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**Current Particulate Matter Emissions
Research at the New York State Department of
Environmental Conservation**

Current Particulate Matter Emissions Research

at the New York State Department of

Environmental Conservation

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NYS-DEC

International ETH Workshop on Nanoparticle Measurement

August 9-13

Zurich, Switzerland

New York State/DEC

Congestion Mitigation and Air Quality(CMAQ)

Project

- US Department of Transportation let RFP on March 4,1996
- Energy and Environmental Analysis, Inc.'s proposal "Characterization and Control of Heavy Duty Vehicle Emissions in the New York Metropolitan Region" awarded contract in January 1998.
- Project Team:
 - EE&A-Overall Project Lead
 - Jack Faucette and Associates- Fleet Demographics Study
 - West Virginia University- HD Chassis Dynamometer Emissions Testing
 - DEC- Contract Oversight and Enhanced Emissions Testing
- Final Project Report due January 2000

CMAQ Project Features

- Fleet demographics study performed to inform truck and test cycle choices.
- 35 in-use light, mid, and heavy heavy duty trucks to be tested using WVU'S transportable dyno running WVU 5-mile and Test D cycles.
- Particle sizing (SMPS) on Test D cycle and size distributions on idle, 20mph and 40 mph steady state runs.
- Subset of trucks tested at multiple inertial weights.
- Smoke tests and lug-downs performed for I/M program assessment.

Emissions Characterization Overview

- Regulated emissions: NO_x, CO, CO₂, HC, PM gravimetric (WVU)
- Real-Time PM mass by TEOM (DEC)
- EC/OC by filter extraction (WVU) and R&P 5100 (DEC)
- Real-Time PAS analyzer for PM -bound PAH (DEC)
- Carbonyls (DEC)
- PM microscopy by SEM with XRF and FTIR (DEC)
- Particle size and size distributions by SMPS (WVU)
- TEOM and gravimetric filters archived for future analysis

CMAQ Project Status

- 12 day instrument 'shake-down' period testing diesel, CNG and hybrid buses with WVU for M.J. Bradley and the National Alternative Vehicle Coalition (NAVC)
- Testing of 35 trucks completed over period June- July 1999
- Emissions data in QA/QC process at WVU and DEC
- One day comparison of particle size distributions from diesel vs. gasoline light duty Dodge pick-ups running unloaded steady states
- Will return in September to test hybrid buses for NAVC and National Renewable Energy Lab

New York State/DEC Clean Diesel Vehicle Project

- **August 1998 DEC Announced Availability of \$1 million of Environmental Bond Act Funds for Clean Diesel Vehicle Demonstration.**
- **MTA Proposal for 50 Bus "Fleet Demonstration of JMI-CRT on Diesel Urban Buses" Announced by Governor Pataki, October, 1998.**
- **Emission Testing Element of CRT Project Expanded to Include Environment Canada's Emission Measurement Research Division (ERMD), Jan, 1999.**
- **Project Team:**
 - ◆ **MTA-Overall Project Lead**
 - ◆ **JMI-Provides Engineered CRT Systems**
 - ◆ **Corning-Catalyst and Filter Substrates**
 - ◆ **Equilon Inc-One million gallons 50 ppm S Fuel**
 - ◆ **Rad Oil-NYC Tankage and Local Supply of Fuel**
 - ◆ **Env Canada-Emissions Testing**
 - ◆ **DEC/AEL-Contract Oversight and Emissions Test Support**
- **Final Project Contract Documents Pending, July, 1999**

MTA -CRT Demonstration Project Features

Fifty buses in 100-bus depot fitted w/CRT Systems:

- ◆ 25 1993 6V92
- ◆ 25 1999 Series 50

- **Entire Depot converted to 50 ppm S Fuel**
- **Durability Evaluation for One Year**
- **Emissions Tests on Two Buses of Each Type**
- **Emissions Testing Includes:**
 - ◆ **Base Engines on both Standard and Low Sulfur Fuel**
 - ◆ **CRT-Equipped on Low Sulfur Fuel**
 - ◆ **Testing at Start and End of Durability Operation**
 - ◆ **CBD and NYC-Bus Test Cycles**
 - ◆ **Other Off-Line Tests @ ERMD**

- **Comprehensive Emissions Testing:**
 - ◆ **Regulated Emissions**
 - ◆ **PM Characterization**
 - ◆ **Chemistry of PM-Bound and Volatile Species**
 - ◆ **Real-Time PM mass (TEOM), NO₂ (FTIR)**

Emissions Characterization Overview

- **R-T PM Mass by TEOM (DEC)**
- **EC/OC by Filter Extraction (ERMD) and R&P 5100 (DEC)**
- **VOC Speciation (ERMD)**
- **Carbonyls (ERMD, DEC) and PAH (ERMD)**
- **R-T NO₂ by FTIR (ERMD)**
- **Particle size by SMPS, ELPI (DEC)**
- **PM Microscopy by SEM with XRF (DEC)**
- **Real-Time PAS Analyzer for PM-bound PAH (DEC)**
- **Continuous Trace Recording of Regulated Emissions (ERMD)**

MTA-CRT Demonstration Project Status

Successful Pilot Demonstration

- ◆ **Single buses of Both 6V92 and Series 50 types in Revenue Service**
- ◆ **Form and Fit of CRT's Verified**
- ◆ **Exhaust Temperature and Back Pressure Data Logger**
- ◆ **Minor Changes Before Full Demonstration**

Currently 'shaking down' new ELPI and 3936N SMPS

Designing and building appropriate dilution system

Attempting to calibrate the PAS PAH analyzer

"Stabilizing" the R&P 5100 EC/OC instrument

DOH/DEC Hazardous Air Pollutants and Acute Asthma in Urban Areas Study

- **Primary Objective: Evaluate temporal associations and possible causal role between several ambient air contaminants and acute asthmatic symptoms as measured by emergency room visits for asthma in NYC.**
- **Specific objectives:**
- **Evaluate whether ambient levels of certain hazardous air pollutants, criteria air pollutants, pollens and spores differ in two NYC neighborhoods that have different rates of hospital admissions for asthma and different socio-economic status characteristics.**
- **Compute the overall rates of air contamination-attributable asthma emergency room visits among residents over a 1-year period, and test whether the magnitude of the air pollution effect differs in the two communities.**
- **Investigate which air contaminants, or mix of air contaminants, are most associated with acute asthma exacerbations in each community.**

The study will measure 24-hour average ambient air concentrations of aldehydes, chromium, iron, nickel, manganese, hydrogen ion, sulfate, nitrates, pollens and spores. In addition, daily hourly concentrations for ozone, sulfur dioxide, nitrogen oxides, number of particles between 7 nanometers and 2.5 micrometers, particulate matter <2.5 micrometers (PM2.5), particulate matter <10 micrometers (PM10) are measured and three-hour daily concentrations for elemental and organic carbon. The hourly data will also be used for calculating daily averages, maximum concentrations, and for ozone an eight-hour moving average. Meteorological (temperature, wind speed and direction, humidity) data is also being collected. The ambient air data will be collected for 365 consecutive days at two sites in NYC. The health effects measure will be a visit to the emergency room (ER) resulting in a diagnosis of asthma, other respiratory conditions, or for a panel of other health conditions not thought to be related to ambient air contaminants (e.g. non-infectious gastrointestinal disorders). The ambient air data and health effects data will be analyzed by time-series analysis to determine whether and to what extent various air contaminants contribute to emergency room visits for asthma or other respiratory conditions.

A Technical Proposal in response to the RFA
Particulate Matter "Supersites" Program
U.S. Environmental Protection Agency
**PM2.5 Technology Assessment and Characterization
Study in New York (PMTACS-NY)**
Submitted by
Atmospheric Sciences Research Center
University at Albany, SUNY
in Collaboration with the
New York State Department of Environmental Conservation
and
Aerodyne Research, Inc.
Aerosol Dynamics, Inc.
Brookhaven National Laboratories
Clarkson University
Penn State University
NYS Department of Health
Rupprecht and Patashnick Co., Inc.

PMTACS-NY Program Goals

- Demonstrate through strategic measurement studies the impact of specific control technologies on NYC PM_{2.5} and related air quality.
- Develop, deploy and demonstrate the utility of advanced measurement technologies characterizing the PM-Co-pollutant complex, its formation processes and source attribution.
- Evaluate and transfer technologies to enhance NYS infrastructure and science capacity to effectively monitor and manage air quality impacting the health and welfare of its citizens.

Measure the temporal and spatial distribution of the PM_{2.5}/Co-Pollutant complex including: SO₂, CO, VOCs/Air Toxics, NO, NO₂, O₃, NO_y, H₂CO, HNO₃, NH₃, HONO, PM_{2.5} (mass, SO₄ = , NO₃ - , OC, EC, Trace Elements), single particle aerosol composition, CN, OH and HO₂ to support regulatory requirements to develop cost effective mitigation strategies PM_{2.5} and its co-pollutants and to establish trends in the relevant precursor concentrations to assess the impact of recent and future emission reductions in terms of emission control effectiveness and air quality response.

Monitor individual vehicle emissions impacts through remote open path roadside, mobile platform and fixed site measurements of CO₂, CO, NO, H₂CO, HONO, CN and aerosol chemical composition. Examine impacts of both current on-road vehicles and candidate technologies such as CNG, hybrid electric and Continuous Regenerative Trap diesel buses.

Test and evaluate new measurement technologies and provide tech-transfer of demonstrated operationally robust technologies for network operation in support of the development of process science and observation based analysis tools and health based exposure assessments.

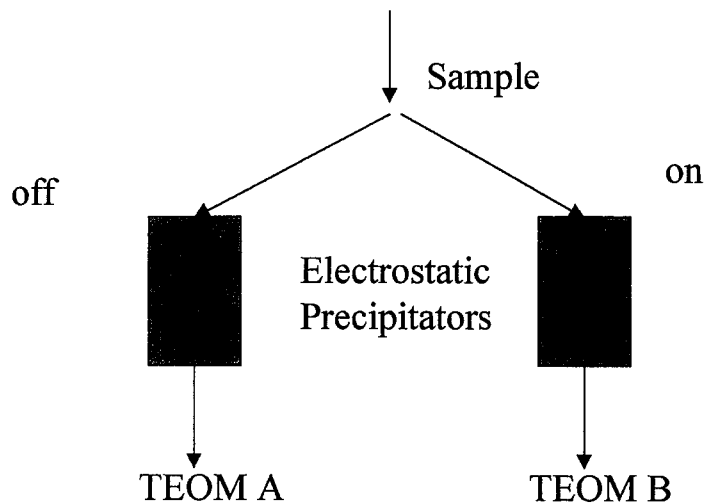
New Measurement Technology Deployment

R&P TEOM (modified Low T/dryer)

A continuous mass monitor based on the tapered element oscillating microbalance has been modified to operate at 30 C and sample a de-humidified ambient air stream passed through a Nafion dryer.

R&P TEOM differential (modified - ESP)

The instrument is based on the direct mass reading and real-time capability of the TEOM system. A matched pair of TEOM sensors (A and B) is run at ambient temperature. Downstream from a common size selective inlet and ahead of each TEOM sensor is an electrostatic precipitator (ESP). The ESP's are alternately switched on and off and out of phase with each other. Each ESP is on or off for a time period ΔT . Frequency data are collected for both TEOM sensors on a continuous basis. The effective mass is the mass that is calculated from the frequency of the TEOM sensor including all sources that affect the frequency during the given time period ΔT . The difference between the effective masses of the TEOM A and B sensors provides a direct measure of the non-volatile and volatile component of particle mass collected during the time interval.



$$M_{TEOM A} = M_{Particles} + M_{Volatiles} + M_{Temperature} + M_{Pressure} + M_{Gas} + M_{Volatiles}$$

$$M_{TEOM B} = M_{Temperature} + M_{Pressure} + M_{Gas} + M_{Volatiles}$$

R&P 8400NS (PM2.5 Nitrate & Sulfate Analyzer)

This automated monitor for semi-continuous measurement of nitrate and sulfate is based on the method of Stolzenburg and Hering (1998, 1999). Particles are collected by a humidified impaction process and analyzed in place by flash vaporization. The approach is based on the manual method that has been used for over twenty years to measure the size distribution of sulfate aerosols (Hering and Friedlander, 1982). In the new instrument design, particle collection and analysis have been combined into a single, integrated collection and vaporization cell, allowing the system to be automated. Particles are humidified prior to impaction to eliminate the rebound of particles from the collection surface without the use of grease (Winkler, 1974 and Stein et al 1994). Interference from vapors such as nitric acid is minimized by use of a denuder upstream of the humidifier. The flow system is configured such that there are no valves on the aerosol sampling line. Analysis is done by flash-vaporization with quantitative detection of the evolved gases. For sulfate the evolved gases are analyzed for SO₂, as described by Roberts and Friedlander, (1974). For nitrate the evolved vapors are analyzed for nitrogen oxides (Yamamoto and Kosaka, 1994).

Aerodyne Research, Inc. AMS (Aerosol Mass Spectrometer)

Ambient aerosol particles in the size range 0.05 to 5 micrometers are focused by an aerodynamic aerosol inlet (U of MN) into a narrow beam and transported into a high vacuum system, where particle time-of-flight measurements determine particle aerodynamic diameter. Volatile and semivolatile chemical components are thermally vaporized and detected via electron impact ionization quadrupole mass spectrometry. Detection sensitivity for the base system corresponds to aerosol loading of 0.1 to 1 microgram/m³, depending on the molecular mass interferences and background levels.

BNL Single Particle Laser Ablation Time of Flight Mass Spectrometer (SPLAT-MS)

Designed to be a universal tool for characterizing the size and composition of individual aerosols from ~10 nm up to tens of micrometers. It utilizes two continuously operative detection modes; VUV photoionization and more conventional light scattering for small and large particle detection respectively. These will be used to synchronize the ablation laser with the particle's arrival for all sizes. Ambient aerosols are focused by the aerodynamic lens system, and accelerated during supersonic expansion through a nozzle to velocities between 100 and 400 m/sec, depending on particle size. Two stages of optical detection are used to indicate the presence of particles larger than 100 nm and for velocity/size determination. To maximize the contrast between particle and gas, the signal is integrated for ~1 microsecond and a requirement for a coincidence between the two laser beams. A continuous VUV light source is used for nanoparticle charging by photoemission and electron detection allows detection and size characterization for particle smaller than 100 nm. An excimer laser is used to ablate particles and generate ions. By operating an excimer laser at 157 nm, the system allows in-resonance particle ionization as oppose to the off-resonance process for longer wavelengths. A reflectron time of flight mass spectrometer is used for single particle composition analysis.

Aerodyne Research, Inc. Mobile Laboratory

The mobile laboratory has a series of sensitive, specific, real-time (~1 second response) sensors for aerosol and ozone precursor trace gases and fine particulates; a global positioning system (GPS); and a central data logging computer. Specifically, the sensors include: an ARI two-color tunable infrared laser differential absorption spectrometer (TILDAS), capable of measuring between 2 and 4 trace gases simultaneously, such as carbon monoxide (CO), nitrogen oxides (NO, NO₂), nitrous acid (HONO), formaldehyde(CH₂O), and sulfur dioxide (SO₂).; a Licor NDIR instrument to measure carbon dioxide (CO₂); a aerosol mass spectrometer (AMS) to measure particulate number densities, size distributions (0.05 to ~2.5 μm), and volatile and semi-volatile chemical composition as a function of particle size. The real-time instruments have been described in detail previously [see Lamb et al. (1995), Nelson et al., (1996), Zahniser (1995), and Jayne et al., 1999]. Data from the individual instruments are logged on a central computer, enabling all data streams to be stored synchronously. A Trimble GPS system with real-time differential correction collects position information at 1 Hz.

New EPA Post-Trap Certification Method

- Project in formation stage w/ EPA, R&P, SWRI and others
- Run R&P 7000 TEOM stack monitor @ 185 C, no SOx condensing?
- Filter media options to be considered
- Dessicate filter before and after measurement
- Phase 1 is to look at 'dry core' particulate
- Phase 2 will include nitrates and sulfates
- Goal is partial flow, fast dilution and slow cooling
- Still mass based method