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Title: PM2.5 Technology Assessment and Characterization Study in New York State (PMTACS-NY)

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Cost Sharing Partners: New York State Energy Research and Development Authority (NYSERDA) and New York State Department of Environmental Conservation (NYSDEC)

Research Category: Particulate Matter EPA "Supersites" Program

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Project Period: January 15, 2000 – December 31, 2004

Objective of Research:

As a result of clinical and epidemiological studies (NRC, 1998) associating adverse health effects in humans and fine particle mass, a new National Ambient Air Quality Standard for PM_{2.5} mass (15 µg/m³ annual and 65 µg/m³ 24-hr average) was promulgated in the United States (Federal Register, 1997). Significant scientific and technical issues surrounding the mitigation of the warm season PM_{2.5}/co-pollutant complex and its interdependence with O₃ air quality through coupled photochemical pathways, common precursors, and similar dependencies upon meteorology must be addressed if effective control strategies are to be implemented. The long-term monitoring of the PM_{2.5}/co-pollutant complex and its precursors at urban and regional representative sites provided under the PMTACS-NY Supersite program provides a unique and unparalleled opportunity to track the impact of emission controls and their effectiveness on air quality and to enhance our understanding of ozone/PM_{2.5}-precursor relationships. The impact of this research is highly significant, providing a sound scientific basis for informed effective decisions in the management of air quality in New York and will benefit its citizens both environmentally and economically.

The PMTACS-NY is designed around three major objectives and addresses a series of science policy relevant questions related to hypotheses that have been and will continue to be tested using measurement data collected under the program.

Objective I. 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, HONO, PM_{2.5} (mass, SO₄⁼, NO₃⁻, OC, EC, Trace Elements), single particle aerosol composition, particle size distribution and number concentration, OH and HO₂ to support regulatory requirements to develop cost effective mitigation strategies for 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.

Objective II. Monitor the effectiveness of new emission control technologies [i.e. Compressed Natural Gas (CNG) bus deployment and Continuously Regenerating Technology- Diesel Particle Filter (CRT-DPF)] introduced in New York City and their impact on ambient air quality, through mobile platform and fixed site measurements of CO₂, CO, NO, H₂CO, HONO, particle size distribution and number concentration and aerosol chemical composition.

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

Summary of Most Important Findings:

- The annual composition of PM at urban New York City sites suggests that the bulk of PM mass is attributed as follows: Carbon-based (~36%), Sulfate-based (~30%), Nitrate-based (~15%) and Ammonium (~15%); the remaining ~5% is metals/soil related and particle bound water.
- Although the contributions to the annual PM mass by season are comparable for cold and warm season months (16.6 and 15.4 $\mu\text{g}/\text{m}^3$ respectively) based on filter based measurement data averaged over three New York city sites in 2002, the PM species composition differs significantly by cold vs. warm season (SO_4 , 22%/34%; NO_3 , 23%/8%; NH_4 , 14%/13%; OC*1.4, 28%/34%; EC, 9%/6%; and soil, 4%/5%).
- AMS (Aerosol Mass Spectrometer) measurements observed that the summer time carbon-based PM contributes up to 45% of the daily PM mass; empirical estimates of PM production based on OH+VOC measurements suggests that ~ 40% of the total PM organic carbon is generated by photochemical oxidation processes (most likely of local origin).
- Summer vs. winter AMS compositional size distribution measurements in Queens, NY indicated a significant shift in mean mode volume size distribution, ranging from 350-400nm to 150-200nm for summer and winter respectively. The observed difference in mean mode size distributions is likely the result of significant summertime photochemical production of secondary aerosol and its condensation/coagulation on the background aerosol.
- Summertime PM secondary organic aerosol (SOA) contributions correlate with photochemical oxidant formation and will vary (i.e. the % SOA contributions to PM mass) as function of the severity of the oxidant season. Estimates of photochemical production of SOA from the direct measurement of OH and VOC are consistent with estimates from AMS analyses that attribute PM organic carbon into Hydrocarbon-based Organic Aerosol (HOA) and Oxidized Organic Aerosol (OOA) species. These estimates suggest that summer time contributions of SOA production from photochemical reactions of OH+VOC in Queens New York can account for 40% of the observed PM organic carbon observed at this location.
- Estimates of PM SO_4 production based on the reaction kinetics of $\text{OH} + \text{SO}_2$ from their respective measurements in Queens, NY in the summer of 2001 indicate that 15-60% of observed PM SO_4 at the site is generated by this photochemical oxidation process (most likely of local origin). These results are consistent with source apportionment estimates that suggest ~ 50% of the observed warm season sulfate observed in New York City is transported into the metropolitan region. Summertime PM SO_4 contributions correlate with local photochemical oxidant formation and the % SO_2 conversion contributing to PM SO_4 mass is in part a function of the severity of the oxidant event.
- Source apportionment techniques utilizing metals analyses from the speciation trends network and enhanced 6-hr filter sampler data collected during PMTACS-NY intensive field studies suggest that these methods are hampered by the limit of detection of many metals key to resolving fuel based combustion sources.

- Wintertime ambient NH_3 measurements are correlated with vehicle emissions, with the highest emission rates associated with cold start vehicles. These results suggest that vehicle emissions are a significant source of the observed cold season ambient NH_3 concentrations.
- On-road vehicle emission flux measurements of residual gases and PM mass and chemical composition using a mobile measurement platform have shown that 1) CNG powered and CRT-DPF equipped diesel buses provide significant reduction in PM emissions as compared to their standard diesel counterparts; 2) CNG powered buses have significant formaldehyde emissions that will require additional controls (oxy-catalyst); 3) CRT-DPF equipped diesel buses significantly change the NO_2/NO_x ratio, which may have to be addressed in the long term; 4) Ultra low sulfur fuels have significant direct benefits with respect to PM, THC, CO and SO_2 emissions, in addition to the control technology benefits requiring these fuels.
- AMS diesel PM organic emissions measured in chase studies during the warm season in New York City show a bimodal distribution (70nm and 400nm modes) that is also reflected in ambient AMS measurements. Ambient AMS measurements made during the cold season at the same location failed to identify a significant secondary small particle mode. This may be the result of the broadened small particle wintertime size distribution masking the 70nm mean mode particles or that the small particle mode source has shifted out of the particle transmission range of the AMS (i.e. 30nm). These results suggest that low ambient temperatures strongly affect size distributions and the formation of lube oil particles either prior to or immediately after exiting the exhaust system.
- The comparison of vehicle chase study and dynamometer emissions for PM are consistent in the mean, but real-world in situ emission measurements suggest significantly more variation than dynamometer tests.
- The observed diurnal pattern in ambient AMS PM organic measurements is consistent with other vehicular precursor emissions and indicates that a substantial portion of PM organic emission can be attributed to mobile sources.
- Continuous PM mass measurement technologies (SES TEOM, FDMS-TEOM, and BAM) have shown continued progress in achieving the “true” measurement of PM mass. The designation of FRM as the mass measurement standard for the “true” ambient PM mass is now being challenged. Recent measurements based on FDMS technology indicate that the “true” PM mass is underestimated by the FRM which loses NH_4NO_3 and semi-volatile organics and that these losses exhibit significant seasonal dependence.
- Continuous PM sulfate and nitrate measurement technologies (8400S and Thermo 5020) show promise for routine network deployment. Sulfate measurements are in good agreement with collocated instruments and 24 hr STN filters. Continuous PM nitrate measurement technology (8400N) shows promise for routine network deployment, but measured PM NO_3 levels are significantly lower (30-40%) than other collocated semi-continuous instruments and 24 hr STN filters. Some measurement data indicate a non-linear response with increasing PM nitrate levels suggesting a changing or limiting reductive capacity of the flash conversion system. Outstanding operational/maintenance issues with these systems remain to be resolved.

Supplemental Keywords: ambient air, atmospheric aerosols, ozone, particulate matter, metals, nitrogen oxides, sulfates, organics, atmospheric chemistry, monitoring, measurement methods, northeast air quality.

Relevant Web Sites: <http://www.asrc.cestm.albany.edu/pmtacsny/>