Organic Aerosol Characterization for Health Studies

(Epidemiological and Toxicological Studies)

James J. Schauer, PhD, PE
Associate Professor
University of Wisconsin-Madison

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Motivating Perspective

- There are many “unknown” sources
- Very large variability within source category emissions
- Very important changes in emissions between source and receptor
- Significant advances in atmospheric science over the past decade in terms of measurements, receptor modeling, and mechanistic modeling
- Accountability for improvements in current air quality regulations needs to be measured at centralized monitoring sites

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…in other words

- Atmospheric studies with a source and atmospheric processing perspective
  - Integrate toxicology and epidemiology
  - Atmospheric science provides the context
    - Representativeness
    - Sources
    - Atmospheric processing
- Complimented by changes in sources, exposure assessment, etc…

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Workshop Questions

- What methods are available that are simple and inexpensive enough to deploy in epidemiological studies?
- What can be done to improve the availability of instrumentation to the health science community?
- What kind of comparability is found among different methods of organic measurement?
- What needs to be done to characterize organic compounds and determine their origin?
- How can we get more information on organic markers from existing sampling networks?
- How does carbon abundance vary in different particle size fractions?
- How can we bridge the gap between fresh emissions and aged ambient organic aerosol?

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Reworded Question

- How can we better infuse atmospheric science tools into health studies?
  - Need to stop asking: "What are the best tracers and how much does it cost to measure them"
  - The optimal measurements for source apportionment studies, toxicological studies, and epidemiological studies are not the same
  - The optimal measurements for different types of source apportionment studies are not the same
  - Need to better exploit data analysis tools

General Comments

- We should not overlook the linkages between organic aerosols and inorganic ions and metals
  - Sources, atmospheric processing, and toxicity
- We should think about the physical and chemical processes of exposure and dosage in the selection of characterization tools
- What we measure needs to be driven by what questions we are asking
  - OC and EC apportionment
  - Quantifying secondary sources and processing
  - Biologically relevant components of OC and EC
  - Sources of biologically relevant components

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Categories of Measurements

- Low Specificity – Low Cost
  - $30-$60 per sample
- Real Time Low Specificity – Medium Costs
  - Considerable capitol and field operation costs
- Medium Specificity – Medium Costs
  - $150-$250 per sample
- High Specificity Measurements – High Costs
  - $500-$800 per sample
- Special Study Measurements – Limited Availability
  - Generally high cost measurements that require considerable data analysis for interpretation

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Low Cost – Low Specificity

- Examples
  - Elemental and Organic Carbon (ECOC)
  - Thermal Evolution Fractions
  - Water Soluble Organic Carbon (WSOC)
  - Simply Bioassays
- Reasons for Low Specificity
  - Emitted from Many Sources
  - High Variability within a Source Category
  - Not Conserved in the Atmosphere
- Data analysis tools can increase specificity

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Low Cost Bioassay Example: Micro-Macrophage Assay

- 24-hour low volume PM2.5 samples collected on 47mm Teflon Filters
- Half of the filter extracted in 900 µL
- Filtered through 0.2 µm filter to remove bacteria and/or particulates
- Leaches were combined with 10X salts/glucose media and used for exposure
- Rat Alveolar Macrophage (NR8383) Bioassays:
  - Formation of Reactive Oxygen Species (ROS)
  - Cell Viability-(LDH release)

Real Time Low Specificity

- Examples
  - Black Carbon (BC)
  - Elemental and Organic Carbon (ECOC)
  - Water Soluble Organic Carbon (WSOC)
- Structure of real time data provides additional specificity
  - Plume analysis
  - Hour-of-Day
  - Day-of-Week

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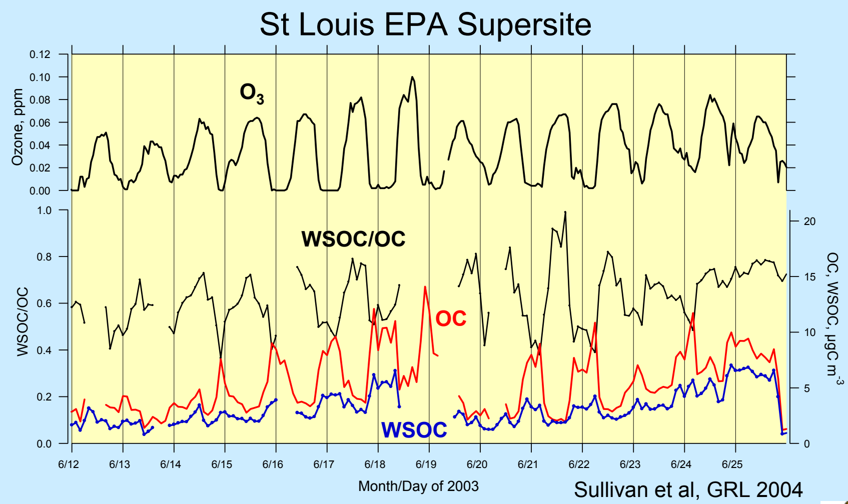
Real Time Measurements of WSOC/OC



Sullivan et al, GRL 2004

Hourly and Daily Patterns of Particle-Phase Organic and Elemental Carbon Concentrations in the Urban Atmosphere

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* 54:823–833

Bae, Schauer, DeMinter, and Turner

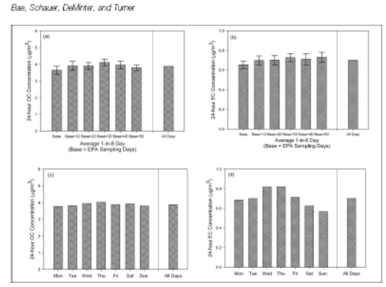


Figure 5. One-in-six and day-of-week average of daily measurement of denuded fine particle concentration at the St. Louis Midwest Supersite for the 2002 data set: (a) One-in-six OC; (b) One-in-six EC; (c) Day-of-week OC; and (d) Day-of-week EC.

Bae, Schauer, DeMinter, and Turner

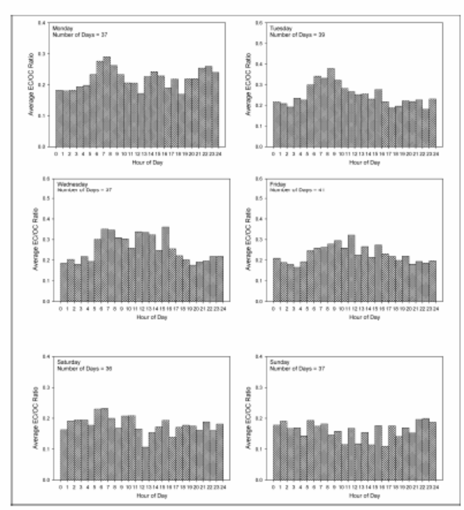


Figure 8. Hour-of-day series of hourly measurement of denuded fine particle EC to denuded fine OC concentration from Friday to Wednesday at the St. Louis Midwest Supersite for the 2002 data set.

Moderate Specificity

- Examples
  - PAH Analysis
  - Thermal Desorption GCMS
    - Non-polar organics – Demonstrated and Available
    - Non-polar and polar organics – Being Demonstrated
  - Low Molecular Weight Organic Acids
  - Simplified solvent extraction GCMS method
- Moderate Specificity
  - Generally highly specific for specific sources but does not provide a comprehensive look at sources
  - Can be biased by “unknown” sources
  - Data analysis tools can increase specificity

Moderate Specificity Example

- 24-hour PM2.5 samples from STL Supersite
  - 730 samples
  - 2 Year Data Set
  - Particle-Phase PAH, Hopanes, Steranes, and wax alkanes
- Insufficient specificity for use as tracers in Chemical Mass Balance (CMB) models without additional constraints
- Used in PMF Models for OC and EC apportionment with trace metals
  - Identify key “unknown” sources
  - Provides information on the specificity of non-polar organic tracers and tracer elements for sources

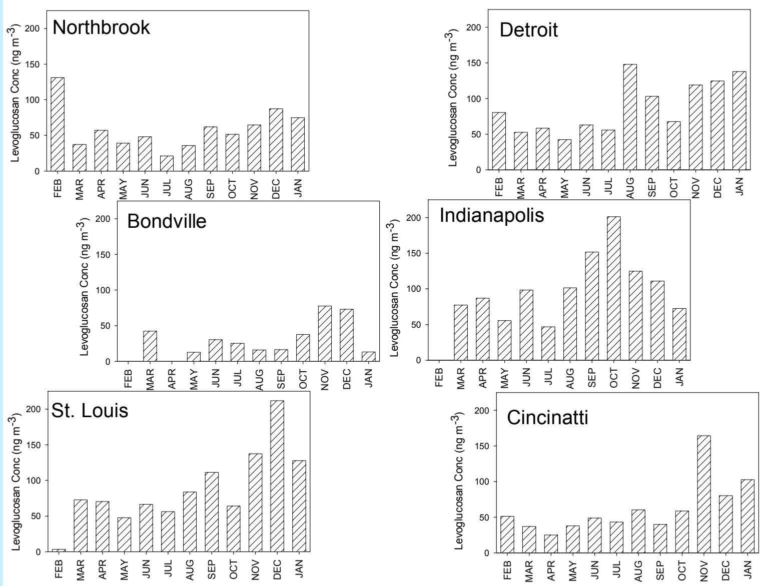
High Cost

- Examples
  - Solvent extraction GCMS – "100 Markers"
  - Secondary Organic Aerosol (SOA) Tracers
  - LCMS Methods for HULIS
- Use for 2-5 year time series is possible but not very cost effective (i.e. 0.5-2.0 Million Dollars)
- Ideal for monthly composites to better understand spatial and seasonal patterns

Example of High Specificity Measurement Studies

- LADCO Midwest Organics Study
  - One year of monthly composites analyzed by for organic tracers that were collected in Six cities
    - Detroit, Indianapolis, Cincinnati, Bondville, St. Louis, and Northbrook
    - Primary source tracers – UW-Madison
    - Secondary Organic Aerosol tracers – US EPA
- Data Analysis
  - Primary source CMB analysis
  - Secondary Organic Aerosol Yield Analysis
  - Multivariate methods

Levoglucosan Concentrations



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Special Study

- Examples
  - Carbon dating (C14)
  - Single compound isotope analysis
  - Analysis of new tracers
  - Single Particle Mass Spectrometers
- Integrated into studies to supplement routine measurements and answer specific questions
- Atmospheric science, chemistry, and data mining research activities

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Health Study Designs

- Traditional approach
  - "If I have X dollars, what can I afford to measure for Y days"
- New Paradigm
  - Hourly and/or daily measurements of low or moderate specificity measurements
  - Multivariate methods to interpret hourly or daily data
  - Complimentary high specificity measurements to validate interpretation of the low and moderate specificity measurements
  - Atmospheric data and analysis used for epidemiological studies and to provide context and guidance for the toxicology studies

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Example 1: 3-10 Year Study

- Real Time Measurements
  - ECOC, WSOC, Water Soluble Ions
- 1-in-3 or 1-in-6 samples
  - ECOC, WCOC, Water Soluble Ions for QA/QC
  - Trace metals
  - Limited GCMS analysis (Moderate)
  - In vitro toxicology studies
- Monthly Composites
  - Full set of molecular markers
  - Secondary organic aerosol tracers
  - In vivo toxicology studies

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Example: 3-10 Year Study

- Data Analysis
  - Epidemiology with EC, OC, WSOC, OC-WSOC, SOA estimated by EC/OC ration method, and Woods Smoke Estimate from WSOC/water soluble K methods
  - Epidemiological analysis with modeled sources of primary and secondary sources of carbonaceous aerosols validated by measurements
  - Analysis of real time data to asses sources
  - Multi-variant analysis of 1-in-6 data to interpret epidemiological metrics
  - CMB analysis of monthly composite data for consistency checks
  - Context for toxicology studies

Conclusions

- Wide range of tools are available for the characterization of carbonaceous aerosols for health studies
- The best tools developed for source apportionment are not necessarily the optimal tools for epidemiological studies
  - Depends on the questions that need to be addressed
- Further advances in the design and implementation need to be done through partnerships between health researchers and atmospheric scientists

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