PROJECT UPDATE

December 2005

New York State Energy Research and Development Authority

Environmental Monitoring, Evaluation, and Protection Program

Chemical Composition of Fine Organic Particles from Urban and Regional Background Locations in New York State

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Project Location

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Keywords

- Emission sources
- Fine particles ($PM_{2.5}$)
- Molecular markers
- Polar organic compounds
- Photochemical reactions

PROJECT FOCUS

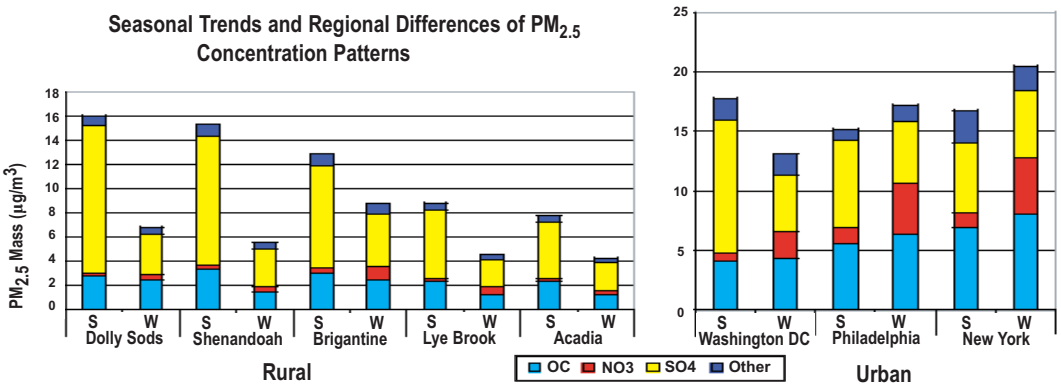
The primary objective of this research is to improve the current understanding of organic compounds associated with fine particles in New York State. This work builds upon a current air monitoring and source apportionment project supported by the Northeast States for Coordinated Air Use Management (NESCAUM) that measures fine particulate matter ($PM_{2.5}$) in the New York City area. Additional chemical measurements of the molecular markers and acidic organic compounds in $PM_{2.5}$ aim to improve estimates of fine carbon particle source contributions in the New York City (NYC) metropolitan airshed over an annual cycle.

CONTEXT

In July 1997, motivated by concerns about the adverse health effects of particulate pollution, the U.S. Environmental Protection Agency proposed a new National Ambient Air Quality Standard (NAAQS) for particulate matter of less than 2.5 microns in diameter ($PM_{2.5}$), including daily maximum (65 micrograms per cubic meter [$\mu g/m^3$]) and annual maximum (15 $\mu g/m^3$) average concentrations. There are about 65 million people in the United States who live in areas with annual average $PM_{2.5}$ levels in excess of 15 $\mu g/m^3$. Recent epidemiological and toxicological studies suggest that particulate matter (PM) health effects can vary by source category.

Airborne PM is a broad class of materials that are transported in the air as solid particles or liquid droplets. These particles are emitted from a variety of natural processes and human activities. The particles can be emitted directly into the atmosphere from primary sources such as motor-vehicle exhaust, home fireplaces and heating appliances, manufacturing plants, commercial and domestic food preparation, tar application, forest fires, wind erosion, and natural and cultivated vegetation. Secondary particles are formed in the atmosphere through photochemical reaction and oxidation processes involving ozone and other gas-phase oxidants. Each of the various emission source types has characteristic chemical and/or physical patterns and signatures. Organic molecular markers are individual compounds or groups of related compounds (homologous compounds such as n-alkanes, n-alkanoic acids, hopanes and steranes), which at a molecular level comprise the chemical profile or "fingerprint" for specific emission source types. An individual molecular marker or groups of marker compounds is linked quantitatively to major emission sources of urban fine particles also with known chemical emission profiles. The molecular-level technology used in the current study matches chemical fingerprints of the PM samples collected to emission sources.

The presence of functional groups containing oxygen or nitrogen atoms on some molecular markers (e.g., carboxylic acids) can increase their solubility in aqueous media (e.g., in atmospheric water vapor, fog, and rain) causing "regional haze." These groups can also impart an acidic or basic character to fine particles, govern their fate and transport in the atmosphere, and influence their uptake by biological systems, including their absorption within the human respiratory tract. Thus, in addition to linking PM composition to emission sources, the presence of polar marker compounds provide additional information on physical and chemical processes influencing the fate and transport of atmospheric carbonaceous particles.



Credit: U.S. EPA IMPROVE, CASTNet and AIRS air quality monitoring programs, NARSTO Assessment, 2003.

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Credit: M. Mazurek

Installation of a clean quartz fiber filter for fine particle collection using a Tisch 2-channel collector.

Project Status

- Initiated 2003
- Project ongoing

New York Energy Smart℠
Public Service Commission — NYSERDA

Since 1975, the New York State Energy Research and Development Authority (NYSERDA) has developed and implemented innovative products and processes to enhance the State's energy efficiency, economic growth, and environmental protection. One of NYSERDA's key efforts, the Environmental Monitoring, Evaluation Protection (EMEP) Program, supports energy-related environmental research. The EMEP Program is funded by a System Benefits Charge (SBC) collected by the State's investor-owned utilities. NYSERDA administers the SBC program under an agreement with the Public Service Commission.

METHODOLOGY

The project has four components:

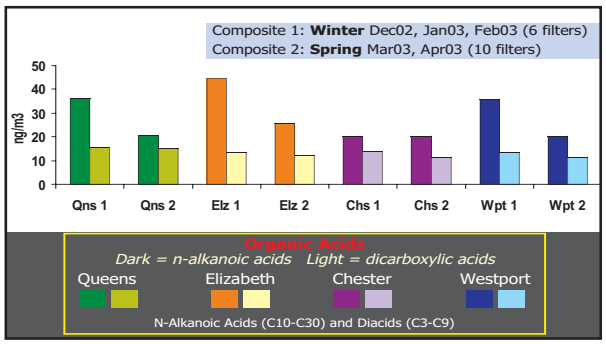
1. Additional detailed chemical analysis of organic molecular markers in samples from NYC, to expand on findings from the NESCAUM-supported air monitoring project, "Speciation of Organics for Apportionment of $PM_{2.5}$ in the New York City Area (SOAP)." The four SOAP locations (see map) are also Speciation Trend Network (STN) sites, where organic carbon (OC) and elemental carbon (EC) analyses are conducted. Collection and analysis of samples from side-by-side filters by project researchers and by STN personnel allow for the long-term comparison of organic speciation data to $PM_{2.5}$ mass measurements.
2. Measurement of organic molecular markers in $PM_{2.5}$ from upwind sources, to be collected in the Bronx (NYC) and at Pinnacle State Park (upstate New York) during two years of sampling, to enable a comparison of urban and regional (background) sites.
3. Updating of emission profiles by measuring organic markers in light-duty gasoline and diesel vehicles for comparison with ambient air samples.
4. Determination of organic emission profiles in seed oils to compare them to ambient air measurements.

Fine particles are collected as 24-hour samples using either a Tisch TE-1202 or TE-1204 sampler. In order to collect a sufficient quantity of material for analysis, filters are grouped by season and location, with identical collection days to produce one "sample" termed a composite. The organic mixtures extracted from the filters measure $PM_{2.5}$ organic marker compounds.

PRELIMINARY FINDINGS

The adjacent figure presents preliminary seasonal and spatial findings from analyses of samples collected at the four NYC area sites. The ambient mass concentrations of n-alkanoic acids (biogenic sources; dark bar) and diacids (photochemical conversions, combustion; light bar) for most sites show higher ambient mass levels in the early winter compared to the spring. This finding is consistent with the general trends seen for OC mass concentrations in $PM_{2.5}$ measured in urban northeastern airsheds, where winter ambient mass concentrations can exceed summer OC concentrations.

Ambient concentrations of acidic organic molecular marker compounds in fine PM samples collected from December 2002 to April 2003 at the four metropolitan receptor sites.



Credit: M. Mazurek

For the winter and early spring, urban emission marker (such as hopane, which is characteristic for motor vehicle exhaust) concentrations were greatest for the urban sites (Elizabeth, NJ and Queens, NYC), followed by Westport, CT (suburban) and lowest or not detected at Chester, NJ - the rural sampling location. Biogenic markers (originating from natural sources, such as microbiota, vegetation, and seed oil or plant waxes) were present at all sites where seasonal composites were compared. Ambient mass concentrations at the Elizabeth, Queens, and Chester sites were roughly the same for biogenic markers. Molecular indicators for secondary photochemical compounds measured at all locations were at roughly the same levels for daily composites.

Higher plants contribute organic acids from the waxy coatings of leaves; the level maximizes in the late summer and fall when leaf aging occurs, then falls off during the winter. Commercial and residential cooking operations, especially frying, consume seed oils, which may become airborne and form fine particles. This fine carbon particle emission source in the metropolitan NYC area is currently unregulated and its strength is unknown.

Further work in progress will determine the updated chemical profile of vehicular exhaust markers emitted from the current vehicle fleet in the NYC area. Mass ratios of these markers to OC and EC masses will allow an estimate of the contribution of vehicular traffic OC mass to the fine particle concentrations.

Note: Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

PROJECT IMPLICATIONS

This project is expected to identify monthly and seasonal concentrations of organic $PM_{2.5}$, offering more detailed chemical information that will be useful for air quality and related health-effects research on the components in PM. Updated chemical profiles for today's vehicle fleets will assist in establishing a baseline with which future vehicle emission systems can be compared in terms of their impacts on air quality, as well as for choosing the best regulatory or technological controls.

In addition, the project's detailed molecular marker work on secondary acidic compounds in the $PM_{2.5}$ organic acid mass will contribute to the development of methods and the characterization of sources of primary and secondary PM emissions affecting NYS. These improved methods, needed to identify important sources both in the state and in the region, should prove invaluable in the process of developing a State Implementation Plan (SIP) for attaining federal standards.