Potential Sources of Atmospheric Organic Carbon

- Direct anthropogenic emissions
  - Combustion
  - Road dusts
- Biogenic emissions
  - Plant waxes
  - Pollens, bacteria, viruses
- Secondary organic aerosols
  - Oxidation followed by condensation
  - Heterogeneous oxidation of adsorbed organics

Determining Sources of Atmospheric Organic Carbon
Determining Sources of Atmospheric Organic Carbon

• Emission Inventories
  – Biogenics?
  – Secondary organic aerosols?

Questions

• Can organic chemicals such as combustion products be useful tracers of carbonaceous aerosol sources?
• Can specific organic chemicals serve as tracers of secondary organic aerosol production?
• Hint: consider atmospheric residence times relative to transport distances from sources.
Outline

• Application of source apportionment techniques to anthropogenic organic chemicals in the atmosphere
  – PAH sources in Baltimore
  – Aerosol sources over the Indian Ocean

• Recent analytical advances
  – Improved sensitivity → better temporal resolution

*Source Apportionment of Polycyclic Aromatic Hydrocarbons in the Urban Atmosphere: A Comparison of Three Methods*

McDonald & Lassey, III and Joel E. Baker

Statistical Methods for Source Apportionment

Multivariate Techniques
- Principal Component Analysis with Multiple Linear Regression (PCA MLR)
- UNMIX
- Positive Matrix Factorization (PMF)

Ratios
- phenanthrene/anthracene
- indeno[1,2,3-cd]pyrene/elemental carbon

Positive Matrix Factorization

\[ X = Y + E \]
where \( X \) = initial data matrix
\( Y \) = calculated matrix
\( E \) = residuals

\[ Y = GF \]
where \( G \) = source contribution matrix
\( F \) = source profile

PMF Algorithm

Minimize \( "Q" \)

\[ \sum \frac{(E_{ij}/\sigma_{ij})^2}{m \times n} \]

Sample Matrix
\( m \times n \)

Error Matrix
\( m \times n \)

Minimize "Q"

\[ \sum (E_{ij}/\sigma_{ij}) \]

Source Contribution
\( m \times p \)

Source Profile
\( p \times n \)

Daily Source Contribution Derived from PMF

- Oil
- Coal

Daily Source Contribution Derived from PMF

- Diesel
- Gasoline
PAH Source Apportionment Conclusions

- Successfully determined the sources of PAHs using 3 methods
- Major Sources of PAHs in Baltimore Are Identified
  - 26% - 34% Coal
  - 18% - 26% Oil
  - 17% - 22% Mobile Sources
    - Diesel ~ Gas
    - 17% - 40% Unknown/Wood
- Source Contributions Change Seasonally
  - Coal Dominant in Summer
  - Oil Dominant in Winter
  - No Seasonal Trends in Mobile Source

Figure 3. Plots of NHcT Bengal 2 and 3 meteorological regime indeno[1,2,3-cd]pyrene (●), benzo[ghi]perylene (○) and coronene (▲) vs (a) EC, (b) OC, (c) SO4-2 and (d) K+. All PAHs were highly correlated with EC, slightly less for K+ and insignificantly for SO4-2 and OC.
PAH concentrations increase dramatically over the northern Indian Ocean, consistent with enhanced anthropogenic emissions from the Indian sub-continent.

Indeno[1,2,3-cd]pyrene/EC ratios suggest that fossil fuel combustion is the dominant source of the particulate phase PAHs to the Northern Indian Ocean atmosphere.

The PAH/EC ratios suggest that biomass/biofuel combustion is not the dominant source elemental carbon-associated PAHs.


**Next Steps: Improving Temporal Resolution**

Greater Temporal Resolution = Less Analyte

1. Greater Sampling Flow Rate
   a. Increased pressure drops (volatilization)
   b. Similar exposure to oxidants (*in situ* degradation)

2. Increase collection surface area
   Greater collection substrate surface area = greater potential for contaminant interference (high blanks)

3. Increase analytical sensitivity
   Greater potential for blank interferences

Clean sampling/large-volume GC injection/optimized mass spectrometer

TSP 20 ug/m³
1 m³ diesel exhaust

Off-road 1994 diesel

Berner Impactor
12 hours, 60 m³

Hi-Vol Filter
24 hours 720 m³
Final Thoughts

• Secondary organic aerosols are the toughest nut to crack

• Discrete measurements provide ground truthing for remote measurements, but will always be at a coarser temporal and spatial scale

• Orders of magnitude improvements in aerosol analytical techniques provide a significant opportunity

• How do we collaborate?

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