New York State Energy Research and Development Authority

Environmental Monitoring, Evaluation, and Protection Program

**PROJECT UPDATE**

**August 2005**

# Formation and Transformation of Particles in Motor Engine Exhaust

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http://genesis.sannet.gov/infospc/templates/cd1/issue_traffic.jsp

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http://www.nyserda.org/programs/environment/emep

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*Keywords*

- Aerosols
- Engine-generated emissions
- Nucleation-mode particles
- Volatile nanoparticles
- Ultrafine particles (UFPs)
- Fuel sulfur content

## PROJECT FOCUS

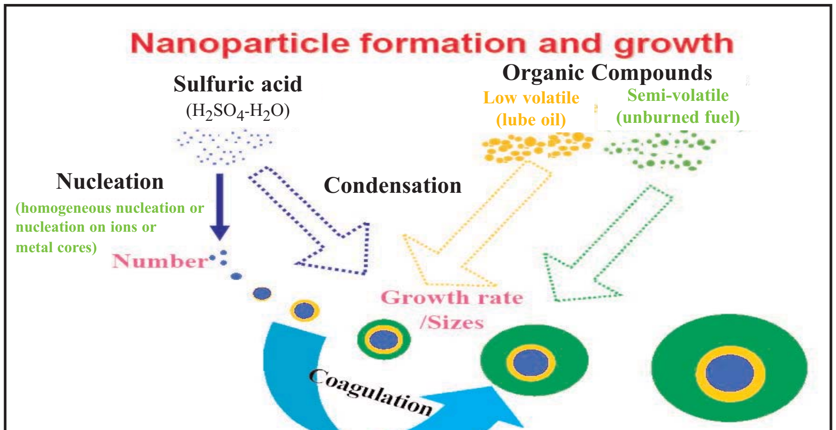
This study aims to improve our understanding of particulate emissions from motor-vehicle engines. The research focuses specifically on clarifying the processes whereby nucleation-mode particles – produced in the conversion of gases to particulate matter – are formed in an engine's exhaust. The contribution of organic compounds to the growth of engine-generated particles is also being explored.

## CONTEXT

Airborne particulate matter (PM) is a broad class of materials, transported in the air as solid particles or liquid droplets (aerosols). These particles are emitted from a variety of natural processes and human activities, including fossil-fuel combustion, forest fires, wind erosion, agricultural practices, industrial manufacturing, and construction. While some particles are directly emitted into the atmosphere (primary particles), others are formed in the atmosphere from precursor gases such as sulfur dioxide, nitrogen oxides, ammonia, and volatile organic compounds (secondary particles). In July 1997, motivated by concerns about adverse health effects, 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 average ($15 \mu g/m^3$) concentrations.

In order to choose the most effective $PM_{2.5}$ control strategies, the relative contributions to $PM_{2.5}$ from different sources need to be determined. Motor-vehicle engines are known to contribute substantially to particulate pollution, especially in urban regions or near heavily traveled roads. Their exhaust emissions are composed of gas molecules and particles. In addition to primary soot particles of the exhaust, secondary "nucleation-mode" particles may also be involved in the formation of $PM_{2.5}$. As exhaust cools down and mixes with ambient air, precursor gas molecules can nucleate to form new particles or condensate on existing particles. Nucleation increases the number concentration (the number of particles per volume air) of particles in the exhaust, while condensation increases the size of the particles. Particles also coagulate with each other, which reduces the particle number concentration while increasing the size of particles, while total mass remains unchanged.

Nucleation-mode particles are generally less than 50 nanometers (nm) or 0.05 microns in diameter. While these particles contribute little to the total PM mass, on which standards are based, their number concentrations can be very high. As a result of a number of factors – high number concentrations and surface area, and a high propensity to penetrate the epithelium – these particles may be directly responsible for the adverse health effects of PM. Moreover, nucleation-mode particles may also pick up and accumulate precursor gases in the atmosphere, which would increase their size, and may thus contribute directly to ambient $PM_{2.5}$ mass. We do not currently have an adequate physical understanding of the mechanisms by which these particles form during combustion in motor-vehicle exhaust, although several theories exist. A clear understanding of the nanoparticle formation mechanisms is critical to designing effective control strategies.




Credit: Dr. Yu

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Credit: Dr. Yu

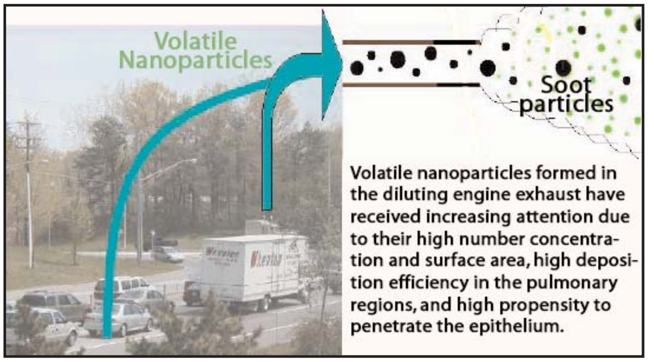
The experimental set-up for the measurements of ions in the exhaust of a Honda gasoline generator.

### *Project Status*

- Initiated 2003
- Project ongoing

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




Credit: Dr. Yu

The Advanced Particle Microphysics (APM) model is the fundamental numerical tool used in this project to carry out extensive data analyses and sensitivity studies, and to delineate the important parameters controlling engine emissions of volatile ultrafine particles (UFPs), particles less than 100 nm in diameter. The project uses an enhanced APM model to simulate detailed aerosol dynamics (nucleation, condensation, and coagulation) of particles in engine exhaust. Studies will include both diesel and gasoline engines run at various speeds on fuels of varying sulfur content. The effect of other key variables on nanoparticle emission, including air humidity and temperature, soot particle concentrations, and residence time, will be explored.

The project focuses on two nucleation mechanisms: (1) nucleation of sulfuric acid and water on ions (the "chemiion theory") and (2) the binary homogeneous nucleation (BHN) of sulfuric acid and water. Other possible nucleation mechanisms will be evaluated as well. Through experiments at the Automotive Emissions Laboratory in Latham, NY, the project team is testing the theory by:

- Measuring chemiions and charged clusters in motor-vehicle exhaust to determine whether the number of ions in the exhaust is sufficient to explain the observed nanoparticles; and
- Measuring the number of nanoparticles formed in the diluted exhaust as the undiluted exhaust is passed through a variable electric field.

The model simulations will also explore the contribution of organic compounds to the growth of engine-generated particles, the nucleation of sulfuric acid and water, and the growth of organic species through condensation.

## PRELIMINARY FINDINGS

**Formation Mechanism of Volatile UFPs**

- Concentrations of chemiions in diesel and gasoline engines were measured to be in the range of $10^6$-$10^8$ per $cm^3$. Simulations taking into account the contribution of these ions to nanoparticle formation can explain some important properties of nanoparticles observed in the engine exhaust. Ion concentrations at the tailpipe exit depend on engine operation conditions, residence time inside the tailpipe, and soot particle concentrations.
- For vehicles running on fuel with typical current sulfur content (~400 ppm), the BHN of sulfuric acid and water may significantly contribute to the formation of nanoparticles in vehicular exhaust when the ambient temperature is low and the relative humidity is high. The same vehicle may emit quite different amounts of volatile nanoparticles when driven in different locations and/or under different weather conditions. The BHN rate is very sensitive to fuel sulfur content: simulations indicate that sulfuric acid-water BHN is negligible under all realistic ambient conditions if the fuel sulfur content is reduced to less than 100 ppm.
- It is likely that both homogeneous nucleation and nucleation on ions contribute to new particle formation for New York State vehicles, which have a typical fuel sulfur content of 300-500 ppm. Under certain conditions, such as cold weather and high relative humidity, homogeneous nucleation controls the number of nanoparticles formed. In other conditions, such as warm weather and low relative humidity or with low fuel sulfur content, nucleation on ions is the dominant process. Nevertheless, it is clear that when fuel sulfur is reduced to below 50 ppm, homogeneous nucleation is negligible in all atmospheric conditions.

**Contribution of Organic Species to Particle Growth**

Organic species of low volatility, such as those associated with unburned fuel and lubrication oil, appear to dominate the growth rate and therefore the mass of the nucleation-mode particles.

## PROJECT IMPLICATIONS

Credit: Benz

The information gathered through this study will make an important contribution to our knowledge of particulate emissions from motor vehicles. An improved quantitative understanding of the dependence of nucleation on ambient conditions and fuel types and of the role of volatile organic compounds in particle growth will be important in designing control technologies as well as in developing emission inventories and appropriate regulatory approaches. This information should prove especially useful for New York State in the process of developing its State Implementation Plan to comply with federal $PM_{2.5}$ standards.