Source Apportionment of Carbonaceous Aerosols using Molecular Markers

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Overview

- Background
- Molecular markers for primary sources
- Development of source profiles
- Overview of source apportionment studies
- Multi-variant methods
- Tracers for secondary organic aerosol
- Method intercomparison studies
- Concluding remarks
Overview: Organic Aerosol

- Carbonaceous aerosols make up a significant fraction of submicron particles in the atmosphere
  - 30-50% in many urban and remote locations
  - Organic Carbon (OC) – Organic Compounds
  - Elemental Carbon (EC) – Black Carbon

- Natural and anthropogenic sources

- Primary and secondary sources
  - Primary – Directly emitted from sources
  - Secondary – Formed in the atmosphere from oxidation of gaseous compounds
Role of Carbonaceous Aerosols

- Climate forcing
  - Elemental carbon – Absorb light
  - Organic Carbon – Scatter light
  - Cloud Condensation Nuclei (CCN)

- Human health
  - Carbonaceous aerosol implicated as important for toxicity and adverse health effects

- Visibility
  - Visibility loss

- Ecosystem impacts
  - Preliminary results suggest deposition to lakes is an important source of carbon in food web
Radiative Forcing (IPCC)

Annual mean radiative forcings from 1750 to 2000

- Halocarbons
- N₂O
- CH₄
- CO₂
- Tropospheric ozone
- Black carbon
- Mineral dust
- Aviation-induced
  - Contrails
  - Cirrus
- Solar
- Land-use (albedo)
- Indirect aerosol effect
- Stratospheric ozone
- Sulphate aerosols
- Organic carbon
- Biomass burning
Measurement of Aerosols

- Historically, chemical measurements of aerosols performed on filters.
- Collection of aerosols are different than the collection of particles from water:
  - Filtration has high efficiency for all sizes.
  - Size segregation done before filtration.
  - Exploit impaction.
- Emergence of real time and semi-continuous methods over the past 10-15 years.
Traditional Chemical Analysis

- **Mass**
  - Gravimetric Determination
- **Secondary Ions**
  - Sulfate, nitrate, and ammonium ions
- **Elemental and Organic Carbon (ECOC)**
  - Several different methods – critical issue
- **Trace metals**
  - XRF analysis provides tracers for crustal materials
helium 2% oxygen

900 °C temperature

laser

calibration peak

FID signal

helium 2% oxygen
Advances in Chemical Analysis

Advanced Chemical Speciation

- Organic Compound Speciation
  - Focus on talk

- Trace Metals
  - ICPMS techniques for trace elements
  - Metal speciation

- Real Time Measurements
  - Aerosol Mass Spectrometers
  - Real time instruments for aerosol species
    - OC, EC, sulfate, nitrate, ions, specific metals
Source Attribution

- A critical question in many locations around the world is to understand the sources of particulate matter in the atmosphere.
- Very large temporal and spatial variability
  - Need representative apportionments
- Very difficult to accurately estimate the inventory of emissions
- Major advances in source apportionment over the past 10-15 years
Source Apportionment Approaches

- Two approaches to assessing the impact of air pollution sources on atmospheric PM concentrations:
  - Emissions inventories and transport models
    - Require spatially resolved “Emissions Inventory”
    - Require models of atmospheric transport
    - Have predictive power to assess the impact of control
    - Well suited to address secondary aerosols
  - Receptor based models
    - Require source fingerprints
    - Require a basic knowledge of sources
    - Do not require a spatially resolved “Emissions Inventory”
    - Ideal for locations were “Emissions Inventories” are not available
- Ultimately we need good agreement by both types of models to assure a accurate understanding of the contributions of different source
Receptor Modeling Approaches

- Utilize “features” or “characteristics” of the pollutants to identify and quantify source contributions
  - Forensic analysis

- Two major approach
  - Factor Analysis
    - Uses temporal changes in particulate matter concentrations to identify “factors,” which are related to sources
    - Requires large data sets
  - Chemical Mass Balance
    - Determine the source “fingerprints” that can re-create the composition of particulate matter measured in the atmosphere
    - Requires measurement of the detailed feature of particulate matter

- Again, agreement between these two approaches would give a high level of confidence in the results
A Simple Example

- Mix together three drinks
  - Milk
  - Diet Cola
  - Lemonade

- Chemical Mass Balance
  - If we know the lactose, fructose, and Vitamin C content of the Milk, Diet Cola, and Lemon Aid
  - If we measure the concentration of lactose, fructose and Vitamin C in the mixture
  - Use this information to calculate the contributions of the three drinks to the mixture

- Factor Analysis Approach
  - We assume that we do not know the composition of the drinks
  - We have many different mixtures of the three drinks
  - Measure sodium, calcium, potassium, and iron in all of the mixtures
  - By understanding the correlation of the four elements in the mixtures, we can identify “factors” that can make up the mixtures
  - Since we know milk is high in calcium, we know the factor with high calcium is milk
Molecular Marker Source Apportionment

- Hundreds of particle-phase organic compounds have been measured in source emissions and in the atmosphere
  - Gas Chromatography Mass spectrometry (GCMS)
- Not all compounds of these compounds can be integrated into tracer models models

Critical Issues
- Atmospheric stability
- Source completeness
- Representative source profiles
- Analytical accuracy and precision
Molecular Markers

- **Molecular Markers**: Particle-phase organic compounds present in the emissions from an air pollution sources that contain unique information about a source category.

- There is a rich knowledge of molecular markers that can be used to understand the contributions of primary sources to the organic aerosol and PM concentrations.

- Source apportionment models that use molecular markers have higher specificity and accuracy than traditional trace element based apportionment models.
Examples of Molecular Markers

- Levoglucosan
- Cholestanol
- Pimaric Acid
- Hopanes
- Steranes
- Picene
Goals of Source Characterization

- **Emission Factors**
  - Often based on regulatory methods
  - Often limited to regulated pollutants
  - Needed for emission inventory

- **Emission Fingerprints**
  - Advanced chemical analysis
  - Needed for receptor models

- **Process Studies**
  - Investigates the fundamentals of pollution formation
  - Supports the development of control technologies

- **Collection of emissions material**
  - Biological and physical characterization
Sources Tested

- Gasoline-Powered Vehicles
- Diesel Trucks
- Food Cooking Operations
- North American Firewood Combustion
- Indian Sub-Continent Biomass
- Coal Combustion – Stoker and Pulverized Coal
- Fuel Oil Combustion
- Resuspended Road Dust and Soil Debris
- Motor Vehicle Brake and Tire Wear
- Vegetative Detritus
- Cigarette Smoke
Coal Combustion

- The particulate matter emissions from coal are very dependent on the properties of the coal combusted and the combustion process.
- In many regions of the world coal combustion is a major source of energy and impact on air quality is significant.
- OC and EC emissions from coal combustion have not been well characterized compared to other important carbonaceous aerosol sources.
PM$_{2.5}$ mass fractions of coal combustion emission

EC   OM(1.2*OC)   Others

Industrial Boilers

Residential Stoves
Mass Fractions of Organic Compound in PM$_{2.5}$

- n-Alkanes
- Aliphatic acids
- Aromatic acids
- PAHs
- Others

Industrial Boilers
- Bituminite Coal
- Brown Coal
- Mixed Coal
- Anthracite Coal
- Sub-bituminite Coal
- Bituminite Coal

Residential Stoves
- Coal Briquette (Lab test)
- Coal Briquette (Field test)
Atmospheric Tracer Studies

- Great interest in understanding sources of atmospheric particulate matter in developing countries
  - Human Health
  - Regional Climate Forcing
- Typically, very limited information exists on emissions inventory in developing nations
- Molecular marker tracer methods have been developed for source attribution and largely employed in parallel to mechanistic models in developed countries
- Molecular marker based source apportionment models can provide efficiently and effectively be used to understand sources of PM in developing nations
Midwestern USA Organics Study

- Regional air quality planning organization (RPO) supported source apportionment study for the Midwestern USA
- Daily PM2.5 Samples collected every 6\textsuperscript{th} day for a year at six locations
- Daily samples measured for bulk chemical composition
- Monthly composites analyzed for molecular markers and used for source apportionment
Chemical Mass Balance (CMB) Model

\[ x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \]

- Fits source profiles (molecular markers and mass) to corresponding receptor concentrations
- Source profiles, receptor concentrations and uncertainty estimates are inputs to the model
- Source contributions to the total mass, molecular markers and uncertainties are outputs

**Pros**

- Primary receptor model for past 20 years

**Cons**

- Difficulties in obtaining a representative source profile that is site and time dependent
Bondville, IL

OC Contribution ($\mu$g m$^{-3}$)

February
March
April
May
June
July
August
September
October
November
December
January
February

Resuspended Dust
Vegetative Detritus
Biomass
Biomass
Other PAH
Diesel
Gasoline
Smokers
Mobile
Other
OC Contribution (µg m$^{-3}$)
MILAGRO Experiment – Mexico City

Urban site PM$_{2.5}$

Peripheral site PM$_{2.5}$

Concentration (ng m$^{-3}$)

Mar 17
Mar 18
Mar 19
Mar 20
Mar 21
Mar 22
Mar 23
Mar 24
Mar 25
Mar 26
Mar 27
Mar 28
Mar 29
Mar 30

Levoglucosan

17α(H)-22,29,30-Trisnorhopane
17β(H)-21α(H)-30-Norhopane
17α(H)-21β(H)-Hopane
Results

Source contribution to OC (µg C m⁻³)

Urban site PM$_{2.5}$

Peripheral site PM$_{2.5}$

Real-time WSOC (µg C m⁻³)

CMB other + water-soluble woodsmoke (µg C m⁻³)

<table>
<thead>
<tr>
<th>y = 1.03x</th>
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<tbody>
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<td>R² = 0.75</td>
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Legend:
- Yellow: Vegetative detritus
- Black: Diesel engines
- Orange: Gasoline vehicle
- Purple: Smoker vehicle
- Green: Woodsmoke
- Green: Other

Mar 17
Mar 18
Mar 19
Mar 20
Mar 21
Mar 22
Mar 23
Mar 24
Mar 25
Mar 26
Mar 27
Mar 28
Mar 29
Mar 30
Multi-Variant Methods

- There are some potential concerns about chemical tracer models that compare source profile to atmospheric concentrations
  - Representative source profiles
  - Impact of “Unknown” sources
  - Stability of tracers in the atmosphere
- Issues can be partially addressed with the use of multi-variant methods
  - Eliminate quantitative use of source profiles
  - Requires much larger data sets
St. Louis Supersite

- Located in East St. Louis, Illinois
- Samples collection April 2001 through July, 2003
  - Daily bulk chemistry
  - Molecular markers measured on 120 samples
- Co-located with a broad range of integrated and semi-continuous aerosols measurements
Positive Matrix Factorization (PMF) Model

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$

- With $p$ factors, resolves **source contributions** and source profiles to fit receptor concentrations
- Receptor concentrations and uncertainty estimates are inputs to the model
- **Source contributions** and molecular marker profiles are outputs

**Pros**

Source profiles are not needed

**Cons**

Factors in the model are not necessarily sources and can be difficult to interpret
PMF Source Contributions

The graph illustrates the contributions of various sources to PMF (Positive Matrix Factorization) source analysis, measured in OC (Organic Carbon) concentration (µg m⁻³). Sources include:

- Winter Comb 1
- SOA
- Point Source 1
- Resuspended Soil
- Wood Comb
- Point Source 2
- Mobile
- Winter Comb 2
- Factor 9
- Factor 10
- Residual

The bars represent different factor solutions:

- 7 Factor Solution
- 8 Factor Solution
- 9 Factor Solution
- 10 Factor Solution
Wood Smokes

PMF results demonstrate that the source profile and apportionment results from CMB are consistent with the PMF profile.

**Graph 1:**
- **Slope:** 0.0058 ± 0.00030
- **Intercept:** -0.033
- **R²:** 0.785

**Graph 2:**
- **Slope:** 0.76 ± 0.045
- **Intercept:** -0.032
- **R²:** 0.735

**Legend:**
- ○ Spring
- ★ Summer
- ▼ Fall
- □ Winter
PMF results demonstrate that the source profile and apportionment results from CMB are consistent with the PMF profile.
Resuspended Soil

- Silicon is a good tracer for road dust as used in CMB
- Source profile used is CMB is not consistent with the PMF profile
- Demonstrates need for regional dust profiles
SOA Tracers

- Laboratory reaction chambers used to simulate the formation of SOA in the atmosphere (Smog Chambers)
  - Single or multiple precursor gases examined
  - Chemical analysis of particulate matter formed in the chambers used to identify tracers for SOA

- Historically, there has been large discrepancies between smog chamber studies and atmospheric studies

- Several reasons have been proposed
US EPA SOA Yield Studies

- 2-methylglyceric acid
- 2-methylthreitol
- 2-methylerythritol

- Toluene
- 2,3-dihydroxy-4-oxopentanoic acid
- Beta-Caryophyllene
- Beta-Caryophyllinic acid
US EPA Yield Studies

alpha-pinene

3-isopropylpentanedioic acid

3-acetylpentanedioic acid

2-hydroxy-4-isopropyladipic acid

3-acetylhexanedioic acid

2-hydroxy-4,4-dimethylglutaric acid
SOA Tracer Method

- Operation of smog chamber as close as possible to atmospheric conditions
- Measured SOA tracers and OC yields
  - Calculated yield of OC per yield of tracer
- Measured SOA tracers in atmosphere
  - Calculated contribution of SOA to OC in atmosphere

- Several issues of concern
  - Stability of tracers
  - Gas-to-particle partitioning of tracers and OC
SOA Yield versus PMF and CMB
Midwest Organic Study

![Graph showing SOA Concentration (µg m⁻³) with data points for Detroit, Cincinnati, East St. Louis, Northbrook, and Bondville. The graph includes lines for CMB SOC, PMF SOC, and Tracer Yield SOC, with peaks and troughs indicating variations throughout the months from March to February.]
Tracer Yield SOC (µg m⁻³, Lewandowski et al., 2008)

PMF SOC (µg m⁻³, This study)

Slope: 1.01 +/- 0.07
Intercept: 0.94 +/- 0.097
Adjusted R²: 0.763 (n=58)

Detroit
Cincinnati
East St. Louis
Northbrook
Bondville
Outstanding Questions/Issues

- Stability of Tracers (Robinson et al. 2006)
- Importance of Semi-Volatile OC on SOA productions (Robinson et al. 2007)
- Sensitivity of CMB to source profiles
  - Mobile sources - Lough et al. (2007)
  - Biomass – Sheesley et al. (2007)
  - Resuspended soil – In progress
Conclusions

- Continue to need to better understand sources of particulate matter in many regions of the world
- Molecular makers can quantitatively be used in source apportionment models
  - Consistency in tracer (CMB) and multi-variant models (PMF)
  - Consistency in SOA yield, CMB and PMF
- Tools can readily be used around the world
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