

Chemical Composition of Fine Particulate Matter from Urban and Regional Background Locations in New York State

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Project Overview

The primary objective of this research is to improve the current understanding of organic compounds associated with fine particles in New York State. This work builds upon the "Sampling and Analysis of Acidic Organic Compounds in the New York City Area" (SOAP) air monitoring and source apportionment project supported by the Northeast States for Coordinated Air Use Management (NESCAUM) and NYSERDA. As part of SOAP, NY City area ambient fine particulate matter (PM_{2.5}) was collected over 5/2002 through 5/2003. Tasks that have been completed or are in progress for this NYSERDA grant are summarized below. Research highlights are presented here.

Task 1. Analysis of acidic organic compounds in SOAP fine PM samples

Task 2. Measurement of acidic organic mass fraction and organic neutral mass fractions

Task 3. Quantify ambient concentrations of known secondary source markers

Task 4. Identify additional potential secondary source markers

Task 5. Add source-apportionment expert to project in an advisory/data interpretation role

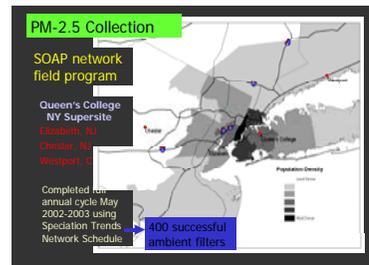
Task 7. Measure the ambient abundances of organic marker compounds and EC, OC, and TC at Bronx, NYC and Pinnacle State Park, NY

Task 8. Determine updated emission profiles for light-duty diesel and gasoline-powered vehicles and mass balance relationships for vehicle markers (hopanes and steranes) to EC and OC mass emission rates

Task 9. Investigate the source(s) of extremely high CPIs for C12 to C30 *n*-alkanoic acids present SOAP ambient fine particle samples to determine the contribution of seed oil emissions from commercial and domestic food preparation activities (fast food frying operations)

Fine PM_{2.5} Sampling

The fine air sampling network sites operated as part of SOAP 2002-2003 were co-located with STN air monitoring sites in NY, NJ and CT operated by the respective state air monitoring agencies. Two new sites (Task 7) began operation, in September 2005, and will continue through August 2007. The two sites are Bronx, NYC and Pinnacle State Park (Addison, NY), called "SOAP-NY". Differences in the ambient concentrations of primary emissions emitted from motor vehicles, wood smoke, cooking activities, and from natural vegetation sources will be compared at the two sites. In addition to individual molecular markers, the organic complex mixtures associated with the fine particles will be evaluated for non-polar and polar constituents. This step will provide greater insight on amounts of "fresh" primary organic aerosol and "aged" secondary aerosol at the urban and rural SOAP-NY sites.



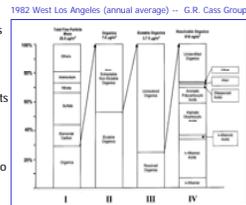
Pinnacle State Park, air quality monitoring site operated by the SUNY Albany and NYDEC. Rutgers Tisch 2- and 4-Channel co-located samplers collect fine particle samples. Pinnacle is upwind of the NY metropolitan area and represents regional background. (July 2005)

Analysis of Atmospheric Organic Compounds

In this project, we use a variety of chemical analysis methods to identify the organic carbon fraction of the fine particulate samples. Molecular level (GCMS, LCMS), bulk carbon (EC, OC), and properties associated with the GC-elutable complex mixtures (GC-FID) are key analytical measurements needed to develop Material Mass Balances for the fine PM mass. Molecular markers are used to apportion the organics mass and total PM mass to the emission sources.

Carbon Chemical Mass Balance

- Accounts for various forms of organic carbon
- Multiple analytical measurements
- Monitor variations in fine aerosol composition from bulk C to molecular organic C



Molecular Markers

Alkanes	PAHs	hopanes	Other
<ul style="list-style-type: none"> pentacosane n-hexacosane n-heptacosane n-octacosane n-nonacosane n-tricosane n-hentriacontane n-dotriacontane antiso-triacontane iso-hentriacontane antiso-hentriacontane iso-dotriacontane antiso-dotriacontane iso-tritriacontane phytane pristane 	<ul style="list-style-type: none"> benzo[<i>b</i>]fluoranthene benzo[<i>k</i>]fluoranthene benzo[<i>a</i>]pyrene indeno[1,2,3-<i>cd</i>]pyrene cd[<i>fluoranthene</i>] retene coronene 	<ul style="list-style-type: none"> nonanal triovalganol galactosan marrisanol cholesterol 7H-benz[<i>b</i>]lanthracen-7-one benz[<i>a</i>]anthracene-7,12-dione 	<ul style="list-style-type: none"> 21 <i>n</i>-alkanoic acids (with C₁₀ to C₃₀) 10 aliphatic dicarboxylic acids (C₁₀ to C₂₀) 1 aromatic polycarboxylic acid cis-9-<i>n</i>-octadecenoic acid

Authentic standards for 63 marker cmpds measured in ambient composites

Sources of Organic Fine Particles

Many sources contribute to the organic mass fraction of urban and rural fine particles. Emission source profiles and known emission inventories help with the identification and apportionment of the organic aerosol and fine particle mass once the molecular level and bulk level analyses are completed.

Urban Sources of Fine Carbonaceous Particles

Obtained from known fine particle emissions inventory

- Oil-fired boiler
- Autos (non- and catalyst-equipped)
- Heavy-duty diesel trucks
- Home heating furnace
- Home fireplace
- Roofing tar pots
- Road dust
- Tire dust
- Brake dust
- Cigarette smoke
- Meat cooking operations
- Vegetation (cultivated, native)

Mathematical Models Accounting for Individual Emission Contributions from Discrete Urban Sources

NYS DEC Automotive Emissions Laboratory

This project will improve the emission source profiles for motor vehicles and for cooking activities in the NY airshed. A collaborative effort with the NYS DEC Automotive Emissions Laboratory will contribute updated chemical profiles from vehicles that are undergoing testing at the NYS DEC AEL (*Shida Tang, Collaboration Project Leader, NYS DEC Mobile Sources & Technology Development*). About 12 vehicles were selected to represent the current vehicle fleet composition in the NYS area. Rutgers will be analyzing the fine PM filter samples for known vehicle molecular markers (steranes, hopanes, PAHs, *n*-alkanes). Potential new markers will be sought using GCMS and LCMS chemical analyses.



Suites of common cooking oils, lard, and fats will be investigated by GCMS to identify sources of the distinct *n*-alkanoic acid patterns found in the SOAP 2002-2003 fine PM samples. Commercial and domestic food preparation activities (fast food frying operations) are hypothesized as the likely sources.

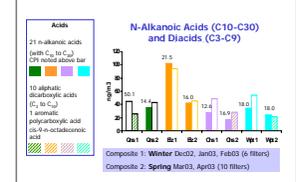


Intermediate School 52, Bronx, NY, air quality monitoring site is operated by the NYDEC (*Dirk Felton, Collaboration Project Leader, NYDEC Bureau of Air Surveillance*). IS52 also is a strategic community-based urban receptor site for the IMPROVE and STN networks. (July 2005)

Results & Discussion

Dominant molecular markers observed in the NY area 2002-2003 fine PM samples are the *n*-alkanoic acids, diacids, *n*-alkanes, steranes, hopanes, and PAHs. Ambient concentrations for these marker compounds have been provided to collaborators at the U.S. EPA NERL (S. McDow, G. Norris) for input into mathematical models such as CMB version 8 for source apportionment.

NYC Area Molecular Markers



Proportions of the acidic and neutral compounds comprising the PM complex organics were determined. In some SOAP 2002-2003 samples, the highest ambient concentrations of organic acids were present during winter. This indicates organic acids are emitted also from primary emission sources in the NYC area, and may dominate seasonally over the contributions of organic acids due to photochemical reactions in the atmosphere. Photochemical processing resulting in secondary organic aerosol (SOA), likely dominates in summer and early fall and is expected to differ at the NY rural and urban sites.

Seasonal Distribution of GCFID Organic Fractions Urban Queens, NY

Elutable Organic fractions are 11-48% of the PM_{2.5} mass

