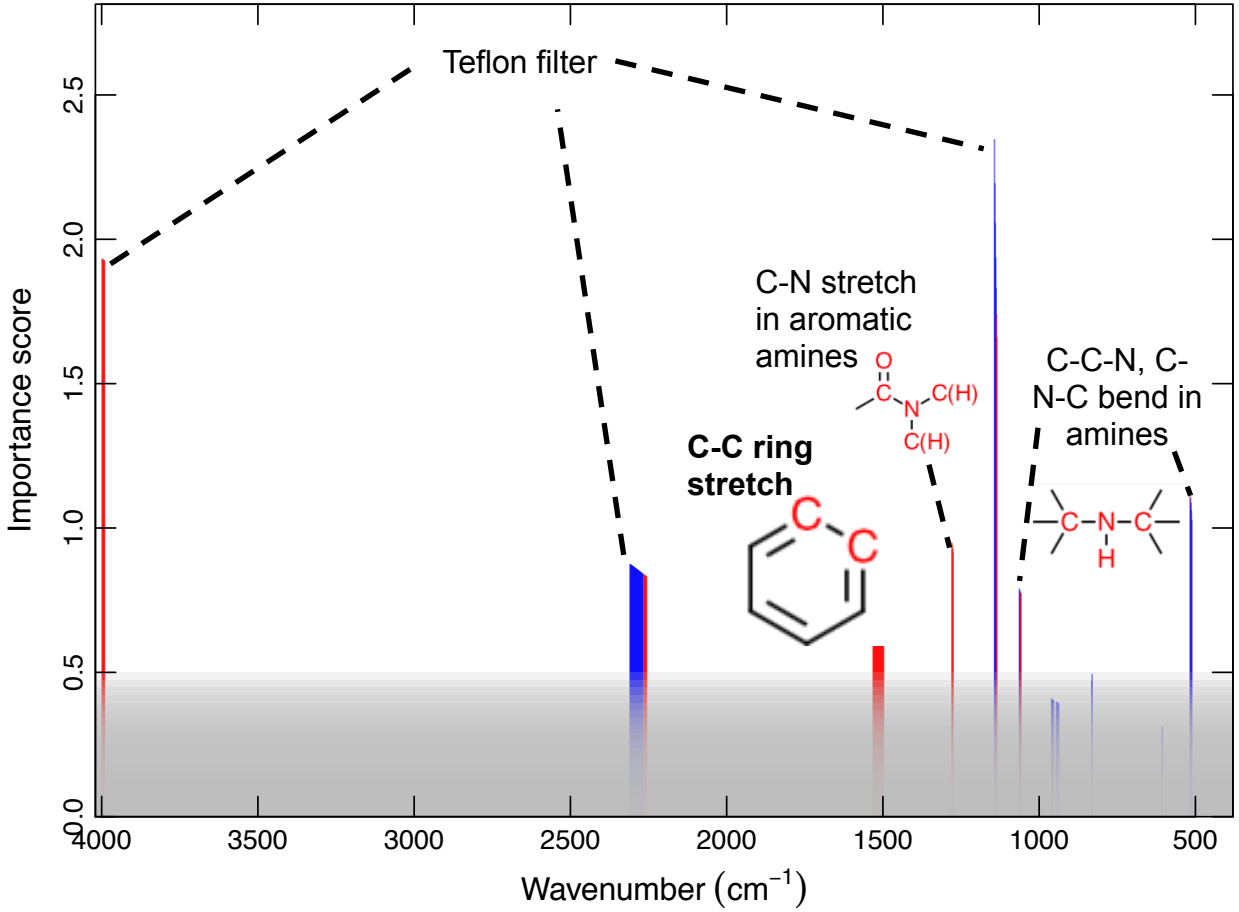
Reggente, Dillner, and Takahama, *Atmos. Meas. Tech.*, 2016
Reggente, et al., *in prep.*, 2016

Why can we quantify elemental carbon with FT-IR?



Seinfeld and Pandis, 2006

Takahama, Ruggeri, Dillner, *Atmos. Meas. Tech.*, 2016



Elemental carbon:

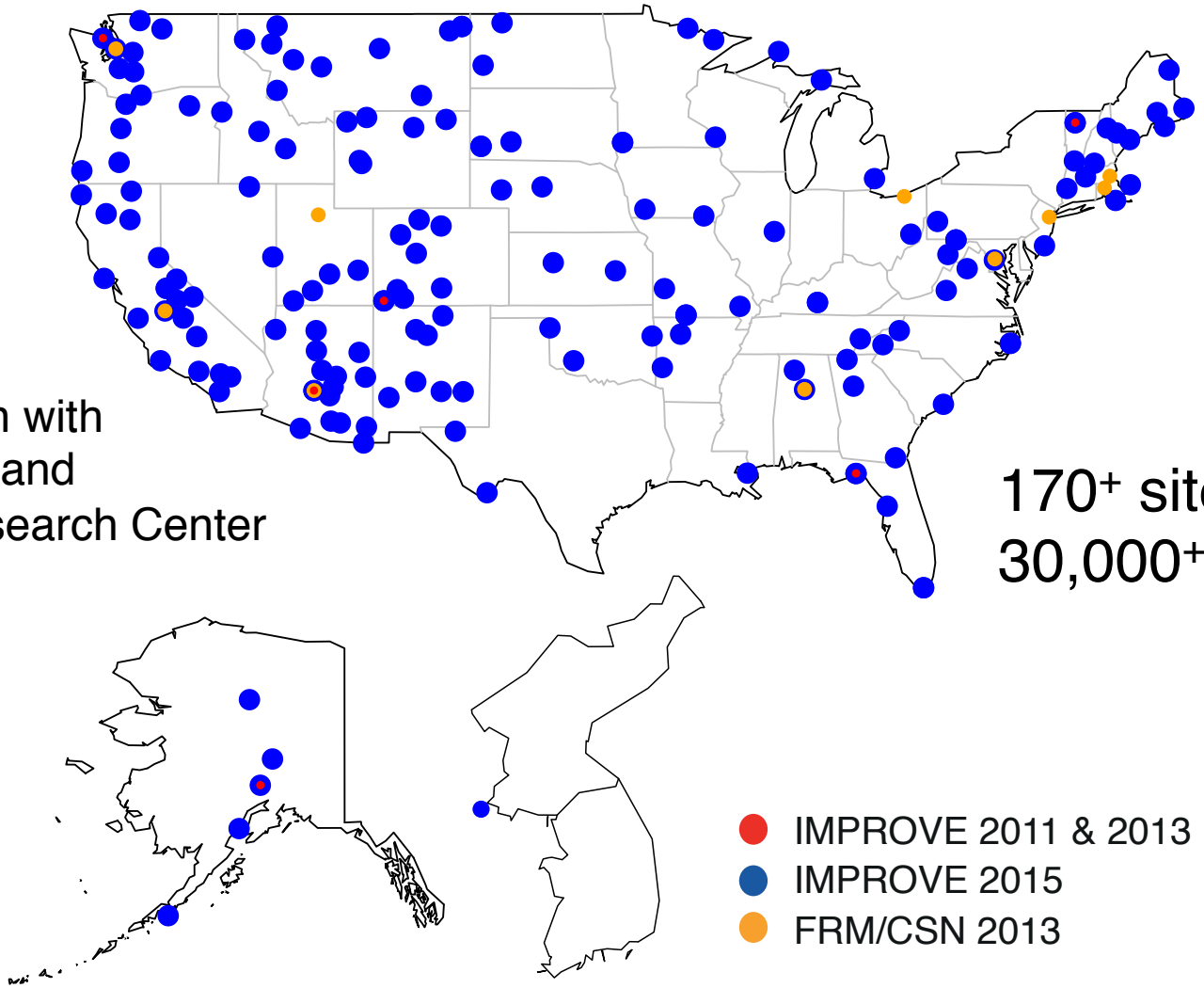
- *chemical definition*: sp^2 carbon not bonded to other elements
- *probable interpretation*: subset of light-absorbing, low-volatility substances emitted primarily from combustion

Peak near ~1600 cm^{-1} observed for ground graphite, graphene:

- *C-C ring stretch*

Present work

extended analysis of TOR OC, EC and FT-IR spectra



In collaboration with
Ann M. Dillner and
Air Quality Research Center

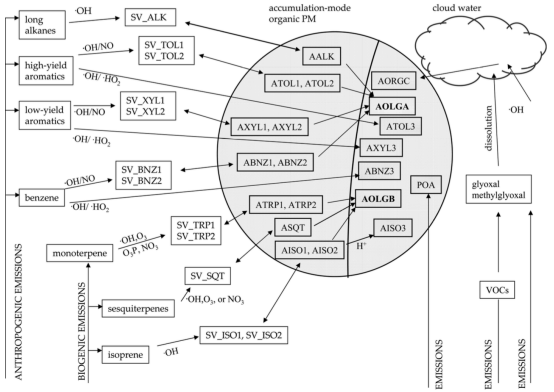
UCDAVIS
UNIVERSITY OF CALIFORNIA

170+ sites
30,000+ samples

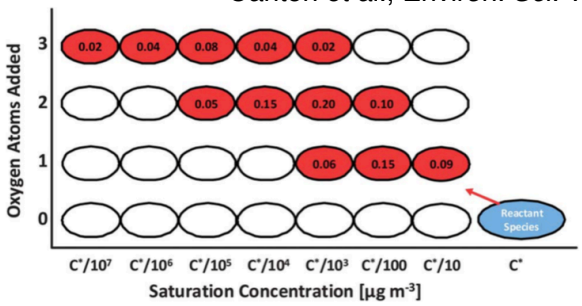
Secondary organic aerosol modeling

Common approaches:

- Yield parameterization
- Surrogate species
- Volatility basis set



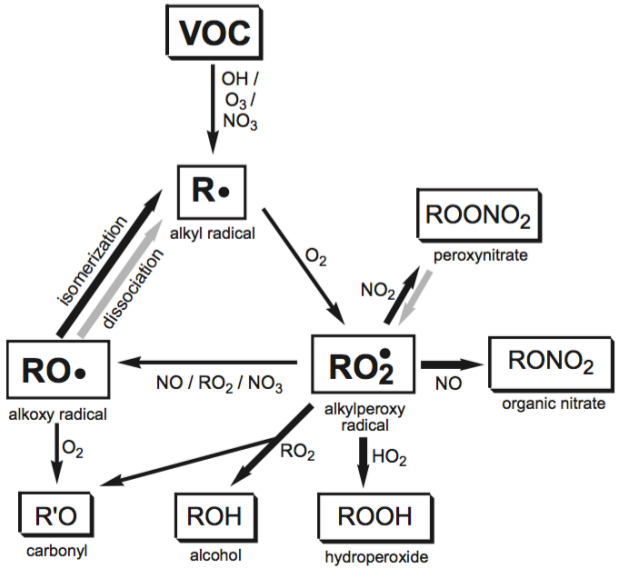
Carlton et al., *Environ. Sci. Tech.*, 2010



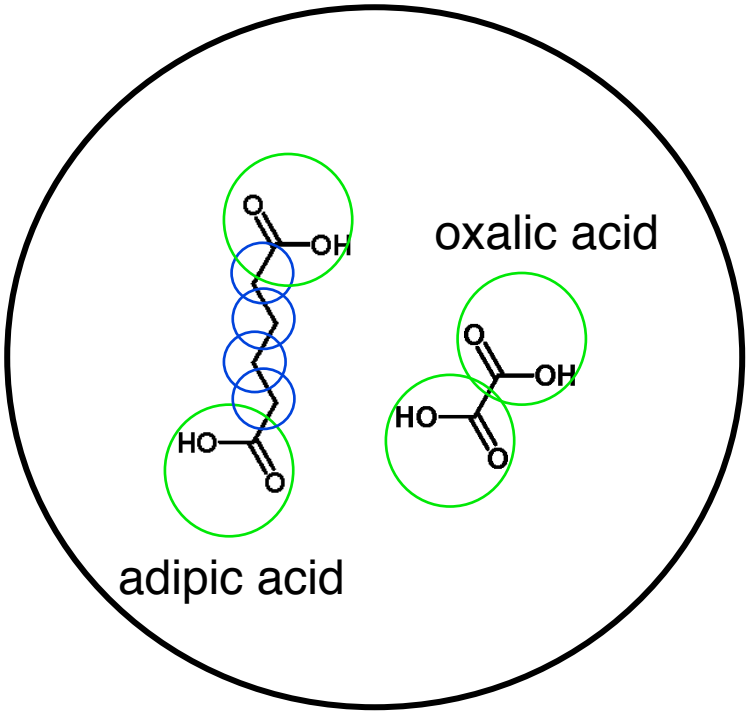
Pandis et al., *Faraday Discuss.*, 2013

Proposed approach:

- Follow functional group transformations
- Functional groups are related to reactivity, volatility, hygroscopicity



Kroll and Seinfeld, *Atmos. Environ.*, 2008



SMILES strings represent molecules

oxalic acid: C(=O)(C(=O)O)O

adipic acid: C(CCC(=O)O)CC(=O)O

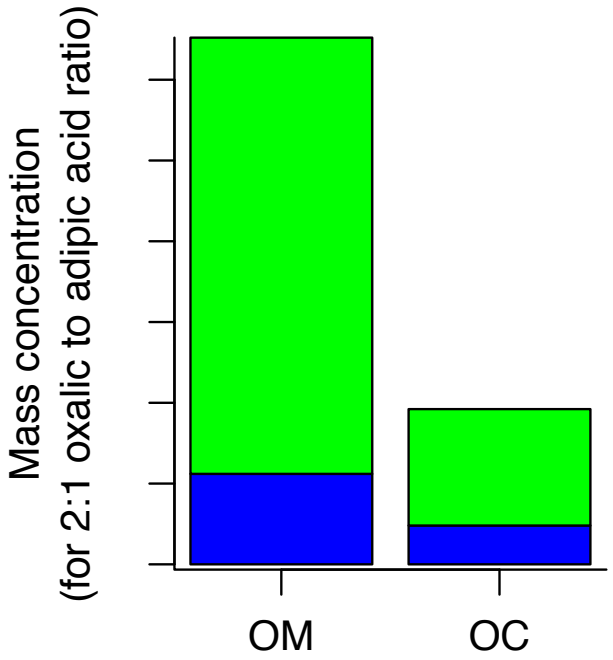
SMARTS patterns represent functional groups

carboxylic COOH: [CX3](=O)[OX2H][H]

alkane CH: [CX4][H]

Example application:

$$\begin{matrix} & \text{oxalic} & \text{adipic} \\ \text{CH} & 0 & 8 \\ \text{COOH} & 2 & 2 \end{matrix} \times \begin{bmatrix} n_{\text{oxalic}} \\ n_{\text{adipic}} \end{bmatrix} =$$



Technical Note: Development of chemoinformatic tools to enumerate functional groups in molecules for organic aerosol characterization

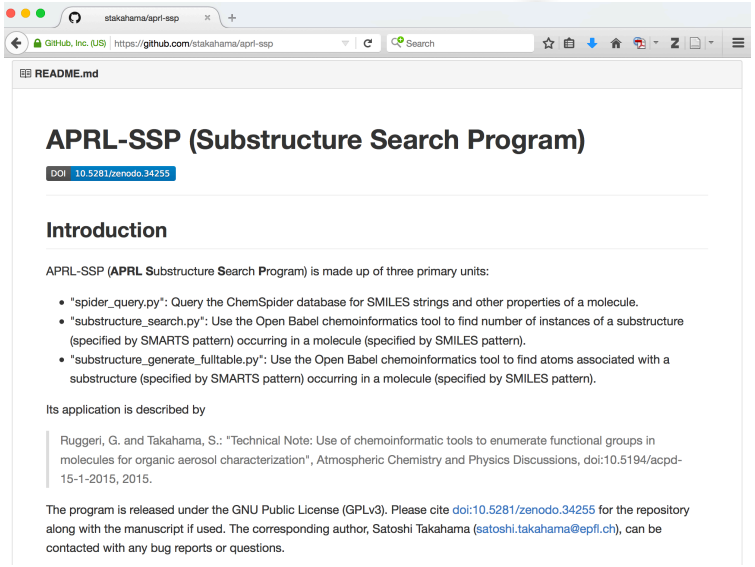
Giulia Ruggeri and Satoshi Takahama
ENAC/IIE Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland

Atmos. Chem. Phys., 16, 4401-4422, 2016
http://www.atmos-chem-phys.net/16/4401/2016/
doi:10.5194/acp-16-4401-2016

No.	Substructure	Definition	Chemoinformatic definition	Matched pattern
8	Ketone	A compound containing a carbonyl group bonded to two carbon atoms.[1]	`[CX3;$(C([#6])(=[O])[#6])](=[O;!$([O][O])])`	
9	Aldehyde	A compound containing a -CHO group.[1] (excludes formaldehyde)	`[CX3;$(C([#1])(=[O])[#6])](=[O;!$([O][O])])[H]`	
10	Carboxylic acid	A compound containing a carboxyl, -COOH, group.[1] (excludes formic acid)	`[CX3;!$([CX3][H])](=O)[OX2H][H]`	
11	Formic acid	Formic acid compound.	`[CX3](=O)([H])[OX2H][H]`	
12	Acyloxy radical	Oxygen-centered radicals consisting of an acyl radical bonded to an oxygen atom.[2]	`[C;$(C=O)](=O)[OX2;!$([OX2][H]);!$([OX2][O]);!$([OX2][N]);!$([OX2]([#6])[#6])]`	
13	Ester	A derivative of a carboxylic acid in which H of the carboxyl group is replaced by a carbon.[1]	`[CX3H1,CX3](=O)[OX2H0][#6;!$([C]=[O])]`	
14	Ether	An -OR group, where R is an alkyl group.[1]	`[OD2]([#6;!$(C=O)])[#6;!$(C=O)]`	
15	Formaldehyde	Formaldehyde compound.	`[CX3;$(C(=[O])([#1])[#1])](=[O;!$([O][O])])([H])[H]`	
16	Phenol OH	Compounds having one or more hydroxy groups attached to a benzene or other arene ring.[2]	`[c;!$(C=O)][OX2H][H]`	
17	Oxy radical (alkoxy)	Oxygen centered radical consisting of an oxygen bonded to an alkyl.	`[#6;!$(C=O)][OX2;!$([OX2][H]);!$([OX2][O]);!$([OX2][N]);!$([OX2]([#6])[#6]);!$([OX2][S])]`	
18	Carboxylic amide (primary, secondary and tertiary)	A derivative of a carboxylic acid in which the -OH is replaced by an amine.[1]	`[CX3](=O)[NX3;!$(N=O)]([#6,#1])[#6,#1]`	
19	Peroxide	Compounds of structure ROOR in which R may be any organyl group.[2]	`[#6][OD2][OD2,OD1][#6]`	
20	Peroxy radical	Oxygen centered radical derived from an hydroperoxyde.	`[O;!$([O][#6]);!$([O][H]);!$([OX2][N]);!$(O=C)][O][#6;!$([C](=O)~OO)]`	

- **50+ substructures**
- validation scheme
- used with GC/MS, MCM, SIMPOL.1
- distributed as Python program

python™



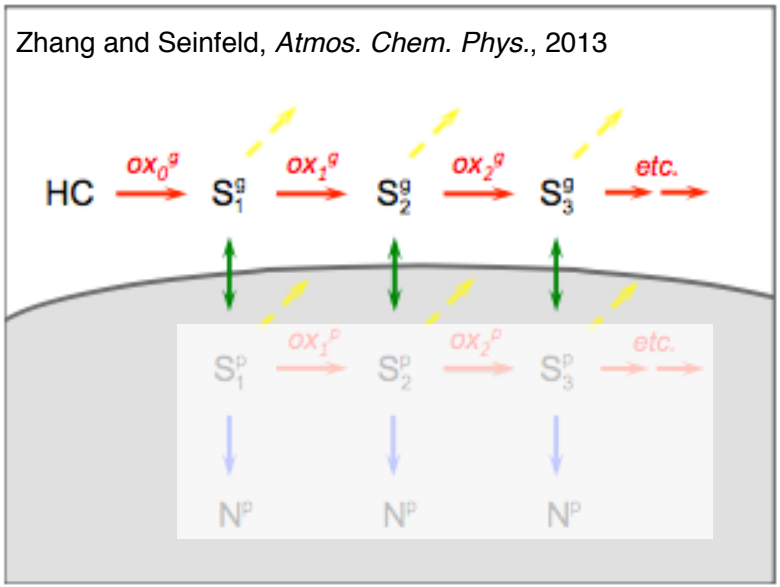
Please visit *http://aprl.epfl.ch*

FNSNF EPFL

Simulation of organic aerosol formation by gas-phase photooxidation chemistry and partitioning

Ruggeri et al., *Atmos. Chem. Phys. Discuss.*, 2016

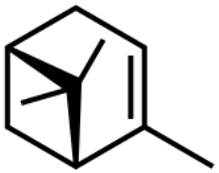
Zhang and Seinfeld, *Atmos. Chem. Phys.*, 2013



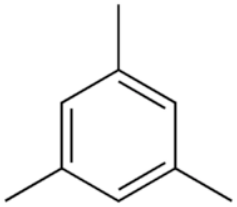
Specifications:

- *Gas-phase chemistry*
  - Master Chemical Mechanism v3.2
  - Automated code generation with Kinetic Pre-Processor
- *Gas/particle partitioning module*
  - Dynamic absorptive partitioning
  - Vapor pressures with SIMPOL.1 group contribution model

α-pinene (APIN)

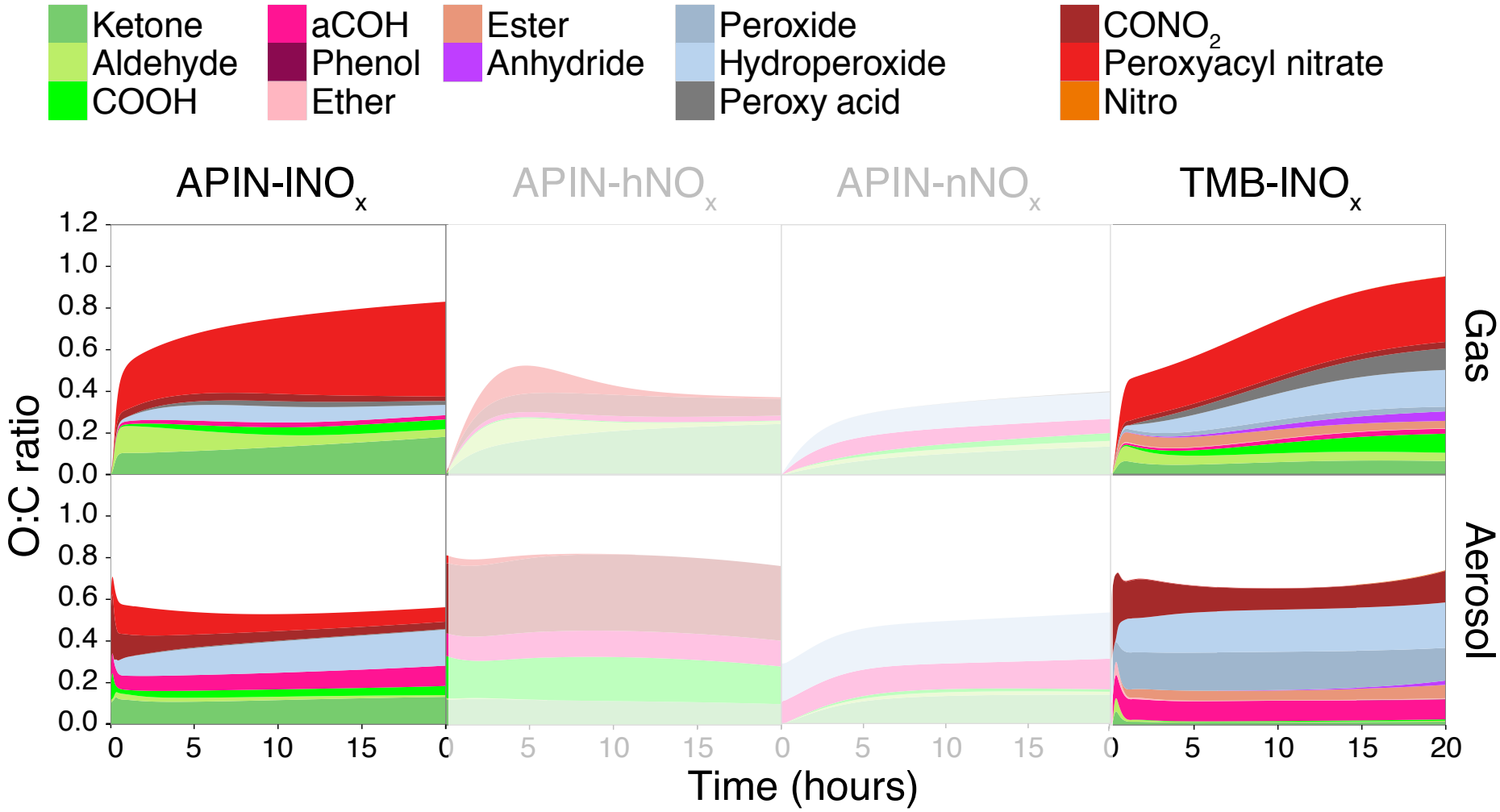


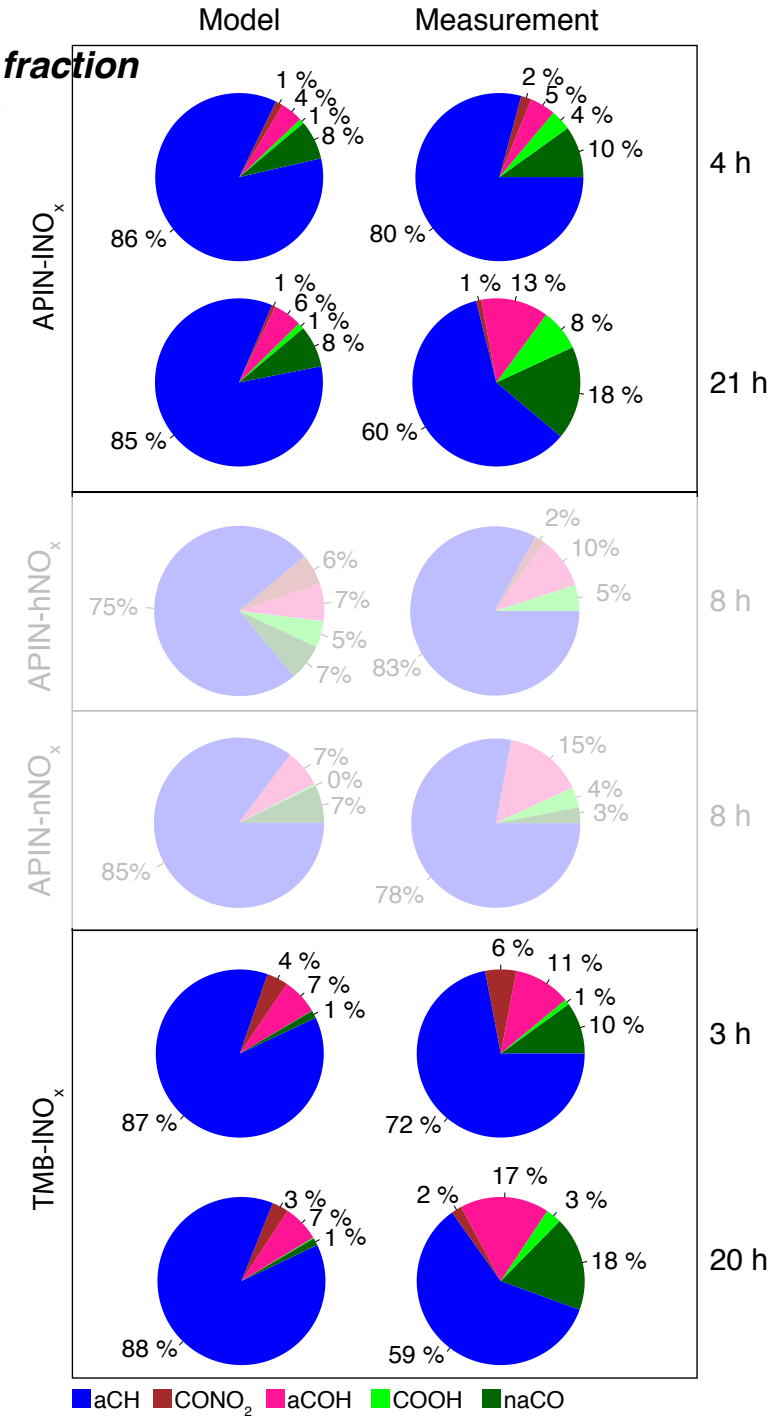
1,3,5-trimethylbenzene (TMB)



Saunders, *Atmos. Phys. Chem.*, 2003
Sandu and Sander, *Atmos. Chem. Phys.*, 2006
Pankow and Asher, *Atmos. Chem. Phys.*, 2008

Evolution of oxygen to carbon ratio by simulation





Comparison with measured functional group abundances

- Increasing discrepancy with time on account condensed-phase oxidation mechanisms not included in the model
- Larger disagreement in TMB on account of dominance by a few polyfunctional compounds in the simulated aerosol phase

Measurements from
Sax et al., *Aerosol Sci. Tech.*, 2005
(PSI chamber)

Current work

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

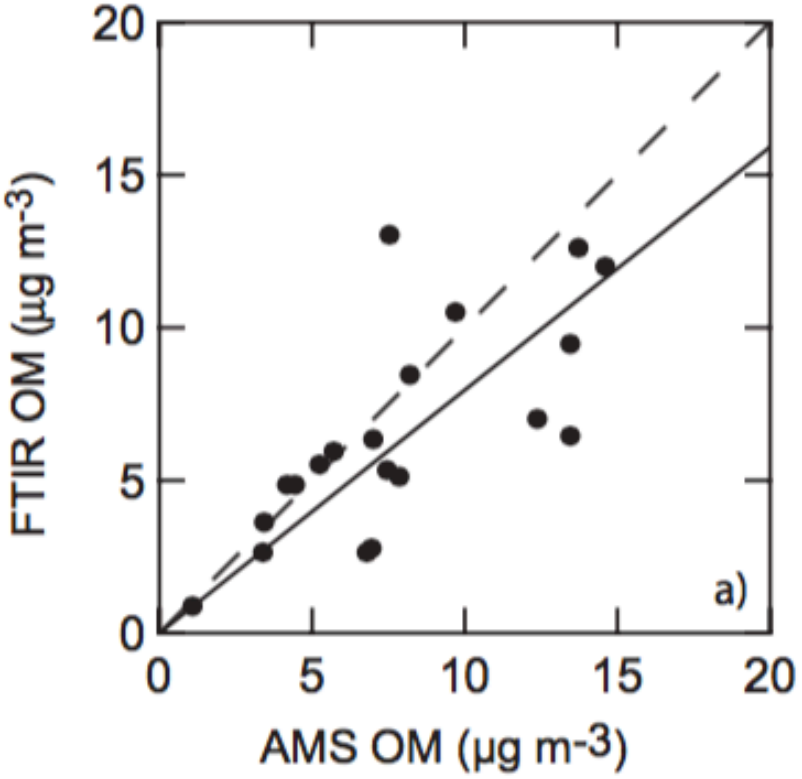
- Mechanism reduction for CMAQ (model-measurement comparison of organic functional groups vs. FTIR measurements)
- Scaling up TOR OC and EC predictions
- More functional groups (peroxides)
- Inorganic species (?)

http://aprl.epfl.ch

Comparison with AMS OM (PM_1)

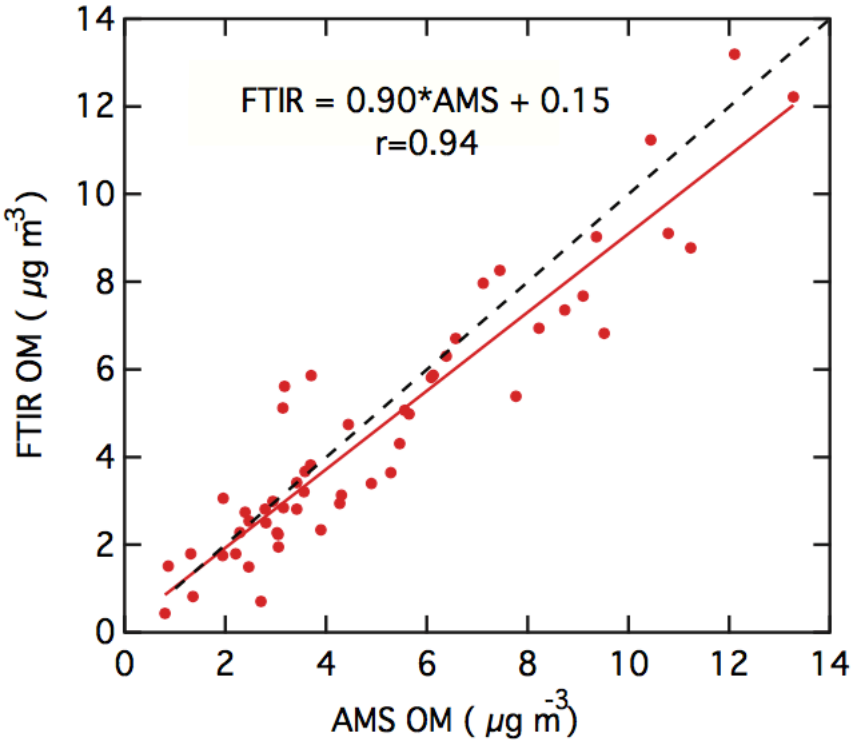
Mexico City, Mexico, 2006

Gilardoni et al., *Atmos. Chem. Phys.*, 2009



Hyytiälä, Finland, 2010

Corrigan et al., *Atmos. Chem. Phys.*, 2013



Generally within 30% of AMS/ACSM organic aerosol