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Title: PM_{2.5} Technology Assessment and Characterization Study in New York State (PMTACS-NY)

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Institution: Atmospheric Sciences Research Center, University at Albany

Research Category: Particulate Matter EPA "Supersites" Program

Sorting Code: 99-NCERQA-X1

Project Period: January - March 2002

Objective of Research:

As a result of recent 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 $\mu\text{g}/\text{m}^3$ annual and 65 $\mu\text{g}/\text{m}^3$ 24-hr average) has been 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 provides the opportunity to track the impact of emission controls and their effectiveness on air quality. These data can be used to verify that implemented PM_{2.5} primary and secondary precursor (including ozone precursor) emission controls are performing according to specifications and verify that PM_{2.5} and ozone air quality has responded to the emission changes achieved as expected. Without adequate monitoring systems to track the progress and effectiveness of implemented control programs, the air quality management approach remains unaccountable.

The PMTACS-NY Supersite program provides a unique and unparalleled opportunity to enhance our understanding of ozone/PM_{2.5}-precursor relationships and track progress in current precursor emission control programs and assess their effectiveness in achieving expected air quality responses. 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 to be tested using measurement data collected under the program. The subject quarterly reports provide highlights on the overall program status, the progress made in the context of the specific tasks associated with the three program

objectives, identification of outstanding issues, project schedule and completion status by task, and a budget analysis.

Progress Summary/Accomplishments:

Data reduction and analysis of findings from the PMTACS-NY 2001 Summer Field Intensive continued through this quarter. The processing of data using the NARSTO format for submission to the NARSTO Permanent Data Archive is nearing completion for the 2001. We expected to make submissions of all trace gas and most PM data sets for 2001 by May 15. In this quarterly report we provide further analyses of the AMS data set and a summary of R&P 8400S continuous PM sulfate data collected during the PMTACS-NY 2001 Summer Field Intensive.

Finally, all investigators providing measurements during the summer campaign are preparing contributions for the PMTACS-NY QA 2001 annual report which near completion.

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, 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.

Measurements at our two rural sites Whiteface Mountain and Pinnacle State Park operated during the quarter as outlined in Table 1 of the QAPP. Our urban sites, IS 52 in the South Bronx and PS219 in Queens are operating most monitoring equipment outline in Table 1 of the QAPP, with the exception of continuous PM sulfate which was taken offline due to persistent equipment failure and PM nitrate which has outstanding performance issues yet to be resolved. Semi-continuous PM carbon measurements (R&P5400) at the urban sites are not online due to delays in needed power upgrades for their operation.

Objective II. Monitor the effectiveness of new emission control technologies [i.e. Compressed Natural Gas (CNG) bus deployment and Continuously Regenerating Technology (CRT)] introduced in New York City and its impact on ambient air quality, thorough remote open path roadside, mobile platform, and fixed site measurements of CO₂, CO, NO, H₂CO, HONO, CN and aerosol chemical composition.

The preliminary findings reported in the last quarter regarding on-road, in-use vehicle emissions of NO₂ slip emissions from CRT carbon particle trap diesel control technologies and methane and formaldehyde emissions from CNG fueled buses have significant health and welfare implications. It is critical that a much larger sample of the on-road in-use emissions measurements of vehicle population be performed. The PMTACS-NY/CEPEX program was designed to demonstrate a new and innovative approach to the measurement of in-use vehicle emissions and it's potential to provide a database of the real-world emissions for in-use operational vehicle fleets. Only with such data can we assess the effectiveness of implemented control strategies and provide quantitative data that can be used to demonstrate "accountability"

in the calculated emissions provide in emission modeling systems. The 2003 winter intensive CEPEX program is an un-funded option, as a result of budget reduction imposed in the initial PMTACS-NY cooperative agreement budget negotiations. We believe this is extremely important work that should be continued. We have briefed several potential sponsors as well as spoken with EPA officials regarding these results and the clear response has been that this is outstanding work that should be continued. But to date we have not identified a source of funds. Further discussions with responsible EPA parties are being planned.

Objective III. 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.

In our previous quarterly report we provided examples of a variety of instrument intercomparison studies that were performed as part of the Summer 2001 Field Intensive. This work continues and for this quarter we focus on mass balance analyses associated with Aerosol Mass Spectrometer.

The total aerosol mass balance was calculated using the complete AMS mass spectrum information and the ‘consensus’ TEOM data (i.e. data from 3 TEOM instruments operating simultaneously during the intensive measurement campaign). The comparison of all AMS species (sulfate, nitrate, ammonium, chloride and organics) with the TEOM data resulted in a good correlation but with only about 55 % of the TEOM mass concentration accounted for in the AMS data: All species – TEOM: slope = 0.538; intercept = 0.435 $\mu\text{g}/\text{m}^3$; correlation coeff. $R=0.951$.

The correlation of the total AMS mass (all masses in the spectrum with the exception of air mass peaks) resulted in a correlation with a larger slope, but also had a much larger intercept: All masses – TEOM: slope = 0.723; intercept = 4.269 $\mu\text{g}/\text{m}^3$; correlation coeff. $R=0.946$. This AMS ‘total mass’ also contains the mass concentration of water. The large intercept is mainly due to water vapor in the air that reaches the ionization region of the AMS and partly due to O_2^{2+} , which interferes with the water and ammonium signal. The O_2^{2+} signal was calculated from the O_2^+ signal and the ratio of $\text{O}_2^+/\text{O}_2^{2+}$ and subtracted from the signal at mass 16 amu. The signal due to water vapor in the air was calculated from the RH, air temperature and ambient air pressure, measured at PS 219 and also subtracted from the total water signal of the AMS. These calculations resulted in an AMS ‘total mass’, that contained all species and particle water. The correlation has a significantly lower intercept and a better correlation coefficient:

All masses + particle water – TEOM: slope: 0.694; intercept: -0.24 $\mu\text{g}/\text{m}^3$; $R=0.949$

On average the AMS was able to identify about 67 % of the total aerosol mass, measured by the TEOMS, ca. 11 % are assigned to particle water. The time series for the TEOM and AMS cumulative species mass contribution data for the intensive period are presented in Figure 1 and the integrated mass balance and species distribution results presented in the Figure 2.

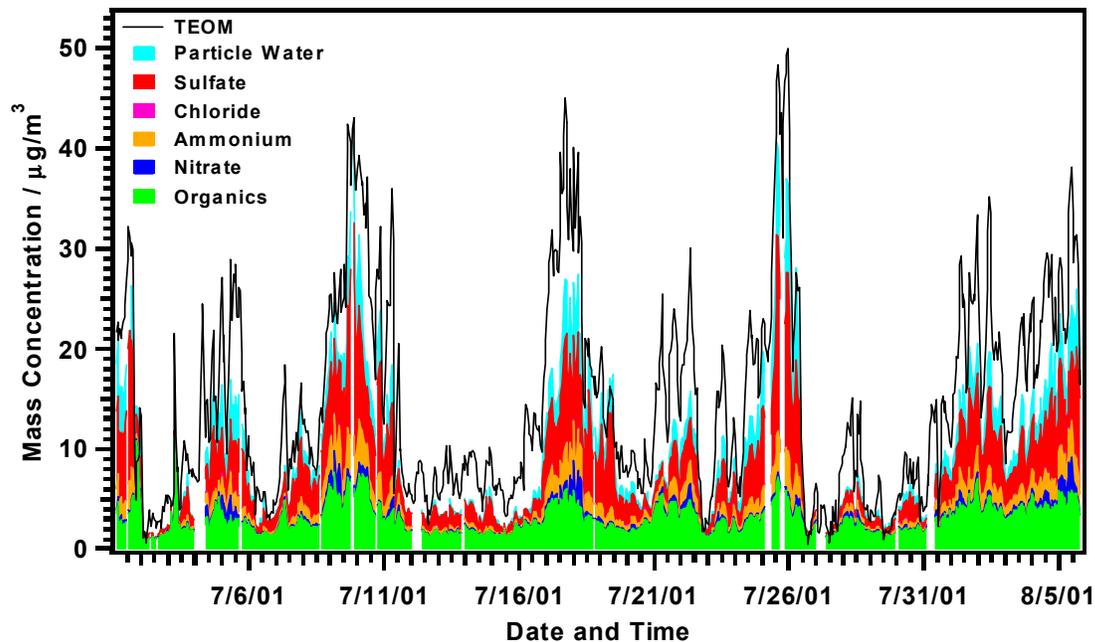


Figure 1. Times series of TEOM and AMS species mass concentrations

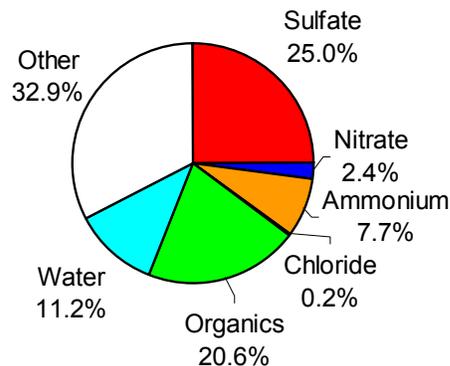


Figure 2. Species mass concentration distributions for entire field intensive period

Finally, using ICP/MS analyses from four ACCU sampler (24-hour) filters operated during the campaign, the average metals concentrations were used to calculate their contribution to the AMS mass balance. The filter analyses reported ~ 3.4 % of the total aerosol mass on the filters was due to metals and another ~ 3.5 % was due to elemental carbon. Using these data, therefore, would explain another 7 % of the 33 % of ‘other’ in the mass balance, leaving ~ 25 % of the mass unidentified. We are currently exploring AMS sources for this mass deficit. Possible explanations include a reduction in the efficiency of the transmission of larger particles into the AMS or the evaporation (and ultimate loss) of semi-volatile material (particle water, organics) in the aerodynamic particle lens, during particle flight under vacuum prior to reaching the thermo-ionization region.

The R&P 8400S, a commercially available continuous PM2.5 sulfate monitoring instrument, was operated during entire PMTACS-NY 2001 Summer Field campaign. It's performance in the field was quite satisfactory; data completeness: 4770 (94.6%) of a maximum of 5040 cycles were reported; 124 cycles were missed due to routine maintenance, 32 cycles missed due to instrument failures, and 114 due to other. A summary of the PM2.5 sulfate concentration measurements from the R&P 8400S are reported in Table I.

Table 1. A summary of R&P 8400S PM2.5 Sulfate Concentration Measurements, June 30 - August 4, 2001, Queens, NY

Statistic	SO₄²⁻, μg/m³
Minimum	-0.41
25%	1.12
Median	2.70
Mean	3.82
75%	5.64
Maximum	20.91

We are currently reviewing the comparisons of integrated R&P 8400S (and other continuous sulfate monitoring systems) with co-located 6-hr filter based sulfate analyses that show good correlation, but indicate a systematic under prediction in comparison with the filter data.

Publications/Presentations: Demerjian, K.L, The Chemical and Physical Characterization of Ambient Particulate Matter: Recent Results from the PMTACS-NY Summer 2001 Field Intensive, City College of NY, February 29, 2002

Future Activities and Outstanding Issues:

During the next quarter planned activities include: 1) continued data reduction and analysis of the Summer 2001 Field Intensive measurements; 2) completion of the annual quality assurance report; 3) first round archive submission of NARSTO formatted data; and 4) preparation of draft manuscripts highlighting the Summer 2001 results.

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/>