SUMMARY COMMUNICATION

DEVELOPMENTS IN CONTINUOUS FINE PARTICLE MASS MONITORING: SAMPLE EQUILIBRATION AND DIFFERENTIAL PARTICLE SAMPLING

Prepared for the

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EXECUTIVE SUMMARY

NYSERDA's Environmental Monitoring, Evaluation, and Protection Program (EMEP) has recently supported two product developments to improve continuous monitoring of fine particulate matter (PM) mass in ambient air—the air that people breathe. These products are based on the use of the Tapered Element Oscillating Microbalance (TEOM®)[1] inertial mass measurement method. The two goals of these efforts were (1) to increase correlation with measurements made using the Federal Reference Method (FRM), a 24-hour filter-based method; and (2) to develop a continuous measurement system that more closely represents the mass of fine particles found in ambient air, rather than that found following the techniques described in the FRM.

Policy Implications

Two major advances in real-time monitoring of fine particles were supported under this research. These include reducing the moisture content of the sampled ambient air so that the temperature of the device could be reduced from 50°C to 30°C, and developing an innovative approach to account for the loss of semi-volatile materials on the filter surface. The devices have the potential to provide highly time resolved and accurate fine particle mass data that can be used to improve health effects studies, verify the impact of state implementation for controlling PM2.5, as well as to reduce monitoring costs.

To achieve the first goal, a sample equilibration system (SES) was developed to reduce the moisture content of the sampled ambient air stream so that the temperature of the TEOM filter could be reduced from 50°C to 30°C, which is closer to the typical ambient collection temperature of the FRM. The lower temperature also reduces the loss of semivolatile components of PM mass. Performance of the SES-TEOM was assessed both under controlled laboratory conditions and in a year-long side-by-side field test by Atmospheric Sciences Research Center (ASRC) of the State University of New York at Albany.

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[1] The TEOM® is manufactured by Rupprecht & Patashnick, Albany, New York.

To achieve the second goal, a new measurement concept—the Differential TEOM Mass Monitoring System, or Differential TEOM—was developed and tested. In this system, sharing SES components, an electrostatic precipitator (ESP) is inserted between the sample inlet and the TEOM mass sensor, operated at 30°C, but theoretically at ambient temperature. The ESP is regularly cycled on and off to selectively remove particles from the sample stream. The sampled ambient air stream first passes through a size-selective inlet that allows small particles to enter the monitoring system. Mass measurements made with the ESP on (when particles are trapped before reaching the sample filter-mass sensor), are **subtracted from** those made with the ESP off (when particles are collected on the filter-mass sensor) to track gain or loss of semivolatile materials on the filter, providing a more detailed time-series record of PM mass.

The performance of the Differential TEOM was assessed at several research institutions through subcontracts and cooperative agreements:

- University of Duisburg, Germany, which used laboratory-generated aerosols to assess the effect of the SES dryer on particle measurement;
- Clarkson University, which, using a similar approach, assessed the efficiency of the ESP and its effect on particle measurement;
- University at Albany Institute of Materials, which focused on the ESP electrode performance relating to material buildup, wear, and cleaning methods; and
- Atmospheric Sciences Research Center of the State University of New York at Albany, which conducted: (1) controlled laboratory aerosol testing using a variety of aerosols; (2) and ambient field measurements with the Differential TEOM, other colocated monitoring systems, and FRM PM samplers.

The Differential TEOM was deployed in Albany and Queens (New York City), as well as Claremont and Rubidoux in California. The devices have the potential to provide real-time fine particle mass data that can be used to improve the quality of health effect studies and verify the impact of state implementation plans for controlling PM, as well as to reduce monitoring costs.

Project Background

The National Ambient Air Quality Standard (NAAQS), as revised by the U.S. Environmental Protection Agency (EPA) in July 1997, added annual and 24-hour standards for particulate matter less than 2.5 microns (PM-2.5) in aerodynamic diameter in ambient air. The ambient air standard is based on measurement of PM-2.5 using an FRM sampler.

Under the FRM procedure, a filter is preconditioned under a defined temperature and humidity and then weighed. Using well-defined hardware, a sample is collected on the filter for 24 hours at ambient temperature and humidity. The filter is then retrieved and weighed under the same laboratory conditions of temperature and humidity. The weight difference divided by the volume of sampled air yields the average 24-hour mass concentration.

Because it is a manual method, the FRM procedure involves significant costs associated with filter replacement and analysis. Such costs could be reduced if continuous-monitoring methods equivalent to the FRM standard were developed. In addition, the mass on the filter can change over time through condensation or evaporation of semivolatile material, adsorption or desorption of gaseous components, and chemical reactions of collected material, since the sample filter and the material it collects are constantly exposed to changing thermodynamic conditions (temperature, pressure, and relative humidity) and changing concentrations of the gaseous components that pass through the filter during sampling. As a consequence, the FRM is only an indicator of PM in the air. It does not precisely represent the mass of PM as it exists and is breathed under ambient conditions.

Compared with the FRM sampling at low ambient temperatures, TEOM monitors that operate at a controlled temperature of 50°C can underreport particulate matter mass when high levels of volatile and semivolatile PM are present in the atmosphere. At a lower temperature, 30°C, a greater fraction of these semivolatile materials is retained, resulting in a greater degree of correlation with the FRM measurements. Studies have shown that when semivolatile particle mass components, such as particulate nitrate or organic compounds from wood smoke, are significant, the TEOM monitor does not provide a one-to-one correlation with the FRM. Although this is not a problem from a sampling perspective, it is an issue when using the TEOM monitor as a continuous monitor for regulatory purposes.

The sample equilibration system for Rupprecht & Patashnick's standard Series 1400a TEOM monitor was designed to partially address those problems by allowing the TEOM to operate at a reduced temperature of 30°C. At this lower temperature, the system collects and retains more of the semivolatile components, such as particulate nitrates and certain organic compounds. The Differential TEOM concept was developed to address sampling issues more completely and to account for short- and long-term changes in mass of the collected filter material over time.

Project Description

The sample equilibration system uses an in-line shell-in-tube dryer made of Nafion® tubing to reduce the humidity level of the sample gases, allowing the TEOM monitor to operate at a temperature closer to the uncontrolled temperature of the 24-hour FRM samples. SES was designed as a retrofit for the standard TEOM monitors. A schematic of the SES TEOM is shown in Figure 1. A testing program was developed and conducted by Rupprecht & Patashnick along with ASRC to verify the performance of the SES-equipped TEOM monitors under controlled laboratory conditions and in extensive field trials. The laboratory tests, performed at the ASRC laboratory, compared the results obtained with the SES-TEOM monitor operating at a controlled temperature of 30°C with those from a standard TEOM monitor operating at 50°C. The field tests allowed for comparison of PM measurements collected using the FRM, the SES-TEOM monitor, and the standard TEOM monitor. The field tests were performed at Queens College in New York City and at Pinnacle State Park in Addison, Steuben County, New York.

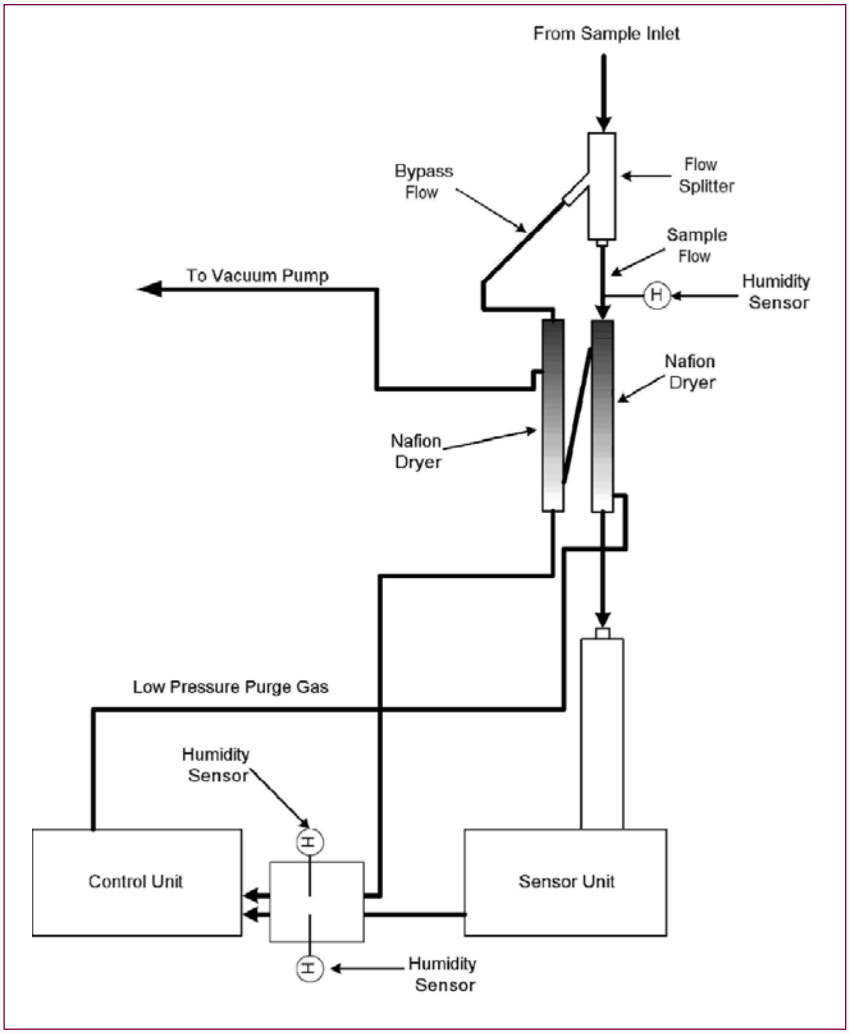

Figure 1.
Schematic of the SES equipped TEOM monitor

The Differential TEOM monitor concept is based on the direct mass reading and real-time capability of the TEOM mass monitor. An electrostatic precipitator is added upstream of the mass monitor so that measurements can be made with the ESP switched on and off for known periods of time. A schematic of the Differential TEOM is shown in Figure 2. When the ESP is off, the TEOM mass sensor samples PM much like a conventional TEOM monitor. When the ESP is on, PM is removed from the sample stream and captured by the ESP. During this ESP-on period, evaporation of collected PM or filter artifacts, such as gas adsorption, desorption, or chemical reactions, may occur. Since these phenomena also occur when the ESP is off, and at the same rates, by comparing the reported mass concentrations from the two periods and determining the resultant mass concentration, the system measures the actual PM in the atmosphere at the time of collection. The system is self-referencing, or self-correcting, and removes from the final reported value the artifacts that are problematic with the FRM.

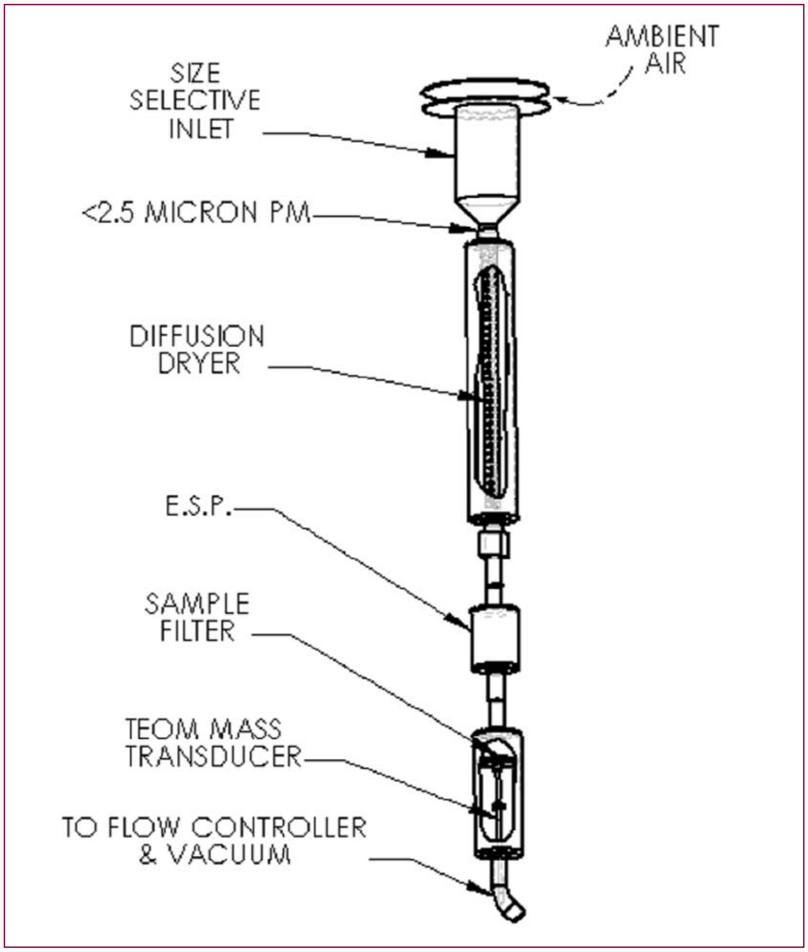

Figure 2.
Schematic of the Differential TEOM monitor

Results

The ASRC laboratory trials were designed to assess the effects of variable humidity on measured PM mass, with and without generated sample aerosols, on both the standard 50°C and the 30°C SES-TEOM monitors. The tests showed that under low humidity, the SES-TEOM monitor and the standard TEOM monitor agreed. With changes in the humidity level in the sample chamber, the standard TEOM monitor showed an effect, but the SES-TEOM monitor was unaffected.

The field trials were performed over multiple seasons at the two locations. The importance of multiple seasons becomes apparent in the results. Overall, the SES-TEOM monitor's 24-hour average mass concentrations correlated more closely with the FRM results than with the standard TEOM monitor results for both sample locations. During warm weather, the TEOM monitor sample temperatures are much closer to the ambient temperatures (the collection temperature of the FRM). Under such conditions, the SES-TEOM monitor and standard TEOM monitor results were both closely correlated with the FRM. During cold weather, the relative difference in sample temperatures was greater for the standard TEOM monitor, and the sample results showed better correlation for the SES-TEOM monitor with the FRM. Correlation of the standard 50°C TEOM and the SES equipped TEOM to the FRM field measurements are all displayed in Figure 3.

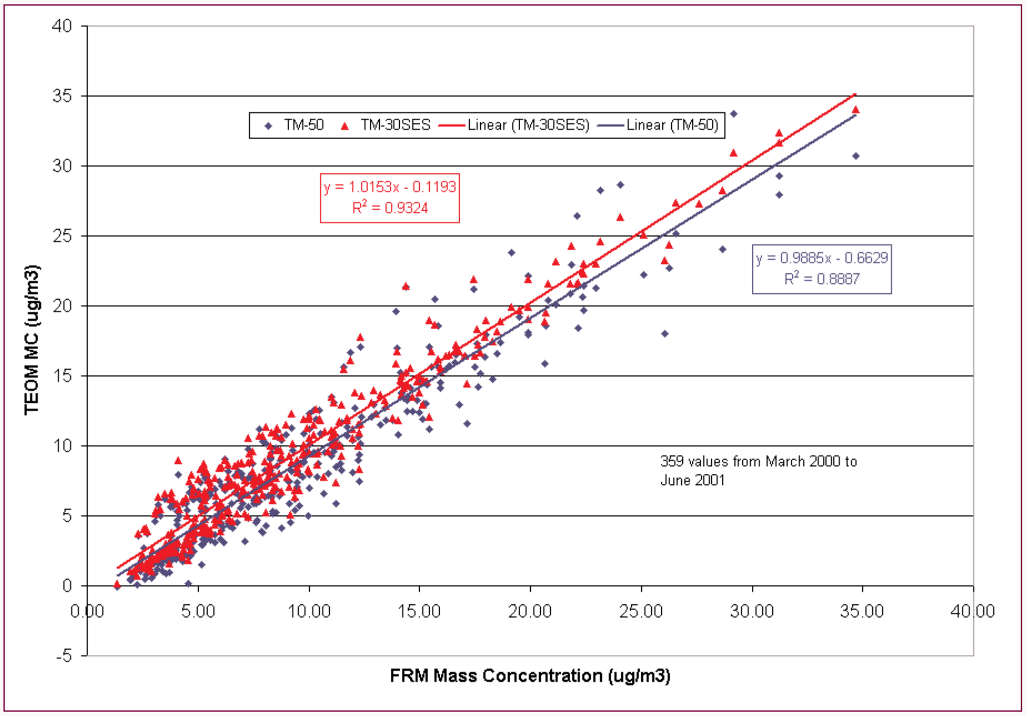

Figure 3.
Comparison of 24-hour average mass concentrations; SES equipped TEOM monitor operating at 30°C (red line), standard TEOM monitor operating at 50°C (blue line), and FRM sample showing better agreement of SES equipped TEOM at 30°C with the FRM. These systems were operated by the Atmospheric Sciences Research Center/University at Albany from March 2000 through June 2001 at Pinnacle State Park in Steuben County, Addison, New York.

The Differential TEOM monitor was evaluated over many months and under many environmental conditions, including laboratory testing. Testing was performed over multiple seasons and at different locations—both in areas with little semivolatile PM in the atmosphere and areas where the level of semivolatile material was quite high.

During testing as part of an EPA-sponsored PM Supersite Program, results from two colocated Differential TEOM monitors were compared with those from a standard TEOM monitor, an SES-TEOM monitor, and the FRM. During the one-month test period, very little semivolatile material existed in the atmosphere in the area. Comparing the results showed that under these conditions, the different methods reported similar results, as expected.

Laboratory testing at the ASRC facilities showed that when sampling sodium chloride aerosol, a nonvolatile aerosol, the Differential TEOM monitor and the SES-TEOM monitor both collected similar amounts and thus reported similar mass concentrations. When sampling ammonium nitrate aerosol, a semivolatile aerosol at room temperature that evaporates at 30°C, the SES-TEOM monitor reported lower mass concentration levels of ammonium nitrate than did the Differential TEOM monitor, as expected. When its ESP was turned off, the Differential TEOM monitor reported a mass concentration similar to that of the SES-equipped monitor during the entire test period. When the ESP was turned on, the Differential TEOM monitor showed that ammonium nitrate was evaporating from the filter. The mass concentration measured during these ESP-on periods indicated the evaporation rate of the ammonium nitrate, and the data were corrected accordingly, yielding a final overall reported mass concentration that was significantly greater than that reported by the SES-TEOM monitor (see Figure 4).

The Differential TEOM monitor was also evaluated at the Los Angeles EPA Supersite in Rubidoux and Claremont, California—areas of high ambient ammonium nitrate levels. The value of the system was shown in the field in the same fashion as illustrated in the laboratory. Comparing the Differential TEOM monitor with the SES-TEOM monitor made it clear that the latter results were affected by the levels of ambient ammonium nitrate. The two colocated Differential TEOM monitors did not exhibit such behavior; rather, their results fell well within the expected accuracy of the instruments.

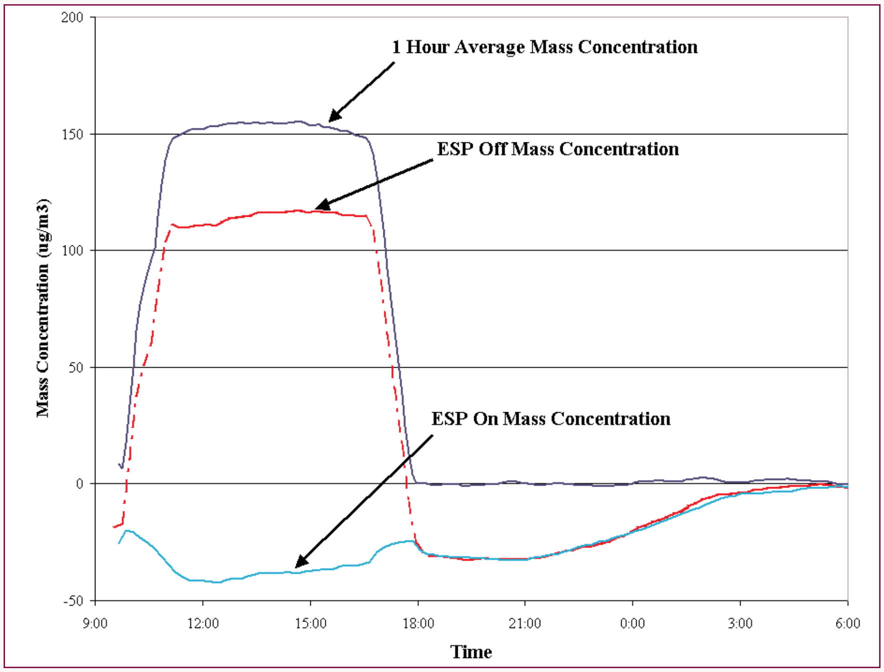

Figure 4.
Performance of prototype Differential TEOM monitor sampling ammonium nitrate from an aerosol chamber at the Atmospheric Sciences Research Center, University at Albany, SUNY. [Measured mass concentration (red line) when ESP is on represents evaporation of ammonium nitrate from sample filter. True net mass concentration (black line) is obtained by subtracting the mass concentration when ESP is on from the mass concentration measured when ESP is off (normal collection).]

Conclusions

The FRM provides a single sample result representing the average ambient PM mass concentration for the collection period. The TEOM monitor was a significant advance over the FRM technology, allowing ambient PM mass concentrations to be monitored in near real-time for extended periods, without the burden of operator intervention. The SES retrofit to the TEOM monitor allows the system to operate at a lower temperature and thus retain a greater fraction of the collected semivolatile compounds, resulting in a greater degree of correlation with the nontemperature-constrained FRM samples. The Differential TEOM monitor technology has shown the ability to resolve issues with adsorption and evaporation of the sample collected by the monitor. As a follow-on to the Differential TEOM project, a simpler filter-based version of the monitor, the Filter Dynamics Measurement System (FDMS) was developed. The Series 8500 FDMS was designed for agencies that need a monitor as part of a routine monitoring network. The FDMS provides results similar to the ESP equipped Differential TEOM Monitor with the same ease of use as the standard TEOM monitor. Since its release, the FDMS has been widely accepted by the industry and received approval from the Air Resources Board of California for both PM-10 and PM-2.5 sampling.

Further information on the SES TEOM and the Differential TEOM can be found in NYSERDA Report 03-06 *Develop and Field Test Rupprecht & Patashnick (R&D)Series-6400 Controlled Sampling Continuos Particulate Monitor* and NYSERDA Report 03-07 *Innovative Instrument for an Ambient Air Particulate Mass Measurement Standard.*

EMEP Program Overview

NYSERDA's Environmental Monitoring, Evaluation, and Protection (EMEP) Program is funded through the system benefits charge (SBC) under the **New York Energy $mart℠** Program. The primary mission of EMEP is to support research to address environmental issues related to the generation of electricity. Since its inception in 1998, the EMEP program has provided objective and policy-relevant research to:

- improve the scientific understanding of electricity-related pollutants in the environment;
- assess the environmental impact of electricity generation relative to other sources of pollution; and
- help develop approaches to mitigate impacts of electricity generation and improve environmental quality.

EMEP has also supported development of advanced environmental instrumentation.

The EMEP program currently supports research in four critical regional environmental issues related to electricity generation: ozone, fine particles, acid deposition, and mercury. Program Opportunity Notices (PONs) are issued periodically to seek proposals that address targeted research areas. Projects are reviewed and selected through this competitive process. The program is guided by a steering committee comprising representatives from the New York State Departments of Environmental Conservation (DEC), Health (DOH), and Public Service (DPS); the U.S. Environmental Protection Agency (U.S. EPA); the National Oceanic and Atmospheric Administration; the New York Academy of Sciences; a utility association; and three environmental and public interest groups. Also, a science advisory committee provides program support and periodic review in critical disciplines.

Under EMEP, NYSERDA sponsors conferences and workshops for policy makers and scientists to share information. They cover a wide range of topics, from asthma in New York City to mercury in remote regions of the Adirondacks. NYSERDA also plans to commission papers to disseminate scientific results in a form useful for policy makers. As research reports become available, NYSERDA and its research partners will post information on-line (see www.nyserda.org). Program Opportunity Notices and information about ongoing projects may also be found on the website.

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