

Additional Chemical/Optical Characterization for IMPROVE/CSN- Type Filter Samples

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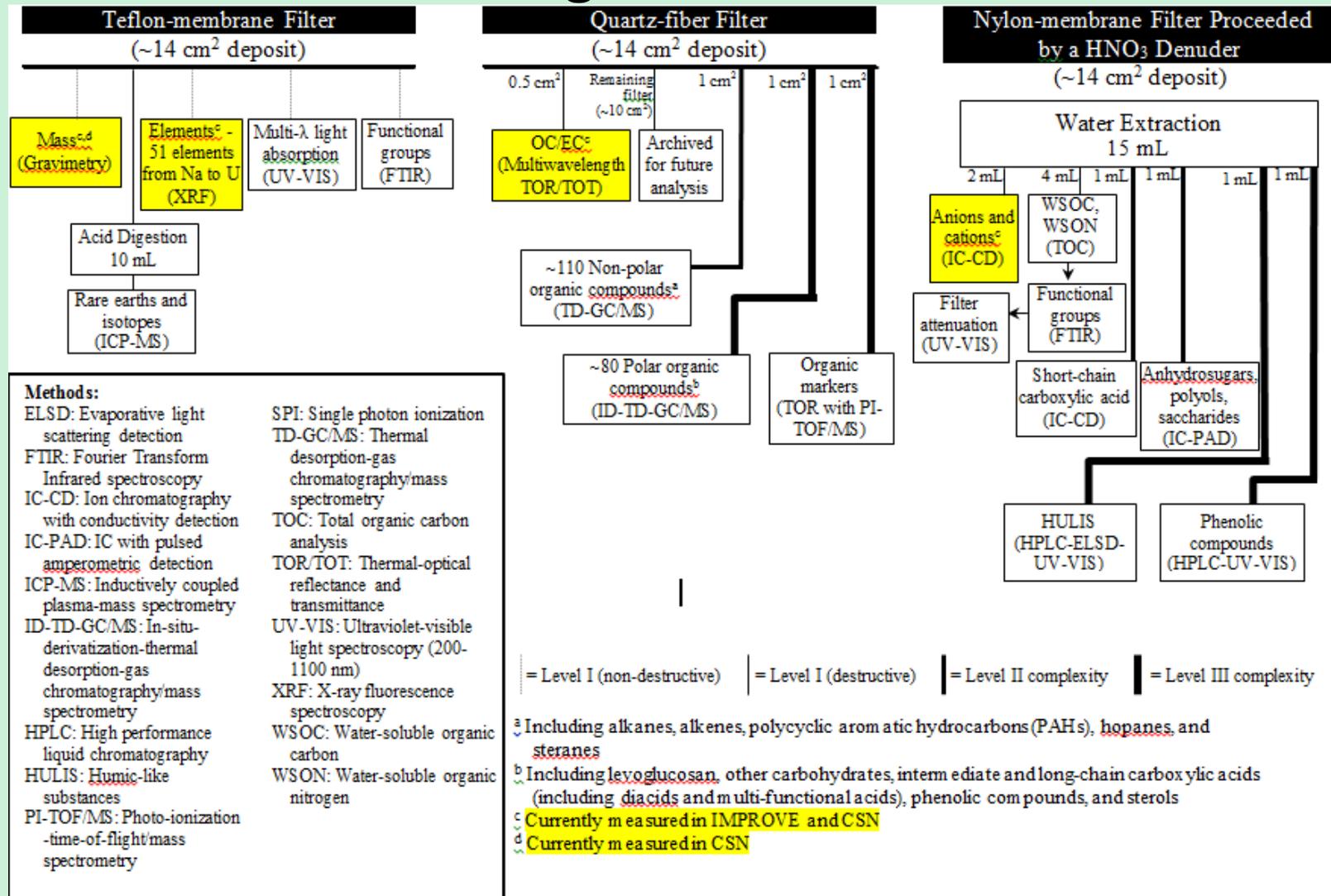
Presented for:
IMPROVE Steering Committee Meeting
Santa Fe, New Mexico

November 1st, 2016

Motivation

- Fingerprint chemical composition with additional analyses
- Direct measurement of OM and OC
- Infer PM chemical nature and source

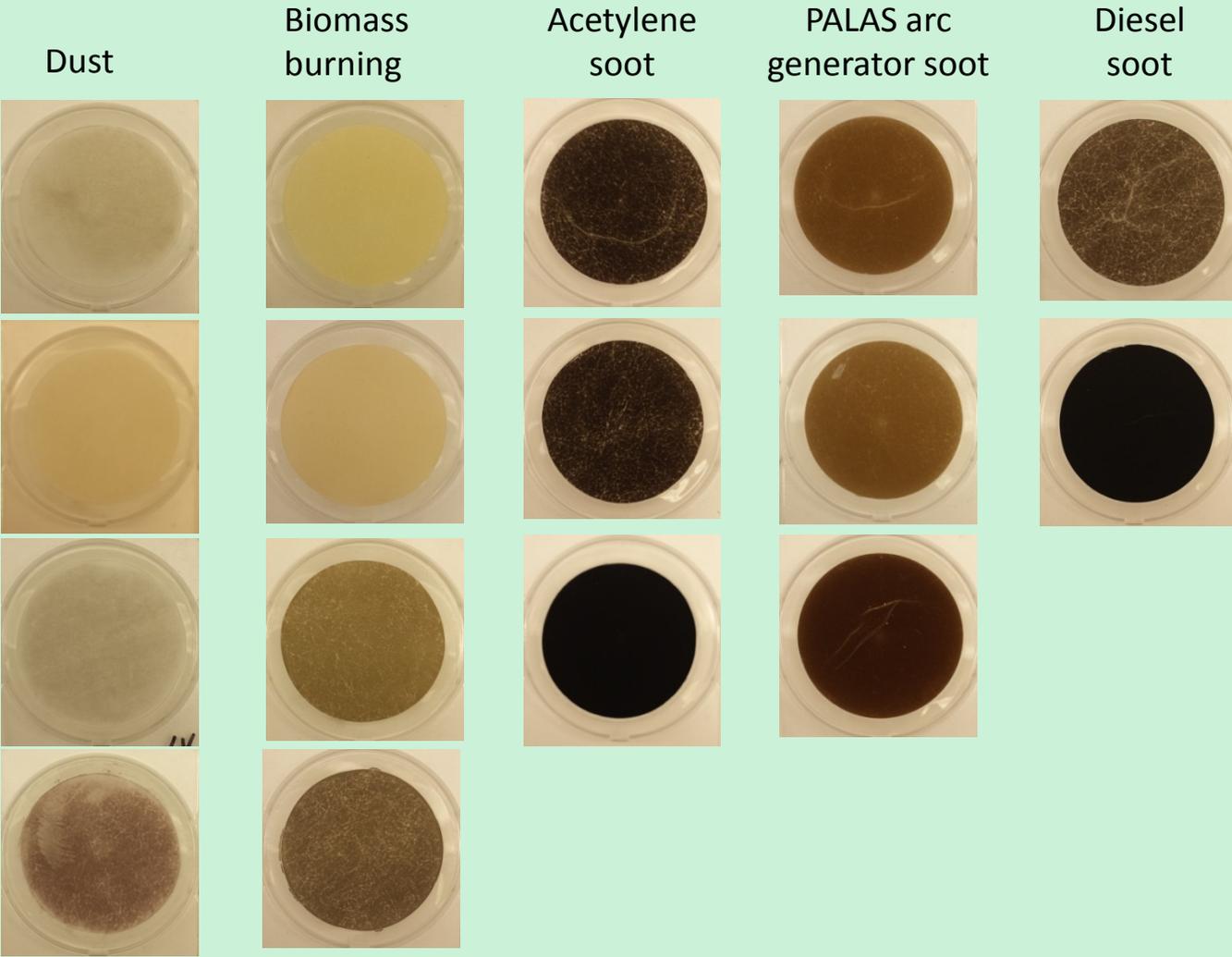
Additional marker compounds can be obtained with long-term networks



Chow, J.C., Watson, J.G., (2013). Chemical analyses of particle filter deposits, Ruzer, L., Harley, N.H. (Eds.), Aerosols Handbook : Measurement, Dosimetry, and Health Effects, 2 ed. Publishre, New York, NY, pp. 179-204.

Watson, J.G., Chow, J.C., Engling, G., Chen, L.-W.A., Wang, X.L., (2016). Source apportionment: Principles and methods, Harrison, R.M. (Ed.) Airborne Particulate Matter: Sources, Atmospheric Processes and Health, London, UK, pp. 72-125.

While the focus has been on “black carbon”, PM comes in many colors that are not black. All of these affect the Earth’s radiation balance



Brown Carbon (BrC) originates mostly from smoldering of biomass burning

- Smoldering forest fires/biomass burning



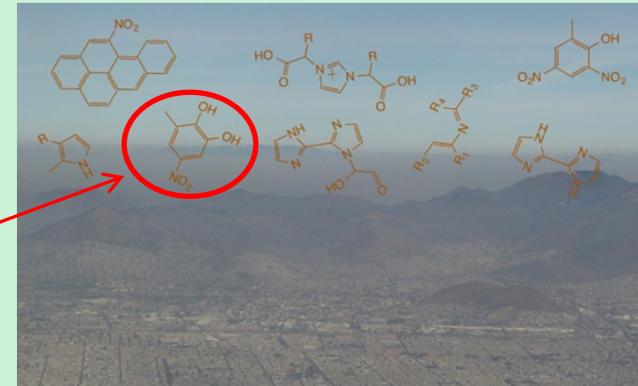
Crop residual burn



- Residential wood/coal cooking/heating

- Bioaerosol, soil humus, and humic-like substances (HULIS)

Nitro-methyl-catechols

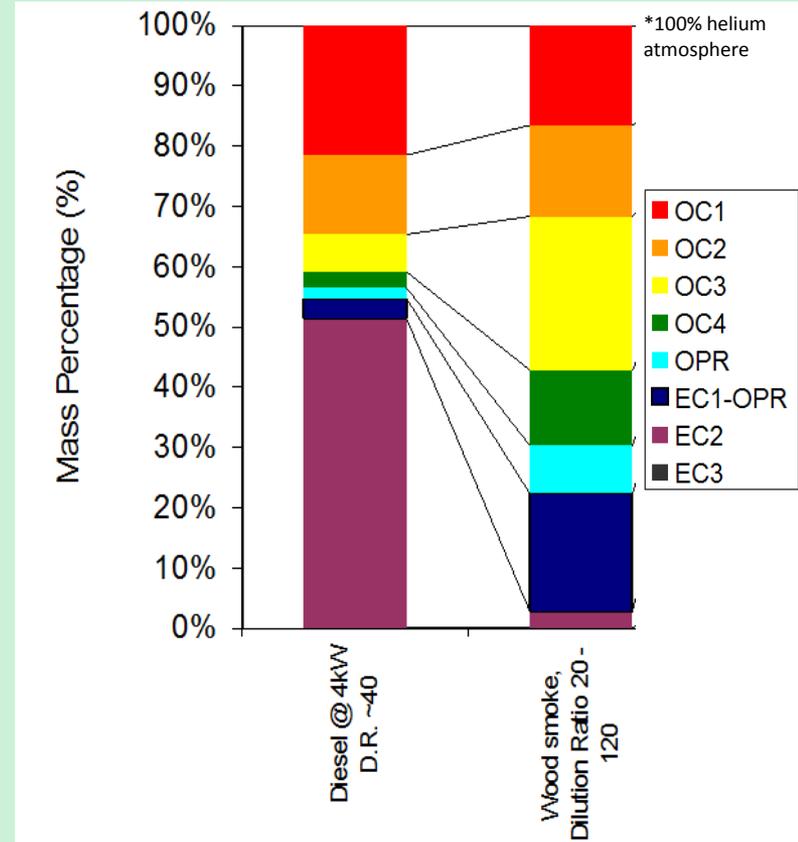
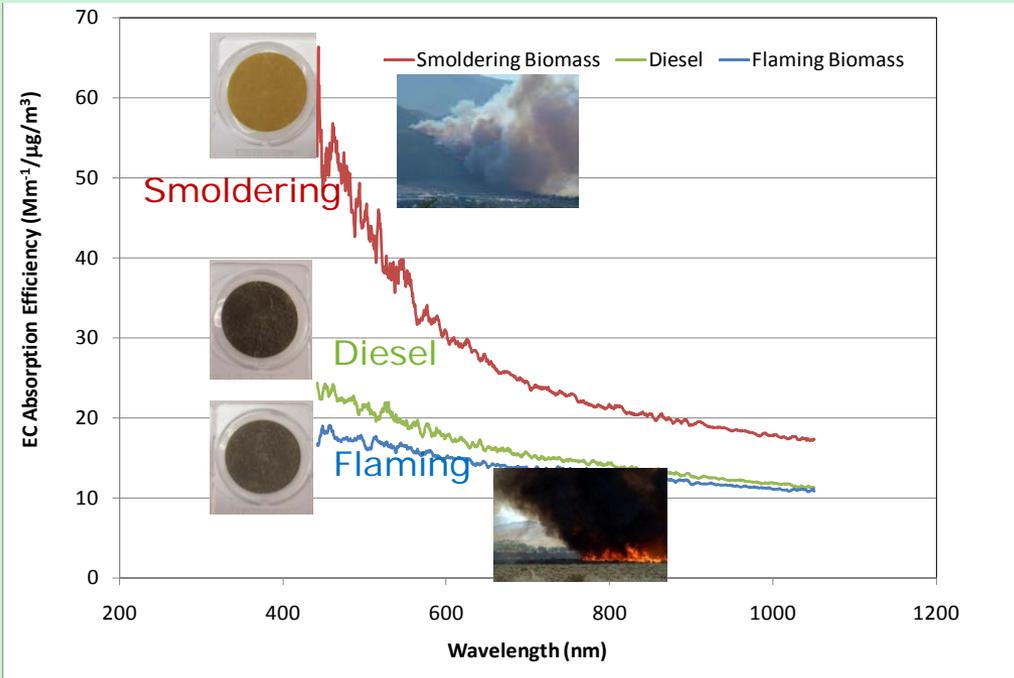


Andreae, M. O., & Gelencsér, A. (2006). Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. *Atmospheric Chemistry and Physics*, 6(10), 3131-3148.

Laskin, A., Laskin, J., & Nizkorodov, S. A. (2015). Chemistry of atmospheric brown carbon. *Chemical reviews*, 115(10), 4335-4382.

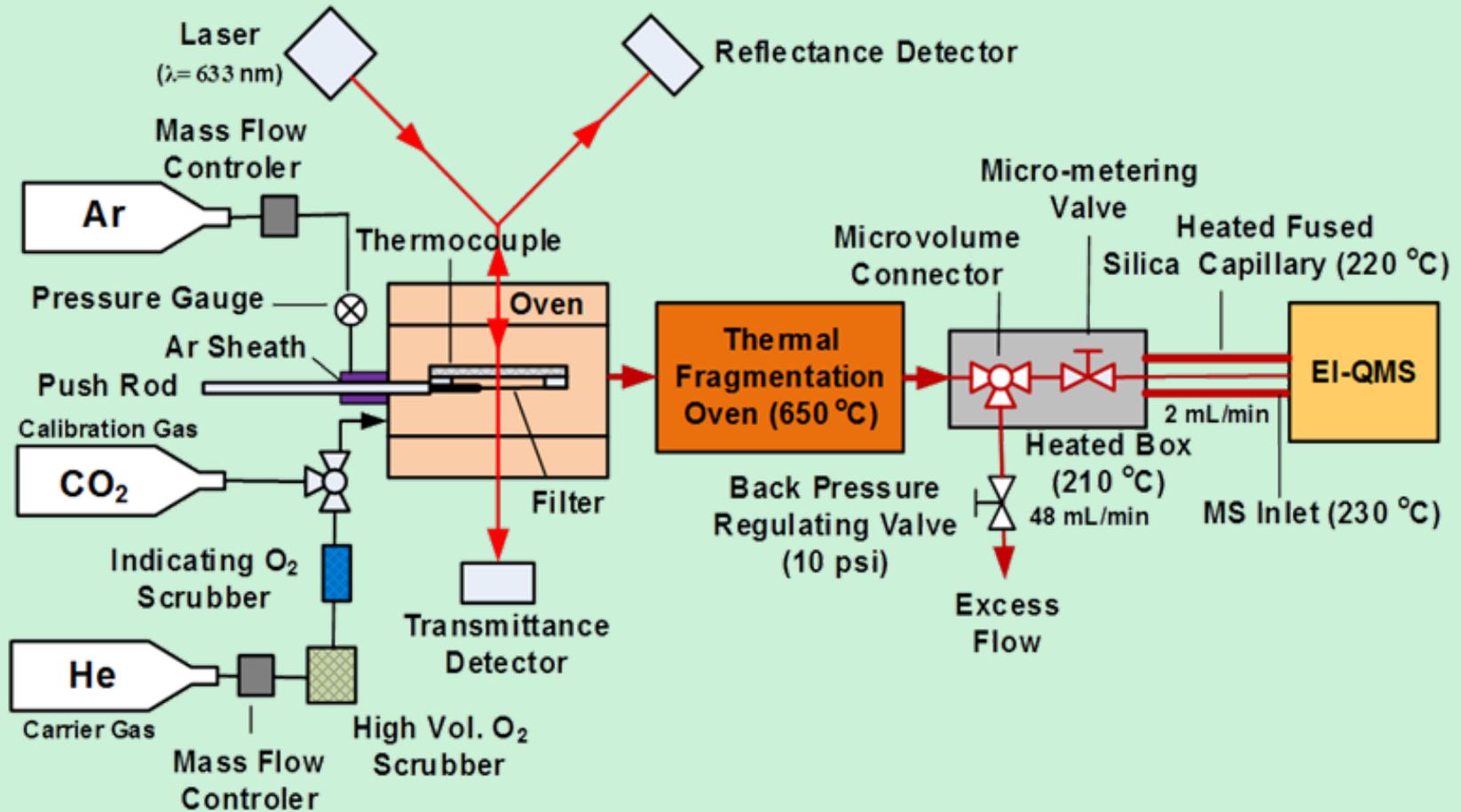
The smoldering and flaming phases of biomass burning show the largest differences between brown and black carbon

(EC absorption efficiency varies by source and wavelength)



Retrofit DRI Carbon Analyzer with MS detector to emulate the AMS spectra

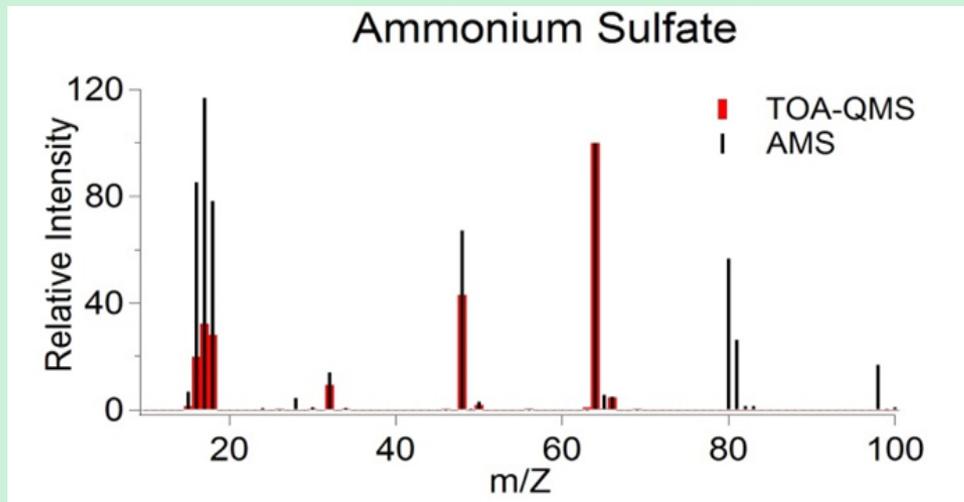
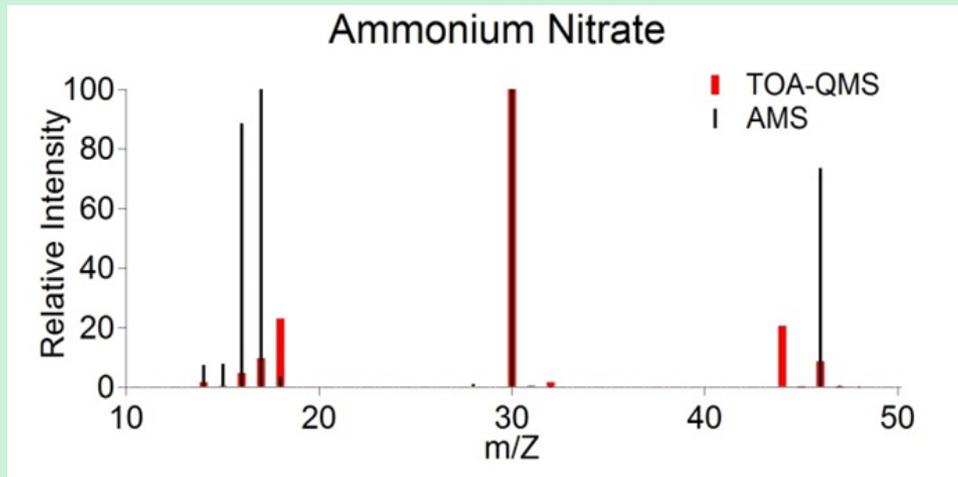
(TOA-QMS)^a



^a Thermal Optical Analysis-Quadrupole Mass Spectrometer

Riggio, G.M. (2015). Development and application of thermal/optical- quadrupole TOA-QMS mass spectrometry for quantitative analysis of major particulate matter constituents., M.S. Thesis, University of Nevada Reno, Reno, NV.

TOA-QMS spectra are similar, but not identical, to AMS spectra



Potential causes of differences:

- Particle collection medium
- **Species transmission**
- Thermal desorption
- **Ionization**

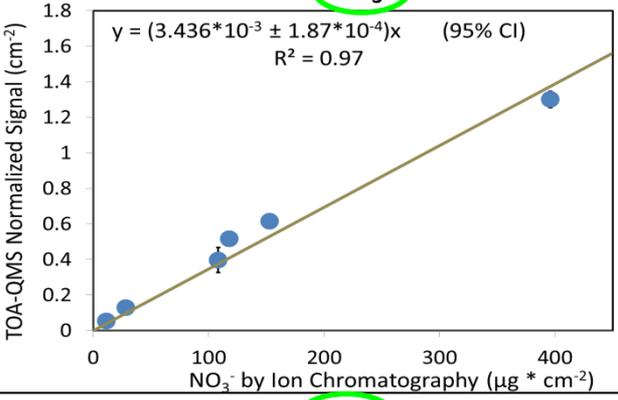
A customized fragmentation table was developed for TOA-QMS.

Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., ... & Jayne, J. T. (2004). A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data. *Journal of Aerosol Science*, 35(7), 909-922.

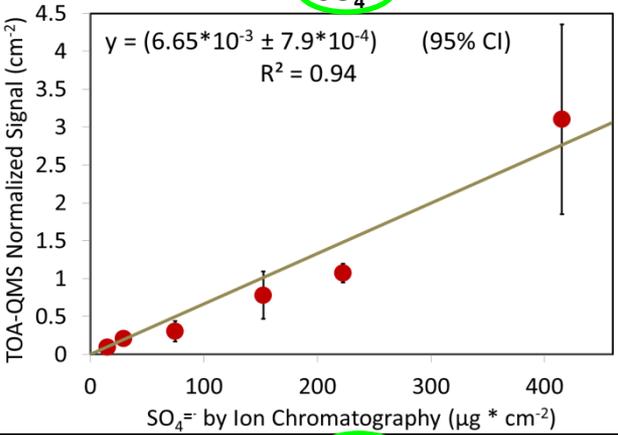
Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., ... & Morris, J. W. (2003). Ambient aerosol sampling using the aerodyne aerosol mass spectrometer. *Journal of Geophysical Research: Atmospheres*, 108(D7).

Signal/response is determined by analysis of quartz filter samples of nebulized NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, and oxalic acid solutions.

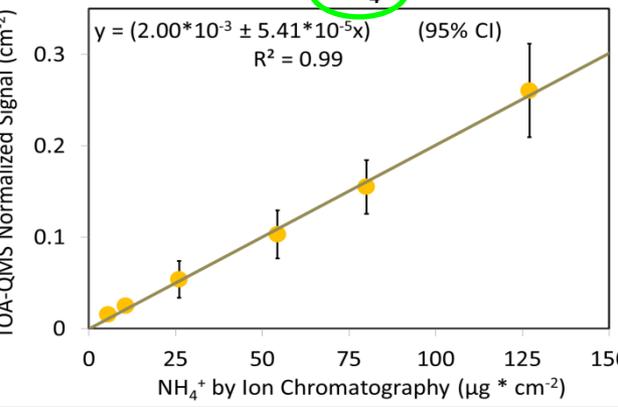
NO_3^-



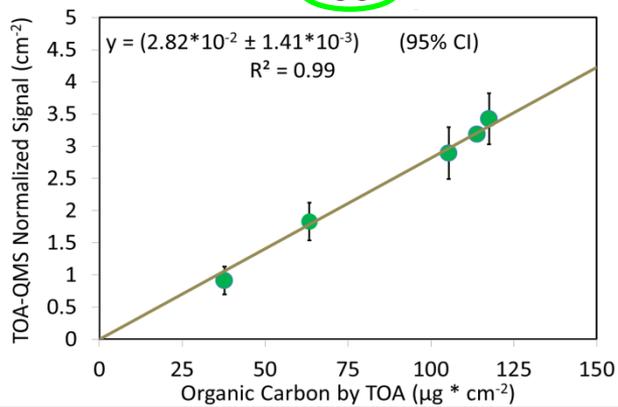
SO_4^{2-}



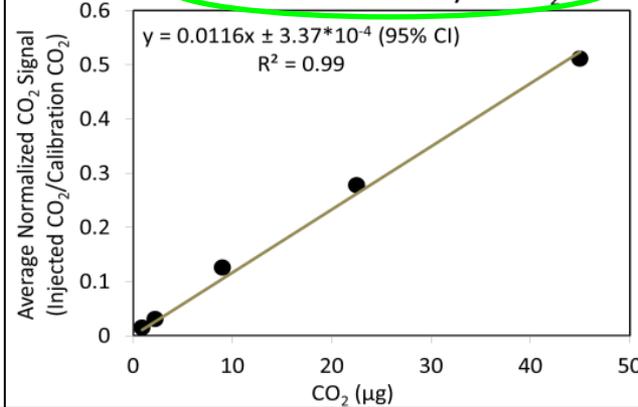
NH_4^+



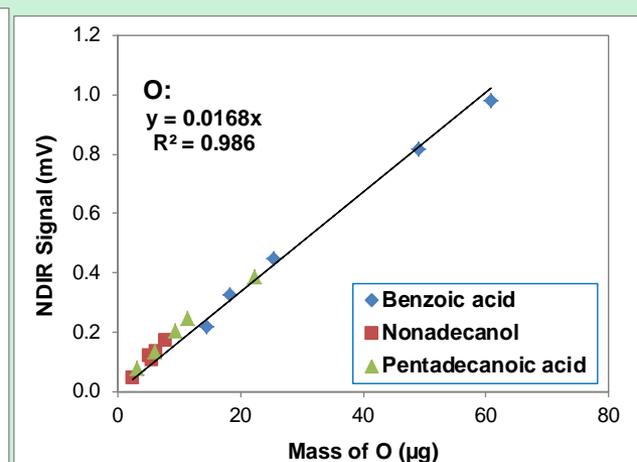
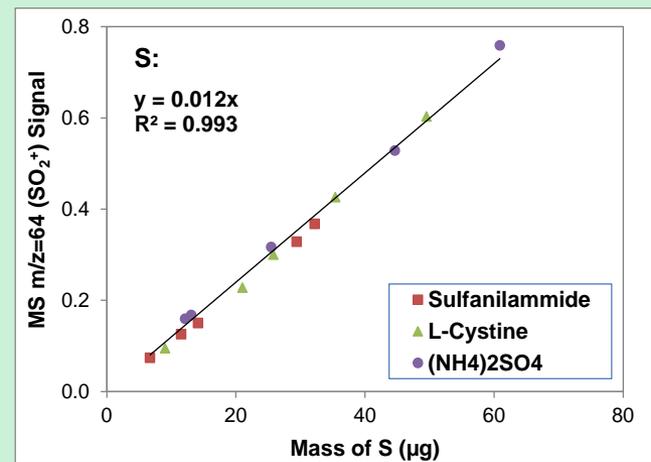
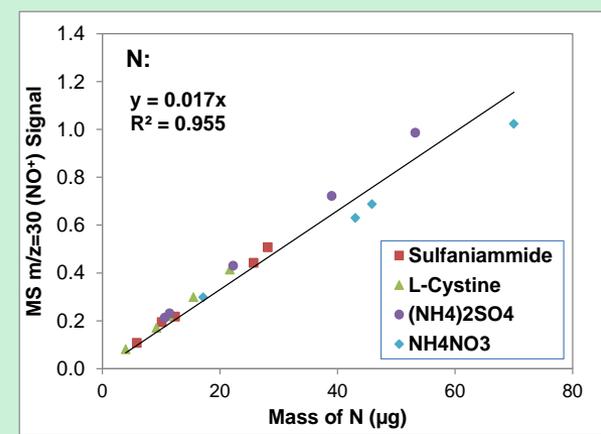
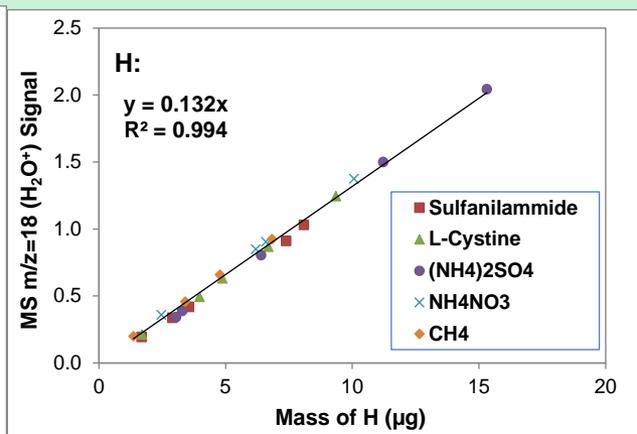
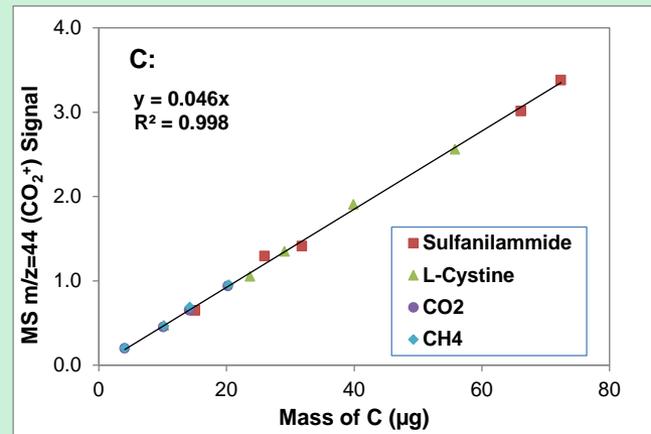
OC



Ionization Efficiency of CO_2



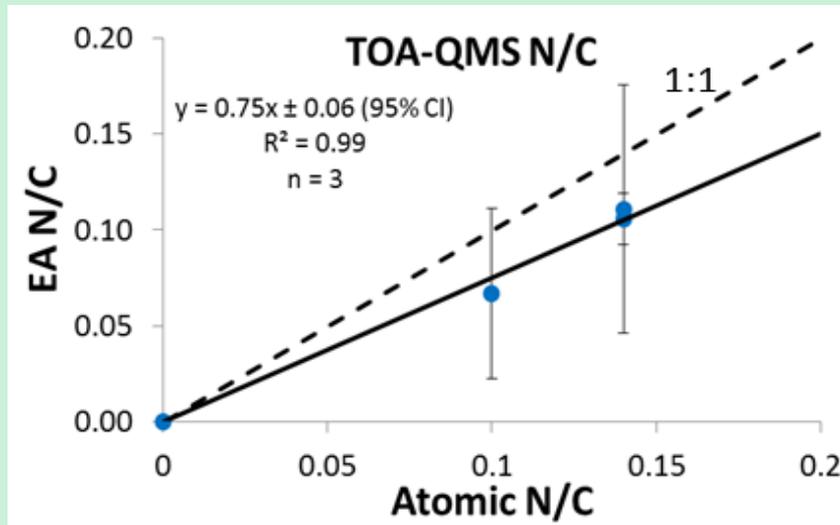
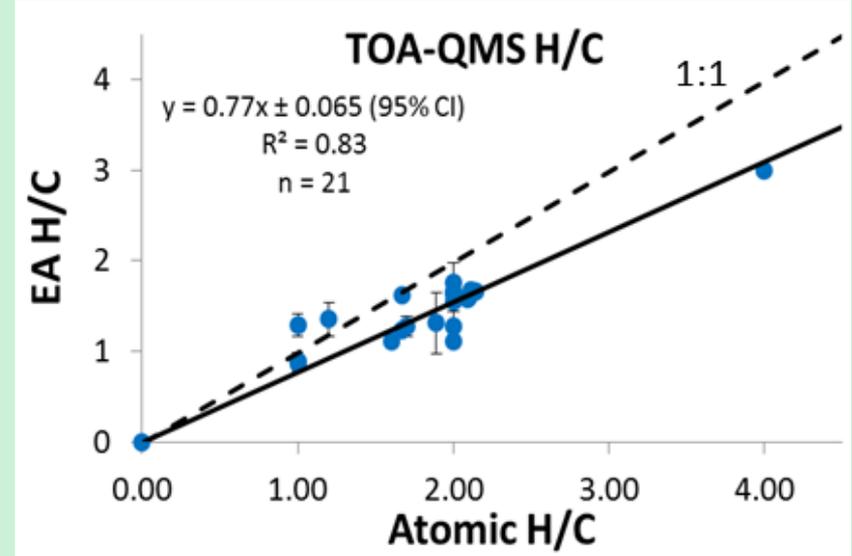
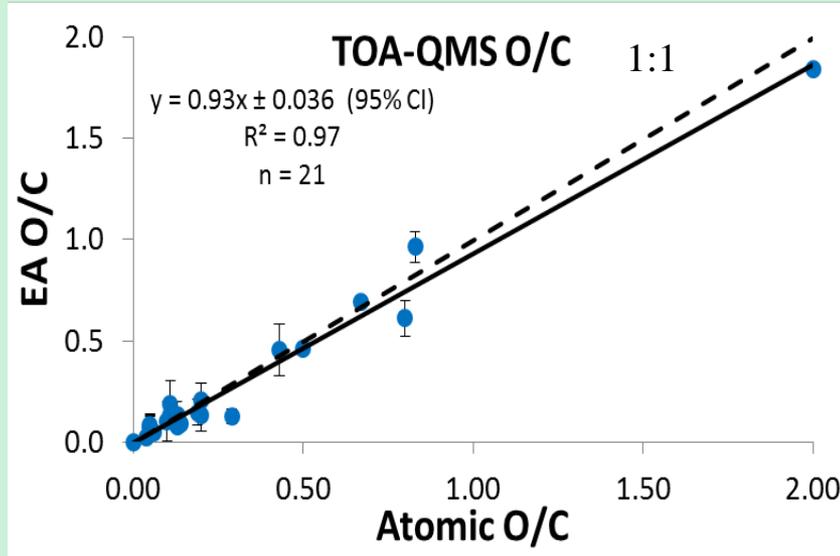
Instrument signals are linear with C, H, N, S, and O quantities for model compounds



Calibration compounds:

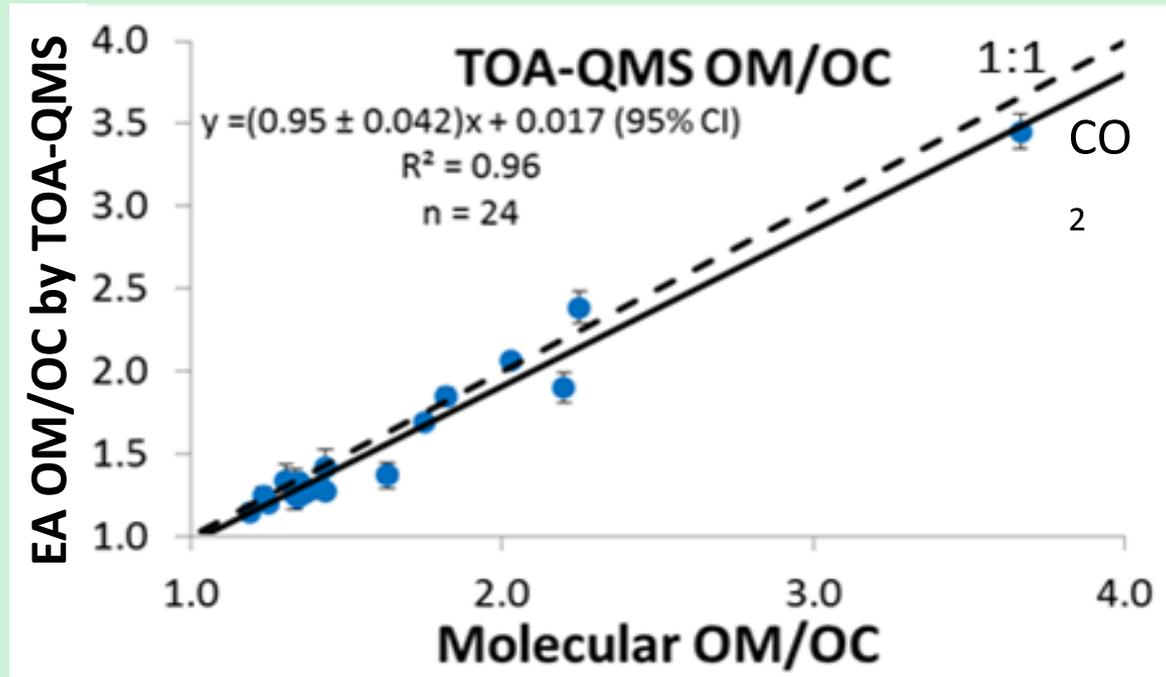
- Ammonium nitrate: NH_4NO_3 ;
- Ammonium sulfate: $(\text{NH}_4)_2\text{SO}_4$;
- Benzoic acid: $\text{C}_7\text{H}_6\text{O}_2$;
- Carbon dioxide: CO_2 ;
- L-Cystine: $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$;
- Methane: CH_4 ;
- Nonadecanol: $\text{C}_{19}\text{H}_{40}\text{O}$;
- Pentadecanoic acid: $\text{C}_{15}\text{H}_{30}\text{O}_2$;
- Sulfanilamide: $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$

Elemental analysis of organic standards shows consistent O/C and H/C relationships



Lower N/C ratio may be due to inadequate number of samples and unaccounted N species

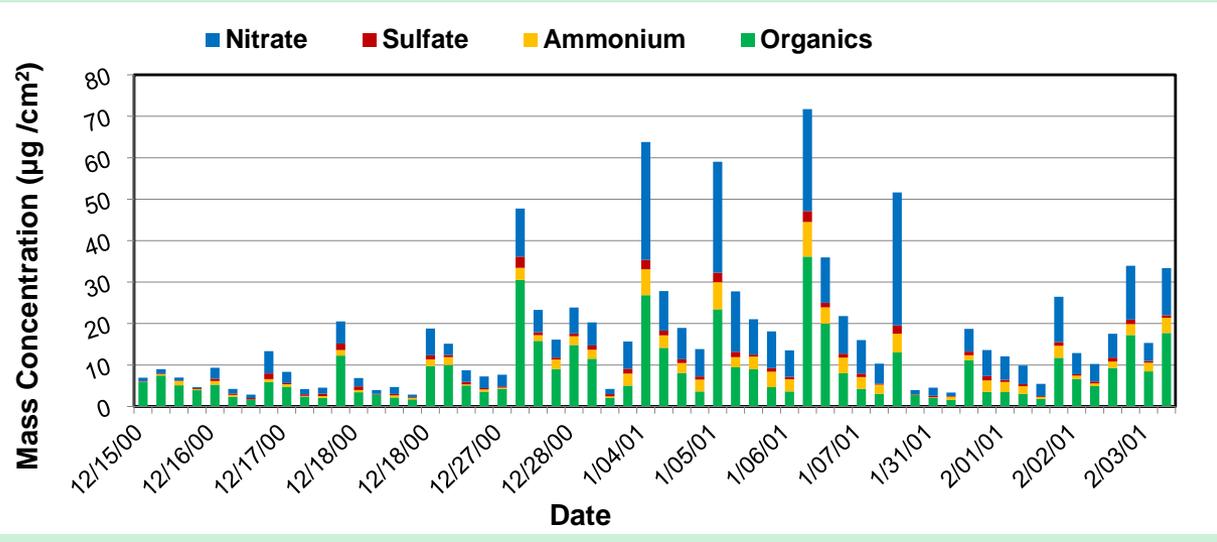
EA estimated OM/OC ratio is comparable to molecular OM/OCa



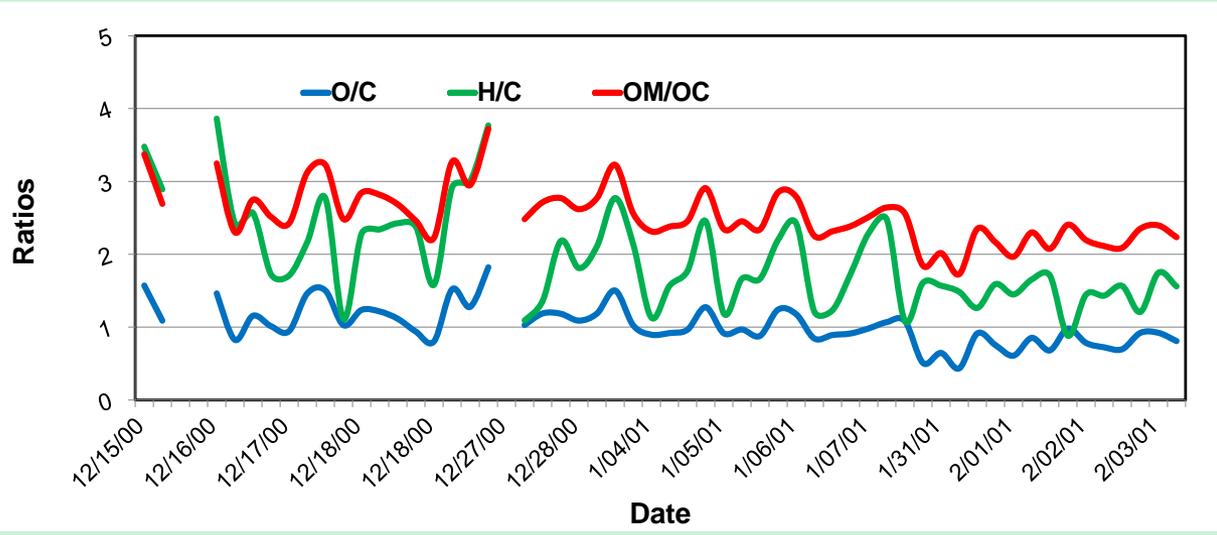
$$\frac{OM}{OC} = \frac{(16 \times C) + \left(1 \times \frac{H}{C}\right) + \left(14 \times \frac{N}{C}\right) + \left(32 \times \frac{S}{C}\right) + 12}{12}$$

^aUsing 24 organic compounds including alkane, PAHs, alcohol, carboxylic acids, aldehyde ester, anhydrides, carbohydrates, amine, amide, organic nitrate, and pyridine

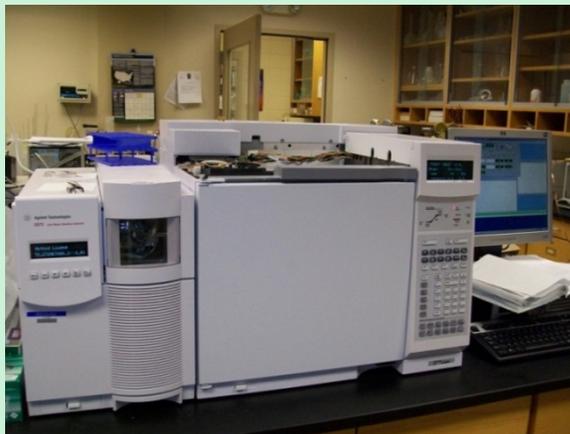
Elemental Analysis of Fresno Samples



Average
O/C 1.03 ± 0.27
H/C 1.95 ± 0.69
OM/OC = 2.55 ± 0.40

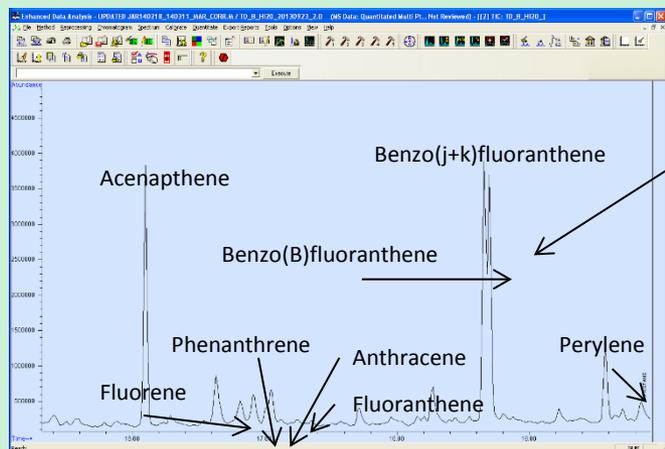


Thermal desorption-Gas Chromatography/Mass Spectrometry (TD-GC/MS) can speciate ~110 non-polar organic compounds^a



Gas Chromatography with
Mass Spectrometry Detector

(Model 6890/5975C, Agilent Technologies, Santa Clara, CA, USA)

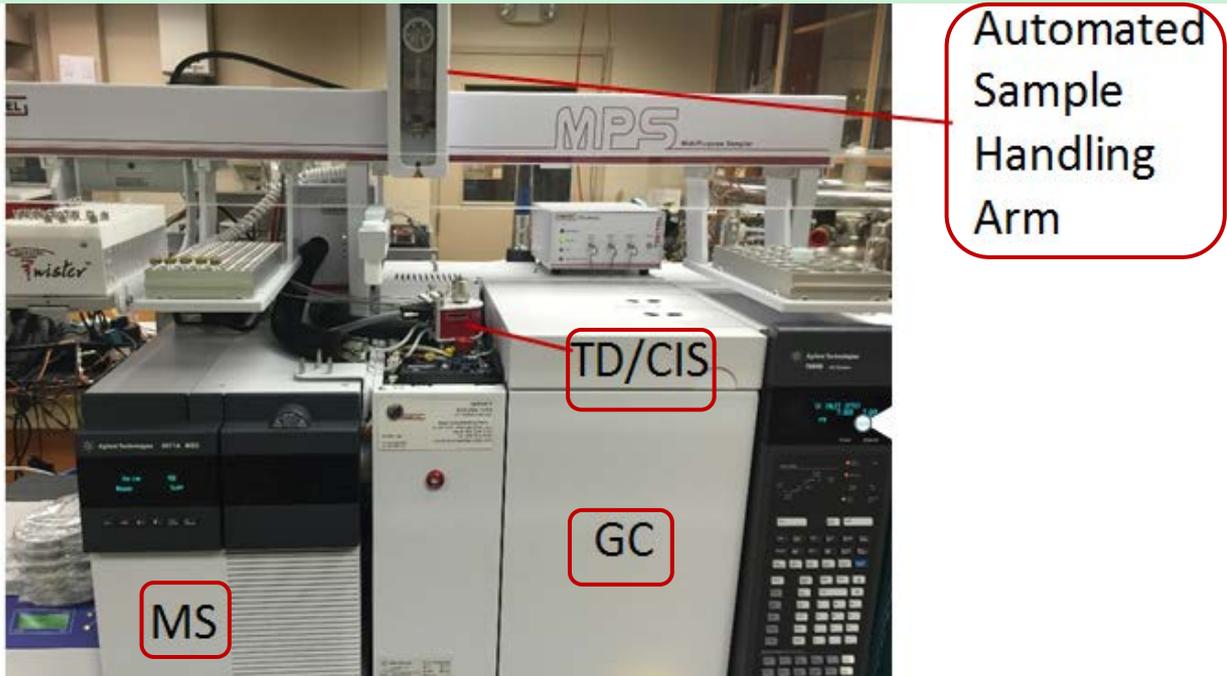


- 37 Polycyclic aromatic hydrocarbons (PAHs)
 - 26 *n*-alkanes
 - 10 iso/anteiso-alkanes
 - 2 methyl-alkanes
 - 3 branched-alkanes
 - 5 cycloalkanes
 - 1 alkene
- 18 hopanes
 - 12 steranes

Ho, S. S. H., Yu, J. Z., Chow, J. C., Zielinska, B., Watson, J. G., Sit, E. H. L., & Schauer, J. J. (2008). Evaluation of an in-injection port thermal desorption-gas chromatography/mass spectrometry method for analysis of non-polar organic compounds in ambient aerosol samples. *Journal of Chromatography A*, 1200(2), 217-227.

^a Using ~1–2 cm² of filter aliquot without solvent extraction

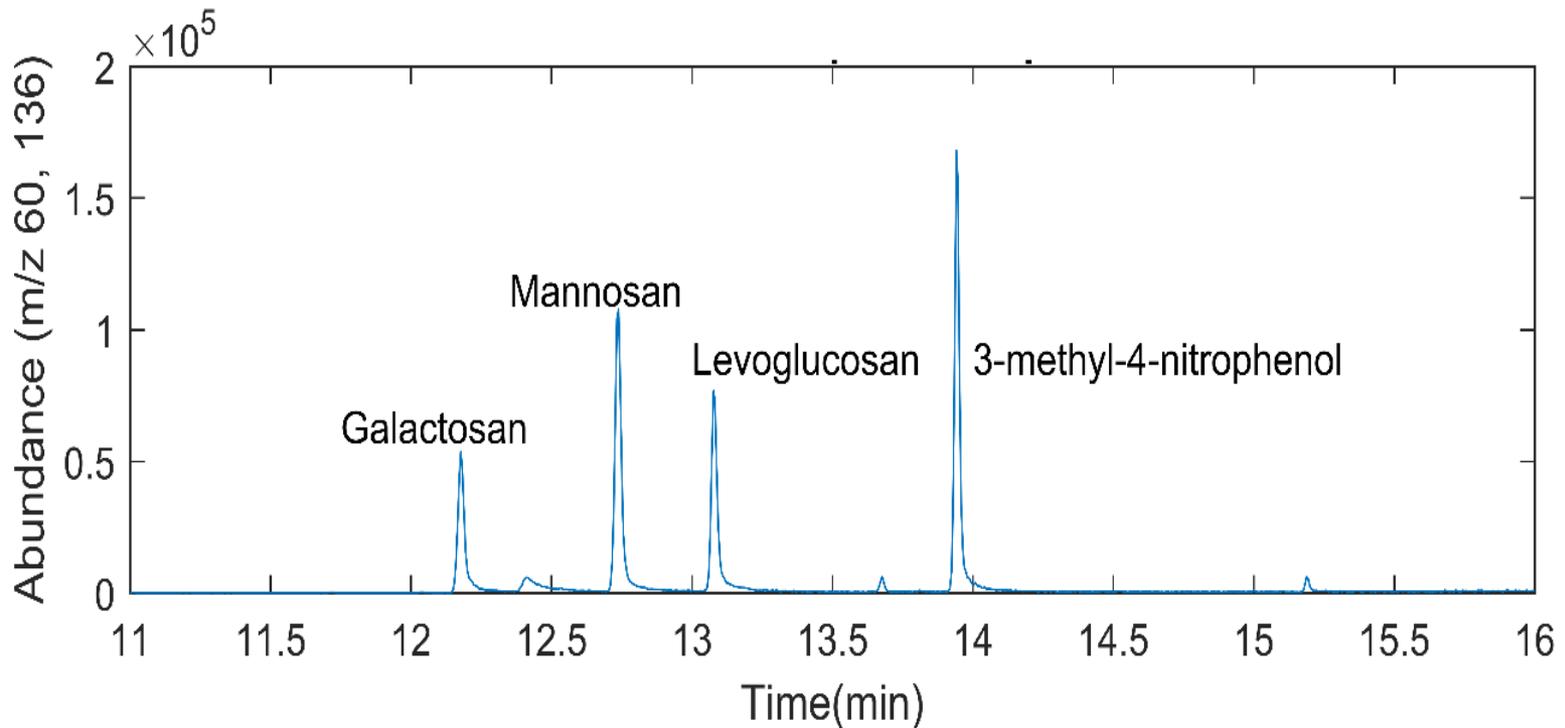
In-situ derivatization GC/MS quantifies BrC and other polar organic compounds



In-situ derivatization gas chromatography (GC)/mass spectrometry (MS) with automatic thermal desorption unit and cooled injection system(TD/CIS)
(Gerstel/Agilent Model 7890B/5977A, Agilent Technologies, Santa Clara, CA, USA)

Examples of Polar Organic Compounds	Examples of BrC
Carboxylic Acids	Carboxylic Acids (e.g., fulvic and humic acids)
C5 Alkene triols	
Carbohydrates	Nitro Aromatics (e.g., 3-methyl-4-nitrophenol, 3-methyl-5-nitrocatechol, 3-methyl-6-nitrocatechol, 4-methyl-5-nitrocatechol)
Sterols	
Phenols	
Aldehydes	PAH's (e.g., 9-fluorenone, phenanthrene, fluoranthene, pyrene, retene, benzo[a]pyrene, benzo[e]pyrene, benzo [g,h,i]perylene, coronene)

Example of TD-CIS-GC-MS Analysis of Polar Organic Compounds without Derivatization



Water-soluble organic carbon (wsoc) is related to cloud condensation nuclei, biomass burning, SOA^a, and health effects



Total Organic Carbon Analyzer
(Model TOC-L, Shimadzu
Corporation, Kyoto, Japan)



High Performance Liquid Chromatography (HPLC) System
(Model 1200, Agilent Technologies,
Santa Clara, CA, USA)

Quantification of WSOC classes

- Neutral Compounds by HPLC-TOC^a
- Mono- and Di-acidic Compounds by IC-PAD
- Polylacidic Compounds or Humic-like substances HULIS by HPLC-ELSD-DAD^a

^a SOA: Secondary Organic Aerosol; HPLC-TOC: High-performance Liquid Chromatography with Total Organic Carbon; IC-PAD: Ion Chromatography with Pulsed Amperometric Detector, HPLC-ELSD-DAD: HPLC with Evaporative Light Scattering Detector and Diode Array Detector (DAD)

Organic functional groups can be quantified by Fourier-transform infrared (FTIR) spectrometry

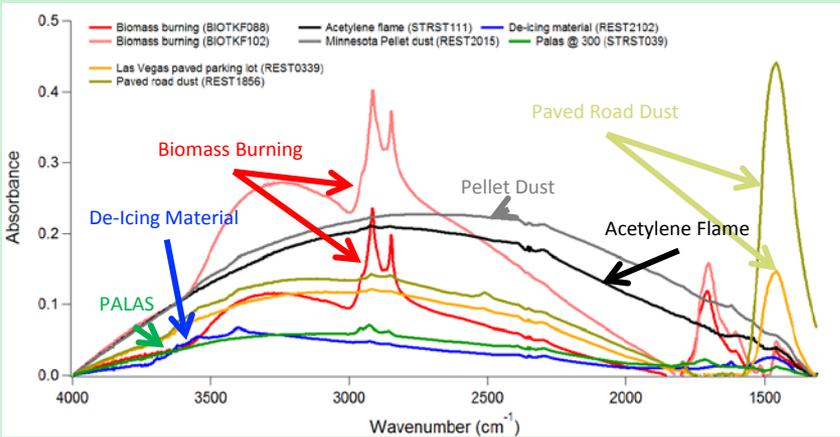


Fourier-transform Infrared Spectroscopy (FTIR)
(Model Vertex 70, Bruker Biosciences Corporation,
BillERICA, MA, USA)

Functional group	Absorbance peaks and/or region cm^{-1}
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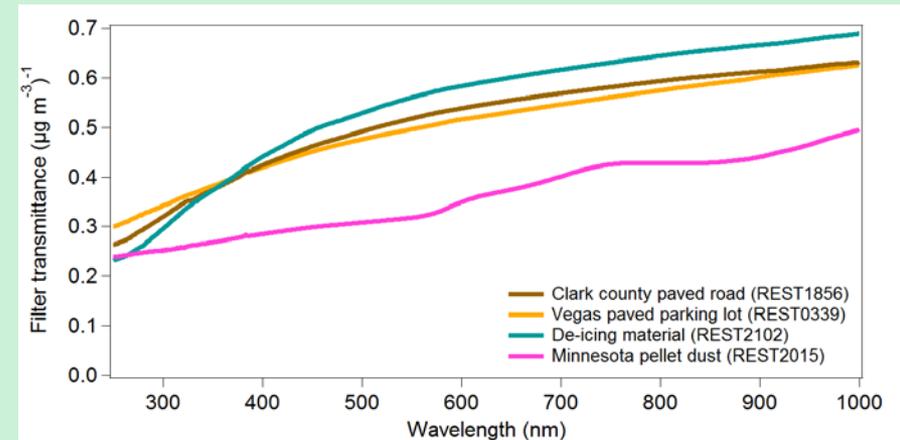
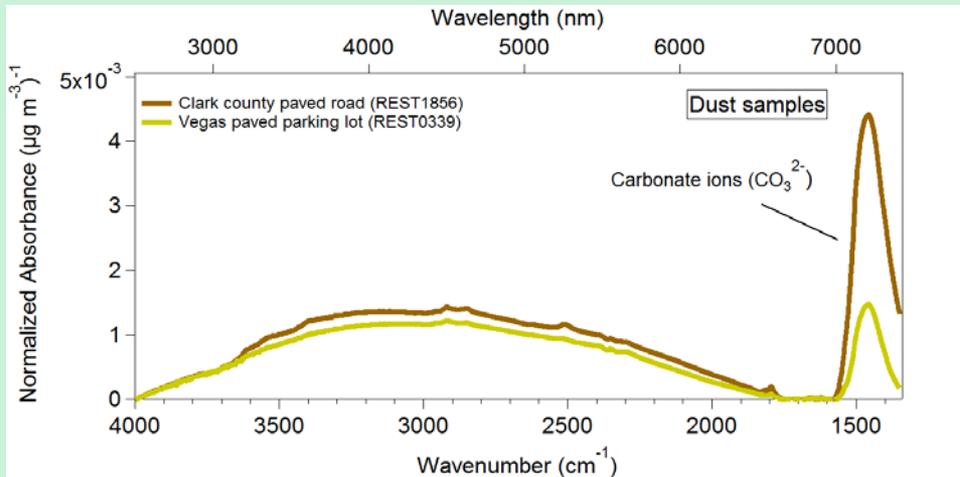
Teflon peaks	1150-1300 (1156,1212), 640, 554, 517
H ₂ O	Sharp peaks 1300-1950, 3480-3960
CO ₂	Sharp peaks 665-672, 2280-2390
Particle H ₂ O	1620-1640, 3350-3750
Aliphatic C-H	Sharp peaks 1370-1480, 2850-2950
Alkene C-H	2900-3100
Aromatic C-H	1000-1290, 3000-3100
Carbonyl C=O	Sharp peaks 1640 - 1850
Aldehyde C-H	2700 - 2860

Alcohol/Phenol O-H	Broad peak 3200 – 3550, 1350, 650±50
Carboxylic acid C-OH	Broad peak 2500 - 3000
Organonitrate	Sharp peak 860, 1278, 1631
Organosulfur	Sharp peak 876
Sulfate SO ₄ ²⁻	612-618, 1080-1140
Ammonium NH ⁺	1400-1470, 2800-3400
Silicate SiO ₃	772-812, 1000-1200
Nitrate NO ₃ ⁻	720, 840-810, 1340-1400



Absorbance for some blank filters can be as high as the actual signal from sample filters. Subtracting an average can increase measurement errors.

Dust samples have unique carbonate peak

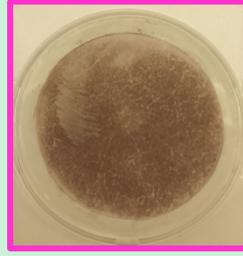
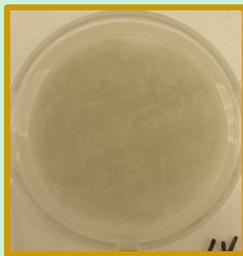


Paved road

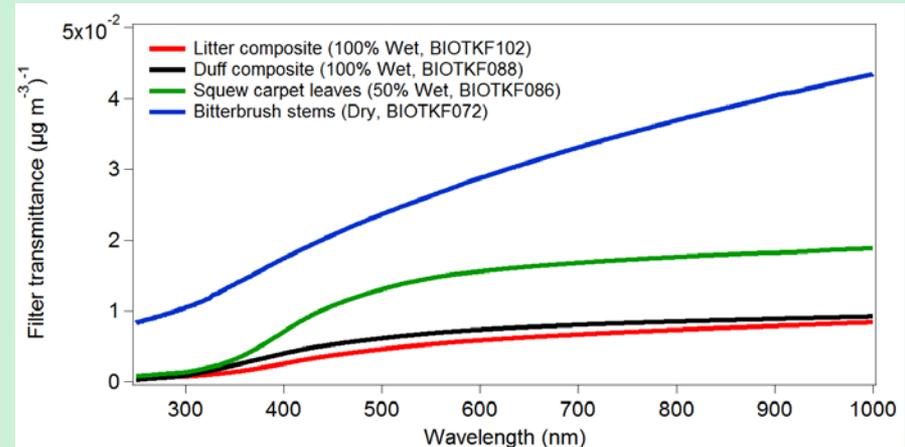
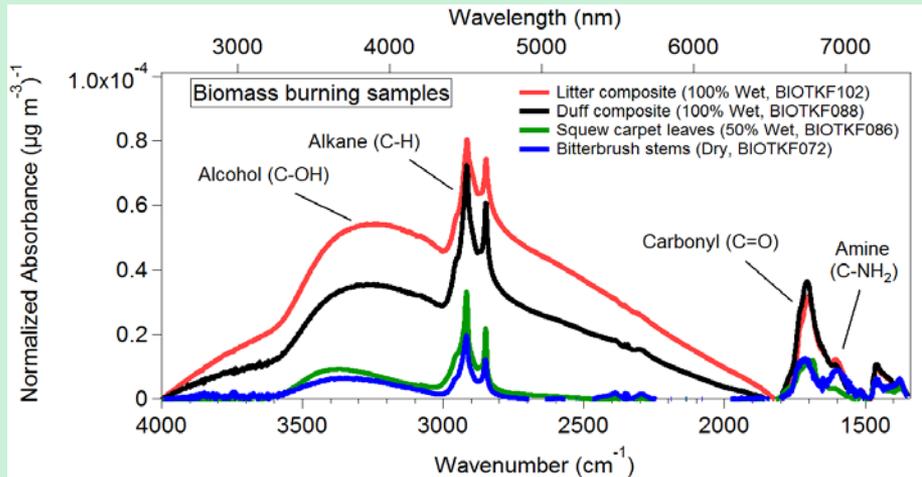
Parking lot

De-icing material

Taconite dust



Biomass burning samples show abundant alcohol, alkane, and carbonyl peaks

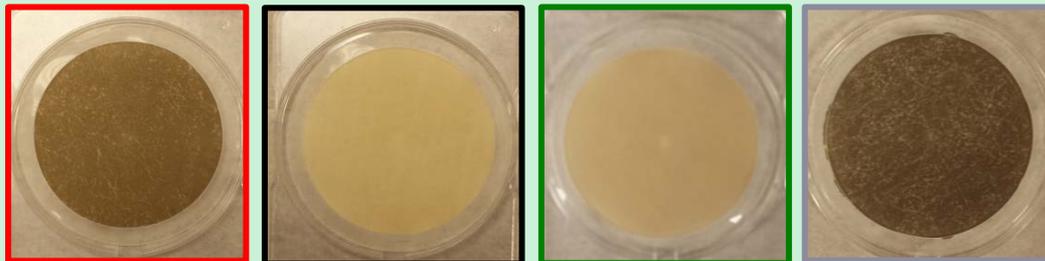


Litter

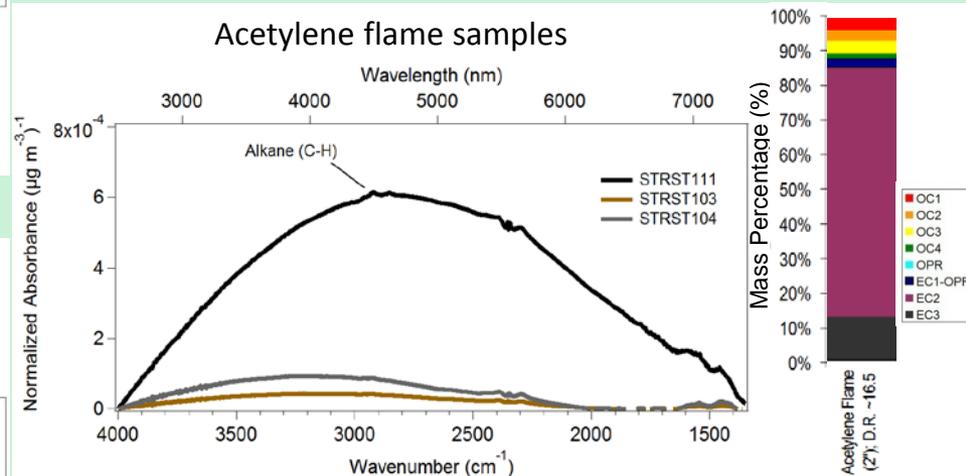
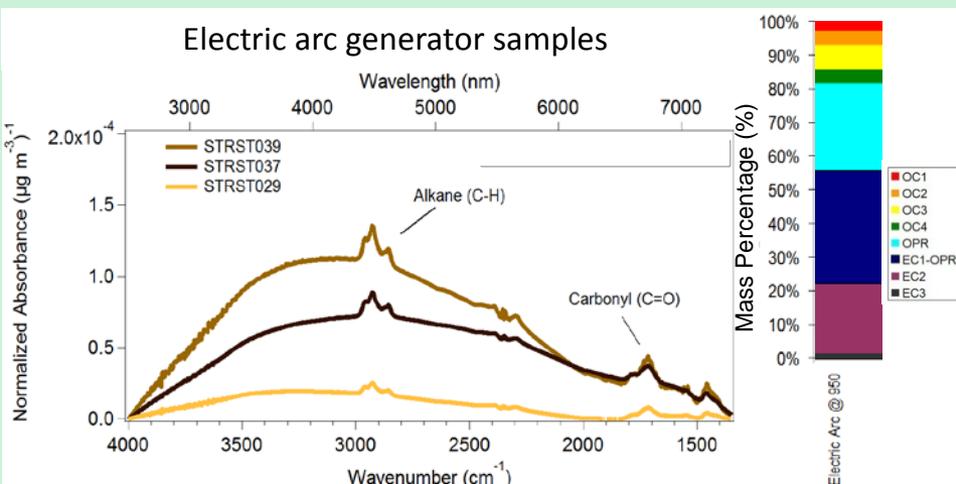
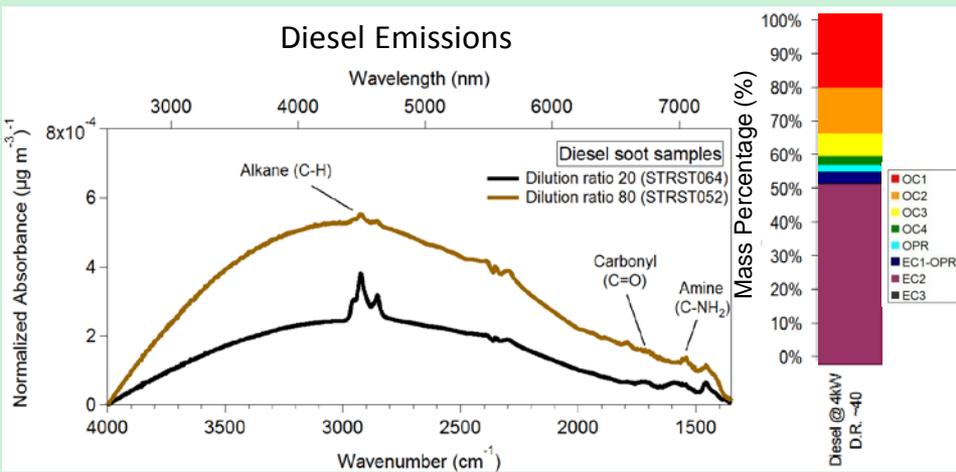
Duff

Squew

Bitterbrush

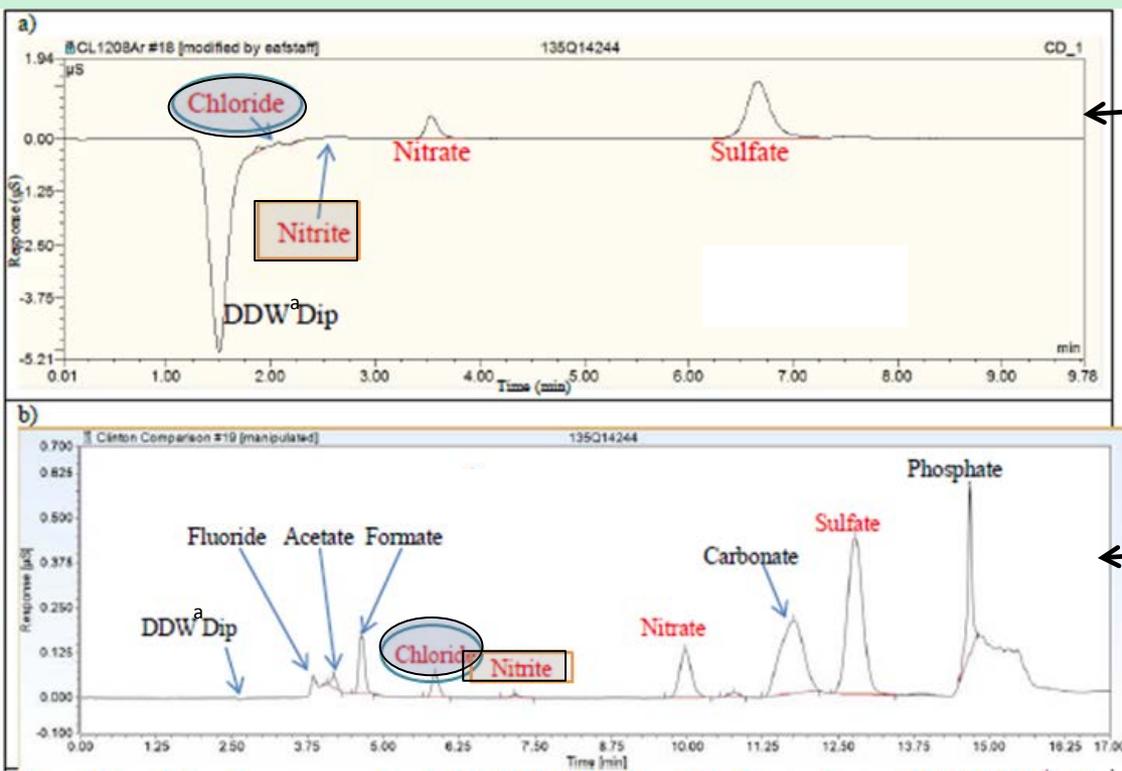


Absorption varies among diesel, electric arc, and acetylene flame emissions



*100% helium atmosphere

Potassium hydroxide eluent in new IC* system eliminated the water dip with constant baseline (Clinton, Texas, 10/15/14)



Dionex ICS-3000



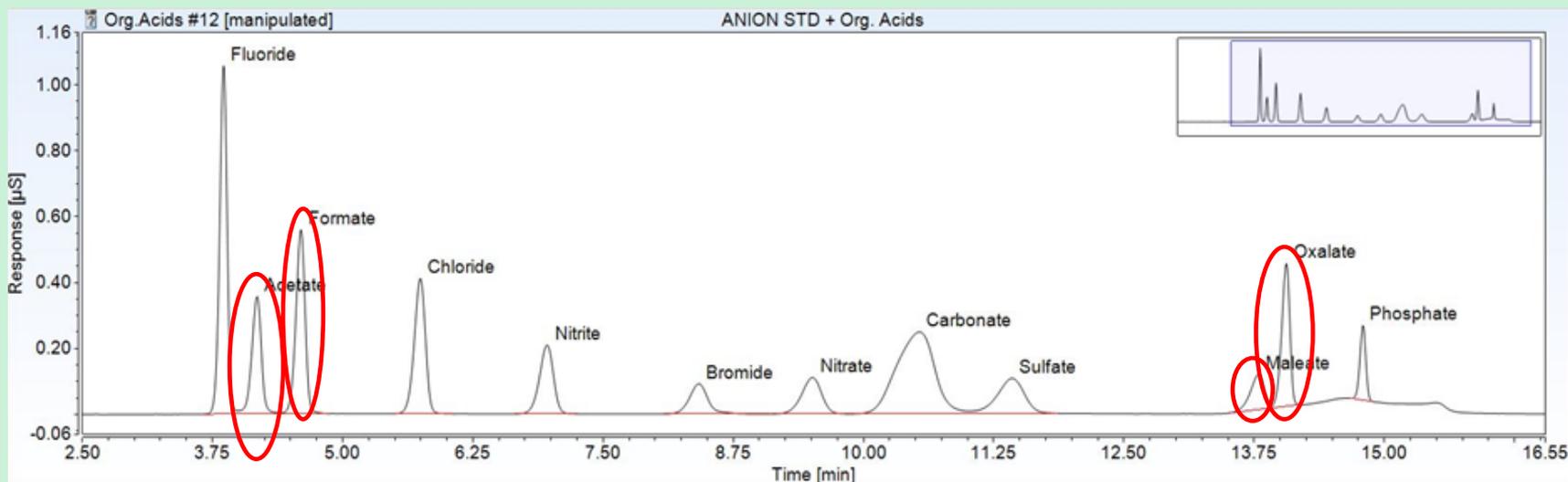
Ion Chromatography

(Dionex ICS-5000+, Thermo Fisher Scientific, Santa Clara, CA, USA)

*IC: Ion Chromatography

^aDDW: distilled deionized water

Organic acids and additional anions can be resolved along with chloride, nitrate, and sulfate in the normal anion analysis



^aOrganic acids: acetate, formate, maleate, and oxalate

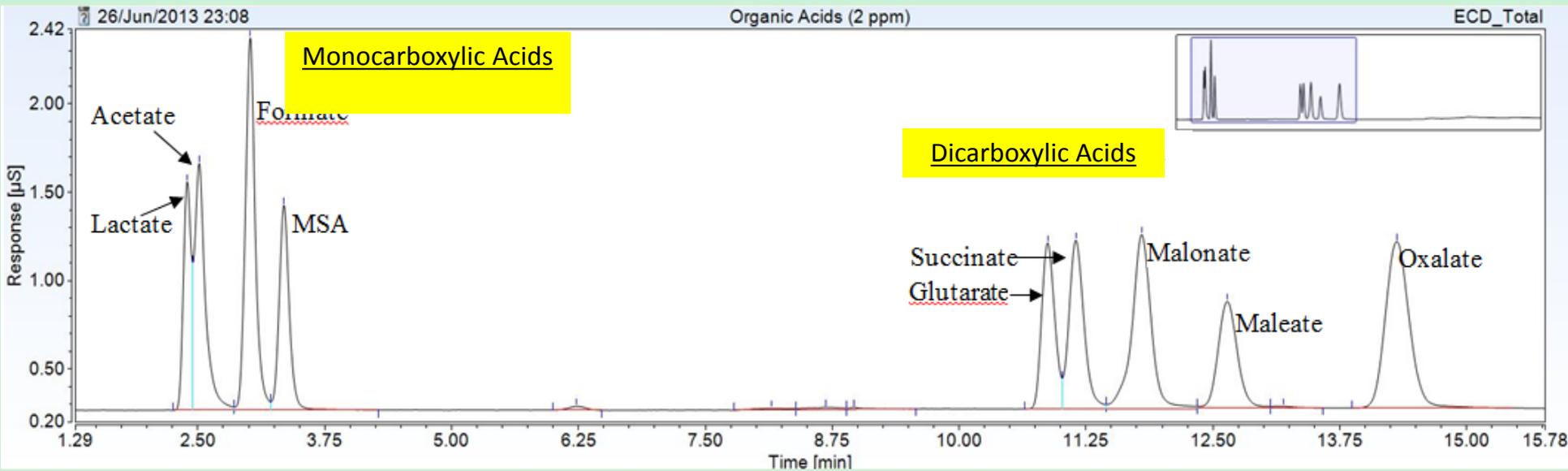
^bAdditional anions: fluoride, nitrite, bromide, and phosphate

Ion Chromatography
(Dionex ICS-5000+, Thermo Fisher Scientific, Santa Clara, CA, USA)

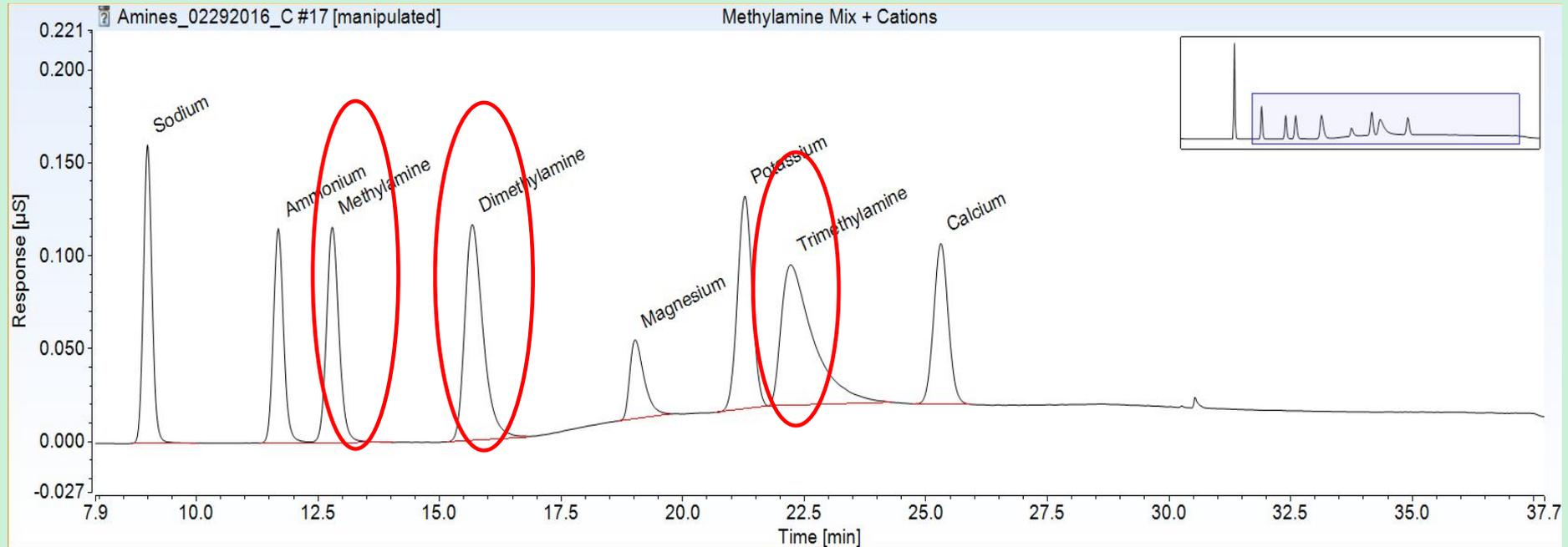


Organic acids are related to biomass burning and cooking emissions

(Modifications to the anion program can yield more organic acids)



Alkylamines can be resolved along with commonly measured cations (Ion Chromatography)



*Three alkylamines, (i.e. methylamine, dimethylamine, and trimethylamine) are derivatives of ammonia

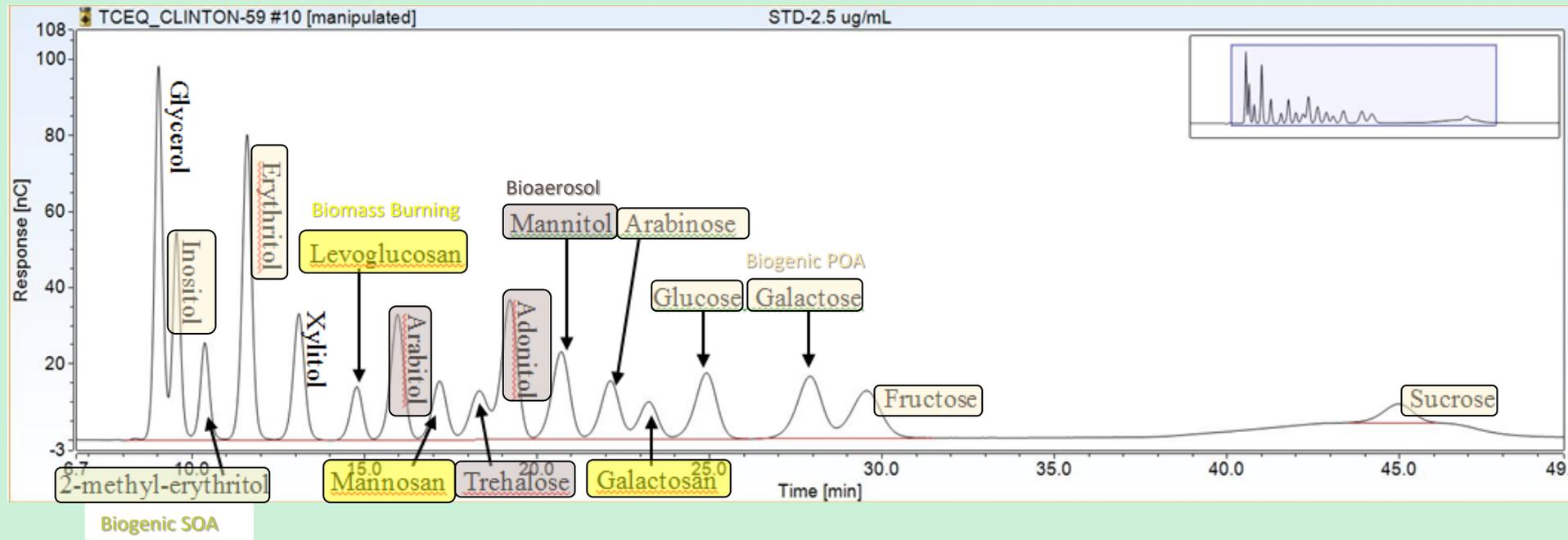
Carbohydrates have been related to various pollution sources

Pollution Source	Carbohydrate Species
Biomass Burning	Levoglucosan, Mannosan, and Galactosan
Biogenic POA ^a	Erythritol, Inositol, Glucose, Galactose, Arabinose, Fructose, and Sucrose
Biogenic SOA ^b	2-methyle rythritol
Bioaerosol	Fungi (e.g., Arabitol, Mannitol, and Trehalose), and Bacteria (Adonitol)

^aPOA: primary organic aerosol

^bSOA: secondary organic aerosol

Carbohydrates can be resolved with IC-PAD^a



^aIC-PAD: ion-chromatography with pulsed amperometric detection

Conclusions

- A large variety of analyses, especially for organic compounds, can be applied to many samples acquired in long-term speciation networks
- Thermal desorption-GC/MS along with carbohydrate and organic acid analyses are cost effective and environmentally friendly for additional organic markers
- Multi-wavelength transmittance and reflectance provides information on sources and radiative transfer, as well as elucidating aerosol changes during filter analysis

Challenges in Chemical Characterization on Filter Samples

- Perfecting, evaluating, and making more efficient procedures for additional characterization
- Modifying instrumentation and procedures to incorporate more specific analyses into long-term networks to obtain more information from existing samples
- Maintaining continuity and consistency with the long-term trends data sets
- Developing more detailed source profiles with these methods for speciated inventories, volatility basis sets, and source apportionment

For more information on this topic

Chow, J.C.; Watson, J.G. (2013). Chemical analyses of particle filter deposits. In *Aerosols Handbook: Measurement, Dosimetry, and Health Effects*, 2; Ruzer, L., Harley, N. H., Eds.; CRC Press/Taylor & Francis: New York, NY, 179-204.

7 Chemical Analyses of Particle Filter Deposits*

Judith C. Chow and John G. Watson

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Source Apportionment: Principles and Methods

J. G. WATSON,* J. C. CHOW, L.-W. A. CHEN, G. ENGLING AND X. L. WANG

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of Protected Visual Environments (IMPROVE)
Carbon Analysis (P16PC00229)



- U.S. E.P.A. PM_{2.5} Chemical Speciation Network (CSN)
Laboratory Analysis Program
(EP-D-15-0250)

