How Can Organic Tracers and Source Apportionment Modeling be Used in Health Studies?

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research and development

Science Question

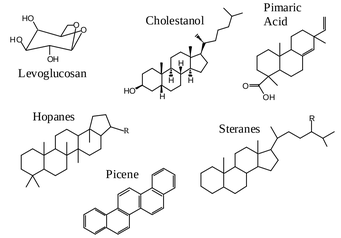
What chemical markers can be used to uniquely identify particle sources of interest to health studies?

Background

Considerable work has been done in the organic characterization of organic source emissions of such major sources as motor vehicle exhaust, biomass smoke, cigarette smoke, and natural gas combustion. Much of this work has focused on the identification and development of molecular markers, or tracers, which can be used in source apportionment modeling of ambient atmospheric aerosol.

There are increasing opportunities to use organic tracers in epidemiology to explore relationships between emission sources and specific health endpoints.

Organic tracers in personal PM samples can be used to track exposure to emission sources compared to ambient apportionment.



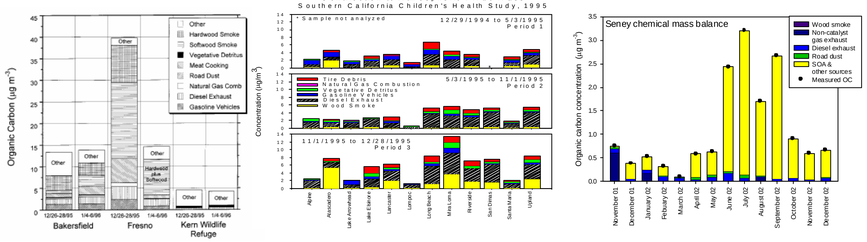


Figure 1: To illustrate the effectiveness of organic tracer techniques and their application under a variety of scenarios, the results of three separate chemical mass balance models are shown above. Figure 1a illustrates a more complete source set where much of the organic carbon has been apportioned to primary emission sources. Figure 1b presents the results from the California Children's Health Study where organic tracers and molecular marker source apportionment techniques were used directly in an exposure study. Figure 1c shows the results of source apportionment at a remote site in Northern Michigan and illustrates the important role that secondary organic aerosol and uncharacterized sources can play in ambient organic carbon concentrations.

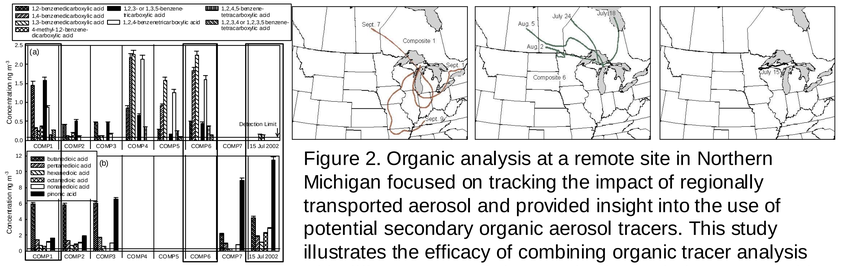


Figure 2. Organic analysis at a remote site in Northern Michigan focused on tracking the impact of regionally transported aerosol and provided insight into the use of potential secondary organic aerosol tracers. This study illustrates the efficacy of combining organic tracer analysis with different types of characterization techniques to provide a more detailed story of the source contributions.

Organic Aerosol Sources	Highly Specific Tracers	Important Fingerprint Features
Natural Gas Combustion		Polycyclic Aromatic Hydrocarbons
Gasoline powered engine exhaust		Hopanes and Steranes Polycyclic Aromatic Hydrocarbons Elemental Carbon
Diesel engine exhaust		Hopanes and Steranes Elemental Carbon
Fuel oil combustion		Hopanes and Steranes Elemental Carbon Nickel Vanadium
Coal combustion – uncontrolled	Picene	Hopanes and Steranes Polycyclic Aromatic Hydrocarbons Elemental Carbon
Biomass burning	Levoglucosan	Resin acids Methoxyphenols
Meat cooking	Cholesterol	Tetradecanoic acid Pentadecanoic acid Hexadecanoic acid Heptadecanoic acid Octadecanoic acid Palmitin Stearin
Vegetative detritus		*n*-Nonacosane *n*-Triacontane *n*-Hentriacontane *n*-Dotriacontane *n*-Tritriacontane
Secondary Organic Aerosol (SOA)	1,2-Benzenedicarboxylic acid Methyl-1,2-Benzenedicarboxylic acid	Not well defined
Cigarette smoke	iso-Nonacosane anteiso-Triacontane iso-Hentriacontane anteiso-Dotriacontane iso-Tritriacontane	
Waste Burning		Not well defined

Current Efforts

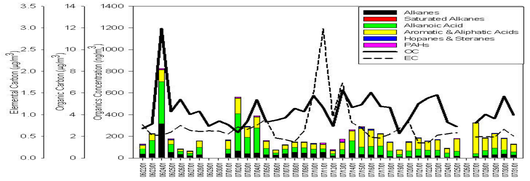
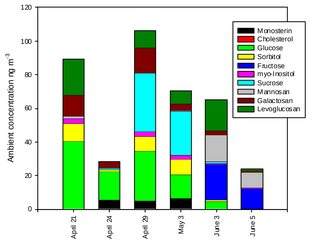


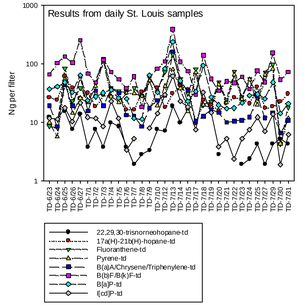
Figure 3. At the St. Louis Supersite, there are efforts underway to characterize 2 year's worth of daily samples for organic tracers. These results can then be combined with epidemiology efforts which have been operating concurrently in the St. Louis area.



A new method is currently being developed for a cost-effective thermal desorption gas chromatography mass spectrometry (TD-GC-MS) technique for the analysis of semi-volatile and particle-phase organic compounds in atmospheric and source samples. By including more polar compounds, such as simple carbohydrates and secondary organic products, a more comprehensive picture of organic aerosol emerges. These tools will result in the broader application of the analysis of particle-phase and semi-volatile organic compounds for air quality studies, health studies, source characterization, and regulatory monitoring and will ultimately enhance efforts to understand the sources of atmospheric fine particulate matter, health impacts, degradation of visibility and climate change, as well as aid regulatory efforts to mitigate these adverse effects.

Polar compounds which merit additional study and potential analysis by TD-GCMS			
Compound Class	**Method of Detection**	**Example Reference**	**Possible SOA**
Aliphatic diacids	derivatization + GCMS	(Kalberer et al. 2000)	yes
Monoglycerides	silylation + GCMS	(Nolte et al. 1999)	no
Mono and Disaccharides	silylation + GCMS	(Nolte et al. 2001)	no
Oxocarboxylic acids	silylation + GCMS	(Jang and Kamens 2001)	yes
Sugar anhydrides	silylation + GCMS	(Nolte et al. 2002)	no
Steroids	silylation + GCMS	(Nolte et al. 2001)	no
Triterpenoids	silylation + GCMS	(Nolte et al. 2002)	no

Figure 5. Parallel to the polar organics work on the TD-GCMS, analysis of non-polar organic tracers using a similar, non-derivatization method on the TD-GCMS is also underway. Because of the reduced organic carbon loading requirements, this technique is ideal for the analysis of personal exposure samples. These samples tend to have much lower carbon loadings than ambient samples, due to the operating conditions of the personal samplers. By lowering detection limits, this allows the expansion of organic tracer analysis into the personal exposure realm.



Future Directions

(1) Some research has shown a relationship between the polar organic fraction of aerosols and toxic effects for in vitro tests. This indicates the importance of further characterization and apportionment of the ambient polar organic fraction using techniques such as advanced derivatization combined with GCMS and TD-GCMS analysis. Quantitative tracers need to be determined for urban and rural secondary organic aerosol, which can be used in source apportionment modeling.

(2) Additional work needs to be done to improve detection limits to enable analysis of samples from remote locations and samples, such as personal exposure samples, which have been collected at low loadings. This type of work can be done with TD-GCMS analysis or the larger injection volumes with current methods.

(3) Due to increased interest in combining organic tracer work with epidemiology studies, techniques such as TD-GCMS, which increases sample throughput, and real-time organic analysis instruments need to be developed to match the growing data needs.

Source to Health Outcome