

# LADCO Organic Molecular Markers Study

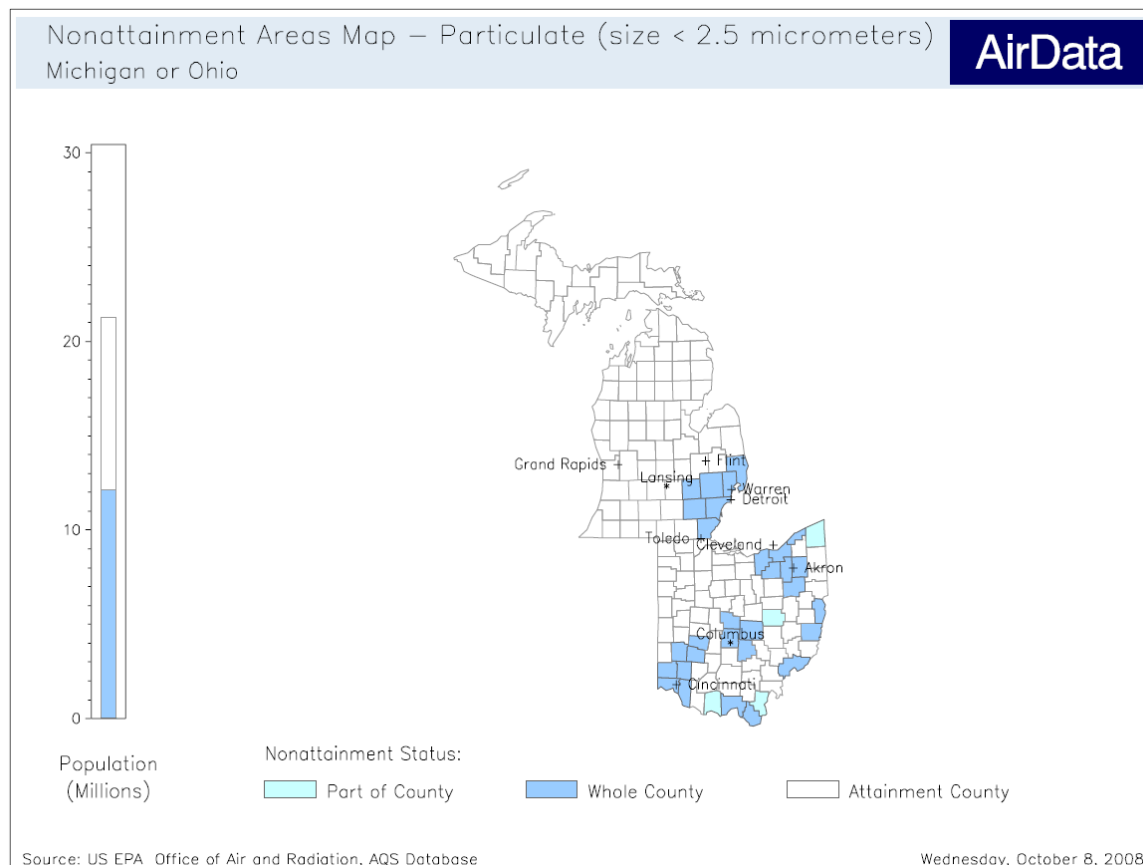
**Final Project Meeting  
October 16, 2008**

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UW-Madison**

**\*- Principal Investigator and Corresponding Author**

# Study Motivation and Objectives

- Detroit, Cleveland, Cincinnati, Mingo Junction all in non-attainment of PM2.5 Standard
- OM contributes to ~1/3 of PM2.5 Mass at these locations
- What sources of carbonaceous aerosol contribute at each site?



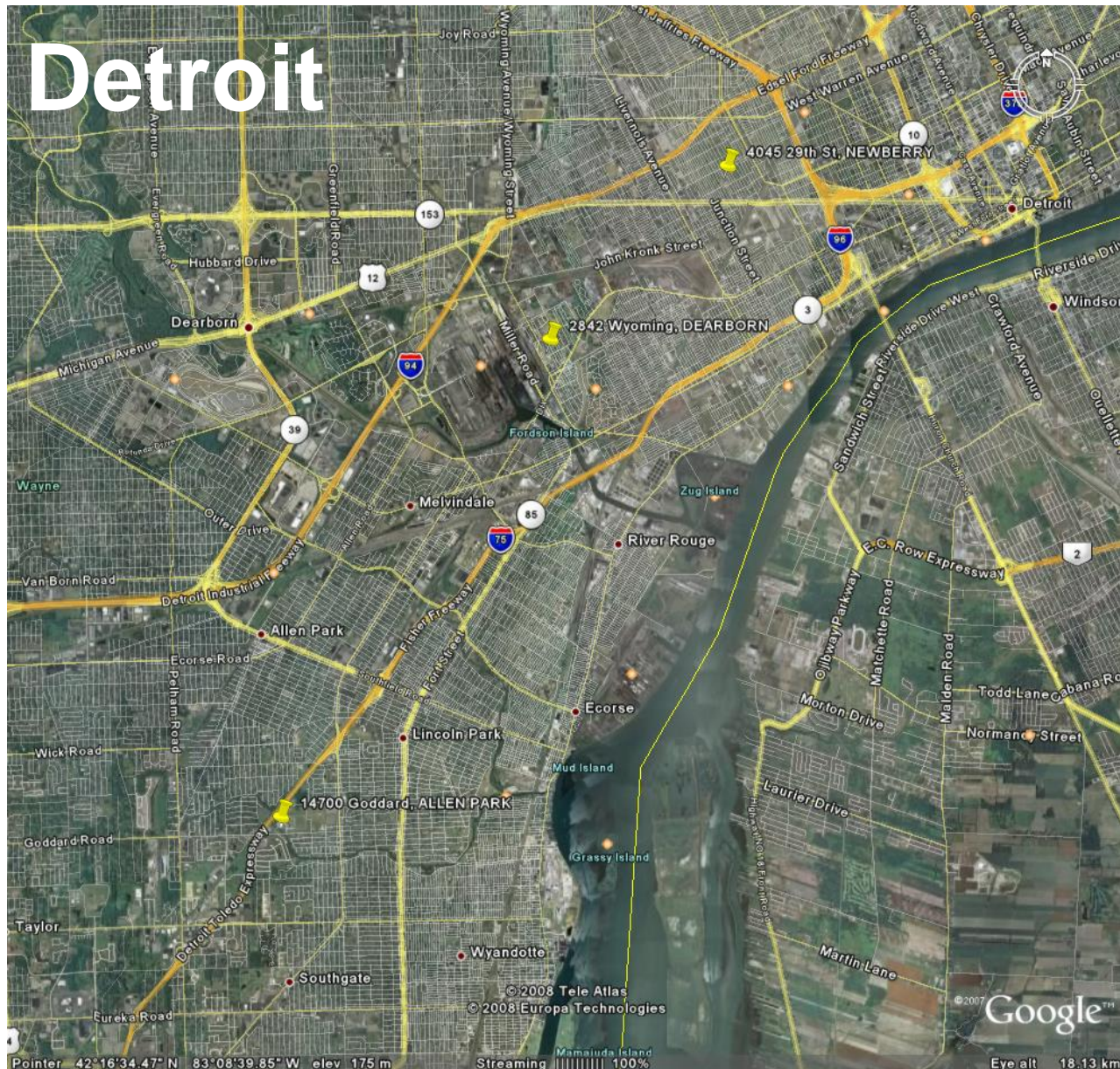
# Research Objectives

- What are the sources contributing to carbonaceous aerosol at each site?
- Are sources local or regional?
- Quantify temporal and spatial contribution changes of OM sources
  - Seasonally, weekend to weekday, day to day
  - Inside each city
  - Between cities
- Quantify biomass burning and SOA contributions to PM<sub>2.5</sub> mass

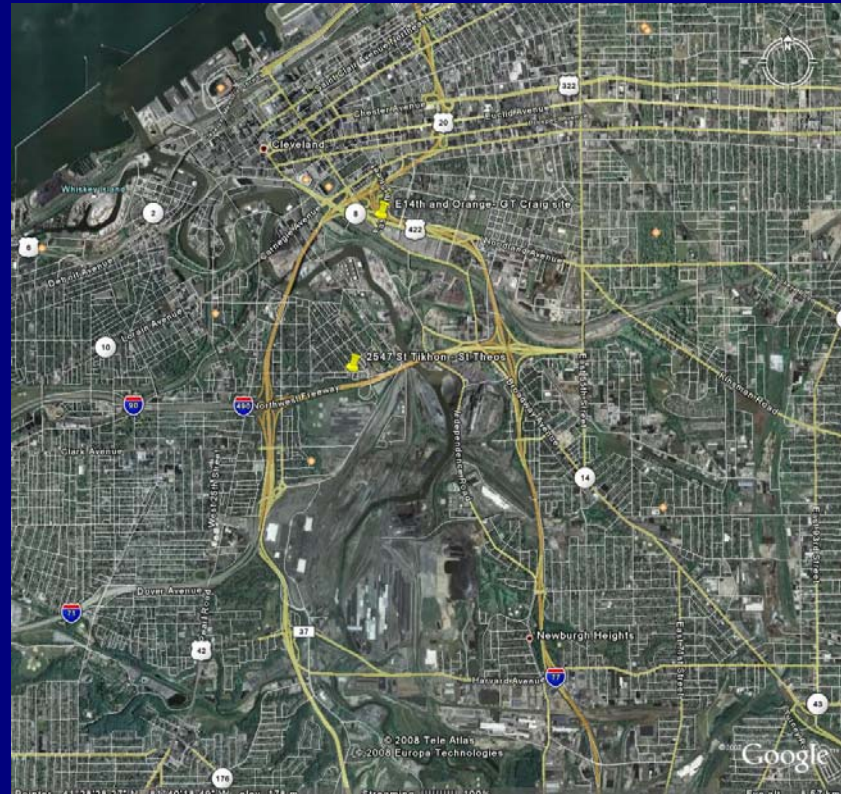
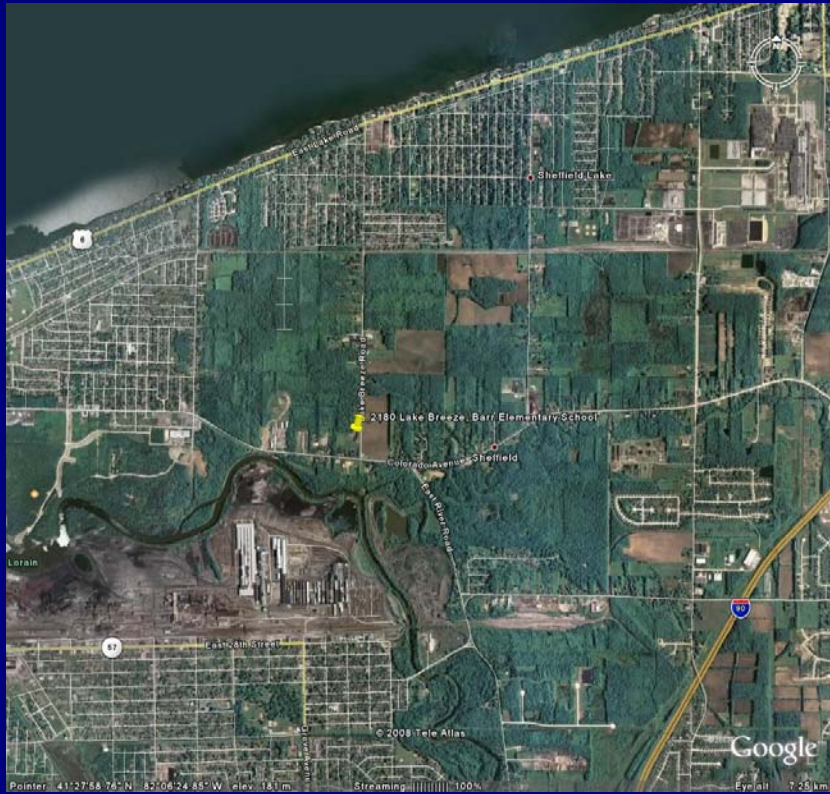
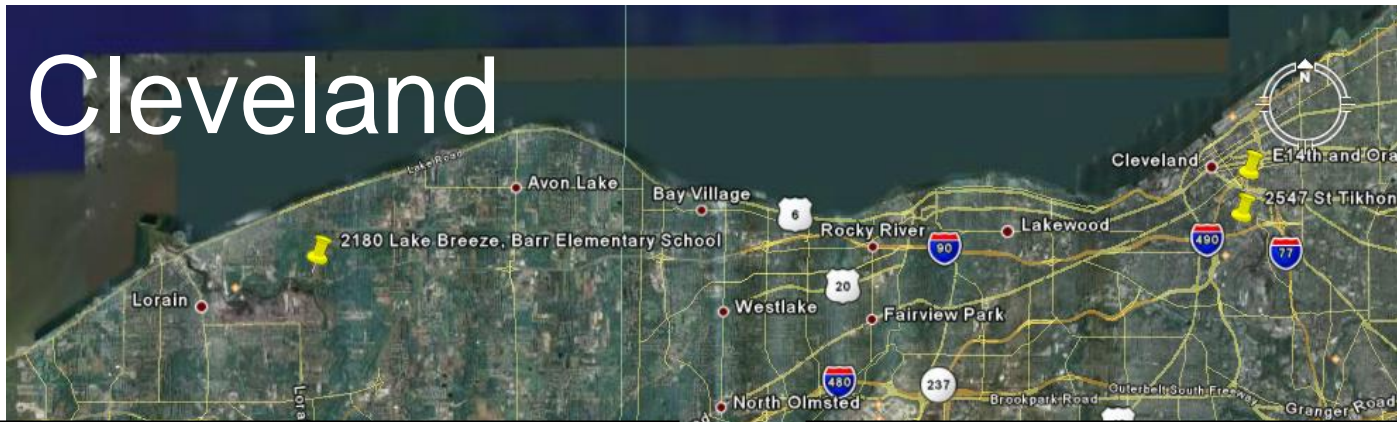
# Sample Collection Strategies

- Summer and Winter Intensives in Cleveland and Detroit
  - 3 sites in each city
  - 1 month each
  - Daily filter collections
  - Real time instruments
- 1 year of 1-in-6 day filter collections at Cleveland, Cincinnati, and Mingo Junction (near Steubenville)

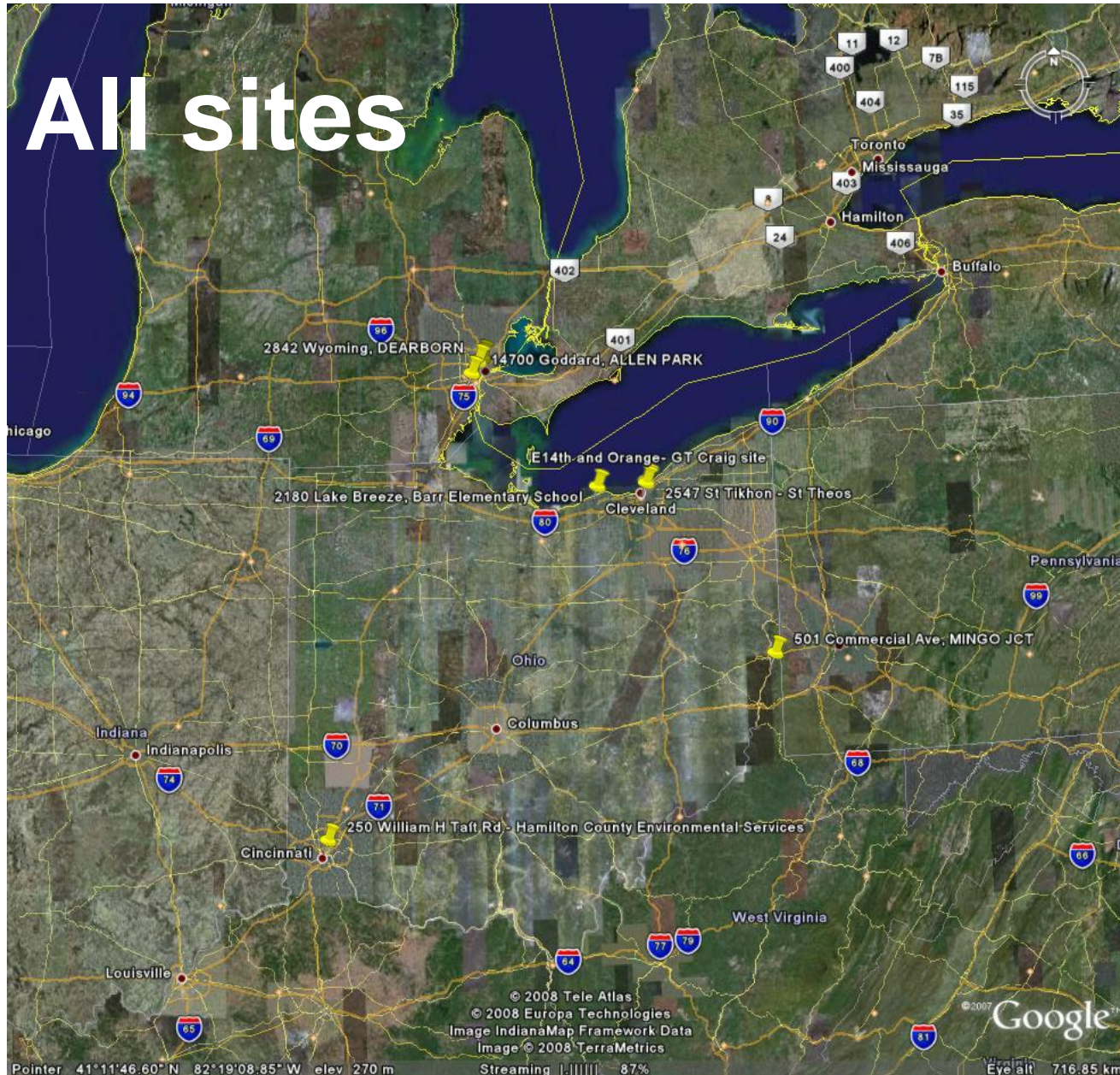
# Detroit



# Cleveland



# All sites



# Measurements

Measurement	Project
<p>24 hr PM2.5 Filters:</p> <p><b>Organic Carbon- Elemental Carbon (OC-EC)</b></p> <p><b>Water Soluble Organic Carbon (WSOC)</b></p> <p>Water Sol. Potassium,</p> <p><b>Water Soluble Sulfur,</b></p> <p><b>Water Soluble Sodium,</b></p> <p>Water Soluble Magnesium,</p> <p>Water Soluble Calcium,</p> <p>Water Soluble Iron,</p> <p><b>Organic Molecular Markers (OMM)</b></p>	1 in 6 & Intensives
Real time OC-EC, Black Carbon	Intensives only; both not available at every site

# Objectives for 1-in-6 Day Study

- Source Apportionment by Chemical Mass Balance Modeling
  - Variation in source apportionment between cities and seasons
  - Local source impacts evident?
  - New SOA tracers
- Contributions of SOA and Biomass Burning to Monthly Averages
  - Evaluate low cost apportionment method
  - Comparisons of WSOC, WSK, Levoglucosan, new SOA tracers, low molecular weight acids

# Chemical Mass Balance

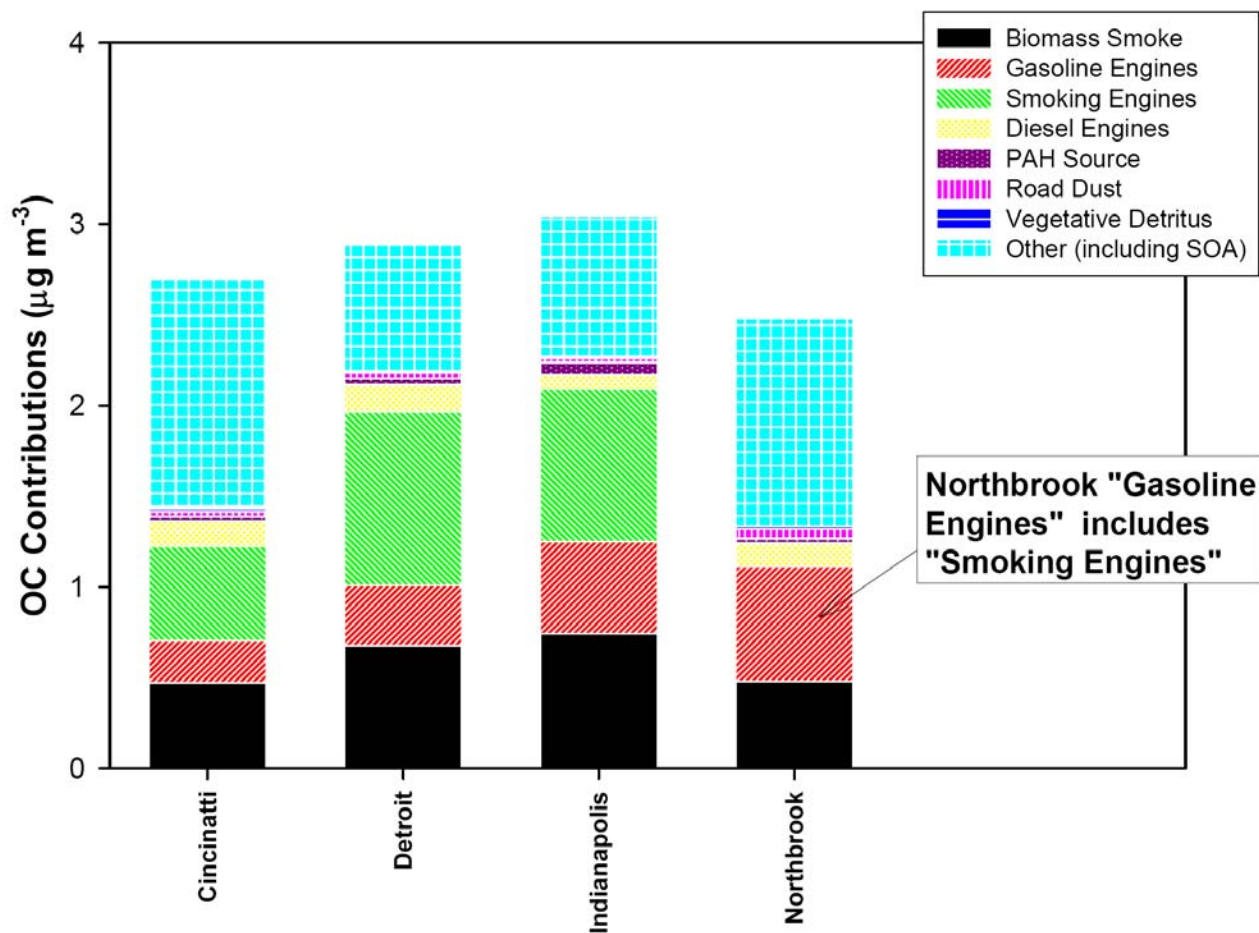
- Resolves source contributions to OC
- Uses previously measured source profiles
- Source profiles contain organic molecular markers specific to processes
- Performs a mass balance between marker : OC ratios from source profiles and markers present in the sample.

# Organic Molecular Markers used in this Study

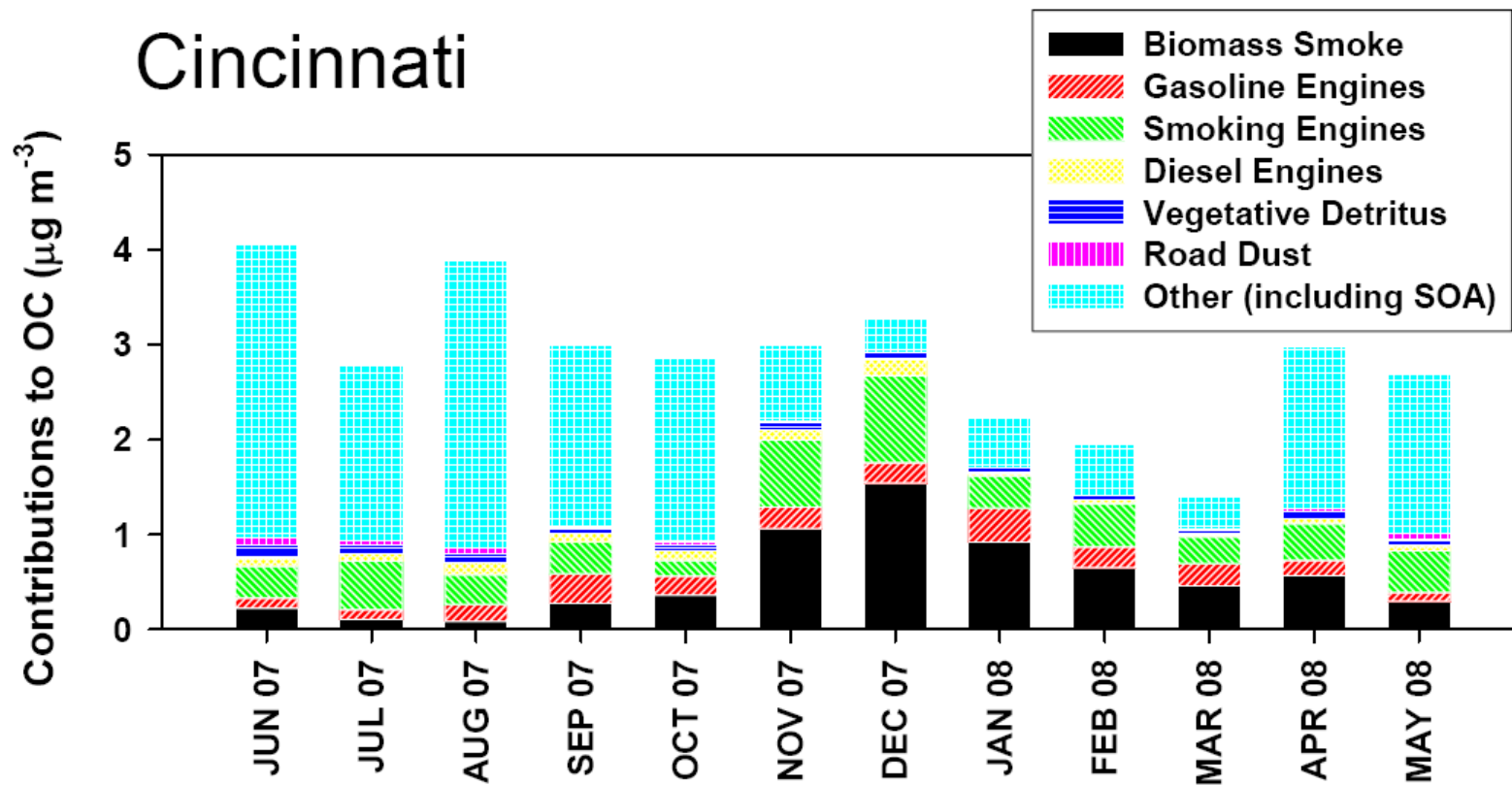
<b>Most important Compound Classes to CMB fit</b>	<b>Emission source</b>
EC, PAHs	Diesel Engines
PAHs	Gasoline Engines,
Hopanes	Smoking Engines
Alkanes	Vegetative Detritus
Silicon and Aluminum	Road Dust
Levoglucosan	Biomass Smoke
Water Soluble species, particularly oxidation products of isoprene, alpha pinene, beta carophyllene, and toluene	Other (including SOA)

# Urban Organics Study

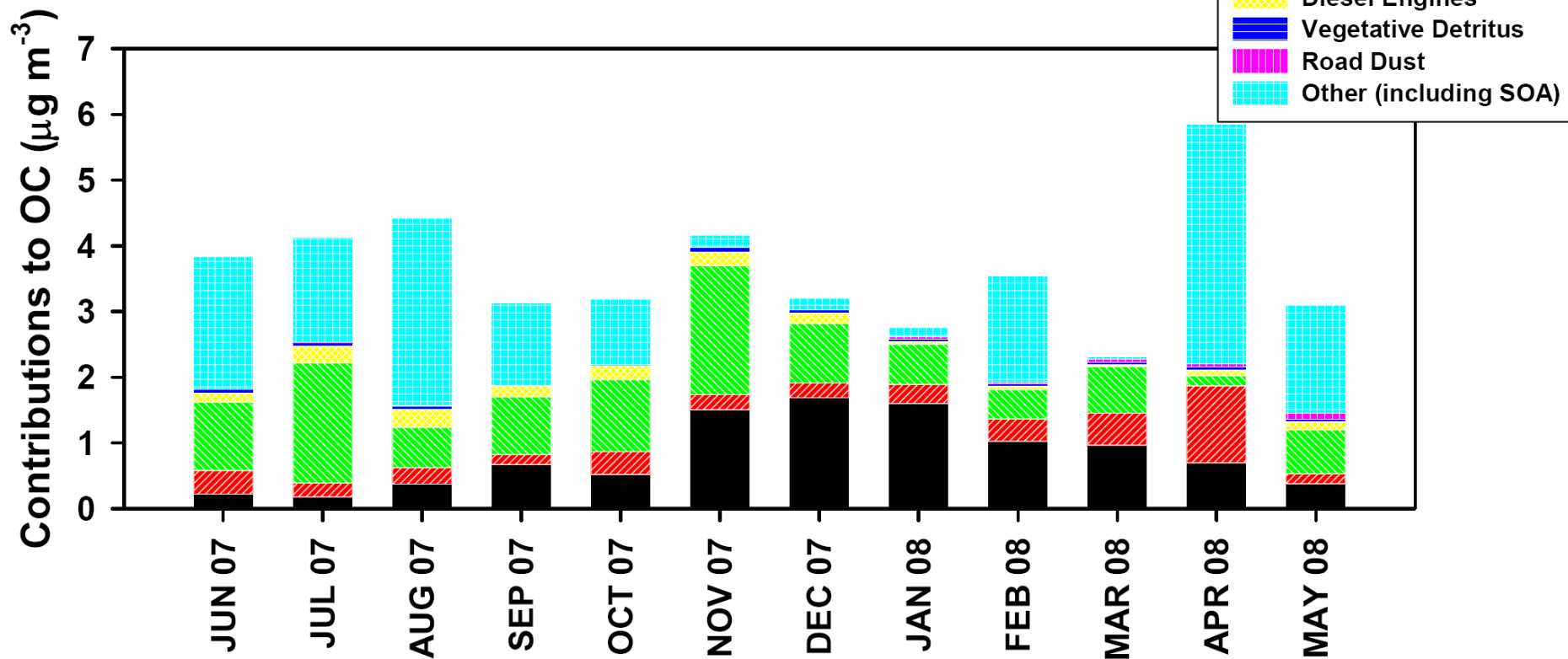
## Annual Average Source Contributions to Fine Particle OC



# This Study



# Cleveland

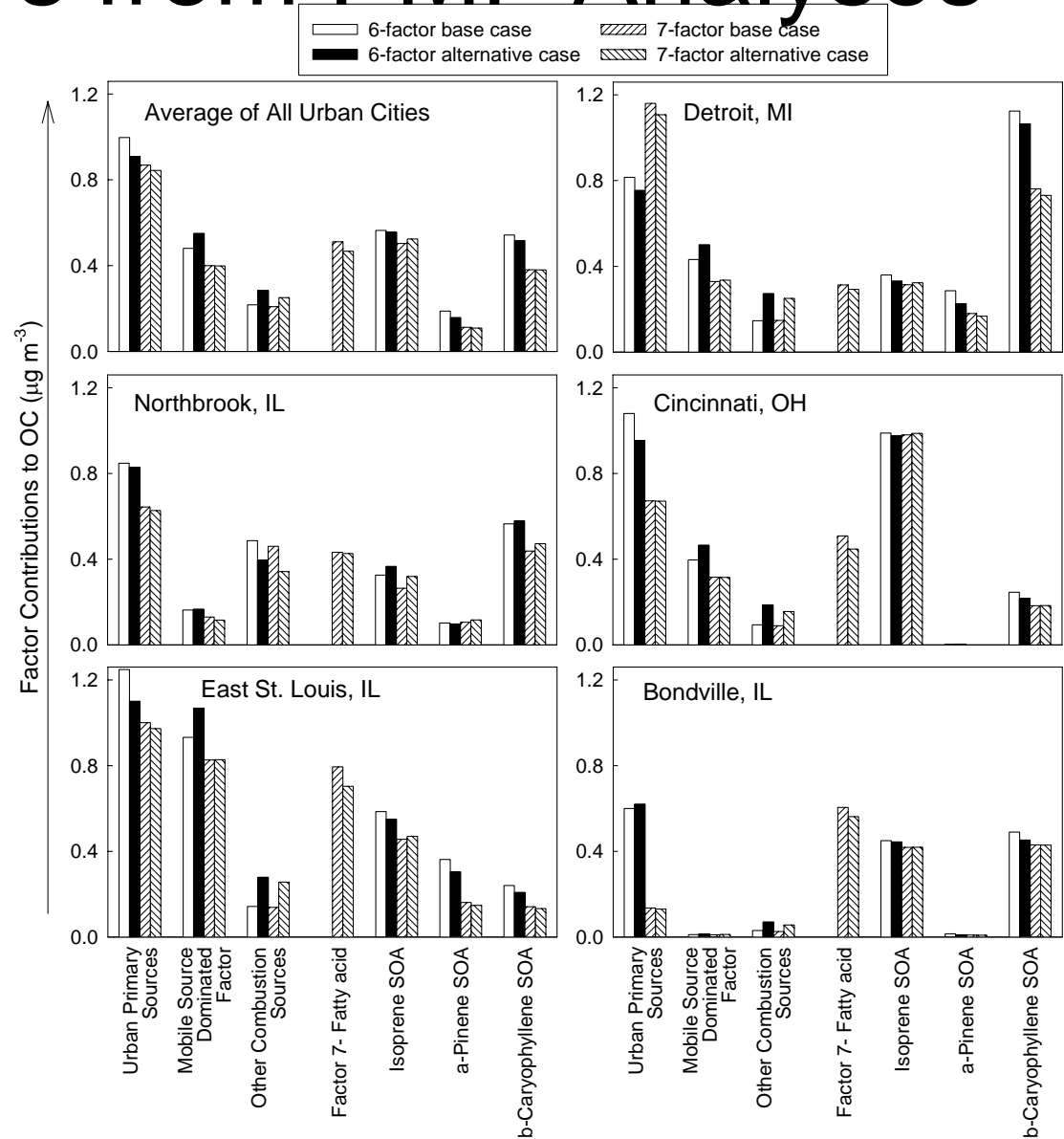


# CMB Conclusions

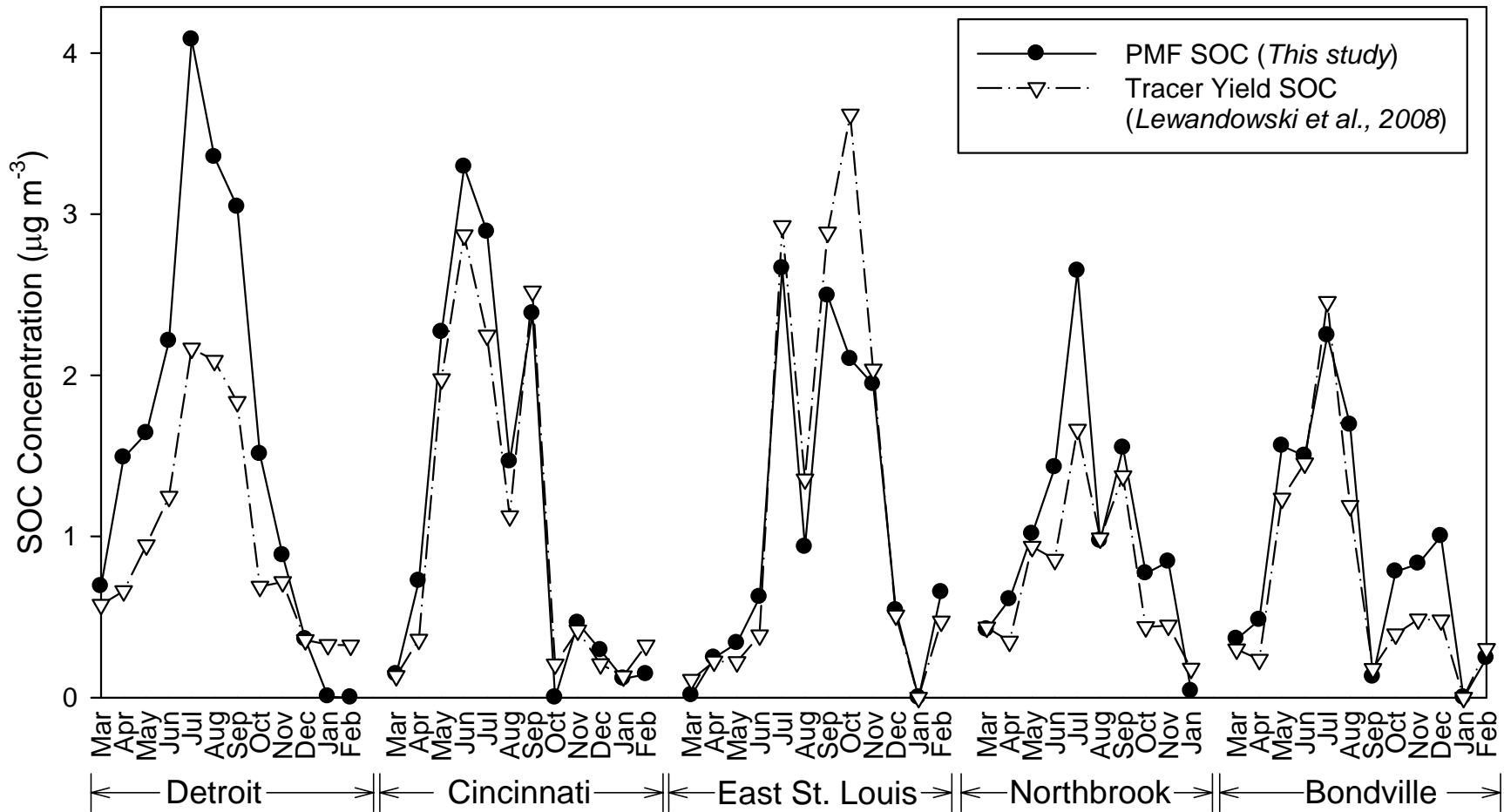
- Cincinnati CMB consistent with previous study
- Cincinnati and Cleveland CMB show similarities
  - Motor vehicles, particularly smoking engines, are important to POA all year
  - Biomass smoke is important in winter (residential wood burning), and minimal during summer (wildfire season)
  - Maximum of Other in summer likely due to photochemical oxidation
- Mingo Junction shows contribution of a local source that we are currently addressing

# SOA Tracers from PMF Analyses

LADCO 2004-2005 study

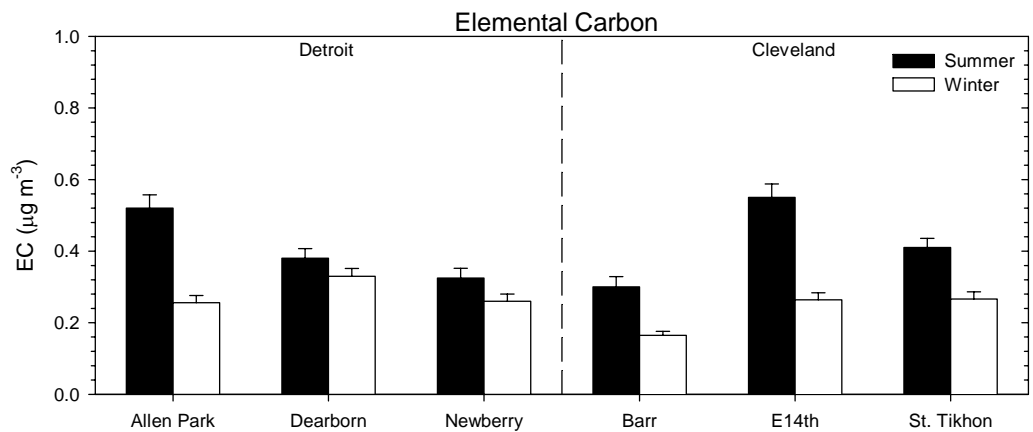
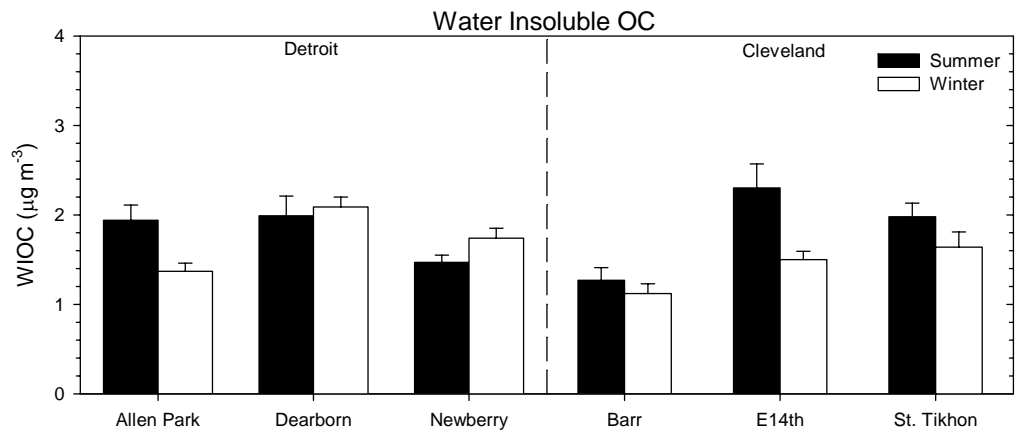
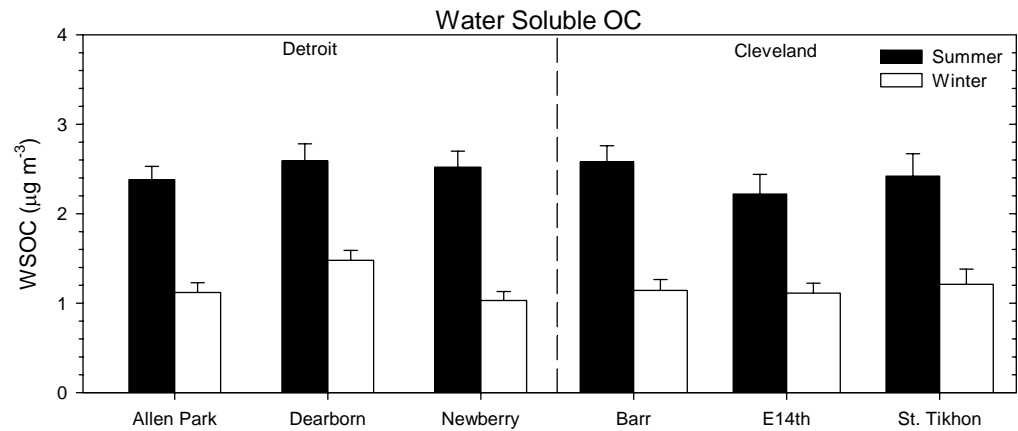


# Tracer Yield Method for SOC



# Intensive Studies

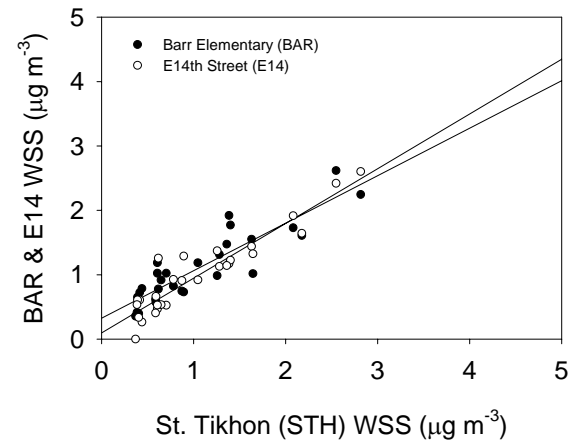
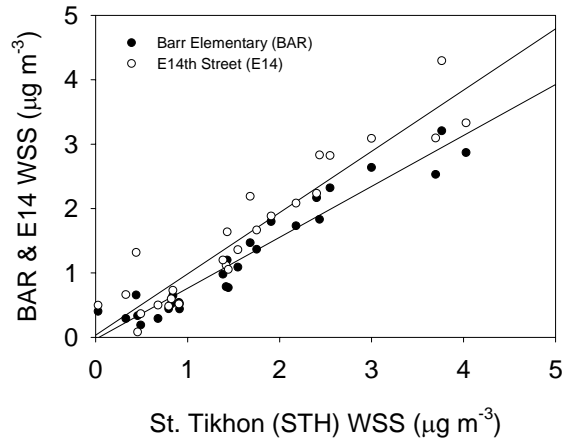
- Reveal influence of region or local sources
  - Explore Intercommunity Variability
  - Spatial trends
  - Temporal trends
- Investigate the use of 'low-tech' analyses
  - Contribution of SOA & biomass smoke
  - Compare WSOC and WSK analyses to SOA tracers



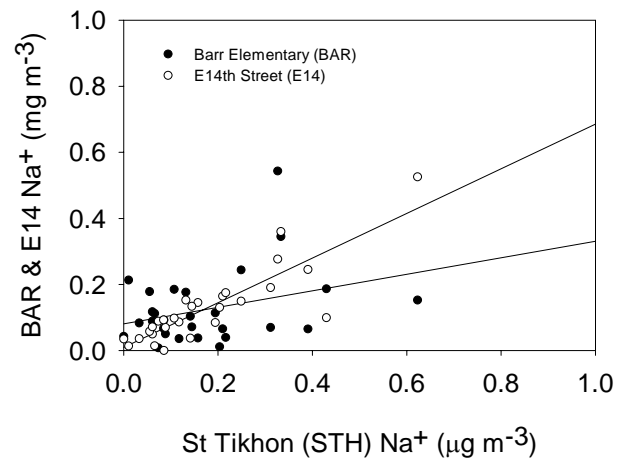
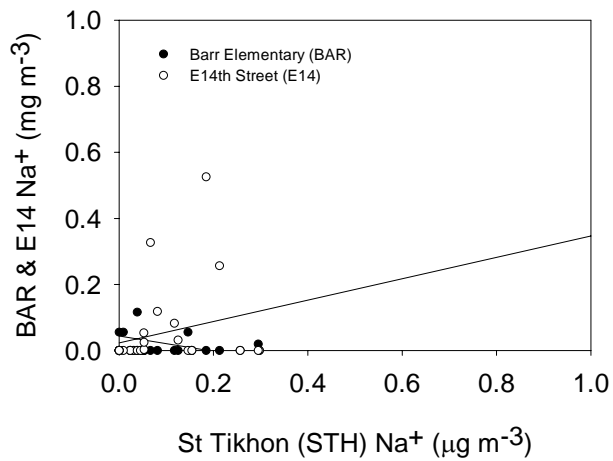
# Summer

# Winter

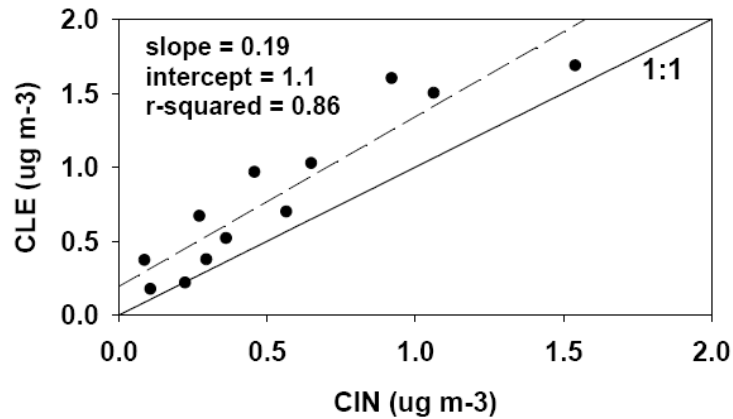
## Cleveland: Water Soluble Sulfur (WSS)



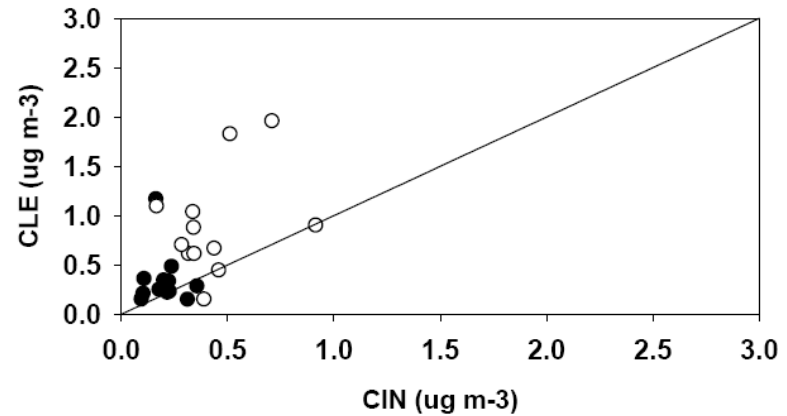
## Cleveland Sodium ( $\text{Na}^+$ )



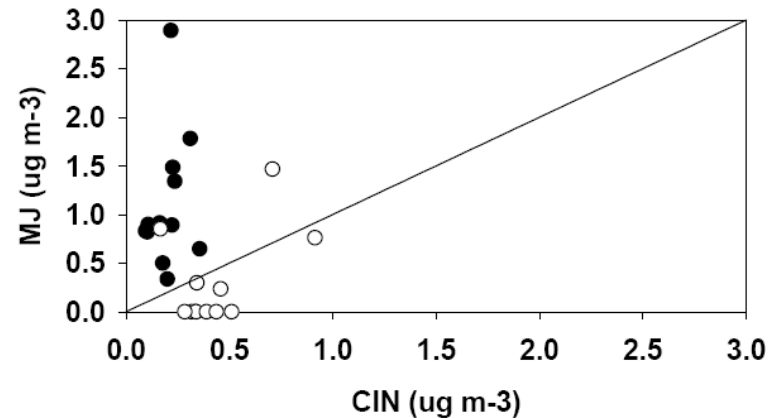
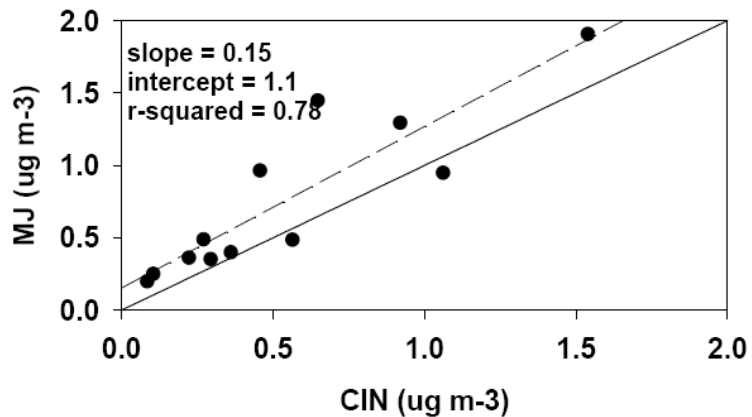
# Using CMB results...



● Wood Smoke



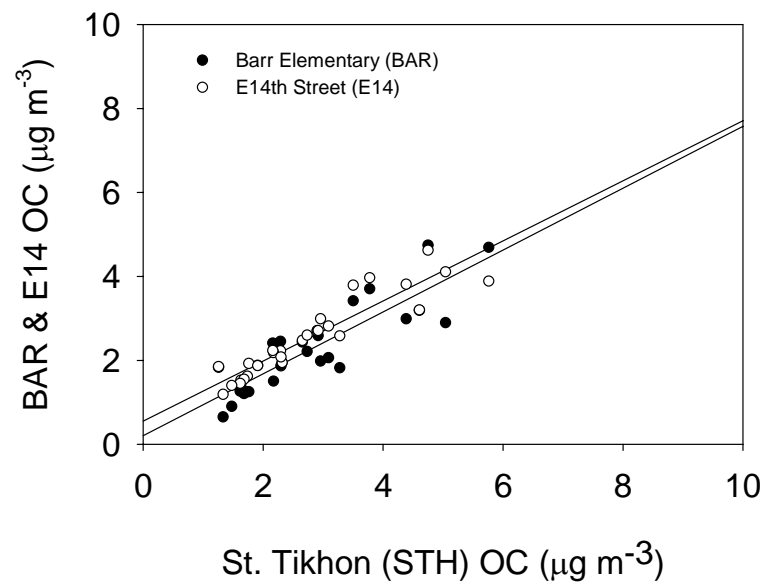
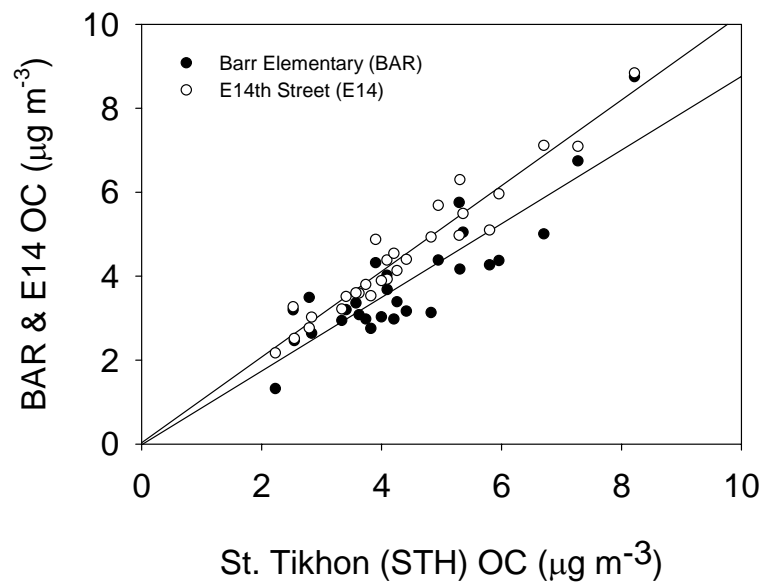
● Gasoline Engines  
○ Smoking Gasoline Engines



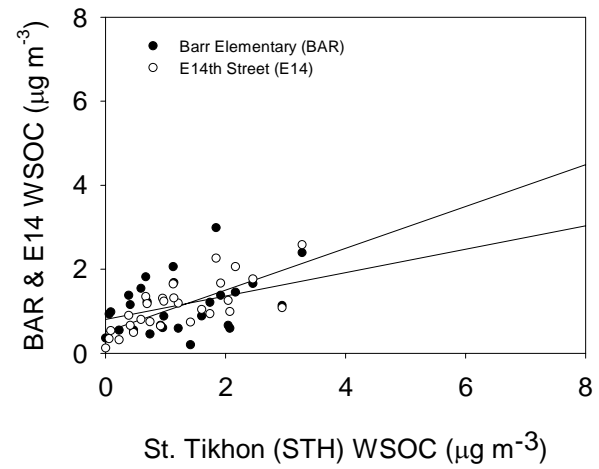
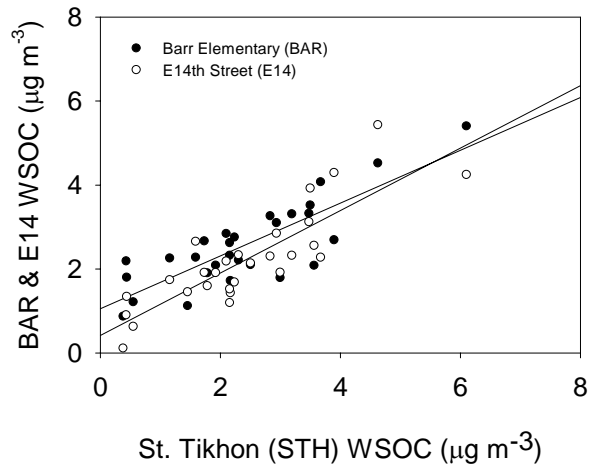
# Summer

# Winter

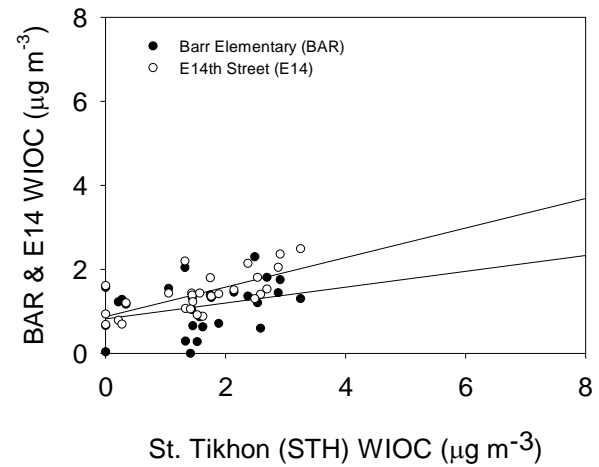
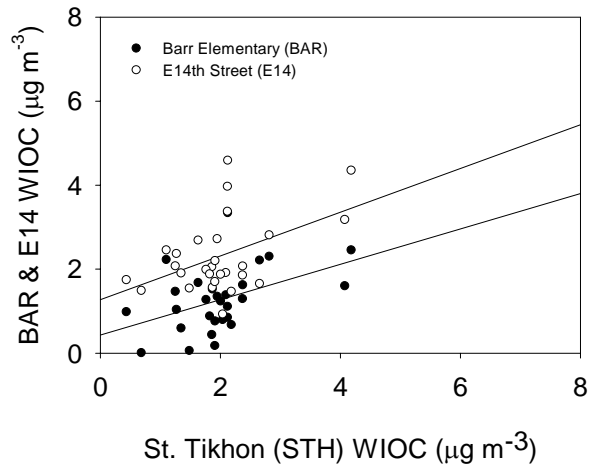
## Organic Carbon (OC)



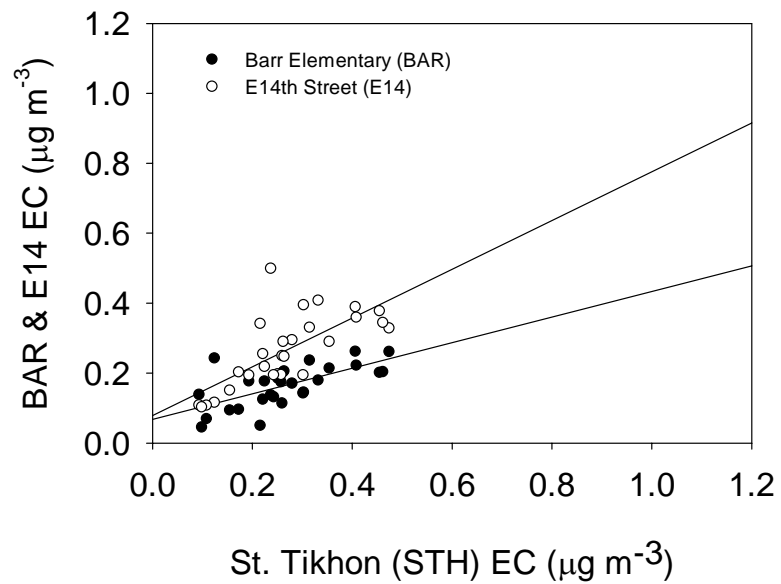
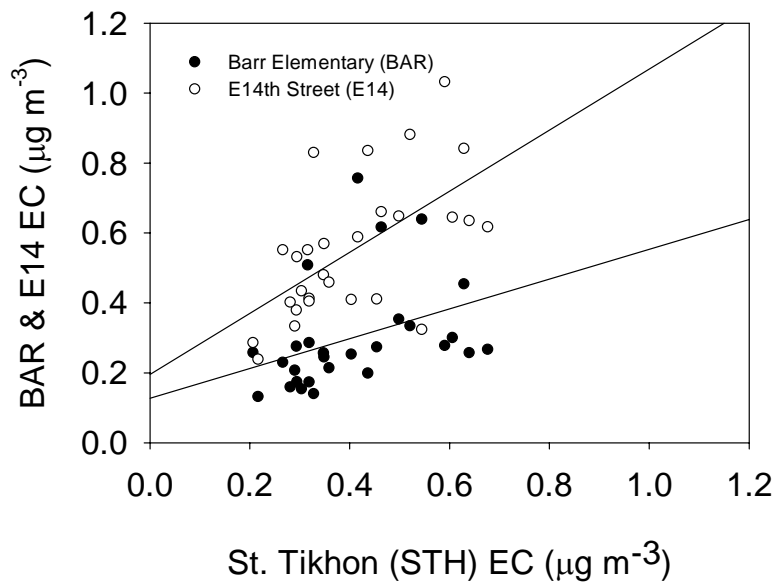
## Water Soluble Organic Carbon (WSOC)



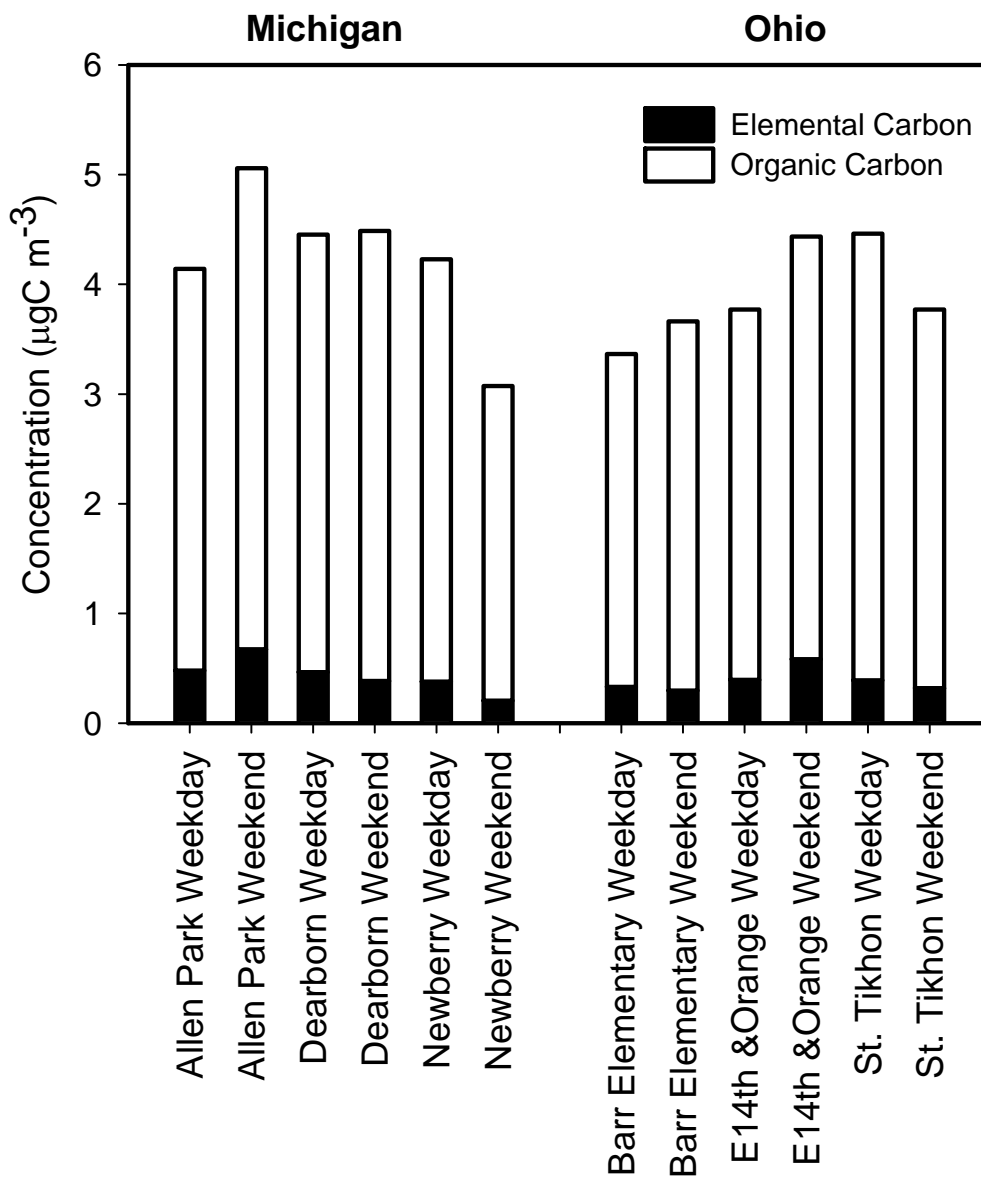
## Water Insoluble Organic Carbon (WIOC)



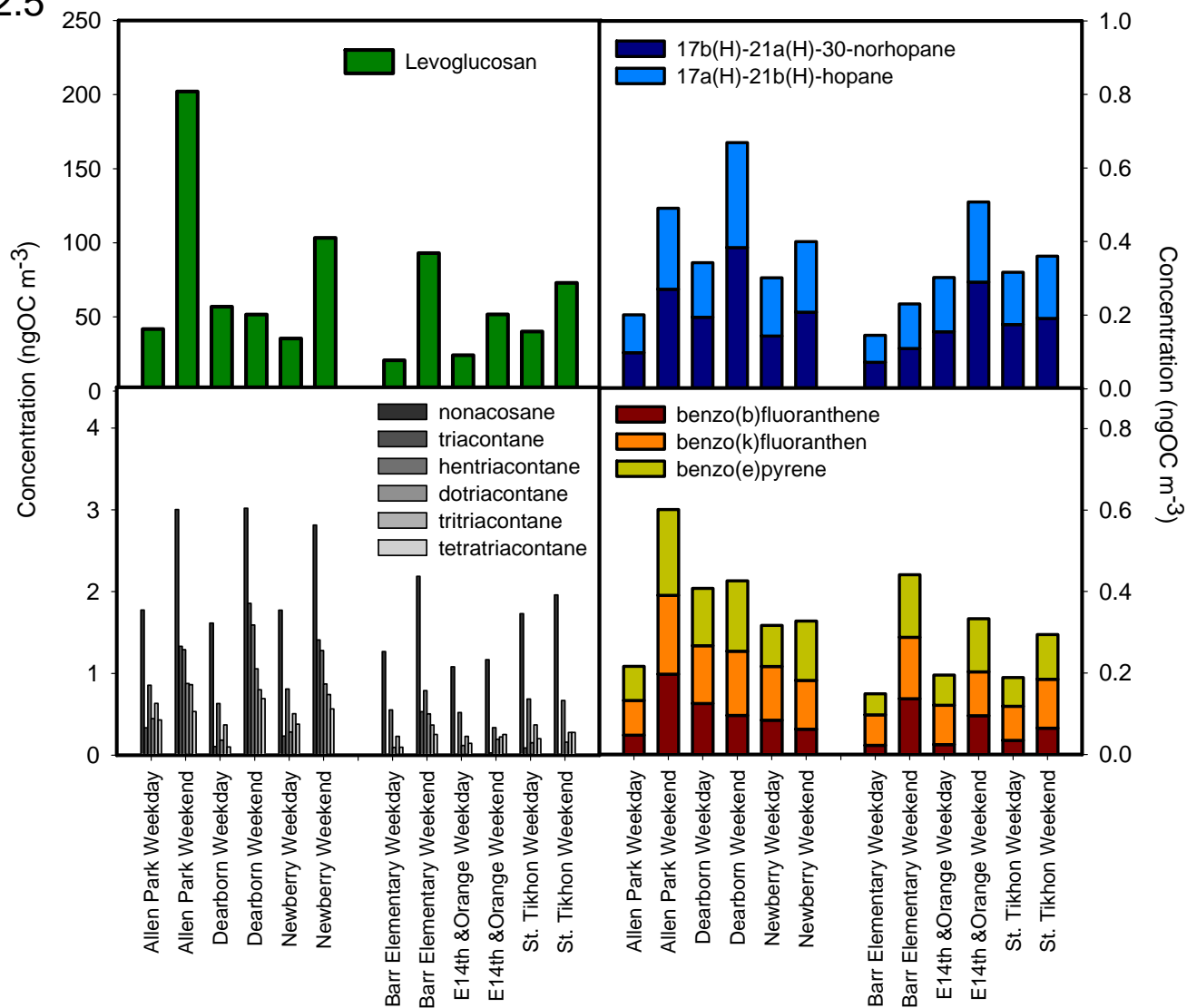
## Elemental Carbon (EC)



# Carbonaceous Aerosol in Composite Samples



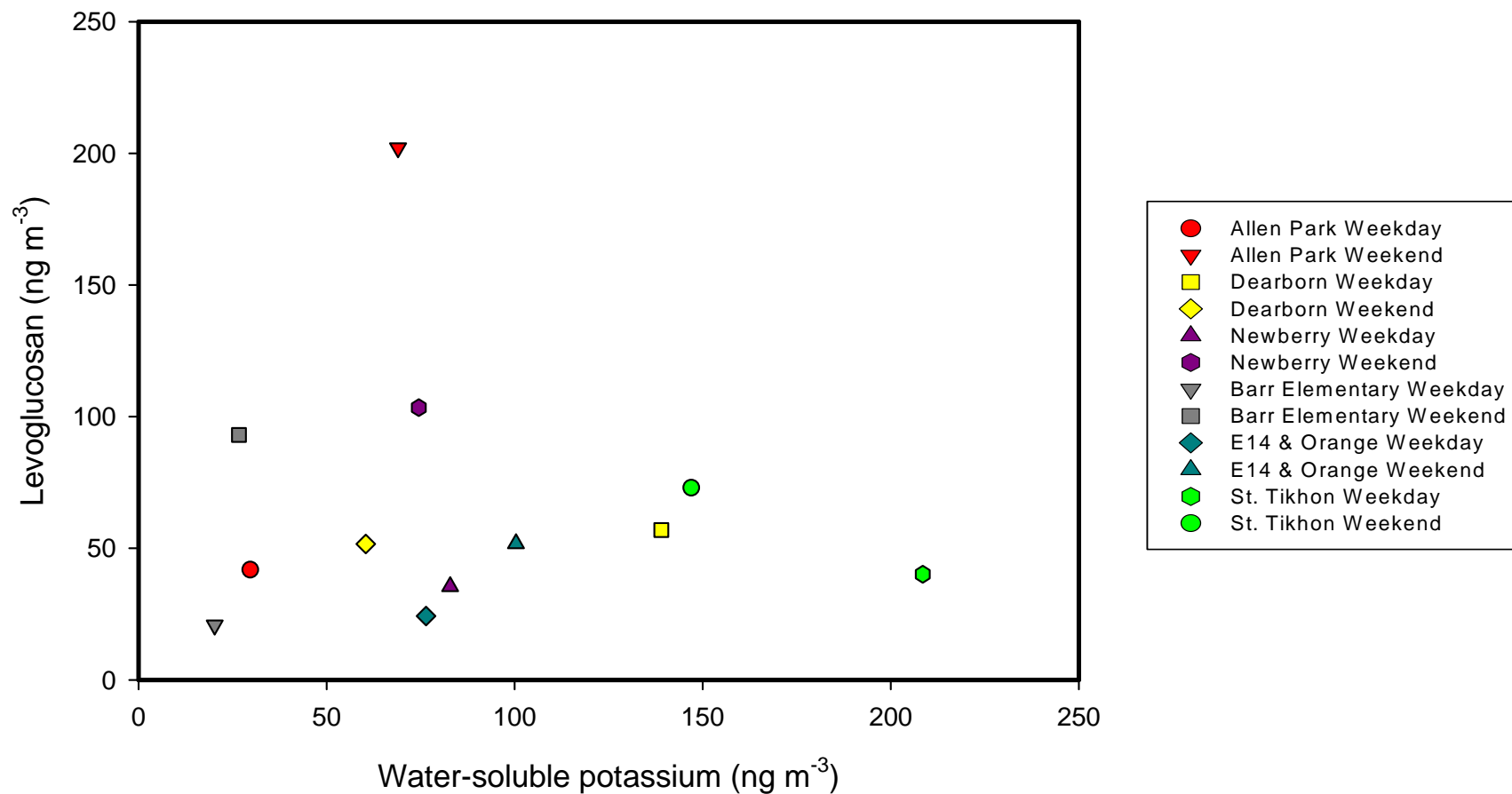
# Organic Molecular Markers in PM<sub>2.5</sub>



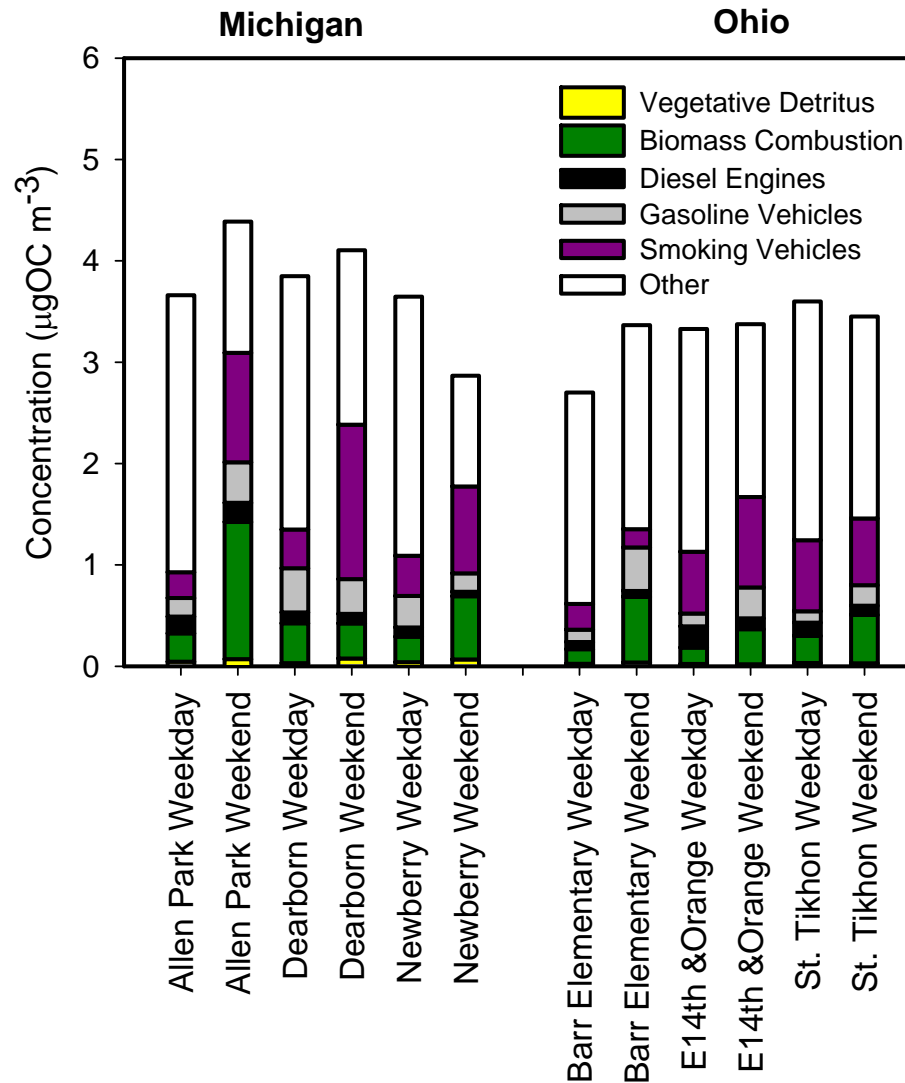
# Summer Intensive Study

## Michigan and Ohio, Summer 2007

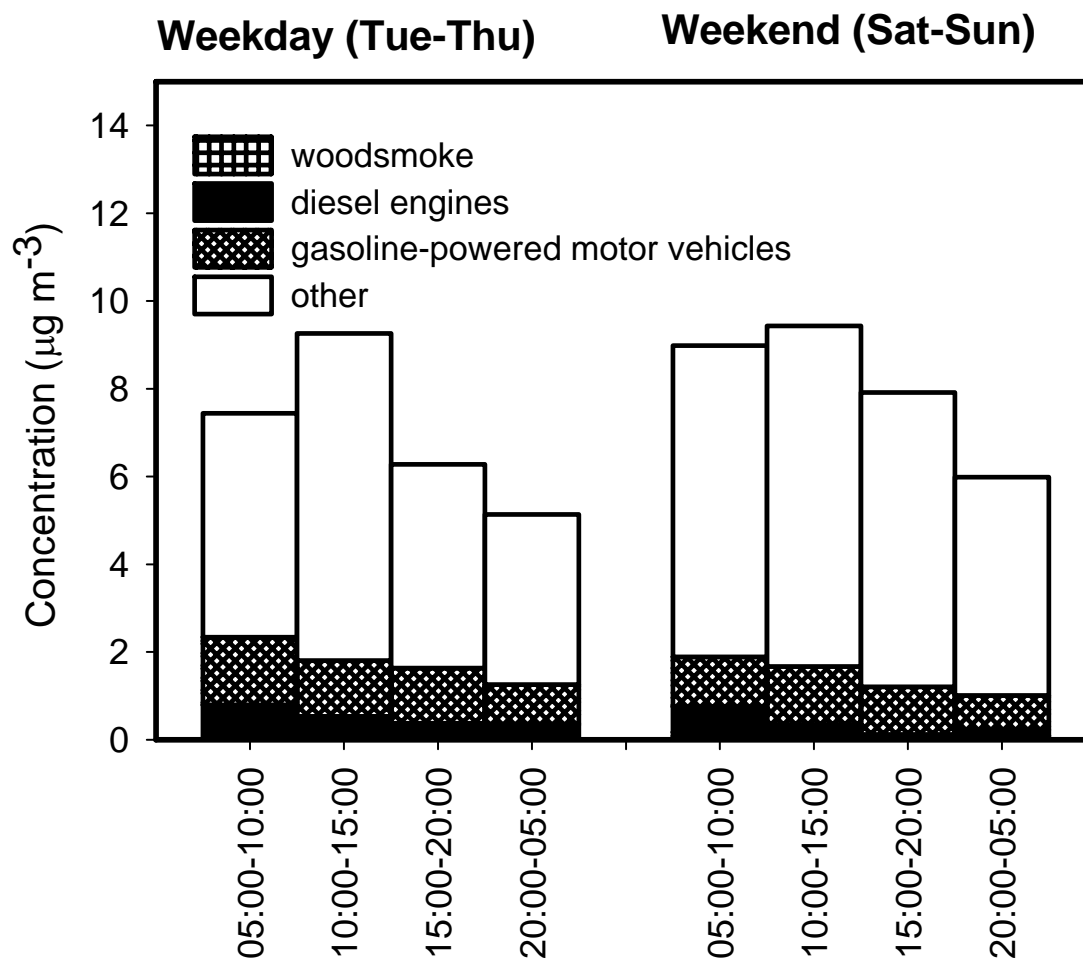
### Comparison of Levoglucosan and Water-Soluble Potassium



# Source Contributions to PM<sub>2.5</sub> Organic Carbon



# Source contributions to PM<sub>2.5</sub> Organic Carbon Riverside, CA, July-August 2005





# Intensive Conclusions

- WSOC regional in nature; similar behaviour to sulfate
- WIOC more local in nature
- Possible point source of WSOC at Dearborn which we are currently addressing

# Intensive Conclusions

- Intensive CMB shows significant spatial and temporal heterogeneity with respect to biomass combustion and motor vehicle emissions
- Significant differences in OC contributions in Midwest versus classically studied LA Basin
  - Significant biomass contributions even in summer at Midwest sites
  - Much greater difference in weekend vs weekday apportionment in Midwest than in Riverside, CA.

# Remaining Tasks

- Complete source apportionment by Chemical Mass Balance Modeling:
  - Development of SOA tracers in CMB
  - Intensive composites; weekend, weekday and monthly
  - Work to deepen understanding of apparent local source impacts
- Evaluate low cost methods for evaluating SOA (WSOC) and biomass burning contributions (WSK) against molecular markers and CMB results
- Sensitivity of previous LADCO CMB studies to midwest vs LA soil profiles (soil profiles completed)



# Acknowledgements

- LADCO
- City of Cleveland Dept of Public Health : Air Quality
- Hamilton County (Cincinnati) Dept of Env. Services: Air Quality Management Ohio EPA (Lorain county and Mingo Junction)
- Michigan Department of Environmental Quality
- Wisconsin State Laboratory of Hygiene