Method development and application of thermal desorption GCMS

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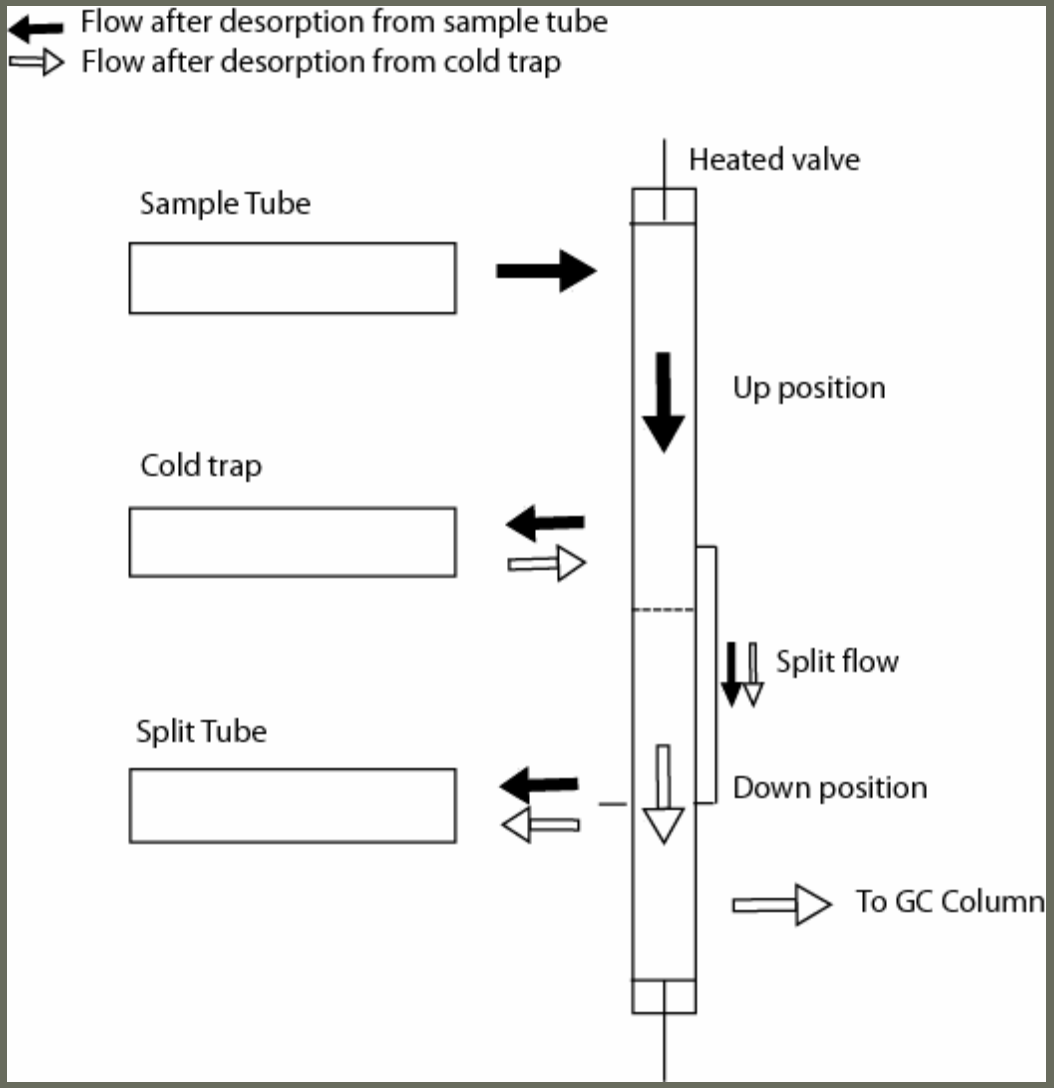
Motivation for TD analysis

- Particle-phase organic compound speciation has been shown to provide a powerful tool to
  - characterize emissions from sources
  - Understand sources of atmospheric PM
- Great interest in broadening tracer application
  - Personal exposure samples (ie. small PM masses)
  - More polar compounds
- Validate and apply TD GCMS analysis on a large scale
  - Establish historical continuity with solvent extraction GCMS
  - St. Louis Supersite
- Develop derivatization techniques for polar compounds compatible with thermal desorption
  - Methylation
  - Silylation

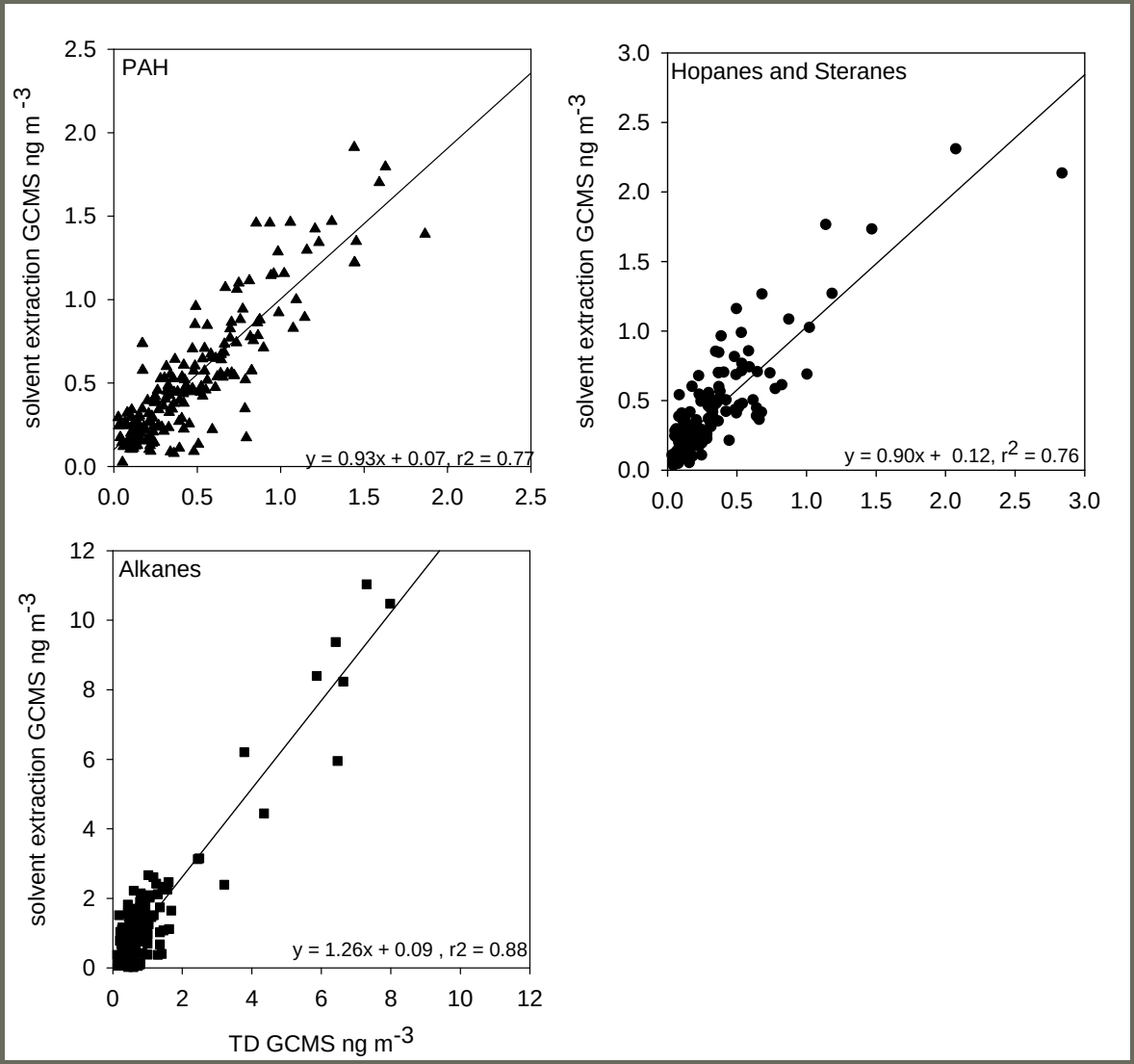
TD methods

- Filter analysis by TD GCMS
  - A blank filter punch is spiked with labeled internal standard and allowed to dry
  - The sample filter punch and the spiked filter punch are placed in a glass thermal desorption tube
  - The tube is placed in the Markes automated thermal desorption unit
- Non-polar
  - Developed to focus on combustion and mobile source markers including hopanes, steranes, PAH and alkanes
  - Requires no additional sample prep
- Methylation
  - Adds analysis of organic acids to non-polar method
- Silylation
  - Adds analysis of organic alcohols and polyols

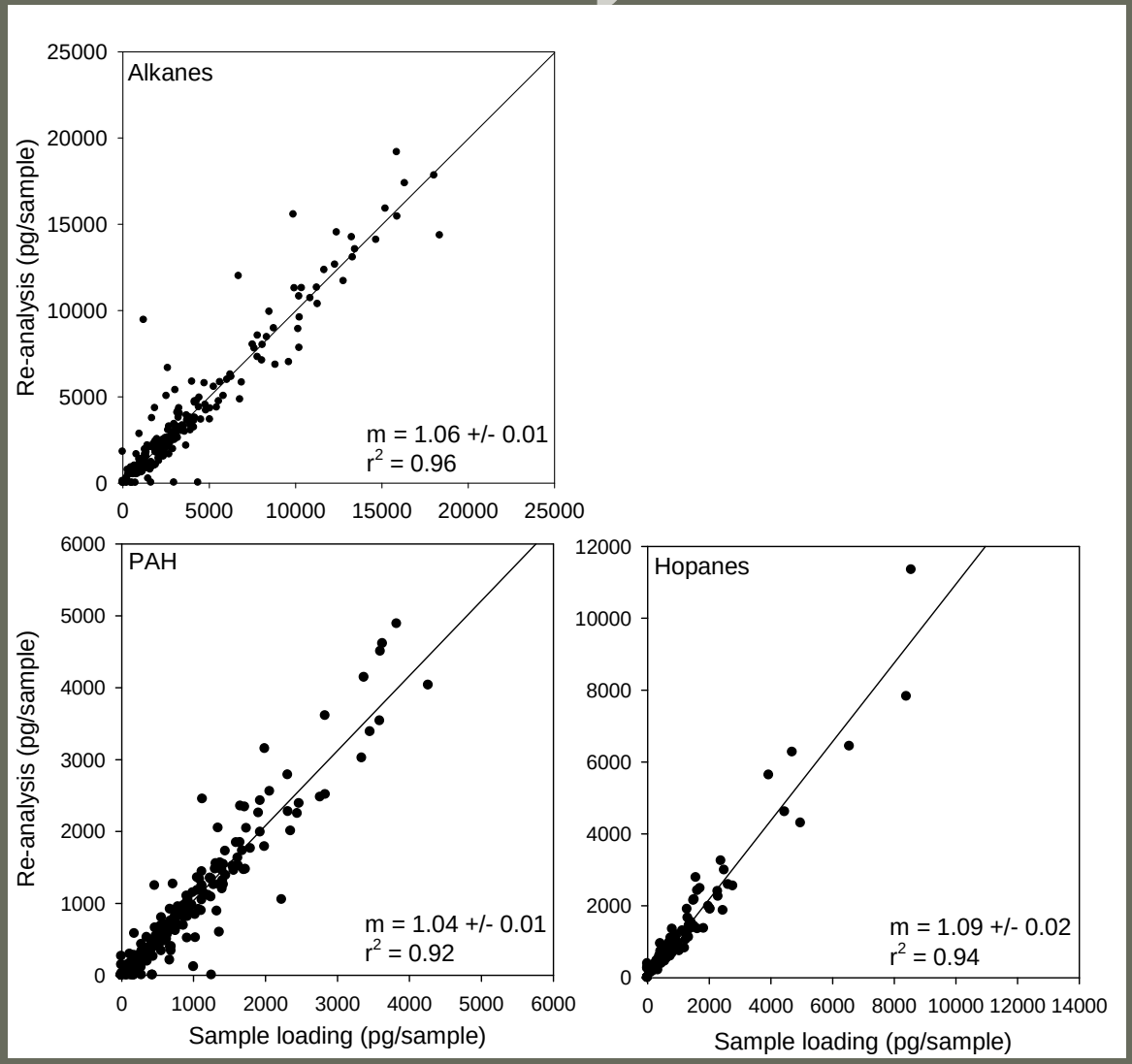
TD schematic



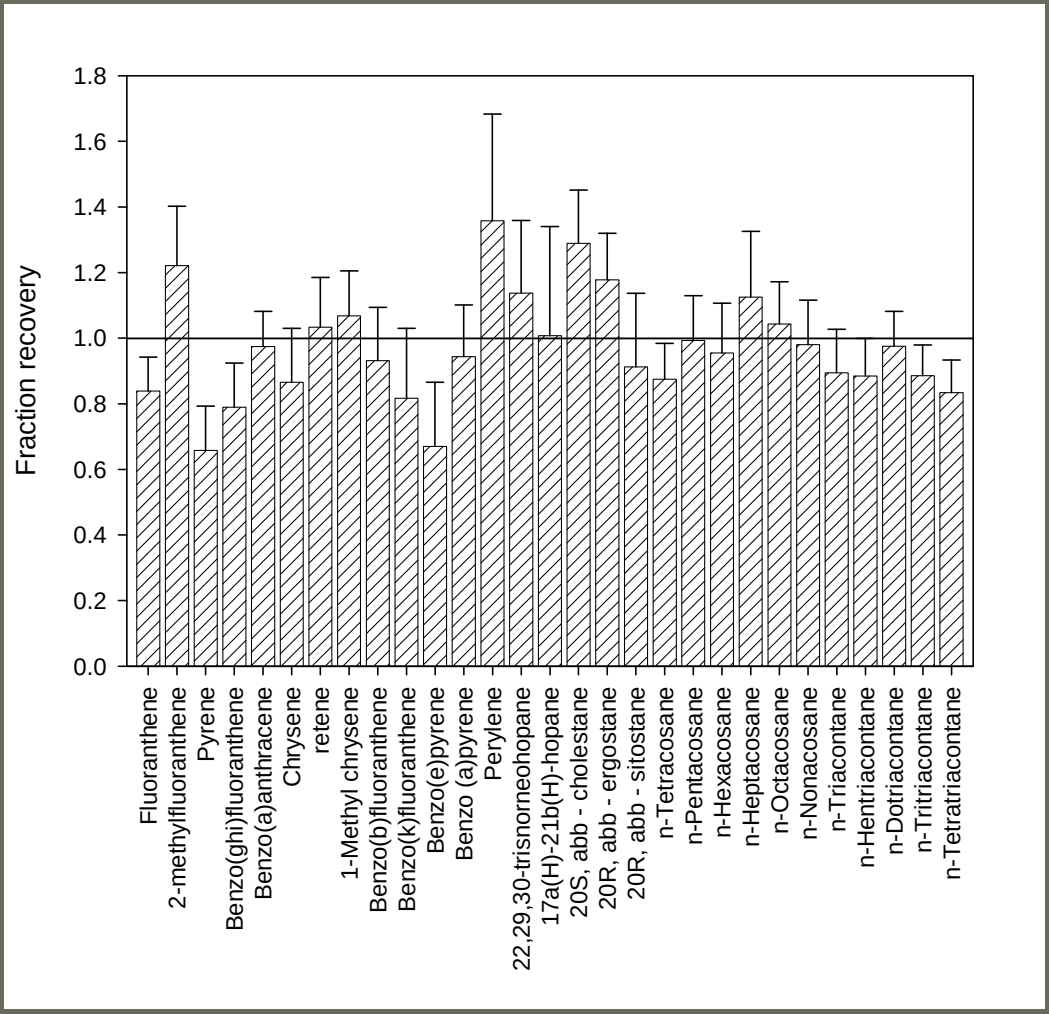
TD GCMS vs solvent extraction GCMS intercomparison



Non-polar TD GCMS duplicate analysis



Non-polar TD-GCMS matrix spike analysis

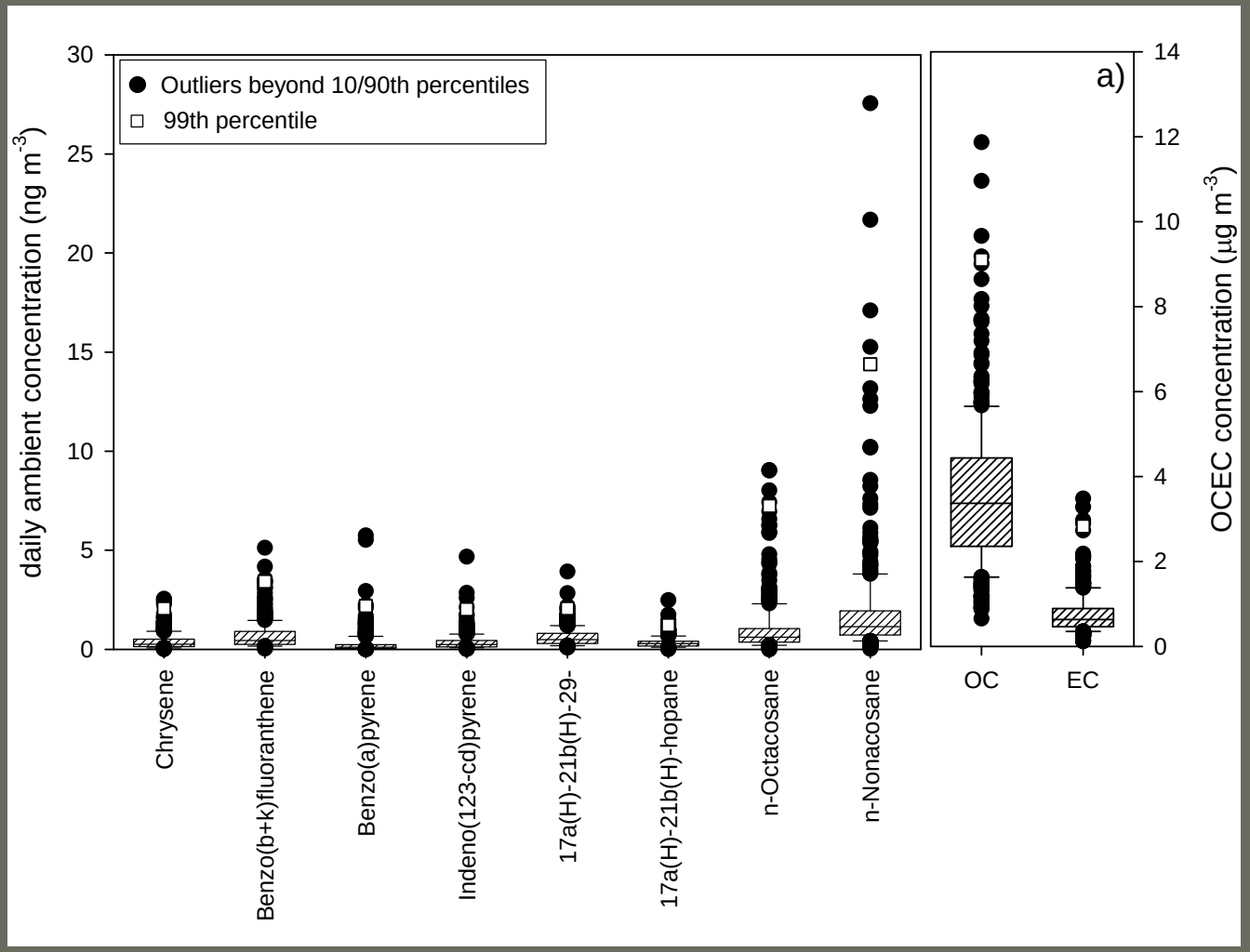


STL GCMS analysis

- 1 full year of daily 24 hour samples was collected in East St. Louis, IL
  - 1 in 6 samples were analyzed by solvent extraction GCMS
  - Remaining samples were analyzed by non-polar TD-GCMS
- Study looks at daily variability in organic tracers
  - Day of the week trends
  - Differences by sources

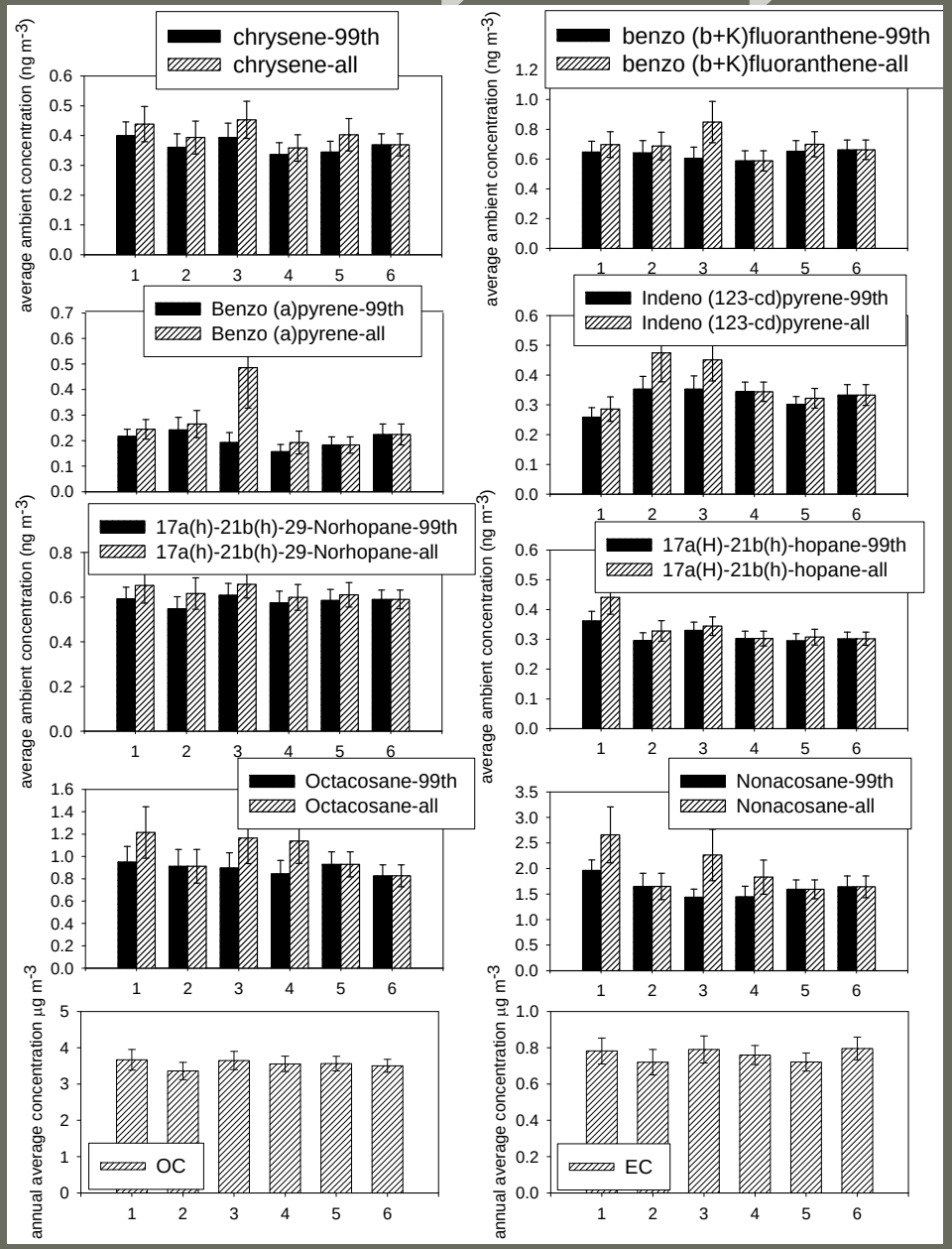
Box plots of select daily molecular markers, OC and EC

St. Louis Supersite study



Every sixth day analysis

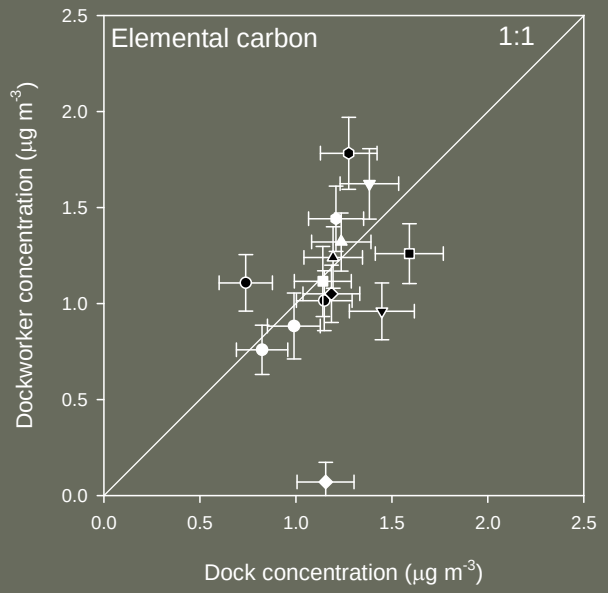
St. Louis Supersite study

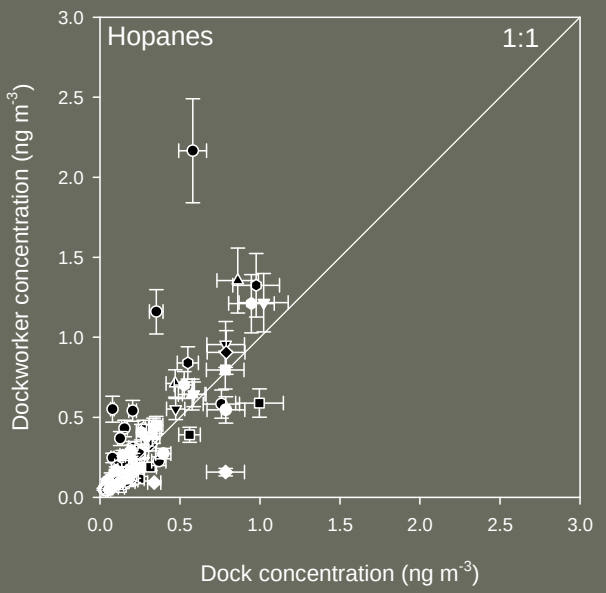


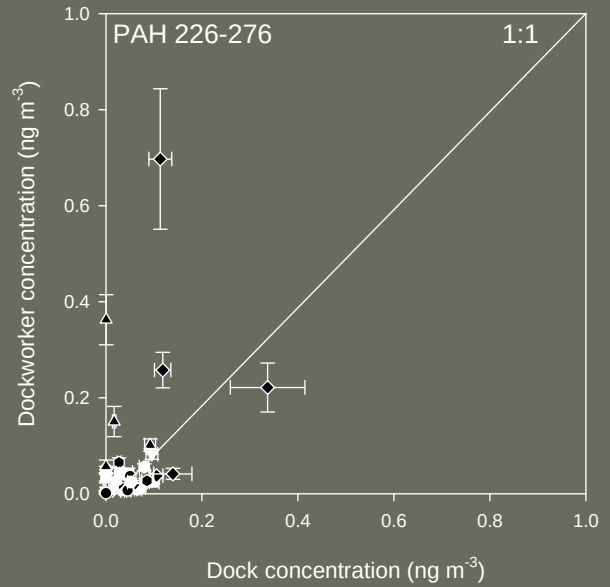
Study design – Personal exposure study

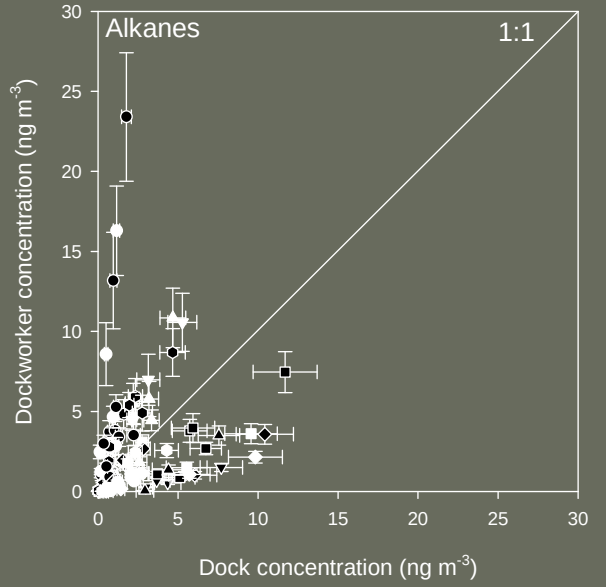
- Assess the relationship of ambient, worksite and personal exposure to carbonaceous aerosols in a highly diesel exhaust impacted environment
  - trucking terminal in St. Louis, MO
- Personal exposure = urban background + work site background + personal activity
  - Ambient site: East St. Louis, IL Supersite
  - Worksites: yard, dock, shop
  - Job types: dockworker, hostler, mechanic, and drivers (2)
- Focus on carbonaceous particulate matter
- Primary components of diesel exhaust are elemental and organic carbon
- Tracers for the organic carbon fraction
  - Hopanes and steranes – lube oil in exhaust

Dock and dockworkers n=14

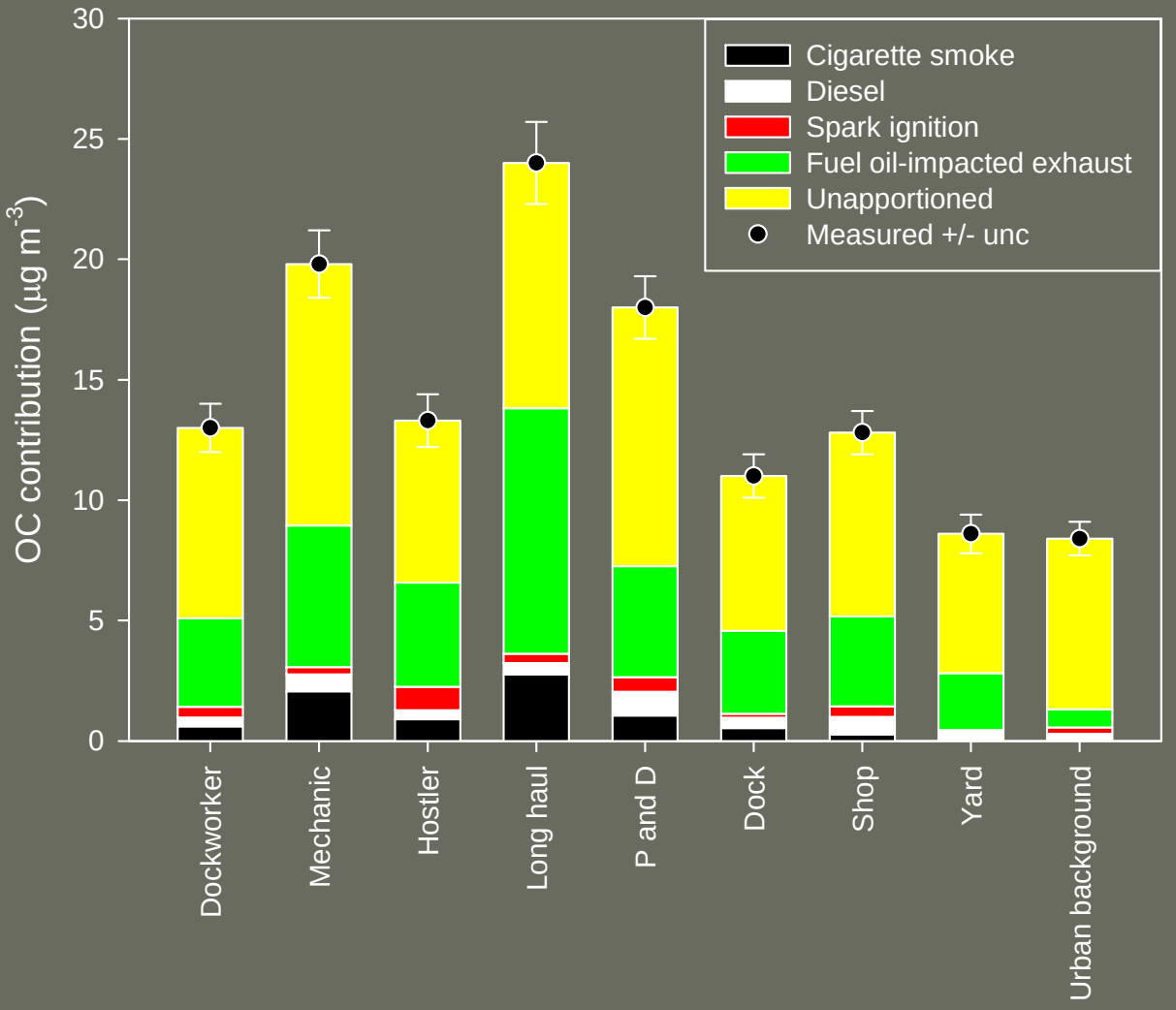








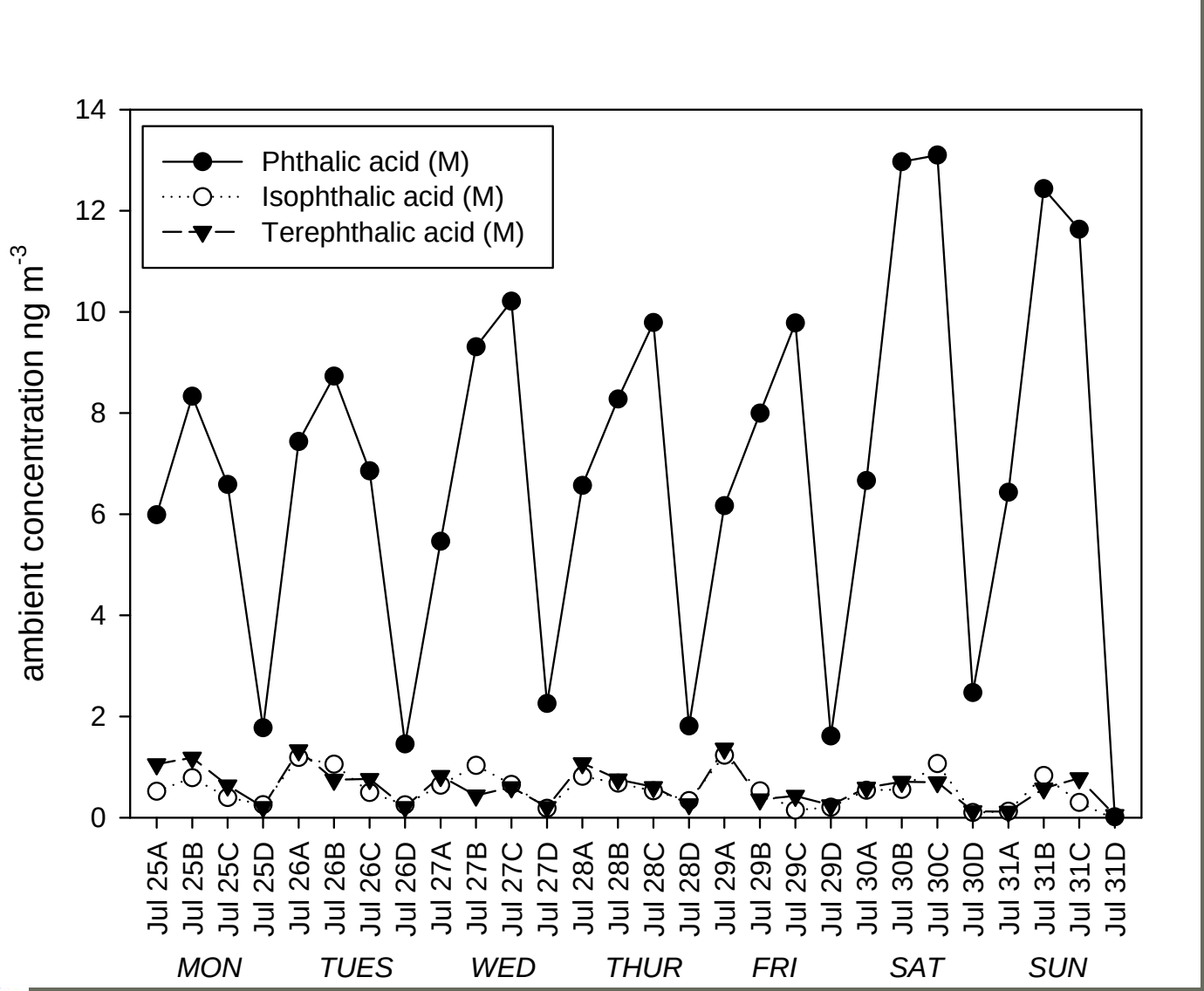
CMB OC apportionment



TD methylation

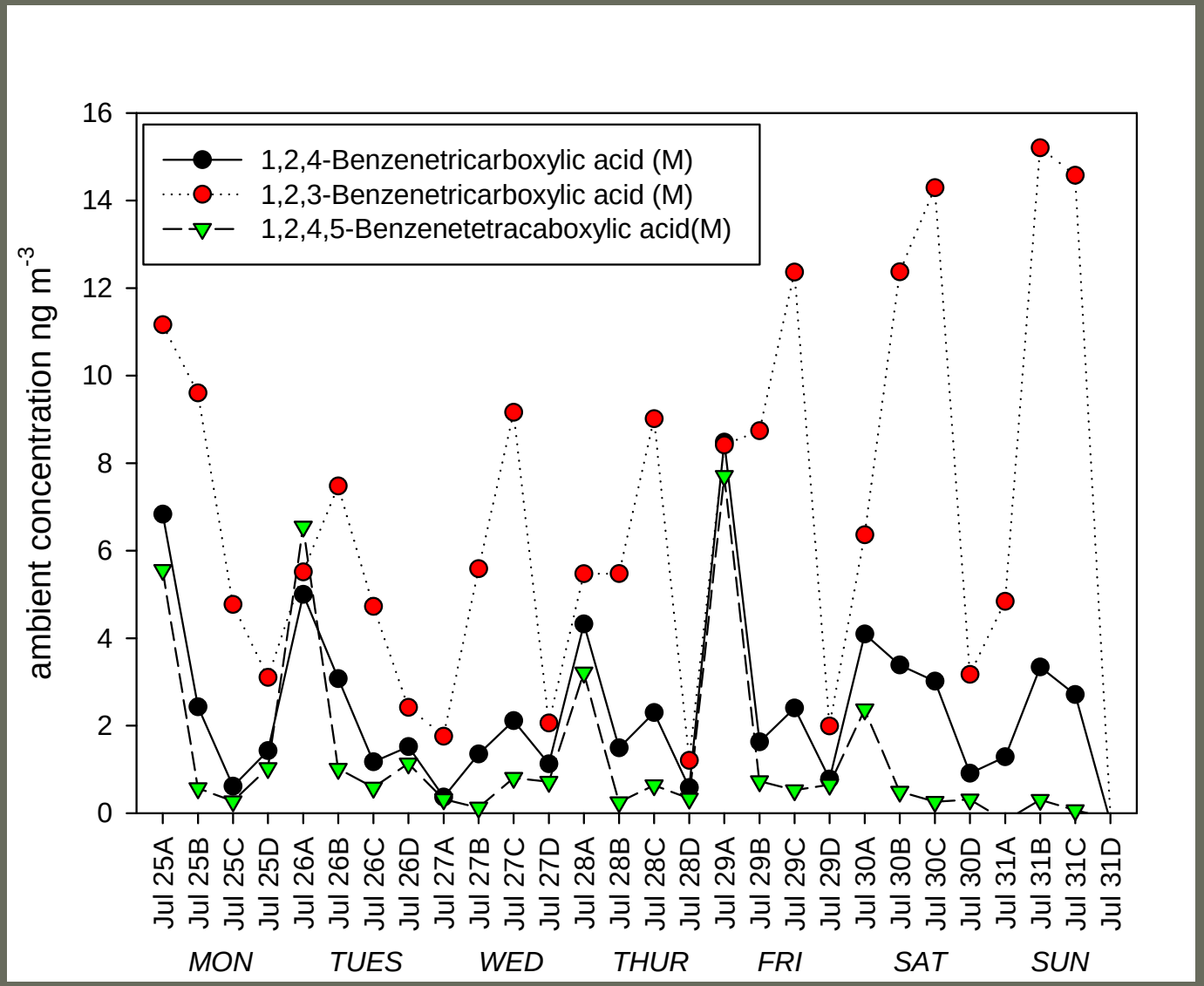
- Parallels solvent extraction GCMS method
- Uses an in-situ diazomethane derivatization to methylate organic acids on the filter prior to analysis
  - N-alkanoic acids, aliphatic diacids, aromatic acids
- Has been combined with non-polar analysis
    - Hopanes, steranes, PAH, alkanes

SOAR aromatic acids

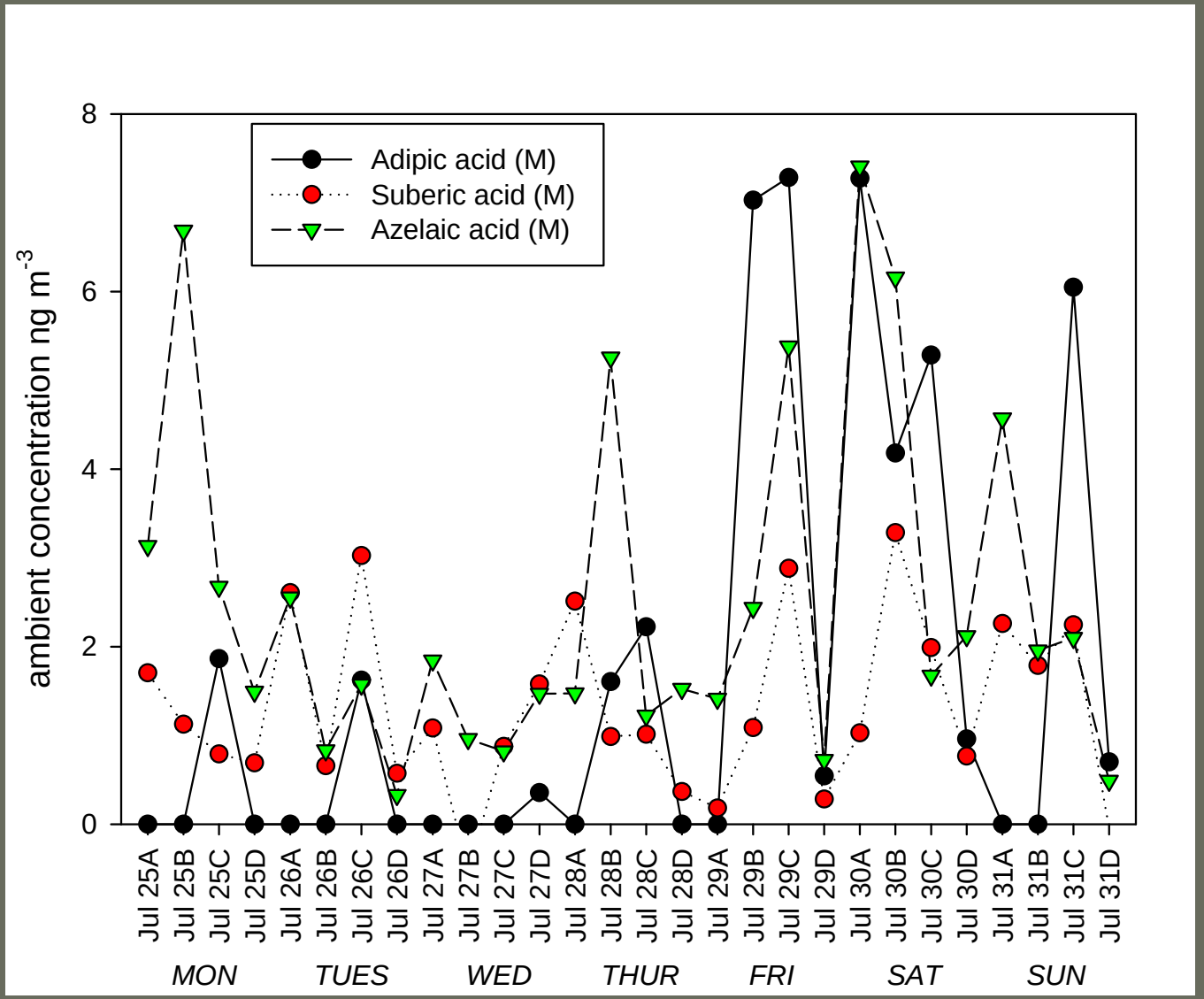


A = morning
B = midday
C = afternoon/ evening
D = night

SOAR aromatic acids



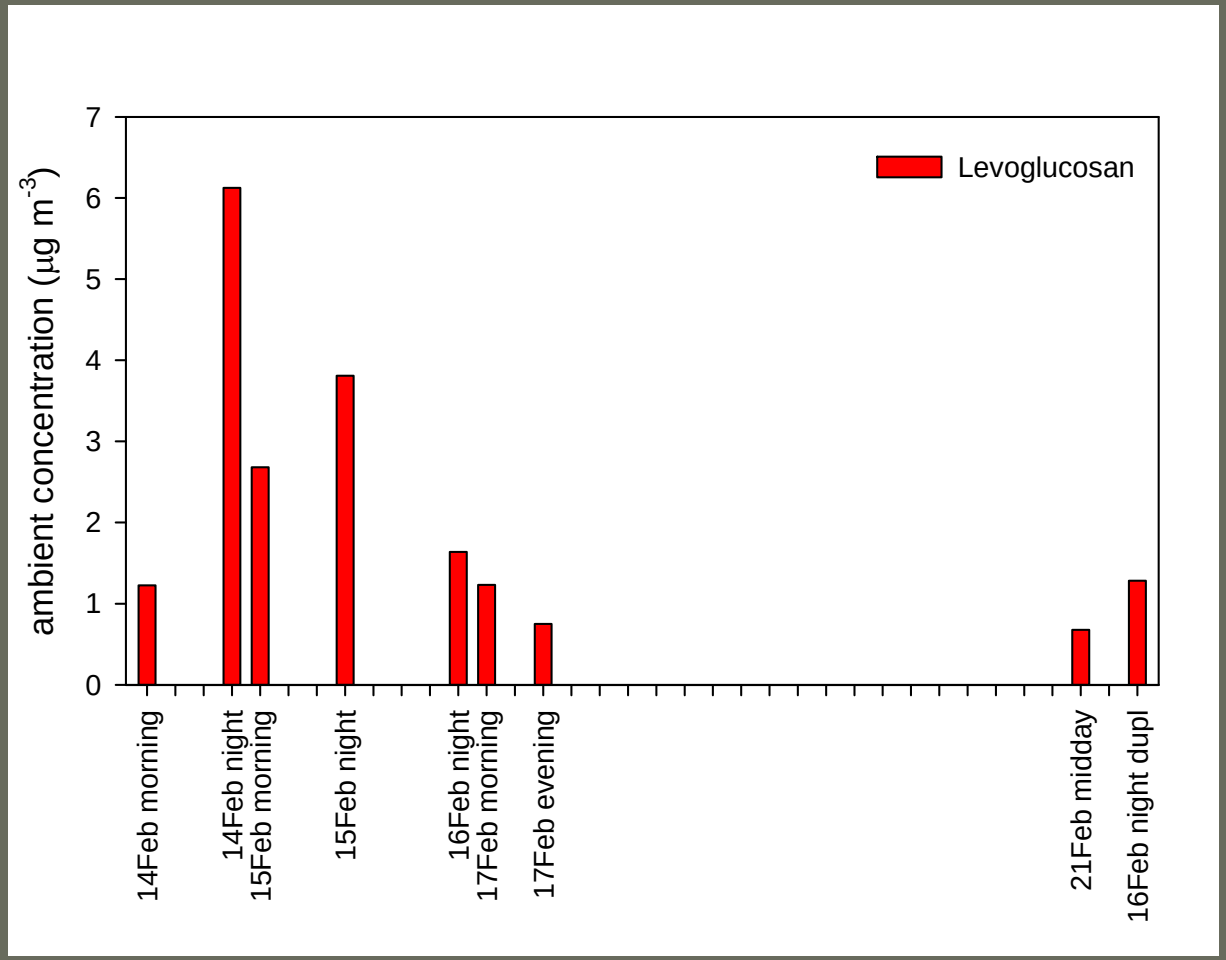
SOAR aliphatic diacids



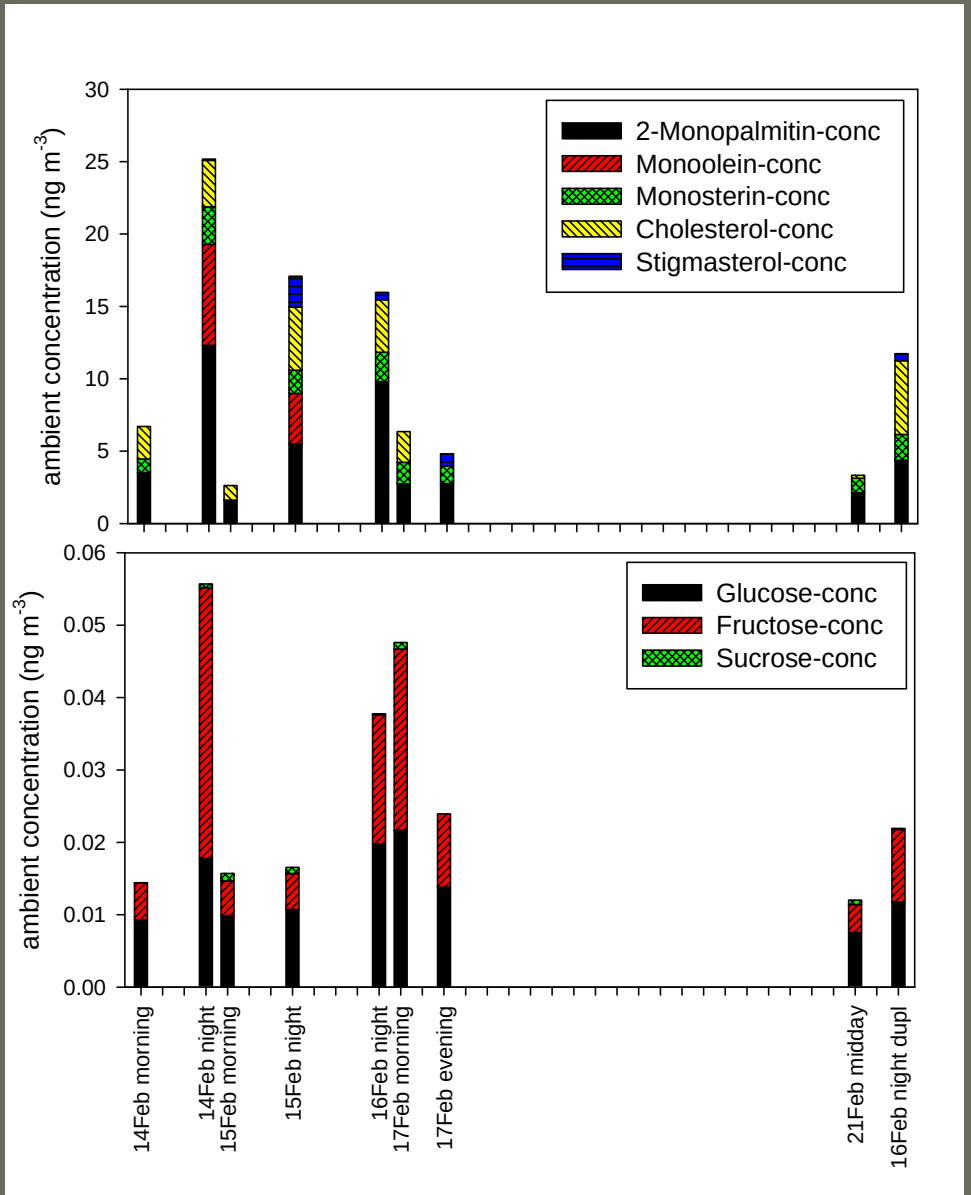
Silylation TD GCMS

- Uses an in-situ BSTFA silylation derivatization to add trimethyl silyl groups to alcohol groups
  - Levoglucosan, sterols, monoglycerides, simple carbohydrates, methyl tetrols (to be added)
- Extends polar range vs. traditional solvent extraction

Fresno levoglucosan – in progress



Fresno sugar trends – in progress



Method development status

- Non-polar method
  - Fully developed and validated
  - Method paper submitted to Aerosol Science and Technology
  - Currently being used in atmospheric and health studies
- Methylation method
  - Development completed
  - Validation near completion
  - Currently in use in atmospheric and health studies
- Silylation method
  - Currently being validated for a limited number of samples
  - Additional optimization required for large scale use
    - May require different TD system

Acknowledgements

- Project Team:
  - Co-PI: Rebecca Sheesley – UW-Madison
  - Co-PI: B. R. T. Simoneit – Oregon State
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- SOAR study (Study of Organic Aerosols at Riverside)
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  - http://cires.colorado.edu/jimenez-group/Field/Riverside05/ for list of participating researchers
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