Develop and Field Test Rupprecht & Patashnick (R&P) Series-6400 Controlled Sampling Continuous Particulate Monitor

Final Report 03-06

October 2003

New York State
Energy Research and
Development Authority

The New York State Energy Research and Development Authority (NYSERDA) is a public benefit corporation created in 1975 by the New York State Legislature. NYSERDA's responsibilities include:

- Conducting a multifaceted energy and environmental research and development program to meet New York State's diverse economic needs.
- Administering the **New York Energy $mart**℠ program, a Statewide public benefit R&D, energy efficiency, and environmental protection program.
- Making energy more affordable for residential and low-income households.
- Helping industries, schools, hospitals, municipalities, not-for-profits, and the residential sector, including low-income residents, implement energy-efficiency measures.
- Providing objective, credible, and useful energy analysis and planning to guide decisions made by major energy stakeholders in the private and public sectors.
- Managing the Western New York Nuclear Service Center at West Valley, including: (1) overseeing the State's interests and share of costs at the West Valley Demonstration Project, a federal/State radioactive waste clean-up effort, and (2) managing wastes and maintaining facilities at the shut-down State-Licensed Disposal Area.
- Coordinating the State's activities on energy emergencies and nuclear regulatory matters, and monitoring low-level radioactive waste generation and management in the State.
- Financing energy-related projects, reducing costs for ratepayers.

NYSERDA administers the **New York Energy $mart**℠ program, which is designed to support certain public benefit programs during the transition to a more competitive electricity market. More than 2,700 projects in more than 30 programs are funded by a charge on the electricity transmitted and distributed by the State's investor-owned utilities. The **New York Energy $mart**℠ program provides energy efficiency services, including those directed at the low-income sector, research and development, and environmental protection activities.

NYSERDA derives its basic research revenues from an assessment on the intrastate sales of New York State's investor-owned electric and gas utilities, and voluntary annual contributions by the New York Power Authority and the Long Island Power Authority. Additional research dollars come from limited corporate funds. Some 400 NYSERDA research projects help the State's businesses and municipalities with their energy and environmental problems. Since 1990, NYSERDA has successfully developed and brought into use more than 141 innovative, energy-efficient, and environmentally beneficial products, processes, and services. These contributions to the State's economic growth and environmental protection are made at a cost of about $.70 per New York resident per year.

Federally funded, the Energy Efficiency Services program is working with more than 540 businesses, schools, and municipalities to identify existing technologies and equipment to reduce their energy costs.

For more information, contact the Communications unit, NYSERDA, 17 Columbia Circle, Albany, New York 12203-6399; toll-free 1-866-NYSERDA, locally (518) 862-1090, ext. 3250; or on the web at www.nyserda.org

Develop and Field Test Rupprecht & Patashnick (R&P) Series-6400 Controlled Sampling Continuous Particulate Monitor

Final Report

Prepared for the

New York State Energy Research and Development Authority

Albany, NY
www.nyserda.org

Barry Liebowitz
Senior Project Manager

Prepared by

Rupprecht & Patashnick Co., Inc

Albany, NY

Jeffrey Ambs
Project Manager

NYSERDA Report 03-06

NYSERDA 5060

October 2003

PREFACE

The New York State Energy Research and Development Authority is pleased to publish this report on the demonstration of the Rupprecht & Patashnick Co., Inc., controlled sampling continuous particulate monitor, the SES-equipped TEOM® Monitor. This report was prepared by Rupprecht & Patashnick Co., Inc., with assistance from te State University of New York at Albany - Atmospheric Sciences Research Center - who conducted independent laboratory and field tests. It is our hope that such a development and demonstration effort will further advance automated and continuous methods of measuring ambient levels of particulate matter mass.

This project was funded as part of the New York State Energy $mart℠ Environmental Monitoring, Evaluation and Protection Program and represents one of several studies of the measurement and assessment of fine partiulate matter underway in New York State.

NOTICE

This report was prepared by Rupprecht & Patashnick, Co., Inc. in the course of performing work contracted for and sponsored by the New York State Energy Research and Development Authority (hereafter "NYSERDA"). The opinions expressed in this report do not necessarily reflect those of NYSERDA or the State of New York, and reference to any specific product, service, process or method does not constitute an implied or expressed recommendation or endorsement of it. Further, NYSERDA, the State of New York, and the contractor make no warranties or representations, expressed or implied, as to the fitness for particular purpose or merchantability of any product, apparatus, or service, or the usefulness, completeness, or accuracy of any processes, methods, or other information contained, described, disclosed, or referred to in this report. NYSERDA, the State of New York, and the contractor make no representation that the use of any product, apparatus, process, method, or other information will not infringe privately owned rights and will assume no liability for any loss, injury, or damage resulting from, or occurring in connection with, the use of information contained, described, disclosed, or referred to in this report.

ABSTRACT

Rupprecht & Patashnick Co., Inc., has developed a modification to the successful Series 1400a TEOM® Ambient Particulate Mass Monitor that allows the system to be used under a wider range of operating conditions. The original TEOM monitor, operating at a controlled temperature of 50°C, can under-report particulate matter mass when compared to the Federal Reference Method (FRM) under conditions when the particulate matter mass present in the atmosphere has a high amount of volatile and semi-volatile material. By adapting the TEOM monitor with a Sample Equilibration System (SES), the TEOM monitor is able to operate at a reduced temperature of 30°C or even lower, depending on the temperature of the enclosure housing the monitor. By operating at a reduced temperature, the SES-equipped TEOM monitor retains a greater fraction of these semi-volatile materials providing with a greater degree of correlation when compared to the non-temperature constrained FRM samples. The SES modification to the TEOM monitor has been a successful addition to the R&P product line, with more than 150 units sold being introduced in the spring of 2000.

Keywords: ambient air monitoring, particulate matter, PM, tapered element oscillating micro-balance, TEOM, Federal Reference Method, FRM, Sample Equilibration System, SES.

ACKNOWLEDGMENTS

Rupprecht & Patashnick Co., Inc., thanks NYSERDA for their support in this project; the Atmospheric Sciences Research Center at the University at Albany for their efforts in both laboratory testing and analyses, and in collecting and analyzing the field data for this project, with both the SES-equipped TEOM® monitor and the standard TEOM® monitor; the New York State Department of Environmental Conservation for collecting and providing Federal Reference Method data for comparison; and the Environmental Monitoring Evaluation and Protection (EMEP) Program Advisory Group and Science Advisors for their comments. The success of this project would not have been possible without the assistance of these cooperators.

TABLE OF CONTENTS

FIGURES

EXECUTIVE SUMMARY

Rupprecht & Patashnick Co., Inc., specializes in the development and manufacturing of technology-leading instrumentation to accurately measure particle mass and determine chemical speciation of samples collected from ambient as well as selected source applications. These instruments are intended to aid in improving air quality at the sampling locations and to reduce the pollutants emitted from the designated source applications.

The TEOM® Series 1400a Ambient Particulate Monitor is the world's best-selling USEPA-approved PM-10 continuous ambient particulate monitor. It is used by air monitoring organizations, industry and research organizations worldwide to measure ambient particulate concentration continuously. The time resolution of the Series 1400a Monitor allows users to identify high pollution episodes and determine trends in real time. When used in conjunction with meteorological data or information from gaseous criterial pollutant analyzers, the instrument can provide vital information in the study of human health effects. Other applications of time-sensitive data include source identification and control, short-term compliance monitoring, emergency response, forensic investigations and numerical modeling.

The TEOM monitor is well known for exacting near real-time (minute resolution) particle mass measurement with the unique characteristic of providing direct PM mass measurement without calibration uncertainty. By default, the instrument is usually operated using a 3 l/min sample airstream flow rate and a 50°C filter and sample airstream conditioning temperature. The TEOM mass sensor is operated at a constant temperature and flow rate so that the net mass change is strictly due to material retained on the sample filter and not influenced by changes in operating or sampling parameters.

Specific attention has recently been focused regarding semi-volatile species retention using the TEOM method. Some studies have presented data and discussion concerning the retention of semi-volatile mass on the sample filter of the TEOM monitor relative to the FRM. By operating the TEOM monitor at a fixed temperature of 50°C the issue of retaining semi-volatile species on the TEOM sample filter becomes important. Studies have shown that under atmospheric conditions where there is a significant presence of semi-volatile particle mass component, such as particulate nitrate or organic compounds from wood smoke, the TEOM monitor does not provide a one-to-one correlation with the FRM. While this is not a problem from a sampling perspective, it is an issue when using the TEOM monitor as a continuous monitor for regulatory measurements.

The apparent solution, to reduce the operating temperature of the TEOM monitor to retain more of the light molecular weight chemical components, such as particulate nitrates and certain organic compounds, was not a practical solution as this raises other sample issues. When exposed to normal temperature fluctuations as observed in many sampling trailers, the influence of small changes in particle-bound water and water vapor becomes significant.

A new system was developed to maintain the sample stream flowing into the TEOM monitor at a lower temperature and relative humidity than has been possible in the past. This Sample Equilibration System (SES) continuously conditions the flows of the TEOM monitor, allowing the operation of the instrument year-around at a temperature that is closer to that of the gravimetric FRM filter equilibration temperature. The system incorporates a Nafion® dryer that has been designed for low particle loss. The SES continuously conditions both the sample and bypass flows of the TEOM monitor.

As long as the environment in which the TEOM monitor is housed is maintained at 25°C or less, the instrument can be operated at a temperature set point of 30°C, even in hot and humid summertime conditions. While TEOM monitors have been operated during cooler months in the past at user-definable temperatures in the range of 30 to 40°C, such operating parameters were not feasible under summertime conditions with higher temperature and absolute humidity levels. The new system enables filter-based mass measurements by the TEOM monitor under consistent, dry conditions, permitting high temporal resolution even under changing summertime temperatures and relative humidities.

In addition to test results obtained by R&P in Albany, NY, both laboratory evaluations and field tests were performed by the Atmospheric Sciences Research Center (ASRC) at the University at Albany. The laboratory evaluations compared a SES equipped TEOM monitor operating at 30°C with a standard TEOM monitor at 50°C while being challenged by different aerosols, both non-volatile and semi-volatile. The aerosols tested were NaCl, ammonium nitrate, and ammonium sulfate. In all cases the size of the generated aerosols were less than 1 µm.

During these tests, a constant aerosol level was introduced to an aerosol chamber at the beginning of the tests with a low chamber humidity. As the test progressed, the humidity levels were changed, while the aerosol concentration remained constant. In general the behavior of the two instruments was the same for the NaCl and sulfate aerosols. As the aerosol concentration was increased at the beginning of the sample period, the concentration measured by the two TEOM monitors was identical and remained so until the humidity was stepped up from near zero to 90%. As the humidity was changed, the concentration monitored by the SES equipped TEOM monitor remained constant. However, the standard TEOM monitor operating at 50°C showed dramatic changes in mass concentration with each humidity change. The mass concentration measured using the standard TEOM monitor would return to matching the SES TEOM monitor mass concentration given sufficient time for equilibrium to be reached.

Similar responses to humidity changes were observed when sampling ammonium nitrate from the aerosol chamber. The SES Equipped TEOM monitor did not show appreciable influence due to the changing humidity levels in the chamber, while the standard TEOM monitor was affected. However, due to the nature of ammonium nitrate, there were significant differences between the two instruments in sampling the aerosol. Ammonium nitrate decomposes as the temperature increases above 10ºC. Since the SES TEOM monitor collects sample at 30ºC, the loss of ammonium nitrate from the TEOM sample was a concern. To monitor the overall collection of the nitrate by the two TEOM monitors, a manual gravimetric sample was also collected. Comparing the two TEOM monitors to the manual sample, it is apparent that the standard TEOM monitor essentially does not measure the ammonium nitrate present while the SES equipped TEOM monitor does measure the ammonium nitrate properly.

ASRC also performed field comparisons between the SES TEOM monitor, the standard TEOM monitor and FRM samples. The field comparisons were performed at a rural location, Pinnacle State Park, and an urban location, in Queens NY. Samples were collected at Pinnacle State Park (Steuben County) from March 2000 through June 2001 and in Queens, NY from February 2001 through July 2001.

The results show excellent correlation between the two TEOM monitors and the FRM samples over the duration of the comparison period. The FRM reports values that are approximately 2% lower than the SES equipped TEOM monitor and approximately 2% higher than the 50ºC TEOM sampler results. In both cases the intercept of the correlations is essentially zero indicating that there is no bias with one method compared to another.

Like the results obtained at Pinnacle State Park, the FRM results agree well with both the SES TEOM monitor and the 50ºC TEOM monitor over the entire sampling period. The results from the two TEOM monitors are nearly identical and both collect samples slightly higher than the FRM during this period.

The SES system developed for use with the TEOM particulate mass monitor advanced the ability of continuous monitors to accurately determine the particulate matter mass suspended in ambient air. Thermodynamic sample conditions are clearly a factor in the measurement of ambient aerosol. Reducing the collection temperature, by altering the standard TEOM monitor collection temperature of 50ºC to a temperature of 30ºC, can significantly increase the amount of semi-volatile material collected. In addition to the temperature aspect of the thermodynamics, the removal of water from the sample airstream is also required for proper measurement of the ambient aerosol under the reduced temperature used in the SES system. The SES adaptation for the TEOM particulate monitor has been highly successful in the marketplace as well, with over 150 units sold since its introduction to the market during the spring of 2000.

INTRODUCTION

Problem Statement

In recent years, scientific discussion has included the influence of thermodynamic conditions (e.g., temperature, relative humidity and filter face velocity) on particulate matter (PM) retention efficiency of filter-based samplers and monitors. Method-associated thermodynamic conditions can, in some instances, dramatically influence the presence of particle-bound water and other light molecular weight chemical components such as particulate nitrates and certain organic compounds. The measurement of fine particle mass (e.g., $PM_{2.5}$) presents a new challenge for all PM measurement methods since a relatively greater fraction of the mass is semi-volatile.

The TEOM® continuous PM monitor is a United States Environmental Protection Agency (USEPA) PM_{10} equivalent method (EQPM-1090-079). USEPA federal equivalency designation testing generally requires the 24-hour integrated results from the monitor to compare favorably with results obtained using an USEPA federal reference method (FRM) gravimetric sampler. There are several hundred TEOM monitors deployed throughout the United States, and thousands of monitors throughout the world, being used for both regulatory sampling and scientific studies. The TEOM monitor is well known for exacting near real-time (minute resolution) particle mass measurements, with the unique characteristic of providing direct PM mass measurement without the calibration uncertainty inherent in mass surrogate methods such as opacity or beta attenuation monitors. The instrument is usually operated using a 3 l/min sample airstream flow rate and a 50°C filter and sample airstream conditioning temperature. The TEOM mass sensor is operated at a constant temperature and flow rate so that the net mass change is strictly due to material retained on the sample filter and not influenced by changes in operating or sampling parameters.

Specific attention has been focused on the retention of semi-volatile species using the TEOM sample method. Some studies presented data and discussion concerning the retention of semi-volatile mass on the sample filter of the TEOM monitor relative to the FRM[1]. By operating the TEOM monitor at a fixed temperature of 50°C, the issue of retaining semi-volatile species on the TEOM sample filter becomes important. Studies have shown that under atmospheric conditions where there is a significant presence of semi-volatile particle mass component, such as particulate nitrate or organic compounds from wood smoke, the TEOM method does not provide a one-to-one correlation with the FRM. While this is not a problem from a sampling perspective, it is an issue when using the TEOM monitor as a continuous monitor for regulatory measurements.

---

[1] Chow, J.C. (1995). Critical Review: Measurement Methods to Determine Compliance with Ambient Air Quality Standards, J. Air & Waste Management Association. 45:320-382.

Figure 1 illustrates the problem of matching the FRM with the standard TEOM monitor configuration. While the correlation between the two methods is reasonable, the slope of the correlation is such that the FRM overestimates the ambient mass concentration relative to the TEOM sampler results by 25% during this comparison period. While the TEOM monitor operating at 50ºC provides a very accurate measure of ambient particulate mass, the measurement is only truly valid at the reference temperature of 50ºC.

Based on these results, the goal was to develop a simple retrofit for the standard TEOM monitor configuration that would provide a 24-hour integrated PM mass concentration measurement that is more comparable to that of the USEPA FRM. An additional objective was to provide rapid particle equilibration on the sample filter for more representative short time resolution measurements.

The apparent solution was to reduce the operating temperature of the TEOM monitor to retain more of the light molecular weight chemical components such as particulate nitrates and certain organic compounds. However, simply lowering the operating temperature of the TEOM monitor was not a practical solution as this raised other sample issues. By lowering the temperature, the influence of small changes in particle bound water and water vapor becomes significant. Figure 2 shows the behavior of a standard TEOM monitor operating at 30ºC when exposed to normal temperature fluctuations as observed in many sampling trailers. These wide swings in mass concentration are not acceptable when trying to observe changes in ambient mass concentration over short term observations. If the ambient conditions are 20ºC and 50% relative humidity (%RH), typical summer conditions, the %RH at 50ºC is approximately 12%, while at 30ºC the %RH is over 35%. As the temperature cycles inside the sample environment, this influences the amount of water bound to the particles as they pass through the sample tubes. (This temperature cycling is typical of the temperature changes caused by the air conditioning systems present in a standard environmental sampling trailer.) At a low %RH, the amount of water present is small, so these small fluctuations in temperature do not affect the sample results. As the humidity increases, the effect of small changes become problematic, as can be seen in the figure.

Thus, to satisfy the original goal of the retrofit for the TEOM monitor, it was desirable to maintain as low an operating temperature as practical while also removing unwanted particle-bound water and water vapor. Reducing the operating temperature of the TEOM monitor is simple, while reducing the water content of the sample requires a more thorough approach.

Solution Description

A new system was developed to maintain the sample stream flowing into the TEOM monitor at a lower temperature and relative humidity than has been possible in the past. This Sample Equilibration System (SES) continuously conditions the flows of the TEOM monitor, allowing the operation of the instrument year-around at a temperature that is closer to that of the gravimetric FRM filter equilibration temperature. The SES continuously conditions both the sample and bypass flows of the TEOM monitor.

The dryers used in the conditioning system of the SES adaptation for the TEOM monitor incorporate selective membranes made of Nafion® tubing. Nafion is a copolymer of tetrafluoroethylene (Teflon) and perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid. Like Teflon®, Nafion is highly resistant to chemical attack, but the presence of its exposed sulfonic acid groups confers unusual properties. Sulfonic acid has a high affinity to water, absorbing 13 molecules of water for every sulfonic acid group in the polymer. Unlike micro-porous membrane permeation, which transfers water through a relatively slow diffusion process, Nafion removes water by absorption as water-of-hydration. This absorption occurs as a first order kinetic reaction, so equilibrium is reached very quickly (typically within milliseconds). Because this is a specific chemical reaction with water, gases being dried or processed are usually entirely unaffected, which makes the material ideal for removing water from the sample without affecting any of the other semi-volatile compounds present in the air stream.

The water moves through the membrane wall and evaporates into the surrounding air or purge gas in a process called perevaporation. This process is driven by the humidity gradient between the inside and the outside of the tubing. This humidity gradient is achieved in the SES by reducing the pressure of the purge gas, setting up a difference in the water vapor pressure across the membrane, driving the drying process of the system.

As long as the environment in which the TEOM monitor is housed is maintained at 25°C or less, the instrument can be operated at a temperature set point of 30°C, even in hot and humid summertime conditions. While TEOM monitors have been operated during cooler months in the past at user-definable temperatures in the range of 30 to 40°C, such operating parameters were not feasible under summertime conditions with higher temperature and absolute humidity levels. The new system enables filter-based mass measurements by the TEOM monitor under consistent, dry conditions, permitting high temporal resolution even under changing summertime temperatures and relative humidities.

The addition of the SES did not require any hardware modifications to TEOM monitors delivered since January 1996 (Series 1400a Revision b), and can be easily retrofitted onto earlier instruments. The SES fits between the flow splitter that follows the size selective inlet, and the entry point of the TEOM sensor unit (Figure 3). The tested configuration added at most 50 cm to the length of the sample inlet system, and conditioned both the sample and bypass flows that together form a total flow rate of 16.7 l/min (1 m^3/h). Relative humidity sensors monitor the effectiveness of the continuous conditioning process, allowing the TEOM control unit to collect and store this information electronically. The tested system had a diameter of approximately 10 cm, including both Nafion® dryers and the necessary flow interconnections. The system does not contain any electromechanical components other than the associated humidity sensors.

Figure 4 shows a schematic of the flow paths in a TEOM system containing the SES. The sample and bypass flows that exit from the flow splitter pass through a pair of Nafion dryers to remove water vapor and reduce humidity levels. From the exit of the SES, the sample flow is routed through the TEOM mass sensor and the bypass flow is routed to the control unit as in the standard configuration. The dried sample and bypass flows then proceed through mass flow controllers that maintain a constant volumetric flow rate, and are combined just prior to the exit from the TEOM control unit to form a total flow of 16.7 l/min. Due to the pressure drop created at the mass flow controllers, the dried combined air stream forms a lower pressure zone between them and the vacuum pump. This dried, low-pressure merged-system flow then becomes the purge flow through the Nafion drier applied to the sample stream, followed by the dryer on the bypass flow. Relative humidity sensors positioned after the dryers provide an ongoing measurement of the effectiveness of the dryers. This information can be collected and logged in the TEOM control unit.

The Nafion dryers incorporated in the tested system were of a specially designed geometry to minimize the potential for the loss of particles at the entry point. The dryer on the bypass flow line consisted of 50 tubes of 0.025 inch inner diameter (ID), while the sample stream dryer consisted of 18 tubes of 0.06 inch ID. Nafion material can be used effectively in applications such as this because of its specific affinity for water. In the presence of a water vapor gradient, the substance allows the effective passage of moisture. Nafion dryers are similar to shell-in-tube heat exchangers, with an outside shell and strands of Nafion tubing down the center. In the SES, circulating the dried air that exits from the control unit around the18 strands of Nafion tubing in the dryer creates the water vapor gradient. The Nafion dryers also aid in lowering the sample stream temperature toward that of the air monitoring station or shelter, allowing for an operation setting for the TEOM monitor that can sometimes be lower than the ambient air temperature. The TEOM sample stream temperature setting can be about 5ºC higher than the station temperature.

TEST RESULTS

Test Results - R&P

Prototype SES units were evaluated at the R&P facility in Albany, NY. The testing period presented was sufficient to cover a representative range of ambient relative humidity and temperature conditions, including one challenging performance evaluation of the SES during a summertime high temperature, high relative humidity episode. Figure 5 shows National Weather Service hourly temperature, dew point temperature and relative humidity data over a six-day period, 30 July through 4 August 2000. The first two days were generally characterized by daytime temperatures over 30ºC, and more humid conditions as indicated by the broader nocturnal relative humidity peaks at or near saturation. An air mass change occurred during the 1^{st} of August marked by a dew point temperature shift of 8ºC. We can focus on the performance character of the SES by examining the PM mass concentration and exit relative humidity before and after the air mass change.

Figure 6 shows the $PM_{2.5}$ mass concentration from two collocated TEOM monitors, one operated at the default 50ºC conditioning temperature without an SES, the other set for 30ºC with an SES. Both monitors used a 3 l/min sample air stream flow rate. Also shown is the ambient relative humidity and exit sample air stream relative humidity from the SES. The data indicate that the post-dryer relative humidity stayed reasonably low and stable in the 20 to 28% range over the entire period. During the higher humidity conditions experienced over the first two days, the SES was able to maintain a sample air stream relative humidity under 30%. Comparing the temporal patterns in the PM concentration of the two TEOM monitors it is apparent that the system using the SES generally measures more mass. This is likely due to better retention of light molecular weight semi-volatile material associated with the fine particle mass. In general, use of the dryer component at a reduced conditioning temperature should help reduce the tendency for chemical processes (*e.g.*, chemical dissociation, gas-particle interaction) that can lead to positive or negative biases on sample filters. In addition, the dried sample air stream in the SES system encourages rapid sample equilibration by minimizing longer time constant equilibrium adjustments of the particle to the surrounding gas stream. This can help provide a better representative short-term mass concentration that includes a measure of semi-volatile components.

After the completion of the comparison tests between the prototype SES TEOM monitor and the standard system, the 24-hour integrated TEOM sampler data was compared with USEPA FRM collected sample results. Figure 7 shows a comparison of the integrated SES TEOM data and the FRM results over the same period as the data presented in Figure 1. In contrast to the data obtained using the standard TEOM monitor operating at 50ºC, the SES TEOM monitor shows a much closer correlation with the FRM samples. This suggests that, relative to the FRM sampler, nearly 20% of the particle mass sampled is volatile between 30 and 50ºC. Note that the FRM-type sampler may also exhibit semi-volatile mass loss at the near-ambient sample stream temperature that it maintains, however the mass loss from the FRM sample is not measured in the method. Nonetheless, operating the SES system on a TEOM monitor set at 30ºC conditioning temperature provides conditioning that is more conducive to retaining semi-volatile particle mass. Note, however, that exact comparison of time integrated data between automated continuous PM methods and manual gravimetric PM methods can be confounded by the methodologies themselves. Continuous monitors generally utilize a dynamic conditioning approach in order to provide meaningful near real-time data. Reference-type gravimetric samplers, however, employ by definition a hybrid dynamic and static sample filter conditioning scheme. Reference sample collection often occurs during varying diurnal ambient temperature and relative humidity, while post-sampling filter equilibration is applied in a static environment, first at the varying thermodynamic conditions in the sampler itself, followed by the better defined (but different) conditions at the laboratory.

Laboratory Test Results - ASRC

In addition to test results obtained by R&P in Albany, both laboratory evaluations and field tests were performed by the Atmospheric Sciences Research Center (ASRC) at the University at Albany. The laboratory evaluations compared a SES equipped TEOM monitor operating at 30ºC with a standard TEOM sampler at 50ºC being challenged by different aerosols, both non-volatile and semi-volatile. The ASRC laboratory consists of a large aerosol chamber and generators for producing different types and concentrations of aerosols for comparison. The aerosols tested were NaCl, ammonium nitrate, and ammonium sulfate. In all cases the size of the generated aerosols were less than 1 µm.

The initial work at ASRC investigated the behavior of the SES TEOM monitor and the standard TEOM sampler when sampling air with different levels of humidity. As shown in Figure 8, even with large changes in the sample humidity, the change in total mass as indicated by the SES TEOM monitor was very slight. In contrast, the standard TEOM sampler operating at 50ºC was definitely affected by these changes in humidity. This was most likely due to small changes in the monolayer of water on the surface of the filter material.

The next phase of the test program at ASRC was to compare the behavior of the different instruments when sampling different challenge aerosols. Figure 9 illustrates the results obtained when sampling NaCl aerosols from the ASRC aerosol chamber over a period of eight hours. Except during the initial rise in concentration, the two instruments show identical behavior and results. The discrepancy during the initial sample period is due to the instability of the aerosol and generation system settling during the startup phase of the test. Since NaCl aerosols are non-volatile it was expected that the two instruments would show identical behavior.

Two sulfate aerosols, ammonium sulfate and copper sulfate, were also tested. During these tests, a constant aerosol level was introduced to the aerosol chamber at the beginning of the tests with a low chamber humidity. As the test progressed, the humidity levels were changed, while the aerosol concentration remained constant. Figures 10 and 11 illustrate the results of these tests. In general, the behavior of the two instruments was the same for the two different aerosols. As the aerosol concentration was increased at the beginning of the sample period, the concentration measured by the two TEOM monitors was identical and remained so until the humidity was stepped up from near zero to 90%. As observed in the figures, the concentration monitored by the SES TEOM sampler remained constant at each increase in humidity as expected with the constant source being introduced to the aerosol chamber, however, the standard TEOM monitor operating at 50ºC showed dramatic increases in mass concentration with each humidity increase. This is due to two factors. First, the standard TEOM monitor is affected by changes in humidity as discussed above. Second, the sulfate aerosols will also adsorb water vapor as the humidity changes and it is due to these changes that the system shows the most mass gain during these tests. The measured mass concentration for each increase rises as the water is adsorbed by the sulfate and gradually declines. The mass concentration would return to matching the SES TEOM monitor mass concentrations given sufficient time for equilibrium to be reached. Similarly on each decrease in humidity, the 50ºC TEOM monitor underestimates the mass concentration as the collected sulfate releases the water adsorbed during the high humidity sections of the test.

Finally, ammonium nitrate was collected using the two TEOM monitors. In addition, a manual gravimetric sample was collected using a R&P manufactured FRM sampler. This sample was used to verify the collection of the nitrate on the SES TEOM monitor operating at 30ºC compared to the FRM sample at room temperature (20ºC). Ammonium nitrate decomposes as the temperature increases above 10ºC. Since the SES TEOM monitor collects sample at 30ºC, the loss of ammonium nitrate from the collected TEOM sample is a concern. Comparing the integrated the mass concentrations measured by the SES TEOM monitor during the test and the manual gravimetric sample yielded a difference of approximately 2%, well within the tolerance limits of this type of test, illustrating that during the sample period, the SES TEOM is able to properly measure the levels of ammonium nitrate aerosol present.

Figure 12 shows the comparison between the two TEOM instruments when collecting ammonium nitrate aerosol. Again, the %RH was changed in the aerosol chamber during the test. The most obvious feature of the data is that at 50ºC, the TEOM method essentially does not measure the ammonium nitrate present. The concentration of the sample was near 350 $\mu g/m^3$ during the entire duration of the test and yet the standard

TEOM monitor indicated a concentration of approximately 15 µg/m^3. The only changes in measured mass concentrations were due to the step changes in %RH inside the aerosol chamber as observed previously.

Previous studies have shown that the SES TEOM monitor, while able to properly collect ammonium nitrate in the field, does show negative mass concentrations as the ambient concentrations of ammonium nitrate decline. Literature also shows that at 30ºC, ammonium nitrate will completely decompose to NH3 and HNO3. This suggests that there is decomposition and loss of the previously collected ammonium nitrate. The total mass of the ammonium nitrate collected during the previous experiment (figure 12) was monitored during the week after the collection period. Figure 13 shows the total mass during the test as well as the reported mass concentration. As the collection during the test is completed, the total mass increases to 1800 µg, at which time introduction of ammonium nitrate into the test chamber was terminated. Over the next six days, the total mass reported by the SES TEOM monitor decreases at a constant rate, until eventually all of the ammonium nitrate is lost from the TEOM sample filter. This constant loss rate is also observed in the constant negative mass concentration value.

These laboratory tests illustrate the issue of sampling semi-volatile compounds under different instrument operating conditions. For ammonium nitrate, the TEOM monitor operating at 50ºC does not collect appreciable amounts of the material (and was therefore omitted from the last figure), and the SES TEOM monitor, while collecting all of the sample during the high concentration periods, does not retain the material over time when operating at 30ºC.

Field Test Results - ASRC

The final aspect of the ASRC evaluations are the field comparison of the SES TEOM monitor operating at 30ºC with the standard TEOM system operating at 50ºC and also compared against the FRM samples. All systems were configured for $PM_{2.5}$ sampling. Field comparisons were performed at a rural location, Pinnacle State Park, and an urban location, in Queens, NY. Details on the test conditions and sampling issues at the two sampling locations are given in Appendix A, ASRC Final Report Documentation, ASRC.

Figure 14 is a comparison of SES TEOM monitor and 50ºC TEOM monitor results versus FRM samples collected over the entire duration of the testing, from March 2000 through June 2001, at the Pinnacle State Park sampling location. The FRM results show excellent correlation with the two TEOM monitors over the duration of the comparison period. The FRM reports values that are approximately 2% lower than the SES equipped TEOM monitor and approximately 2% higher than the 50ºC TEOM monitor. In both cases the intercept of the correlations is essentially zero indicating that there is no bias with one method compared to another.

Part of the motivation for the development of the SES TEOM monitor was to in response to reports that the TEOM monitor under reports values under conditions with appreciable levels of semi-volatile materials in the atmosphere. The presumption being that at the higher temperatures, not all of the volatile material is collected on the sample filter, or if it is collected, the material evaporates resulting in negative reported mass concentration values. Figure 15 presents the correlation between the two TEOM monitors results and the FRM results during June, July, and August 2000. During these warm months of the year, the correlation between the two TEOM monitors and the FRM are similar to the correlation over the entire test period. Figure 16 presents the correlation for the months December 2000 and January and February 2001. During this period, the FRM over reports compared to the SES TEOM monitor by approximately 5% and the 50ºC TEOM monitor by nearly 20%. Clearly there is an influence of the sample temperature on the material collected on the sample filters during the cold weather periods. Recall that one significant difference between the two TEOM monitors and the FRM samples is that the TEOM monitors are operated and collect the suspended particulate at fixed temperatures while the FRM samples are collected under variable thermodynamic conditions. These variable sample conditions can significantly influence the material collected compared to sampling under fixed conditions. The initial ASRC report on the results obtained from the SES TEOM monitor testing at the rural location at Pinnacle Sate Park is presented as Appendix B, and the complete detailed results from the field testing are given in Appendix C.

The urban location for comparison was located at PS219 in Queens, NY. Due to infrastructure issues, the SESS TEOM monitor was not able to be installed until late January 2001, so that the comparison period was from February 2001 through July 2001. Like the results obtained at Pinnacle State Park, the FRM results agree well with both the SES TEOM monitor and the 50ºC TEOM monitor over the entire sampling period as shown in Figure 17. The results from the two TEOM monitors are nearly identical and both collect samples slightly higher than the FRM during this period. During the warmer months of May, June, and July, Figure 18, the FRM again samples less material than the two TEOM monitors, under reporting the SES TEOM samples by 10%. In both of these representations, the correlation between the samples is quite high, with an R^2 generally greater than 0.95. When comparing the results of the two TEOM monitors to the FRM samples during colder months, February, March, and April, Figure 19, it is clear that the FRM collects significantly higher amounts of particle mass than the two continuous monitors. Again, considering the unconstrained sample conditions of the FRM, this result is not surprising, however, due to the few data sets in each month, care must be taken to avoid invalid conclusions. Complete results are listed in Appendix D.

CONCLUSIONS

The SES system developed for use with the TEOM particulate mass monitor advanced the ability of continuous monitors to accurately determine the particulate matter mass suspended in ambient air. Thermodynamic sample conditions are clearly a factor in the measurement of ambient aerosol. Reducing the collection temperature, by altering the standard TEOM temperature of 50ºC to a temperature of 30ºC, can significantly increase the amount of semi-volatile material collected. In addition to the temperature aspect of the thermodynamics, the removal of water from the sample airstream is also required for proper measurement of the ambient aerosol under the reduced temperature used in the SES system on the TEOM particulate monitor. Without removing water from the airstream, changes in the humidity level can significantly affect the measured mass concentration obtained from any continuous monitor operating at a temperature below 50ºC.

The SES adaptation for the TEOM particulate monitor has been highly successful with over 150 units sold since its introduction to the market during the spring of 2000. The SES allows the TEOM monitor to operate at a lower temperature and provide measurements which approach more closely the results obtained using the FRM.

FUTURE DIRECTION

As the understanding that the changes in the thermodynamic conditions can be significant in the determination of the ambient particulate grows, R&P is ready to take the lead in properly measuring the levels of particulate as they exist in the atmosphere at the time of collection. The FRM collects the sample under actual ambient temperature conditions, however, the sample is then placed in a controlled temperature and humidity environment, potentially affecting the sample collected on the filter. Instead, R&P has developed a Differential TEOM monitor that, in addition to collecting the sample under ambient temperature conditions, also performs the actual mass measurement under the sample conditions in near real-time. This provides an actual and correct mass measurement without the significant delay in time required for the FRM. The SES is an integral part of this new Differential TEOM monitor.

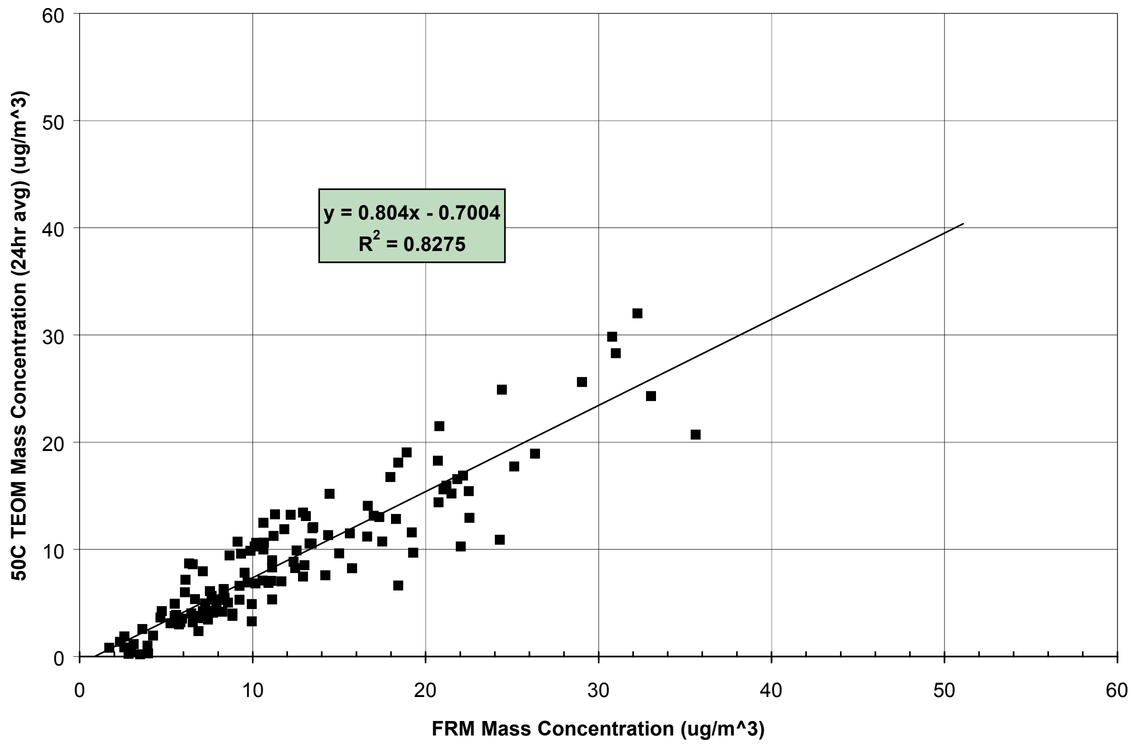


Figure 1. Comparison between standard TEOM monitor operating at 50ºC and FRM mass concentrations (24-hour averages).

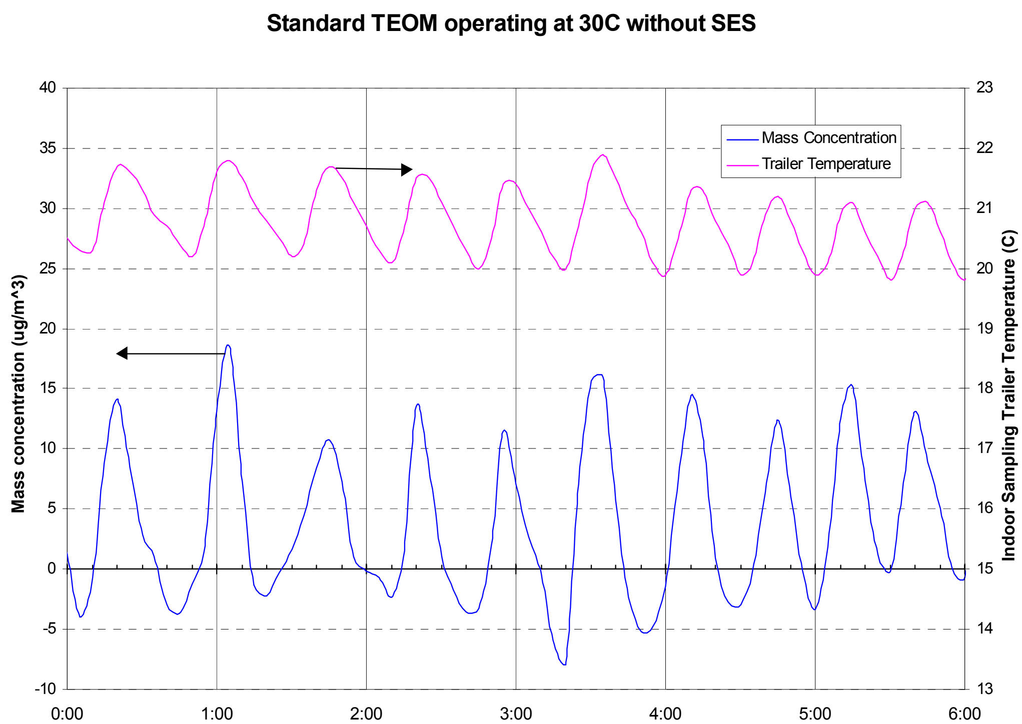


Figure 2. Effect of changing sampling environment temperature on mass concentration in a standard TEOM monitor operating at 30ºC without and SES system.

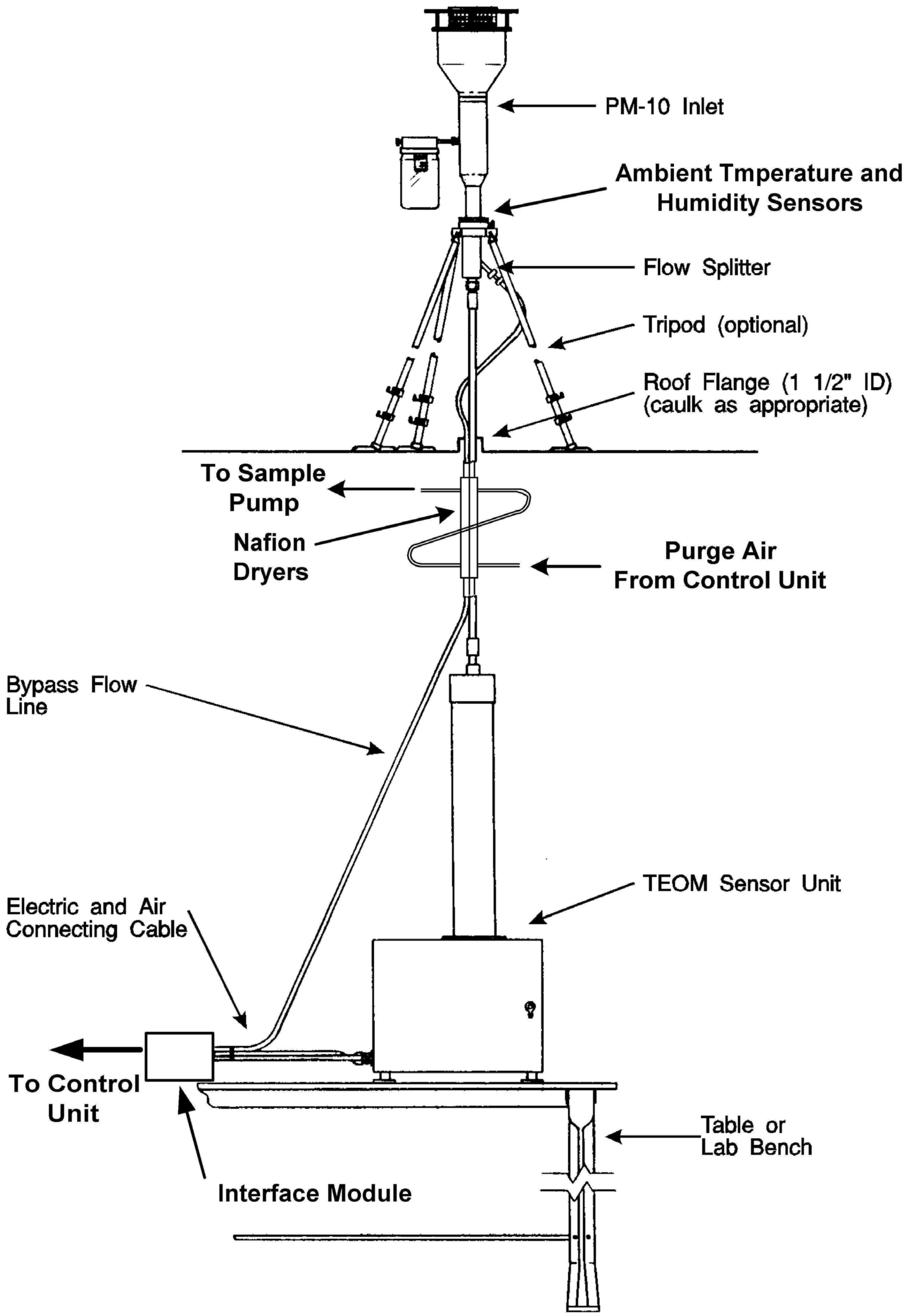


Figure 3. TEOM monitor test configuration with SES system.

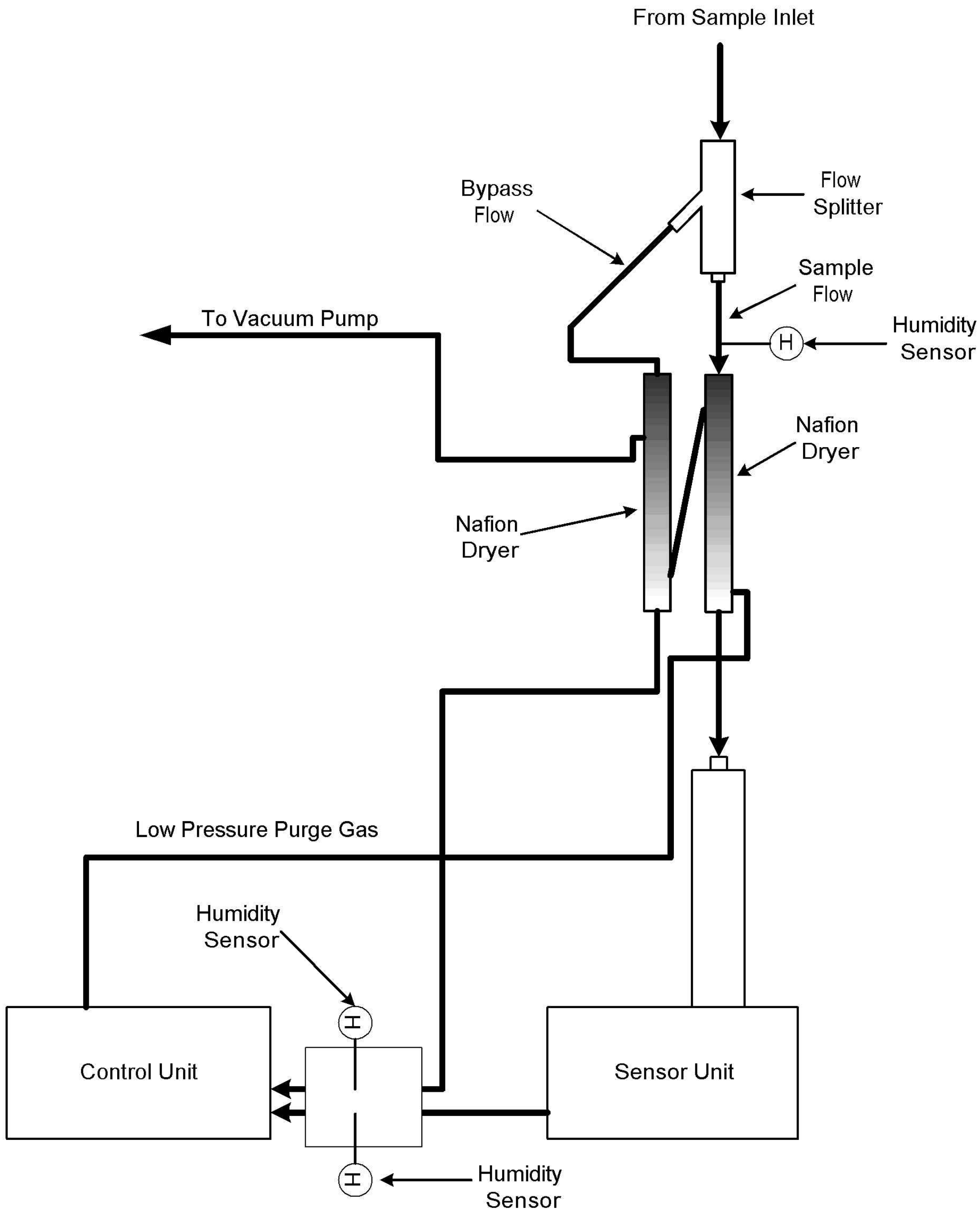


Figure 4. Schematic of SES equipped TEOM monitor.

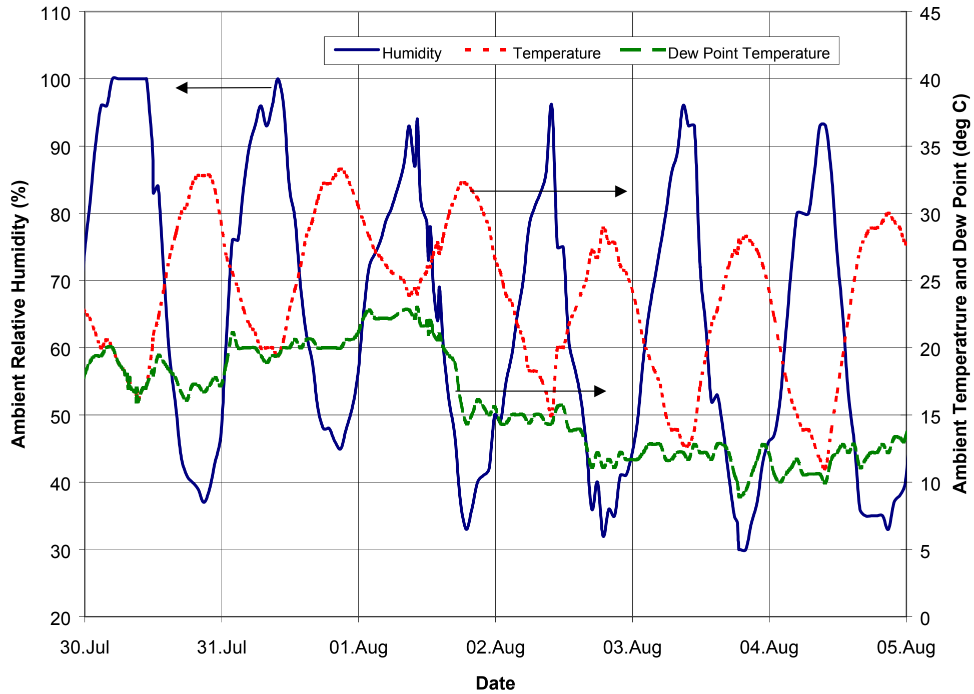


Figure 5. Representative plot of changing ambient temperature, humidity, and dewpoint over a period of six days in Albany, NY (30 July - 5 August 2000).

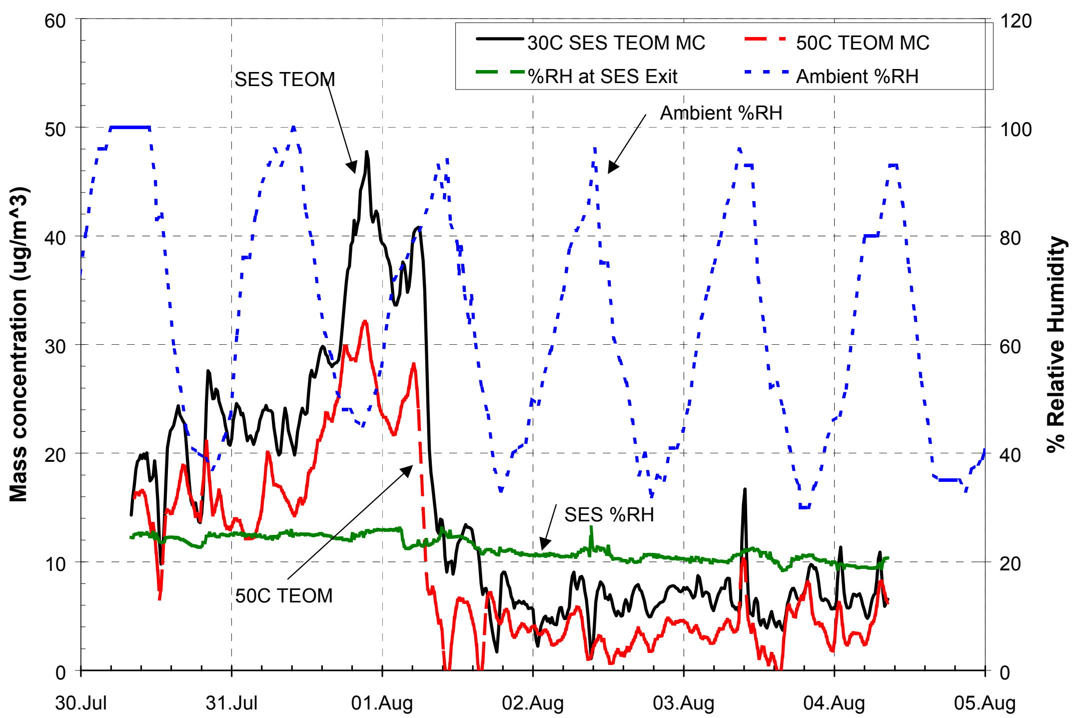


Figure 6. Comparison of mass concentrations for two collocated TEOM monitors; SES equipped TEOM monitor operating at 30ºC and a standard TEOM monitor operating at 50ºC. From 30 July - 5 August 2000.

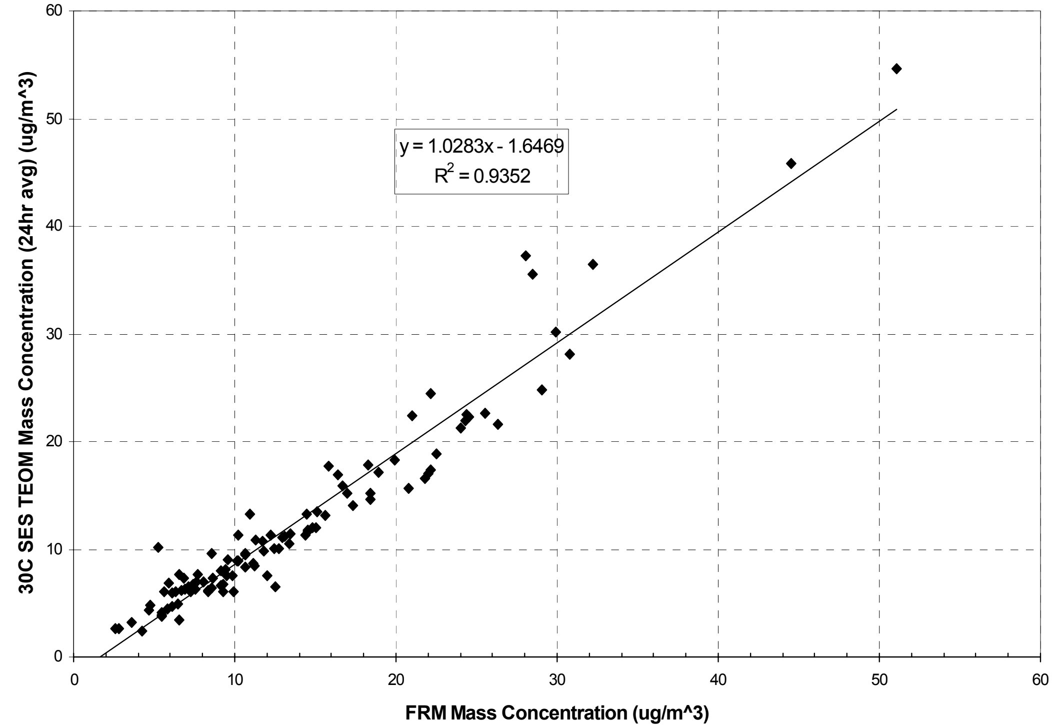


Figure 7. Comparison between 24 hour average 30ºC TEOM monitor and FRM mass concentrations.

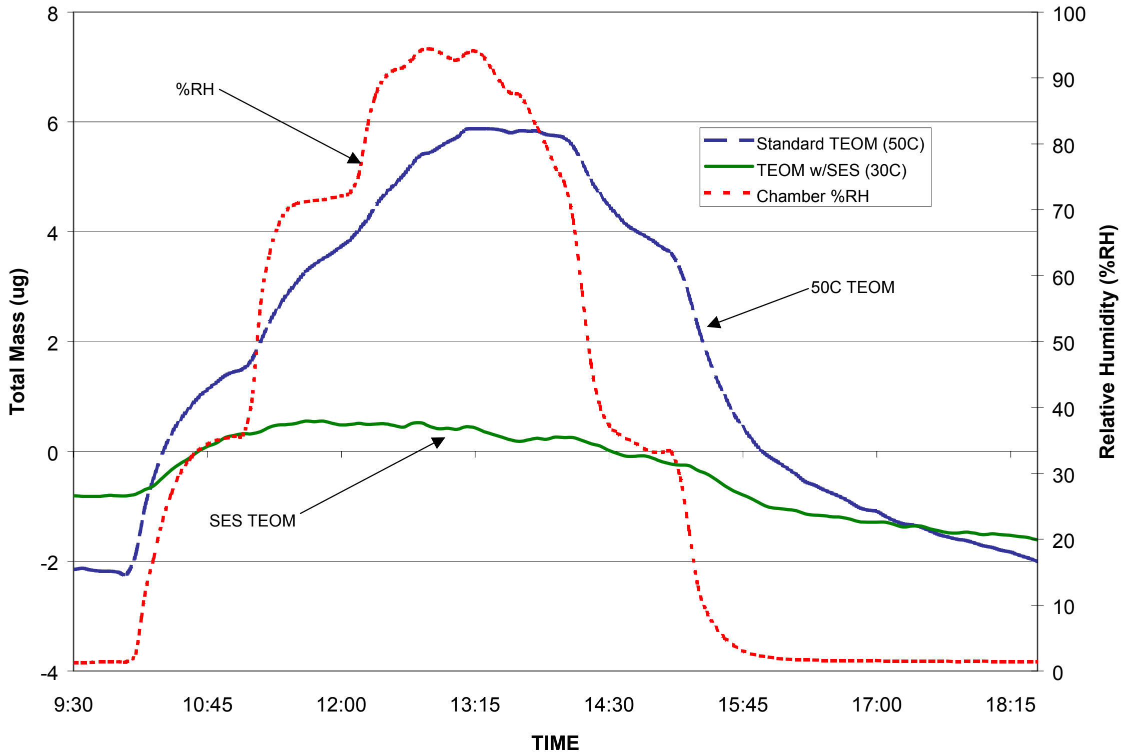


Figure 8. Comparison of the effect of changing sample relative humidity on the reported mass of a standard TEOM monitor operating at 50ºC and a SES equipped TEOM monitor operating at 30ºC.

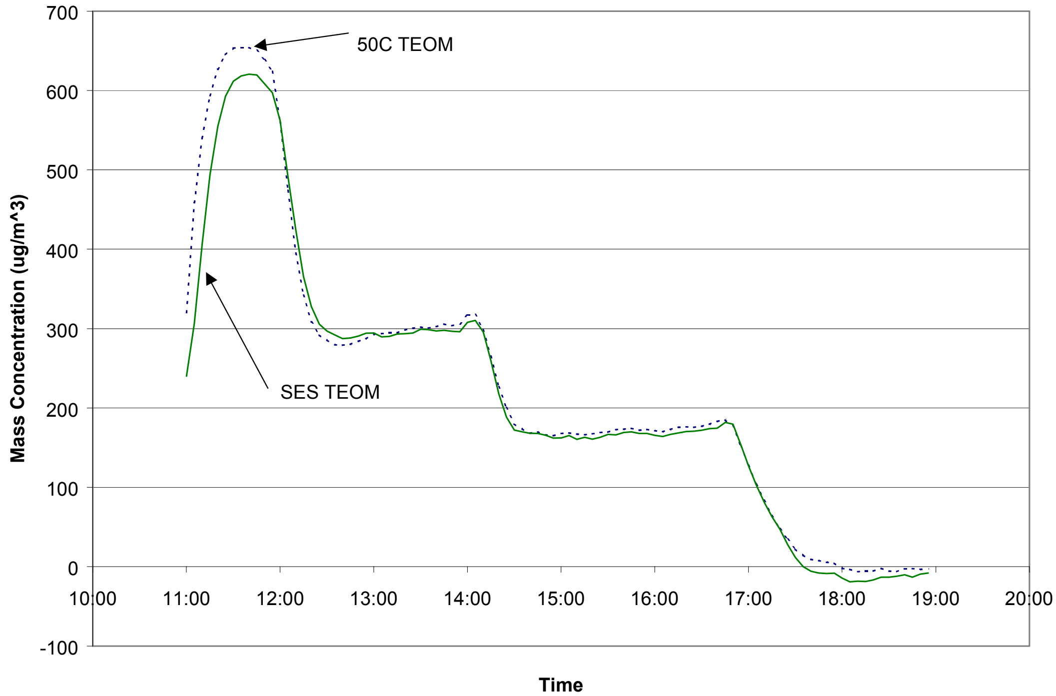


Figure 9. Comparison of SES equipped TEOM monitor operating at 30ºC and a standard TEOM monitor operating at 50ºC collecting NaCl aerosol.

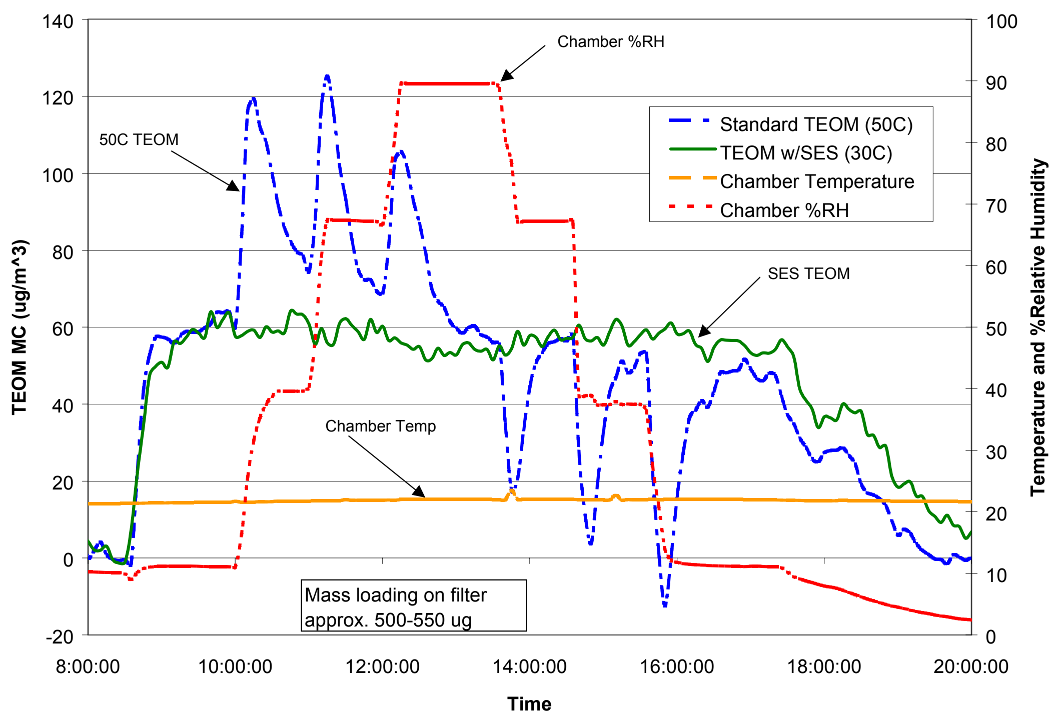


Figure 10. Results comparing mass concentrations of copper sulfate collected by SES equipped TEOM monitor and standard TEOM monitor.

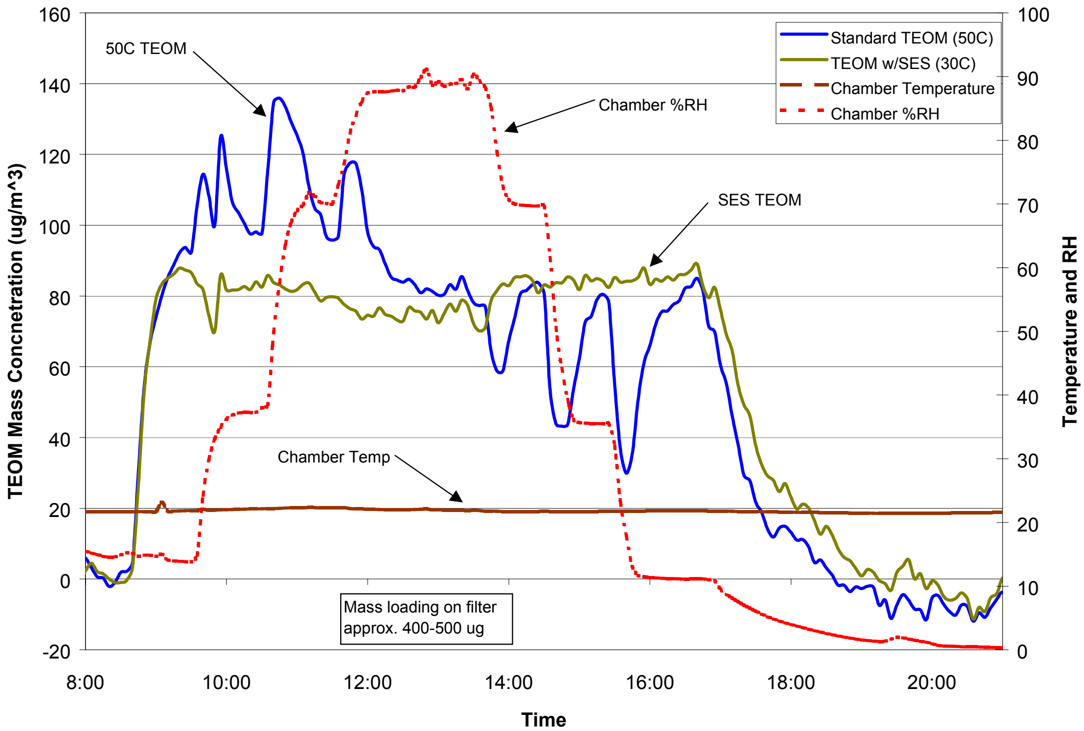


Figure 11. Comparison of SES TEOM and standard TEOM mass concentrations while collecting ammonium sulfate under changing humidity levels.

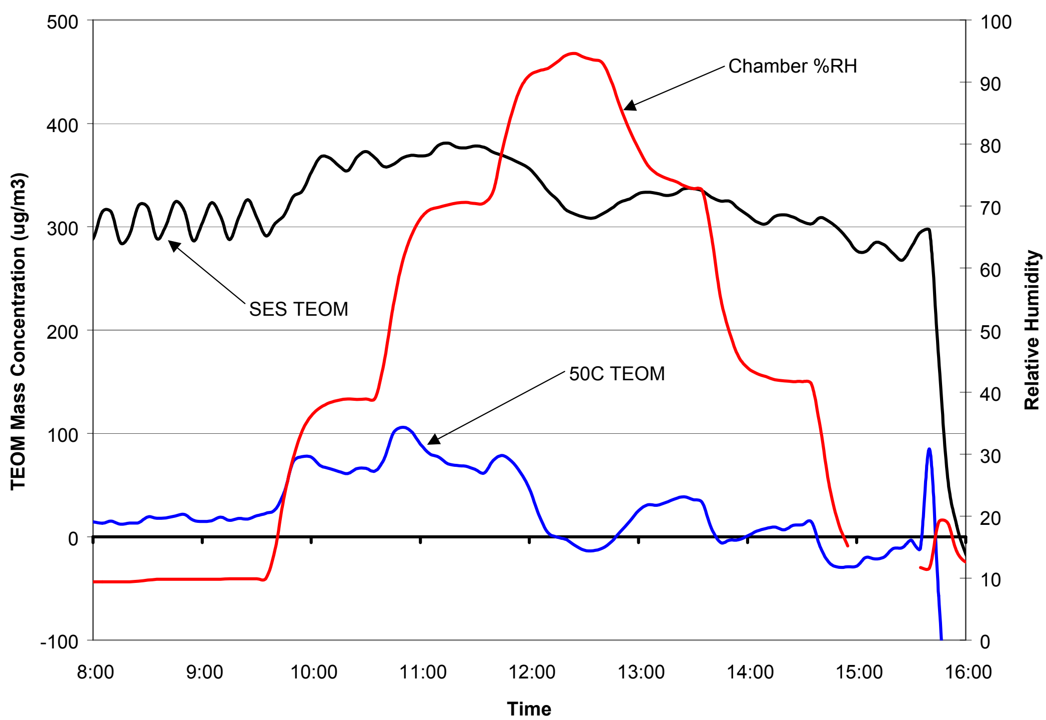


Figure 12. Comparison between SES equipped and standard TEOM monitors collecting ammonium nitrate during changing humidity conditions.

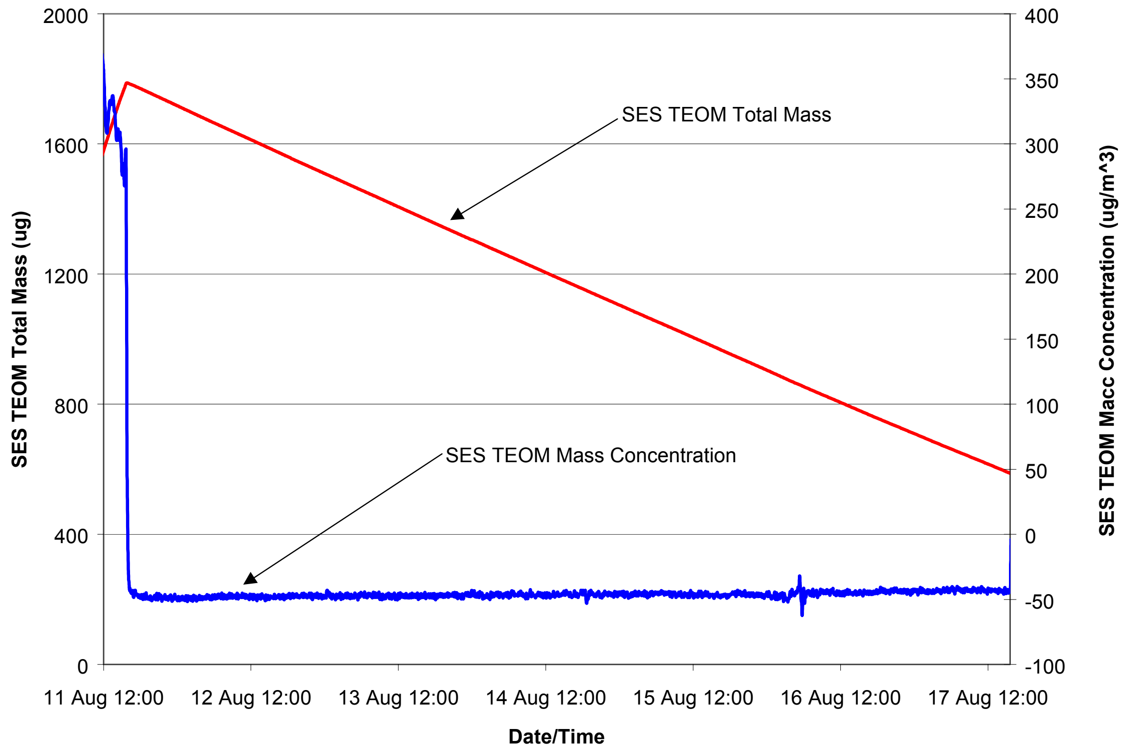


Figure 13. Evaporation of ammonium nitrate from SES equipped TEOM monitor, operating at 30ºC, over a period of six days.

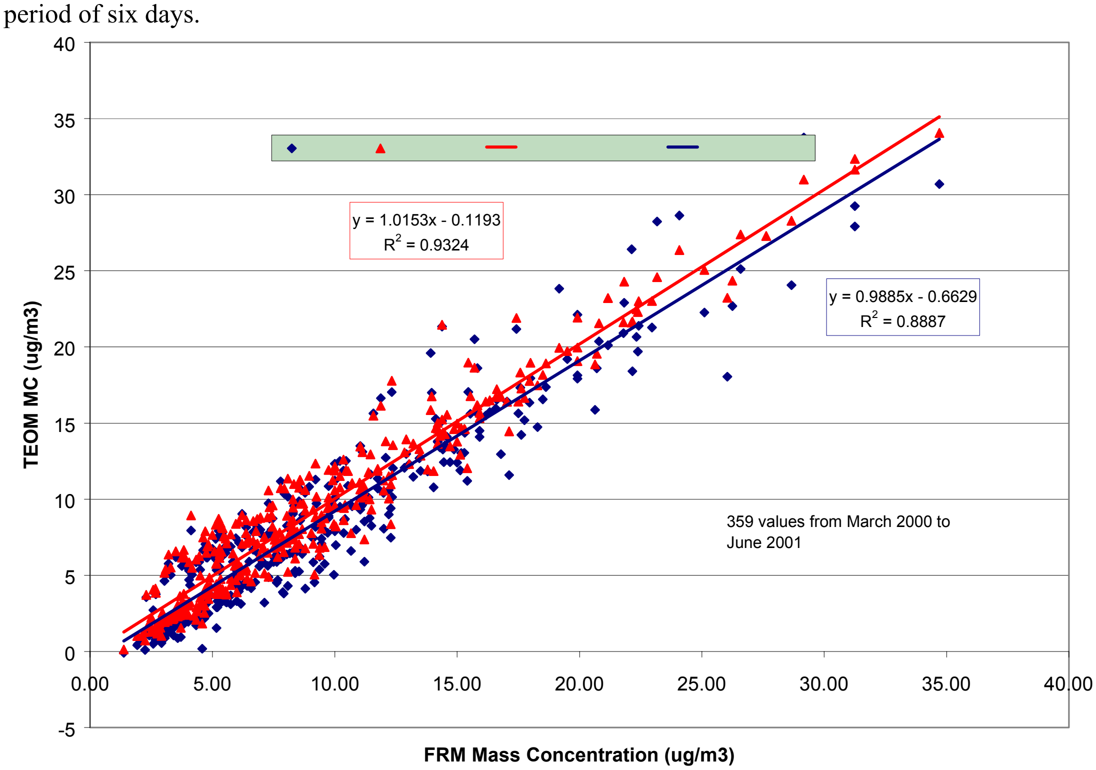


Figure 14. Comparison between SES TEOM monitor (30ºC) and standard TEOM monitor (50ºC) versus FRM samples at Pinnacle State Park sampling location, March 2000 through June 2001.

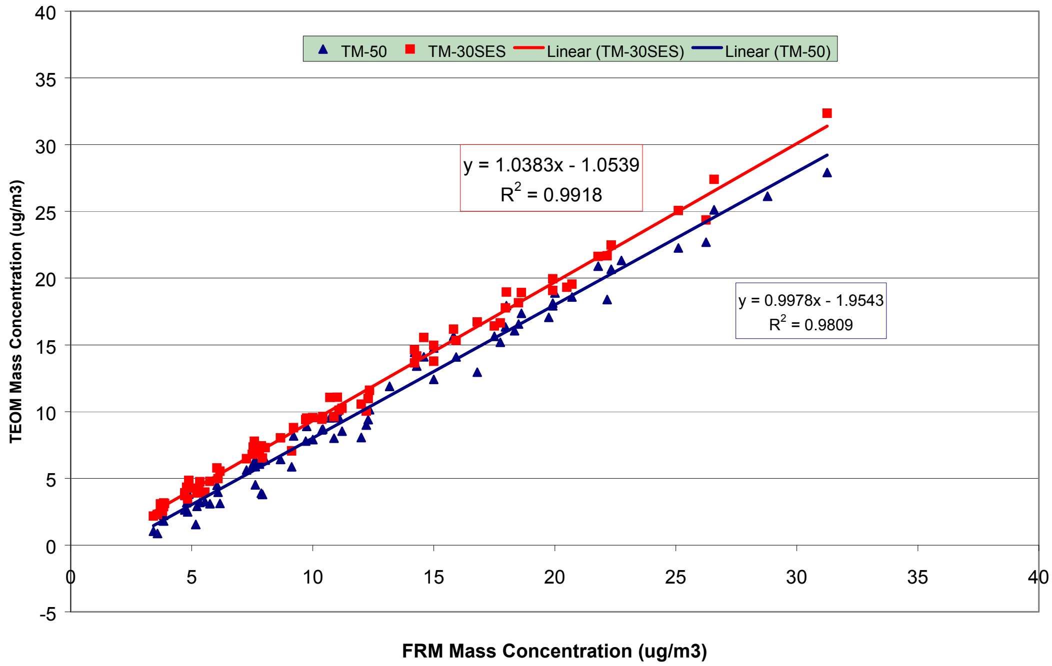


Figure 15. Comparison between SES TEOM monitor and 50ºC TEOM monitor versus FRM samples collected at Pinnacle State Park during the months of June, July, and August 2000.

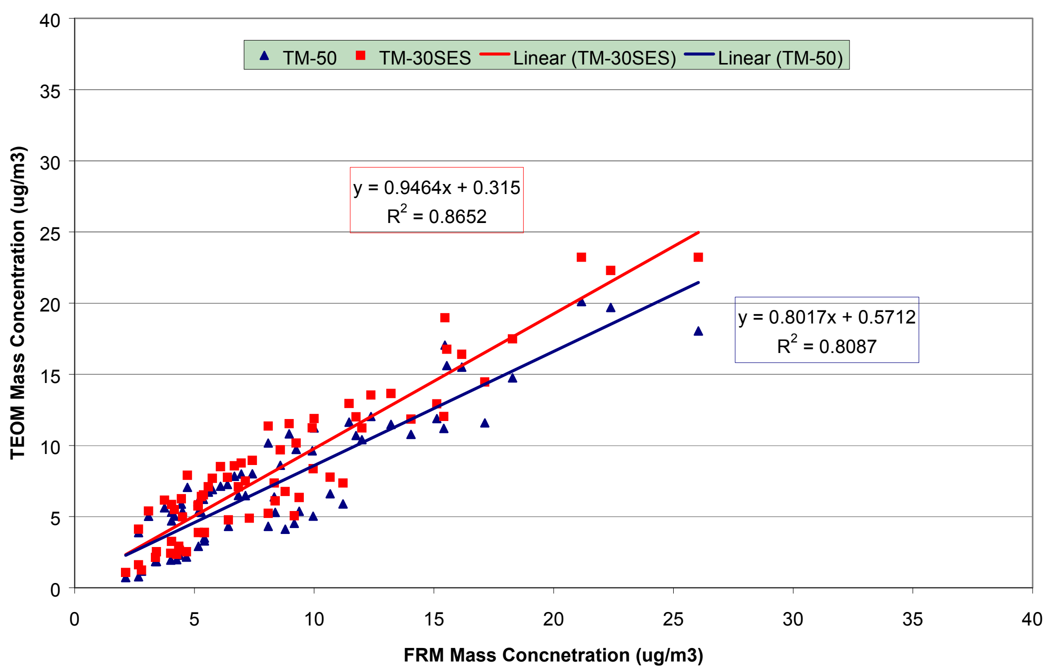


Figure 16. Comparison of SES TEOM and 50ºC TEOM monitor results versus FRM samples collected at Pinnacle State Park during the months of December 2000 and January and February 2001.

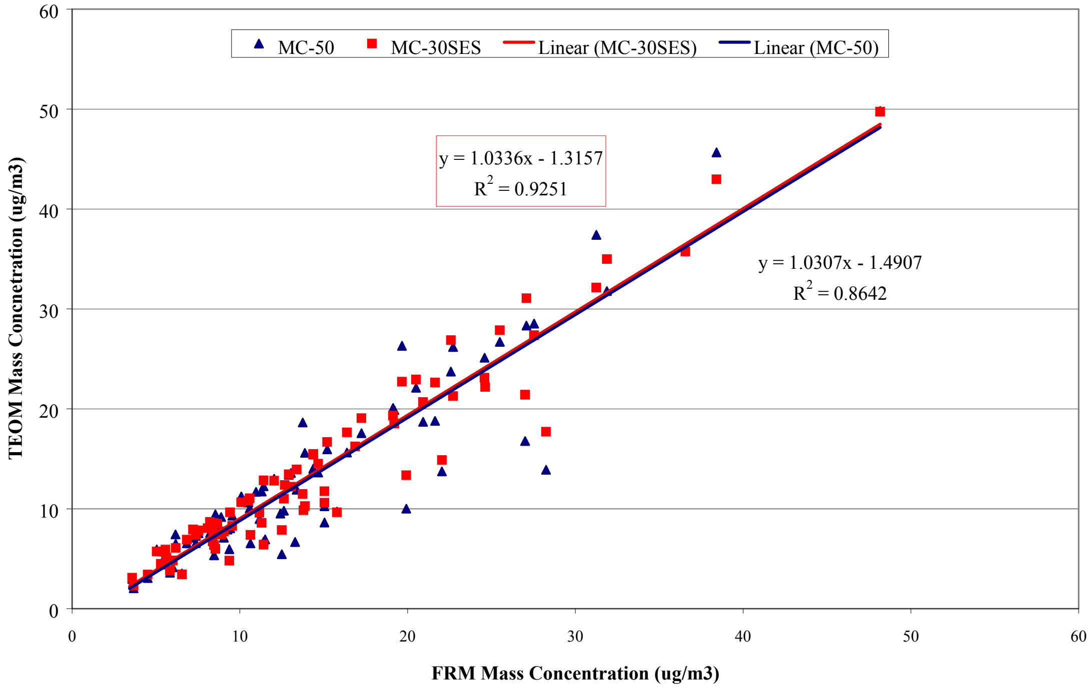


Figure 17. Comparison between SES TEOM and standard TEOM monitor results versus FRM samples collected at PS219 in Queens, NY.

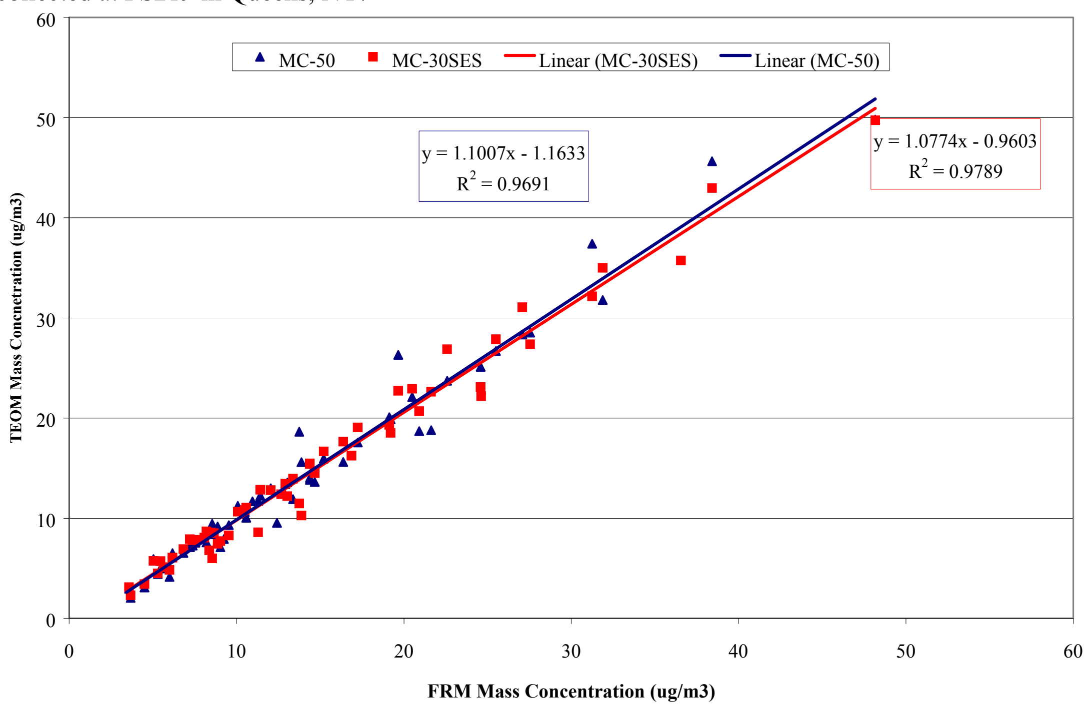


Figure 18. Comparison between the SES and 50ºC TEOM monitors versus FRM samples collected at PS219 in Queens, NY, during May, June, and July 2001.

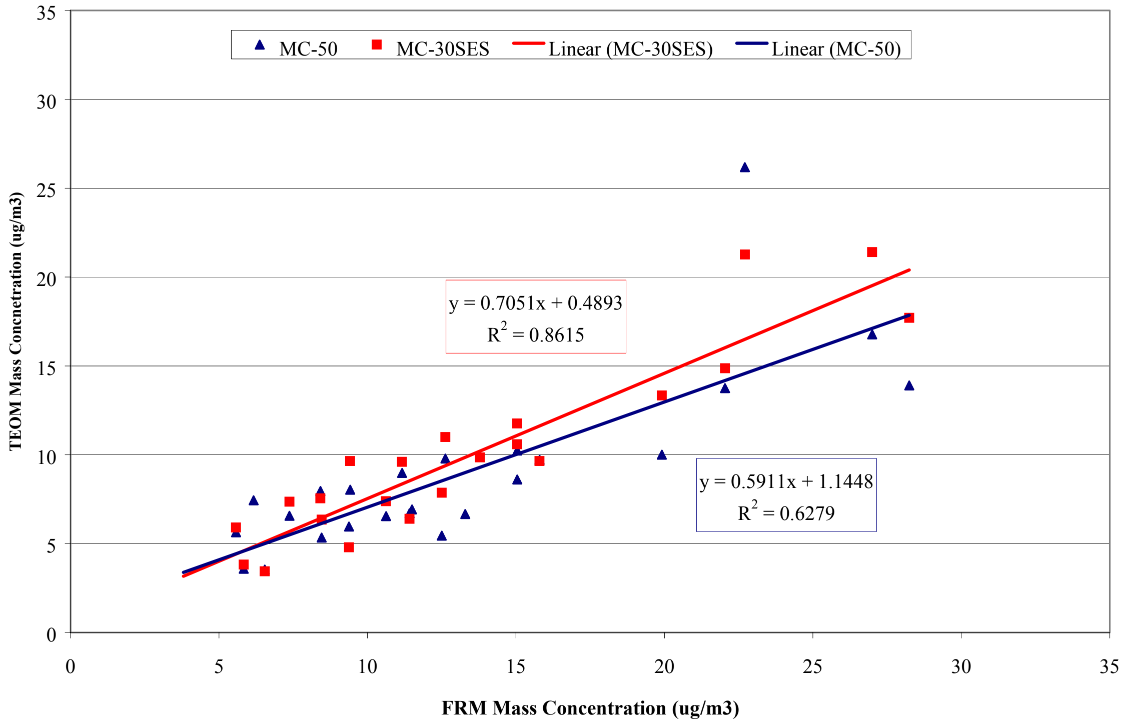


Figure 19. Comparison between SES TEOM monitor and 50ºC TEOM monitor results versus FRM samples during February, March, and April 2001, collected at PS219 in Queens, NY.

APPENDIX A

ASRC FINAL REPORT DOCUMENTATION

Material for Final Report from R&P to NYSERDA

ASRC participation in SES project

Author: Jim Schwab

Date: 10/15/01

Executive Summaries:

Laboratory Work: Oral presentation by Jeff Ambs to Fall 2000 NYSERDA Technical Review (also oral presentation by Jim Schwab at AAAR Fall 2000 meeting)

Field Work: Poster presentation at Fall 2001 NYSERDA conference.

Field Data and Preliminary analyses:

Addison, NY (Pinnacle State Park): SES installed late March 2000. Data comparisons of FRM, 50˚C TEOM and 30˚C SES TEOM from April 2000 through June 2001 in EXCEL workbooks "PSP-monthly-correlations.xls" and "PSP-monthly-correlations2.xls".

Queens, NY (Queens College/PS219): SES installed in late January 2001. Data comparisons of FRM, 50˚C TEOM and 30˚C SES TEOM from February 2001 through June 2001 in EXCEL workbook "QC FRM-TEOM.xls".

Highlights of laboratory data:

Stable concentrations of laboratory test aerosols were generated and measured with a standard 50˚C TEOM, and with the 30˚C SES TEOM. Relative humidity was ramped to test the sensitivity of the mass monitors to changes in water vapor. The 50˚C TEOM responds to step changes in humidity with extreme swings in reported mass conentrations.

Nafion Dryer and 30˚C sensor (SES TEOM) decreases, and in some cases all but eliminates, the sensitivity of the TEOM mass monitor to changing humidity.

Highlights and background information for field data:

The following table gives some additional information for the interpretation of the monthly correlations presented in the EXCEL spreadsheets:

Table 1. Monthly Mean Data for Pinnacle State Park (Addison, NY)

	Mean FRM MC (ug/m3)[1]	Mean Ambient Temp (˚C)[2]	Mean RH (%)[2]	Comments
April 2000	5.95	6.6	72	Very wet month and Spring
May 2000	11.59	14.5	70	Very wet month and Spring
June 2000	13.28	18.2	78	Very wet month and Spring
July 2000	10.90	18.0	78	Quite cool
August 2000	10.39	18.4	81	
Sept. 2000	9.35	14.5	79	
October 2000	9.01	9.5	74	
Nov. 2000	7.34	2.4	79	
Dec. 2000	6.44	-8.4	77	
January 2001	10.64	-4.2	79	
February 2001	8.47	-3.8	70	
March 2001	7.63	-2.7	77	
April 2001	8.58	6.6	67	Gobi Dust event 4/21-4/22
May 2001	10.58	12.8	62	Early hot periods- 5/2-5, 5/12-13
June 2001	14.80	16.9	77	Very hot 6/27-6/30 – Highest monthly average FRM MC yet

Notes for Table 1:

[1] Monthly mean FRM mass concentration calculated using values from those days when valid FRM, 50˚C TEOM, and SES TEOM measurements were available.

[2] Monthly mean temperature and relative humidity calculated from all valid data for the month.

Table 2. Monthly Mean Data for Queens, NY (Queens College/PS219)

	Mean FRM MC (ug/m3)[1]	Mean Ambient Temp (˚C)[1]	Comments
February 2001	14.54	2.6	
March 2001	15.90	2.7	
April 2001	11.38	11.5	Gobi Dust event 4/21-4/22
May 2001	14.41	16.9	Early hot periods – 5/2-5/5, 5/12-5/13
June 2001	15.97	22.0	Warm month – very hot 6/27-6/30

Note for Table 2:

[1] Monthly mean FRM mass concentration and ambient temperature calculated using values from those days when valid FRM, 50˚C TEOM, and SES TEOM measurements were available.

Topics for continued investigation:

1. Reason for unusual behavior of TEOM/FRM and (SES TEOM)/(50˚C TEOM) ratios for April – June 2001. Collect and verify additional data to confirm the transition from this "anomalous" period to more "normal" or "expected" values for these ratios.
2. Further investigations of the relationships between ambient temperature, relative humidity, and precipitation with mass concentration measurements and their ratios.
3. Case studies for:
    a) at least 2-3 events of rapid RH change;
    b) at least 2-3 events of rapid mass concentration change.

Additional product of this collaborative work:

Manuscript for publication in peer-reviewed journal tentatively titled: An Improved Instrument for Measurement of Continuous PM-2.5 Mass Concentrations: TEOM® Monitor Operated at 30˚C with a Nafion™ Dryer compared to a 50˚C TEOM® and FRM Filter Measurements.

APPENDIX B

PM-2.5 Mass Measurement at a Rural New York State Site: Comparisons of FRM Filter Based 24 Hour Measurements and Continuous TEOM® Measurements with and without a Nafion Dryer

James J. Schwab, John B. Spicer, Charles D. Schirmer, and Kenneth L. Demerjian
Atmospheric Sciences Research Center, University at Albany, State University of New York

Introduction

The Federal Ambient Air Quality Standard for Fine Particulate Matter (PM-2.5) is based on 24-hour filter measurements collected and weighed according to a Federal Reference Method (FRM). There is a large network of surface sites making and reporting these mass concentration measurements, both in New York State and across the country. Unfortunately, there are some serious issues with filter based measurements, most notably 1) filter measurements require significant amounts of operator time for setup, collection and shipment of samples; 2) volatile species can be lost from the filter during long collection periods or shipment; and 3) 24 hour averaged samples are unable to capture short duration, high concentration events.

This means there are both scientific and economic reasons to examine and evaluate other PM-2.5 measurement methods. Scientific in the sense that we know information is lost in the consideration of only 24 hour averaged measurements, and in that FRM measurements do not measure a true scientific quantity due to known losses of volatile material. It also seems possible if not likely that a different PM-2.5 measurement method could be significantly less expensive to operate while providing as much or more data to scientists and policy makers.

We are operating a FRM sampler and two versions of the Tapered Element Oscillating Microbalance (TEOM®) at our air quality research site in Addison, NY. Results from these samplers, and comparisons and correlations of these will be presented below.

Site

Pinnacle State Park is located in Addison, New York in the state's Southern Tier Region just below the Finger Lakes. It is located on the eastern slope of Orr Hill (elevation 504 m) and is part of the Allegheny Plateau of southern New York State and northern Pennsylvania. Orr Hill rises steeply from the Canisteo River Valley and the village of Addison. The surrounding area is a patchwork of vegetation types, including a nine hole golf course to the northwest (part of the park), mixed deciduous and coniferous forests, some former pastures and fields, and an approximately 50 acre pond to the south and below the site.

The site became operational in 1995 with a complement of gas measurements, including O_3, CO, NO, NO_y, SO_2, and hydrocarbons. Temperature, pressure, relative humidity, and winds are also measured. In 1999 we began measuring PM-2.5 using the R&P Partisol FRM sampler and a TEOM® mass monitor. The second TEOM® with the Nafion dryer was deployed in spring 2000. We also have deployed at the site a R&P 5400 Carbon Particulate Monitor, a R&P 2300 Speciation sampler, and an IMPROVE speciation sampler.

Measurement Methods

FRM 24 hour Filter Measurements

- Sample Inlet – PM-10 inlet followed by WINS impactor with 2.5 um cut-point
- R&P 2025 Partisol Sampler
- Filter weighing done by RTI under contract to NYSDEC

TEOM® Mass Monitor

- Sample Inlet – URG PM-2.5 cyclone followed by flow splitter
- R&P Model 1400AB – sample flow 3 LPM
- Mass Sensor stabilized at 50˚C
- Continuous measurement – instrument response time approximately 2 minutes

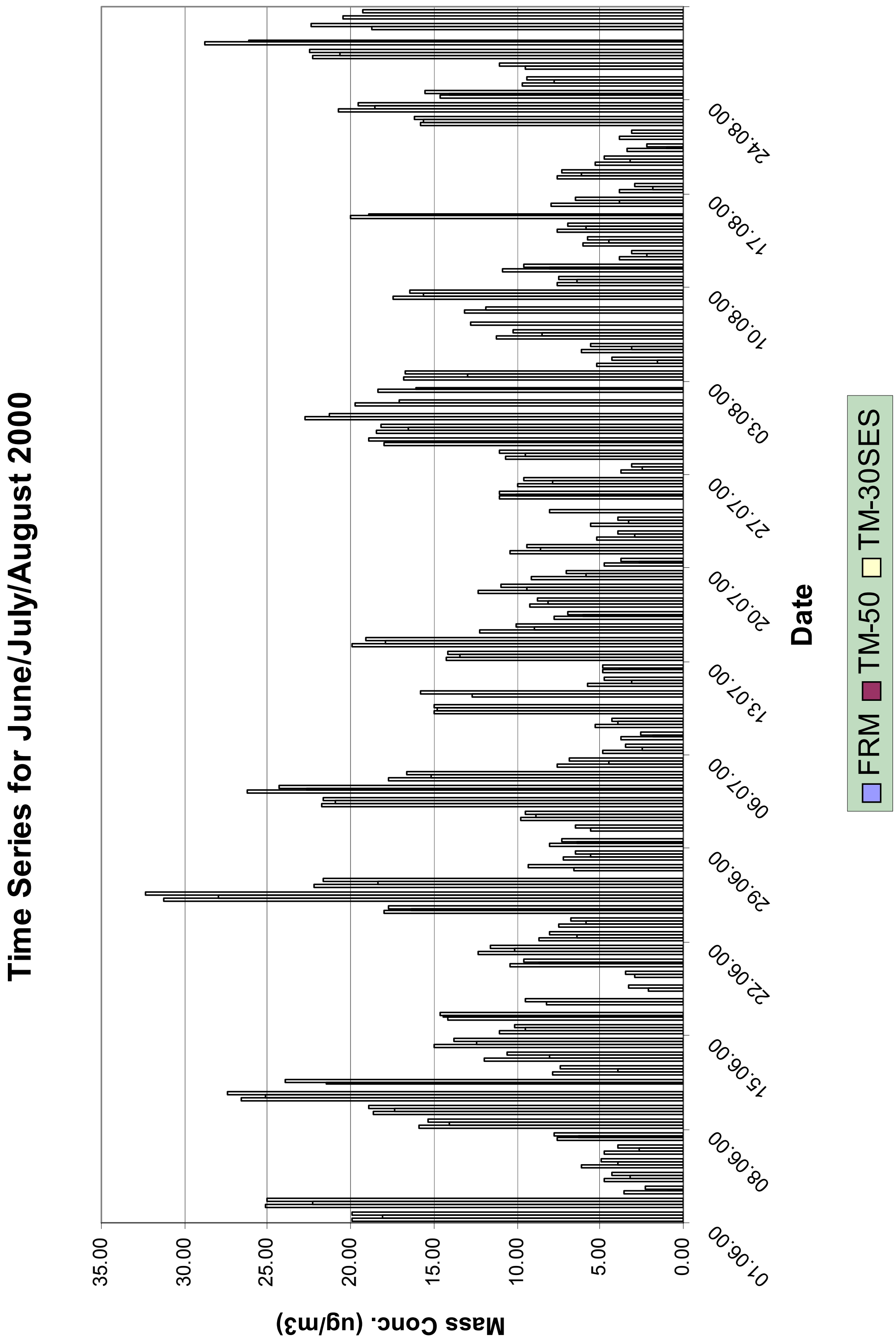
SES TEOM® Mass Monitor with Nafion Dryer

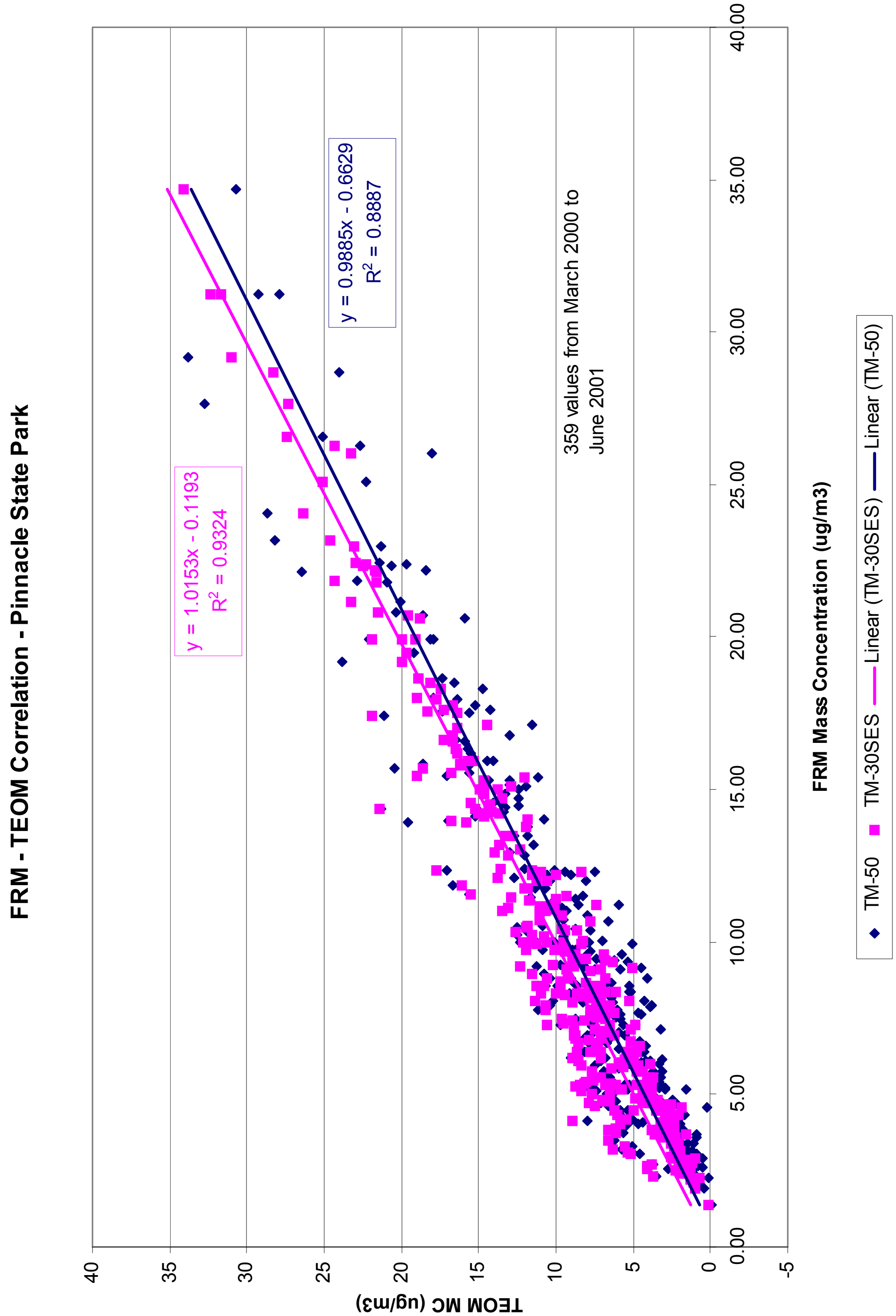
- Sample Inlet – URG PM-2.5 cyclone followed by flow splitter and Nafion dryer
- R&P Model 1400AB – sample flow 3 LPM, dried to RH typically less than 20%
- Mass Sensor stabilized at 30˚C
- Continuous measurement – instrument response time approximately 2 minutes

Conclusions

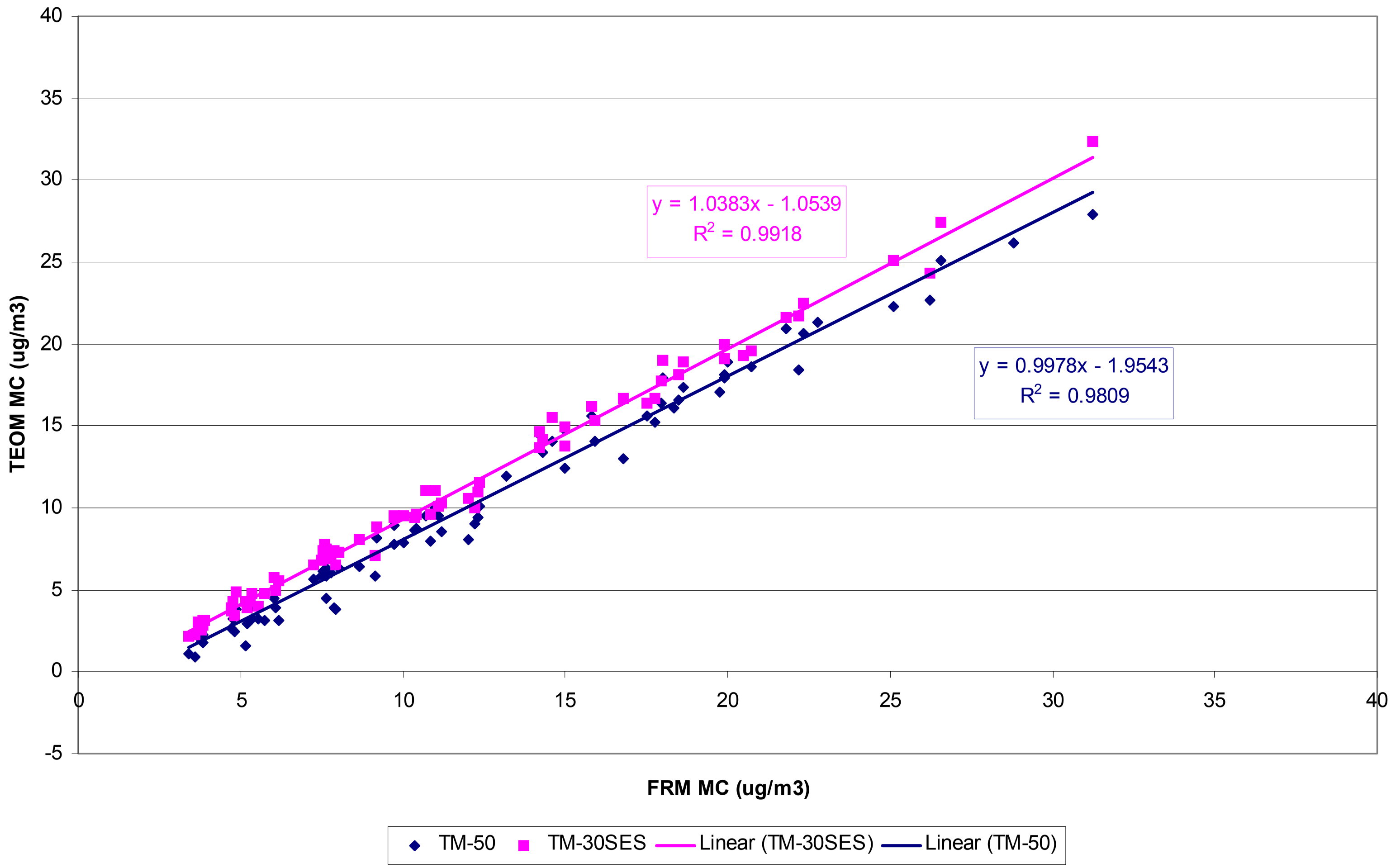
- There is a high degree of correlation between the FRM filter based measurements and the continuous TEOM measurements of PM-2.5
- At low mass concentrations, both TEOM instruments tend to report lower values than the FRM.
- At higher mass concentrations, the standard TEOM measurements approach the FRM more closely, and the SES measurements are virtually identical with the FRM measurements.

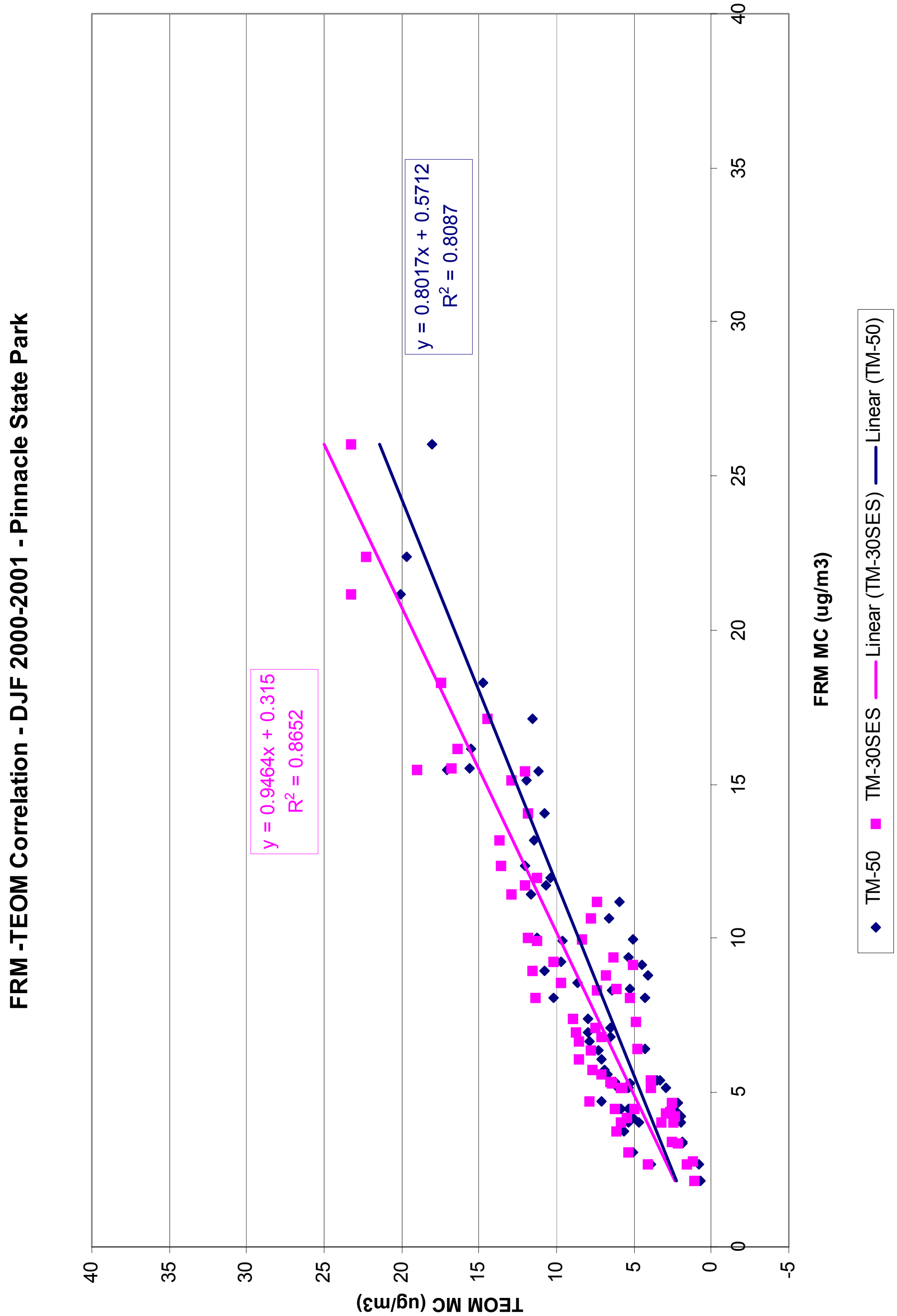
- The SES TEOM, with the Nafion dryer and the sensor at 30˚C, typically captures 5-10% more mass than the standard TEOM at 50˚C.
- The TEOM data from April-June 2001 shows significantly more scatter than earlier data - is this instrument related or related to properties of the aerosol? (Note: Gobi dust event generated some surprising measurements.)
- TEOM measurements of PM-2.5, especially SES TEOM measurements, are simpler to obtain and appear to be every bit as scientifically valid at this site.

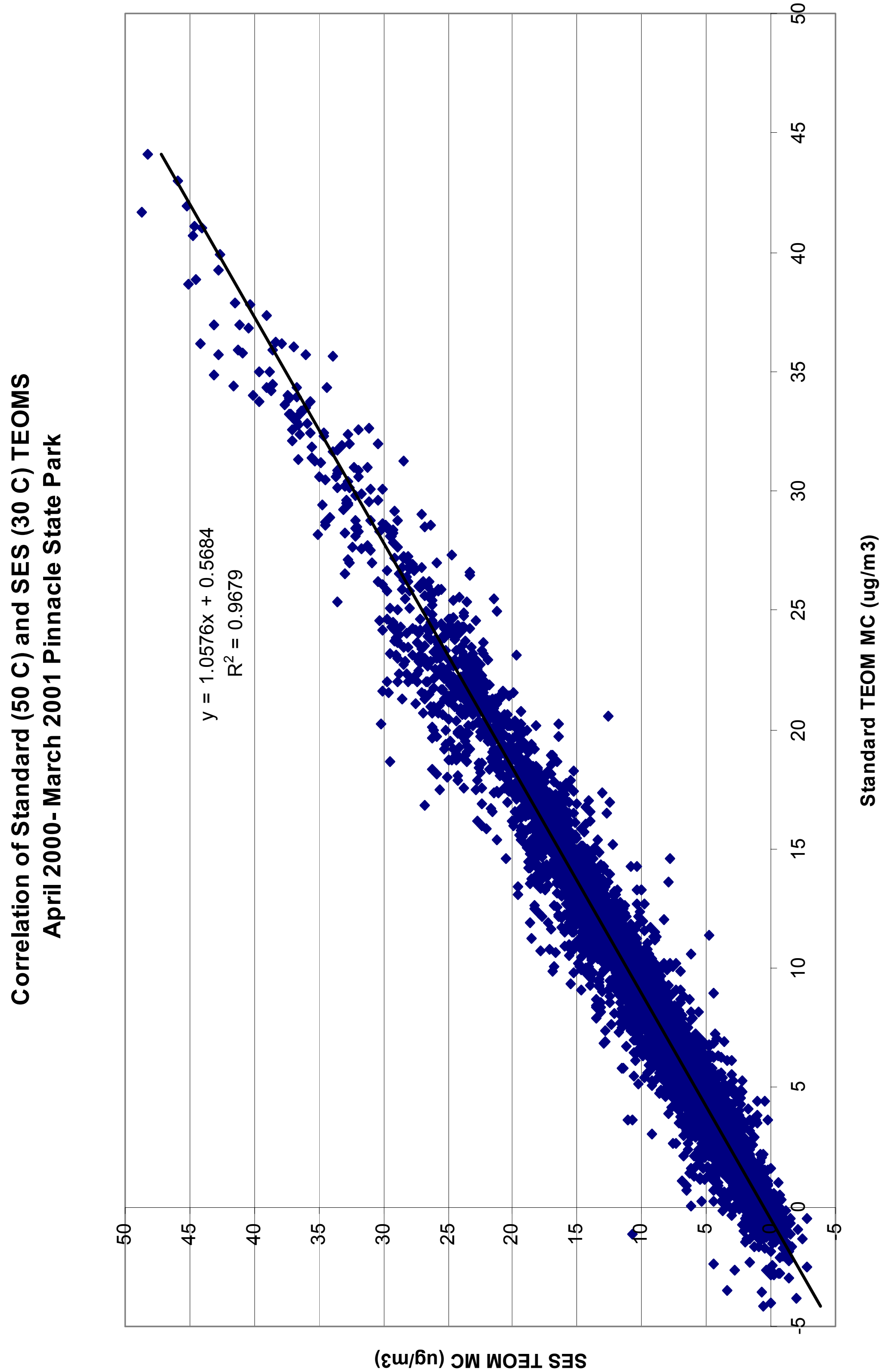

Time Series for June/July/August 2000
Mass Conc. (ug/m3)
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
01.06.00
08.06.00
15.06.00
22.06.00
29.06.00
06.07.00
13.07.00
20.07.00
27.07.00
03.08.00
10.08.00
17.08.00
24.08.00
Date
FRM
TM-50
TM-30SES


FRM - TEOM Correlation - Pinnacle State Park
TEOM MC (ug/m3)
FRM Mass Concentration (ug/m3)
y = 1.0153x - 0.1193
R^2 = 0.9324
y = 0.9885x - 0.6629
R^2 = 0.8887
359 values from March 2000 to June 2001
TM-50
TM-30SES
Linear (TM-30SES)
Linear (TM-50)
-5
0
5
10
15
20
25
30
35
40
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00

FRM - TEOM Correlation - JJA2000 - Pinnacle State Park



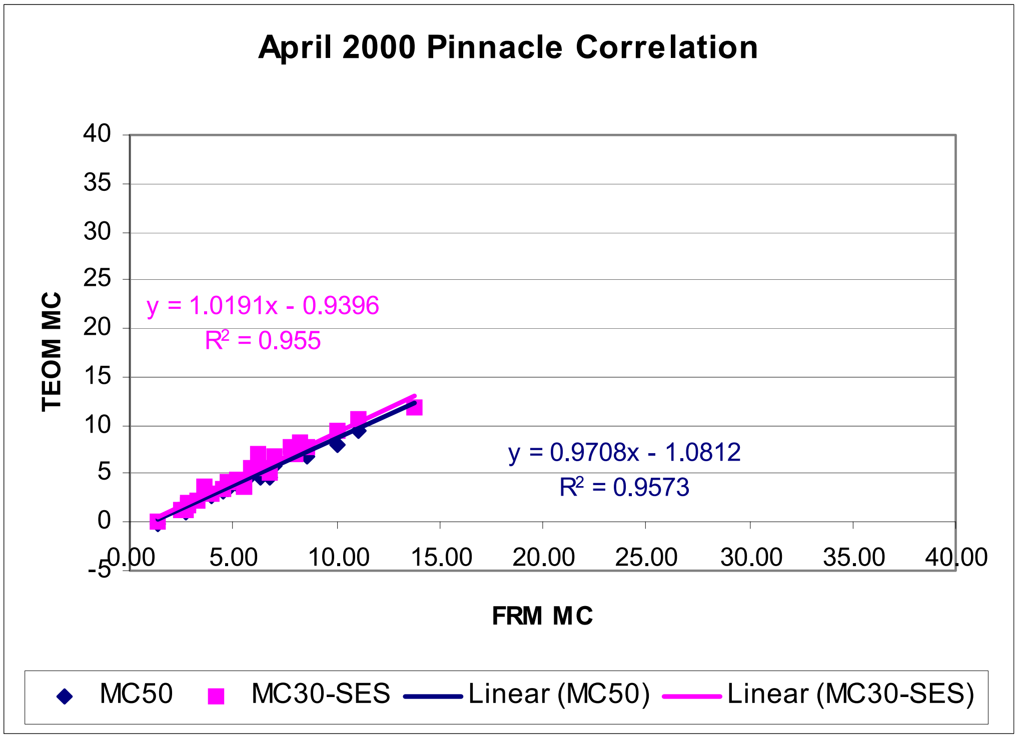

FRM -TEOM Correlation - DJF 2000-2001 - Pinnacle State Park
TEOM MC (ug/m3)
FRM MC (ug/m3)
y = 0.9464x + 0.315
R2 = 0.8652
y = 0.8017x + 0.5712
R2 = 0.8087
TM-50
TM-30SES
Linear (TM-30SES)
Linear (TM-50)
40
35
30
25
20
15
10
5
0
-5

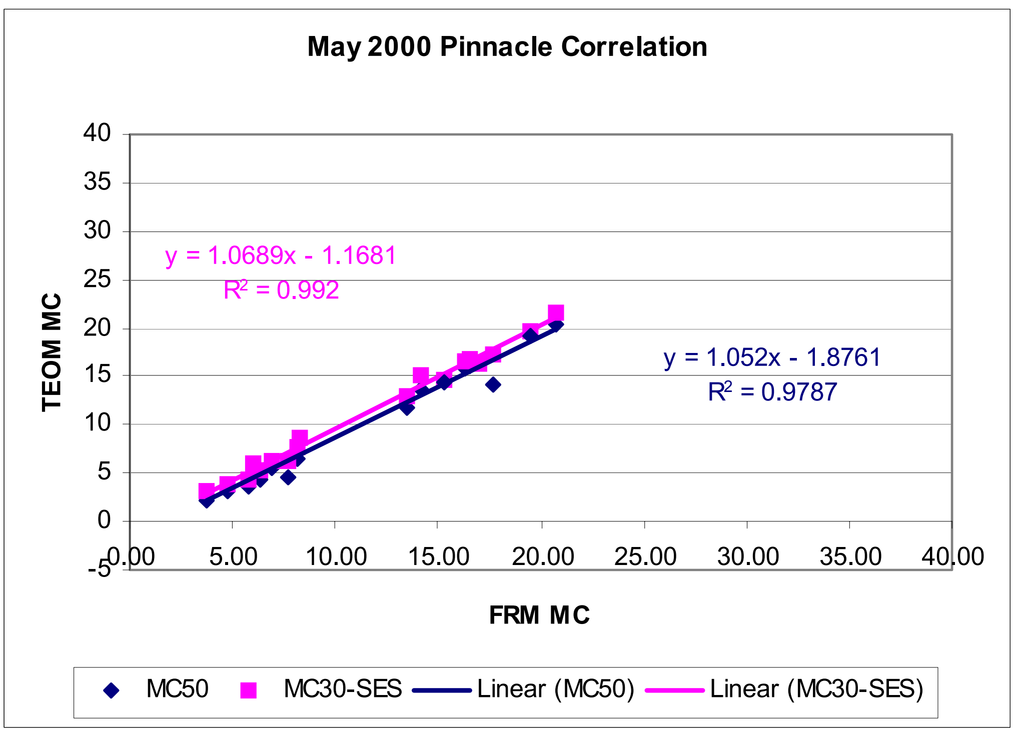

Correlation of Standard (50 C) and SES (30 C) TEOMS
April 2000- March 2001 Pinnacle State Park
y = 1.0576x + 0.5684
R2 = 0.9679
Standard TEOM MC (ug/m3)
SES TEOM MC (ug/m3)
-5
0
5
10
15
20
25
30
35
40
45
50

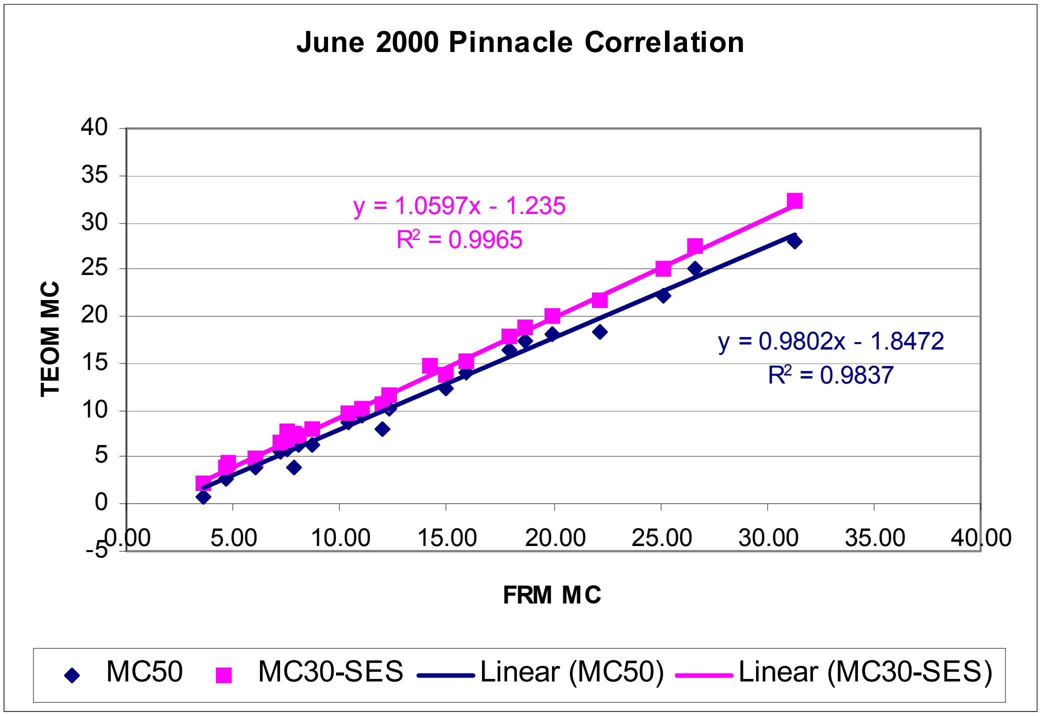
APPENDIX C

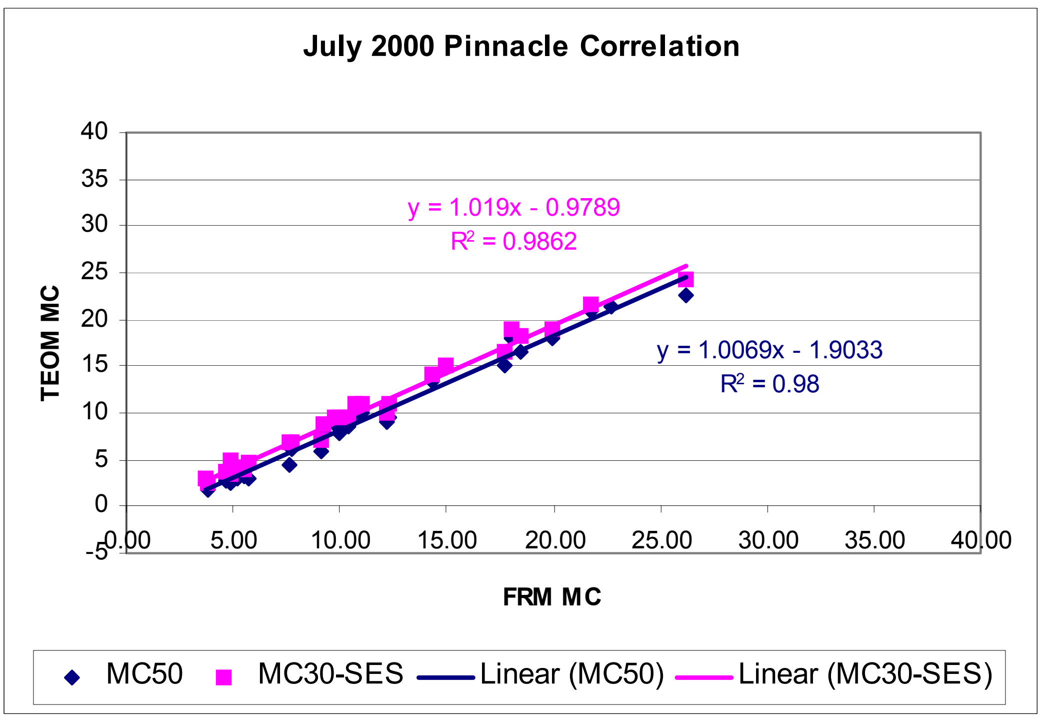
Detailed Results - SES Equipped TEOM Monitor Study - Rural New York State Sampling Location

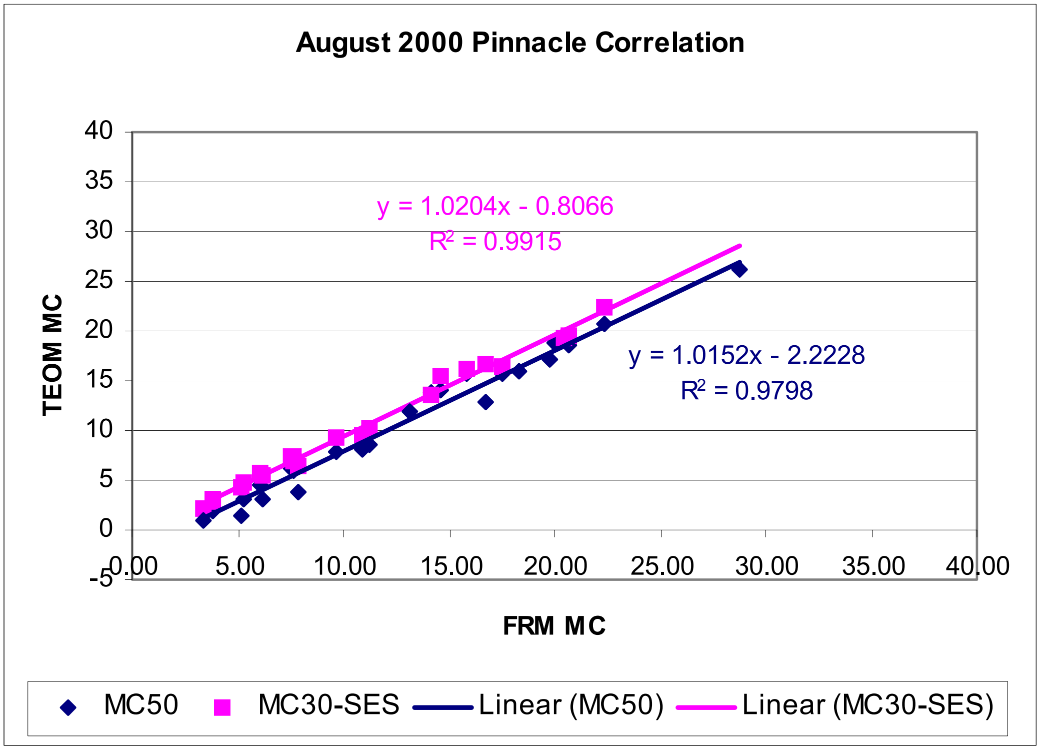
Appendix C contains all of the monthly correlations between the SES equipped TEOM monitor and the standard 50ºC TEOM monitor compared with the FRM samples over the entire sampling period at the Pinnacle State Park rural sampling location. The first set of figures include the correlations where the intercept of the correlation curve is determined by the data. If the resulting intercept is significantly different than zero, then there is a potential bias between the two sampling techniques. The second set of figures includes the correlations where the intercept is constrained to pass through the origin of the graph. If there is no bias between the different sampling methods, then the two sets of figures will be identical.

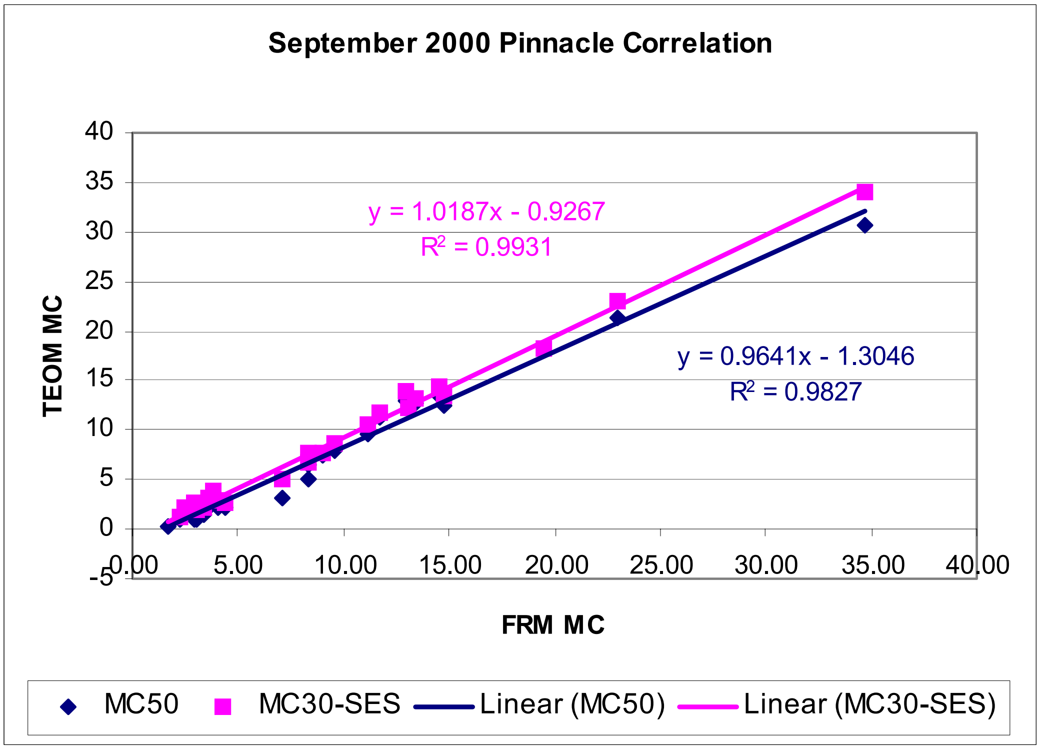

April 2000 Pinnacle Correlation
TEOM MC
FRM MC
y = 1.0191x - 0.9396
R2 = 0.955
y = 0.9708x - 1.0812
R2 = 0.9573
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

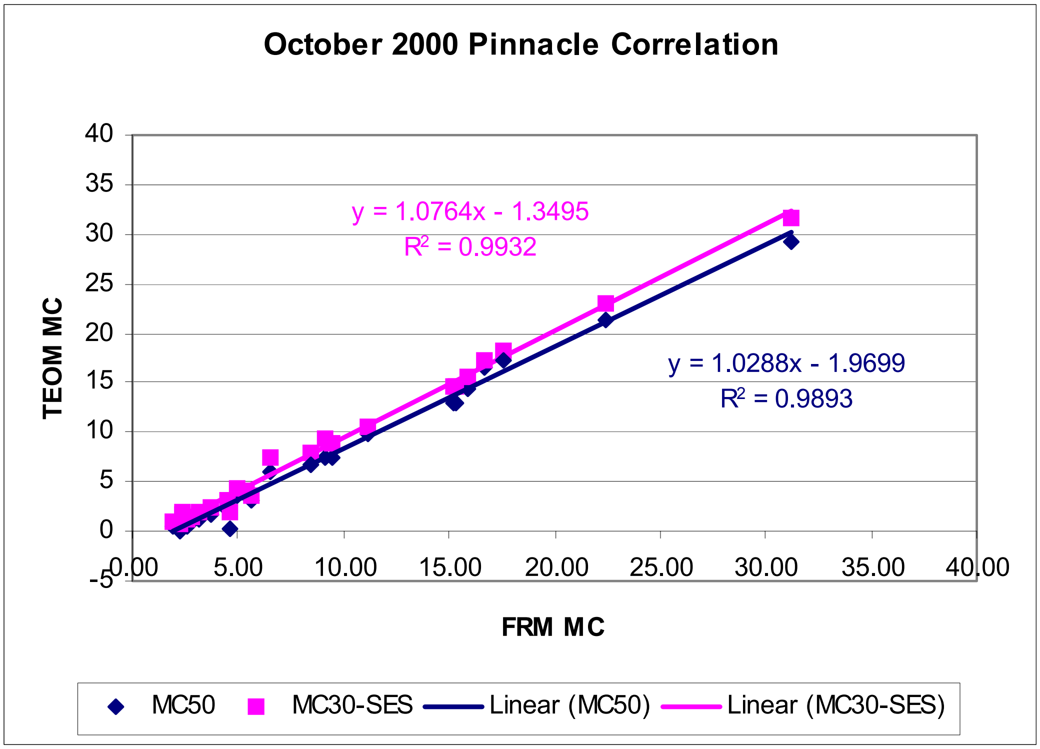

May 2000 Pinnacle Correlation
TEOM MC
FRM MC
y = 1.0689x - 1.1681
R2 = 0.992
y = 1.052x - 1.8761
R2 = 0.9787
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

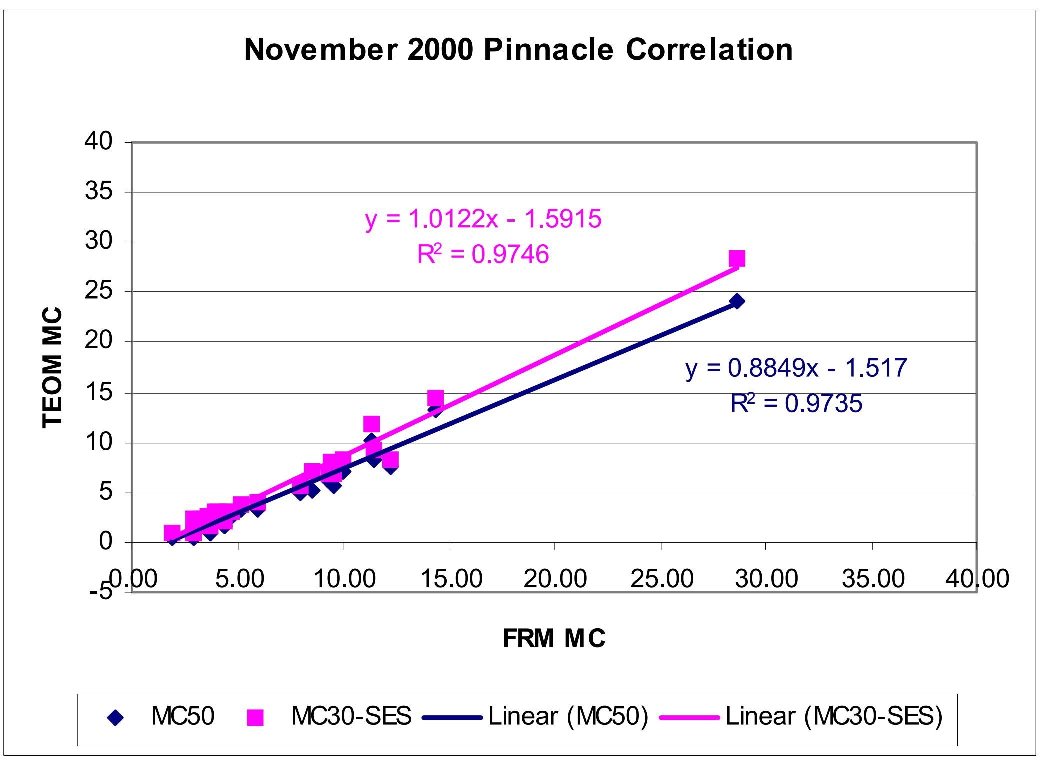

June 2000 Pinnacle Correlation
y = 1.0597x - 1.235
R² = 0.9965
y = 0.9802x - 1.8472
R² = 0.9837
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

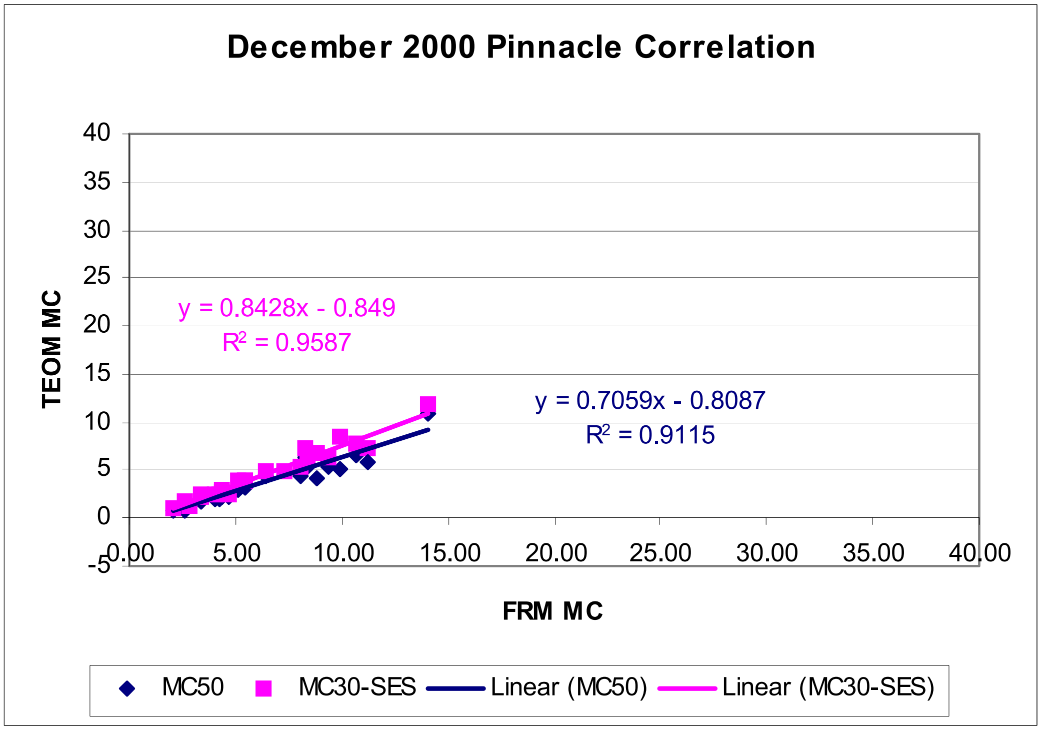

July 2000 Pinnacle Correlation
y = 1.019x - 0.9789
R² = 0.9862
y = 1.0069x - 1.9033
R² = 0.98
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

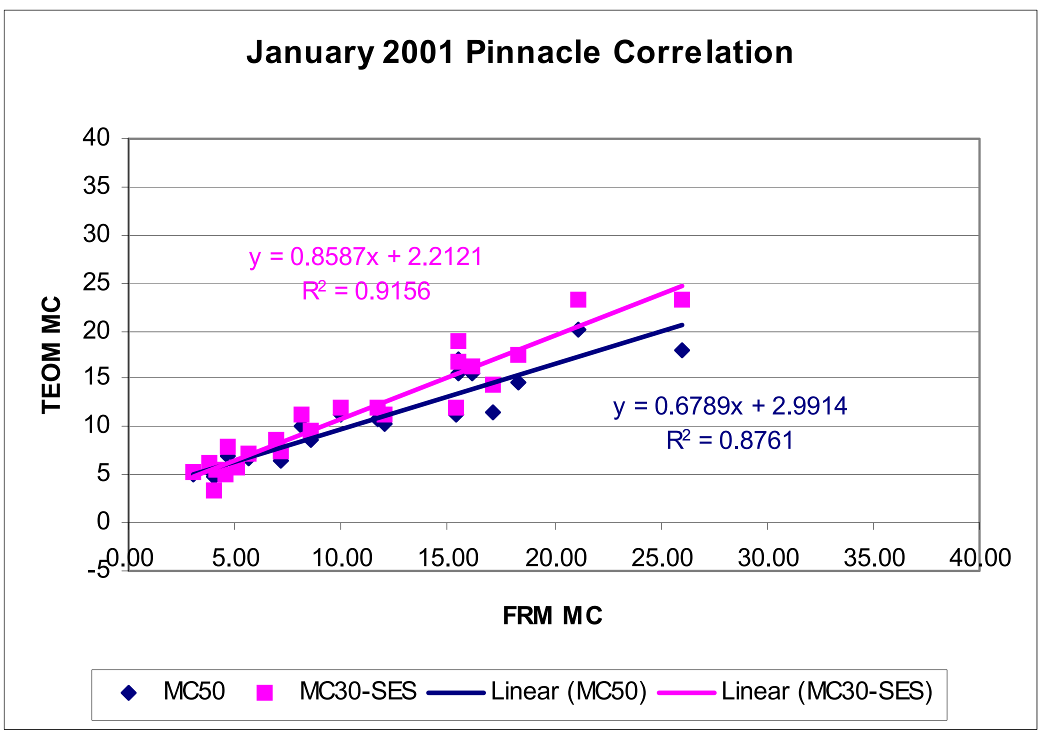

August 2000 Pinnacle Correlation
y = 1.0204x - 0.8066
R² = 0.9915
y = 1.0152x - 2.2228
R² = 0.9798
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

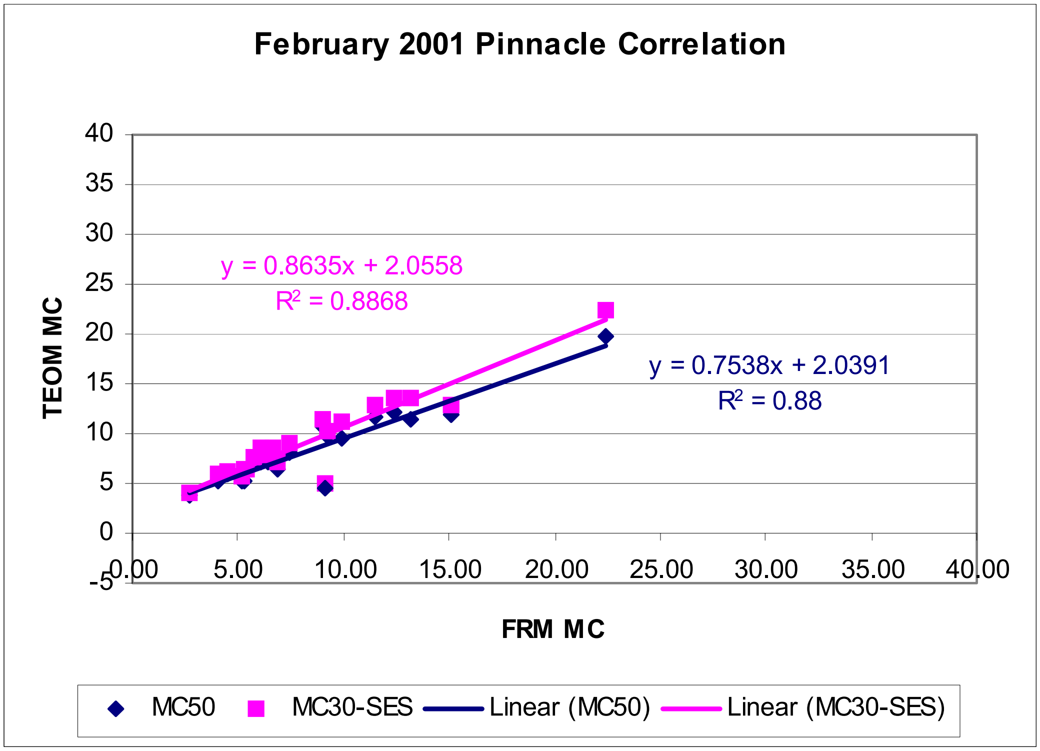

September 2000 Pinnacle Correlation
y = 1.0187x - 0.9267
R² = 0.9931
y = 0.9641x - 1.3046
R² = 0.9827
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

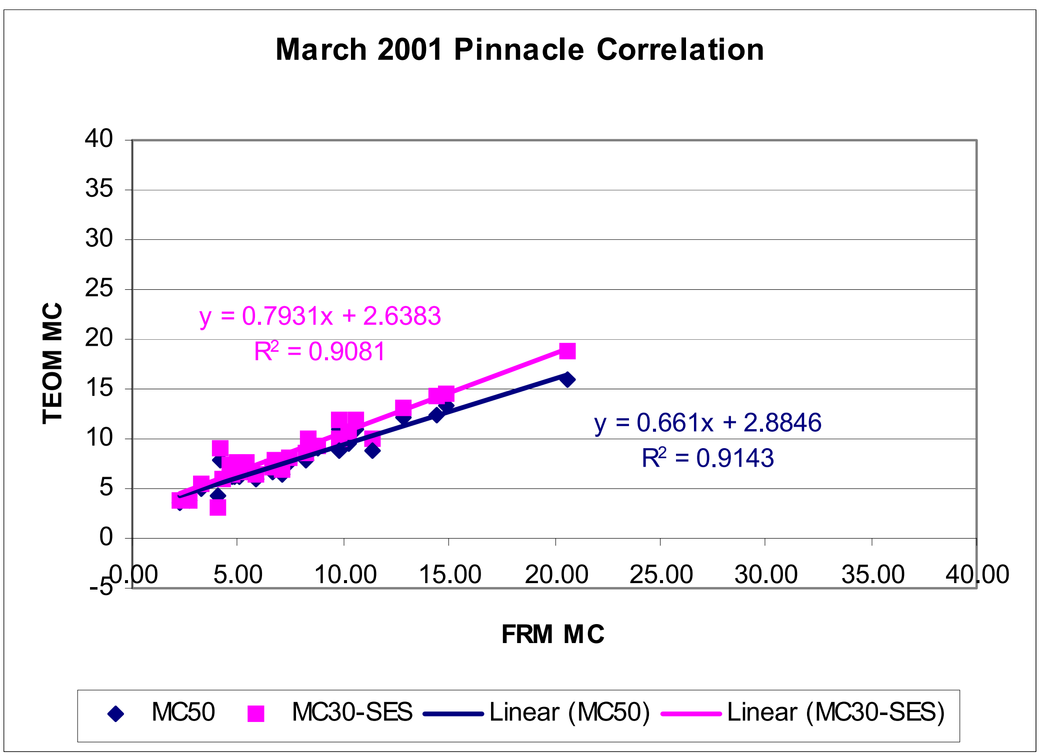

October 2000 Pinnacle Correlation
y = 1.0764x - 1.3495
R2 = 0.9932
y = 1.0288x - 1.9699
R2 = 0.9893
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

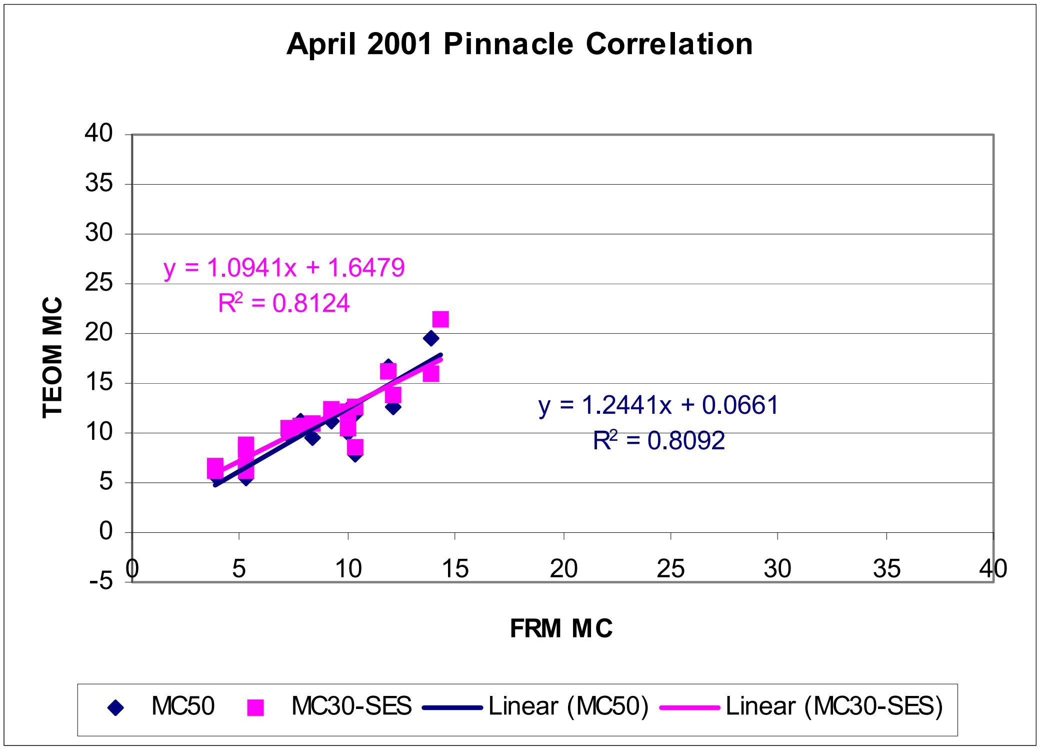

November 2000 Pinnacle Correlation
y = 1.0122x - 1.5915
R2 = 0.9746
y = 0.8849x - 1.517
R2 = 0.9735
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

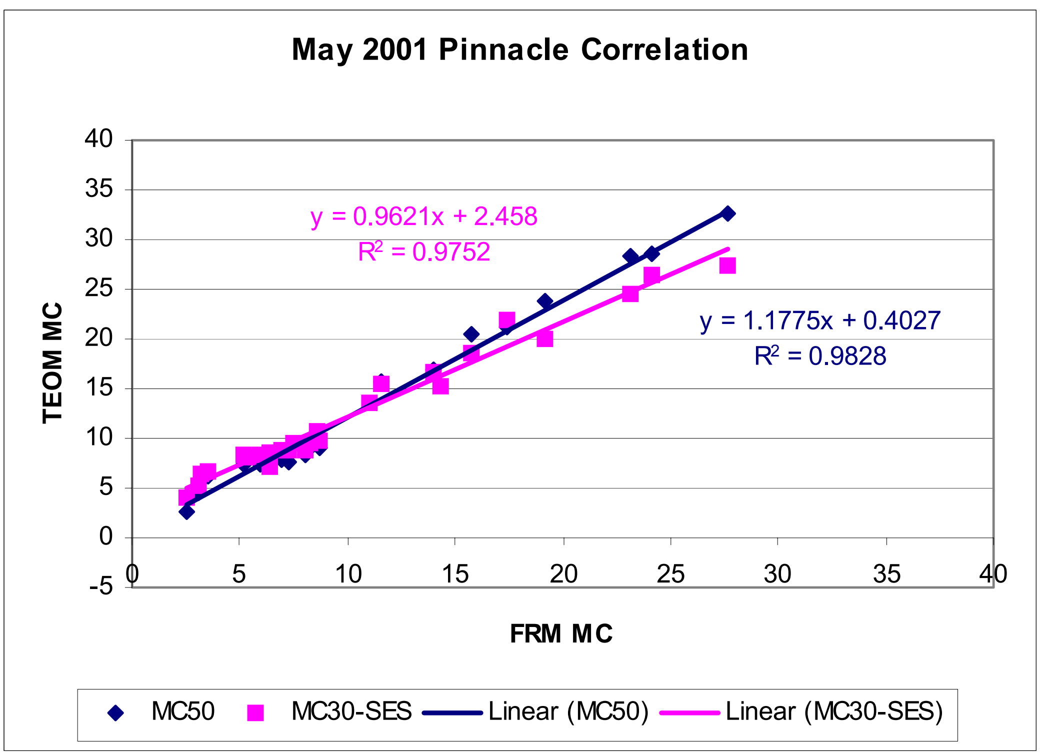

December 2000 Pinnacle Correlation
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
y = 0.8428x - 0.849
R² = 0.9587
y = 0.7059x - 0.8087
R² = 0.9115
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

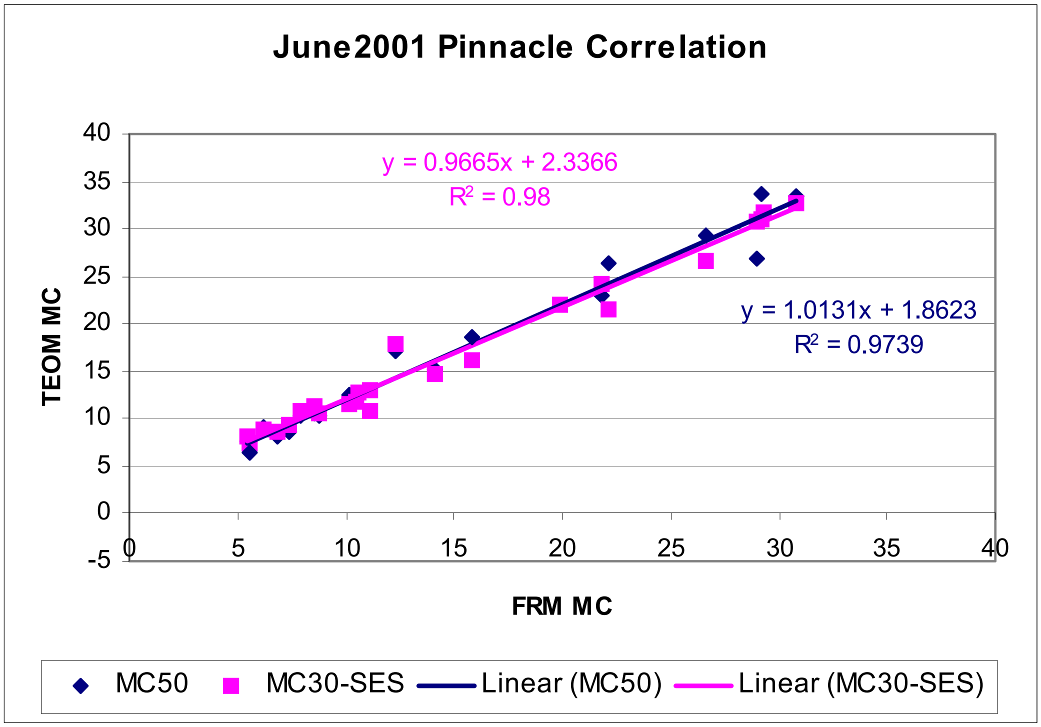

January 2001 Pinnacle Correlation
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
y = 0.8587x + 2.2121
R² = 0.9156
y = 0.6789x + 2.9914
R² = 0.8761
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)


February 2001 Pinnacle Correlation
TEOM MC
FRM MC
y = 0.8635x + 2.0558
R2 = 0.8868
y = 0.7538x + 2.0391
R2 = 0.88
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

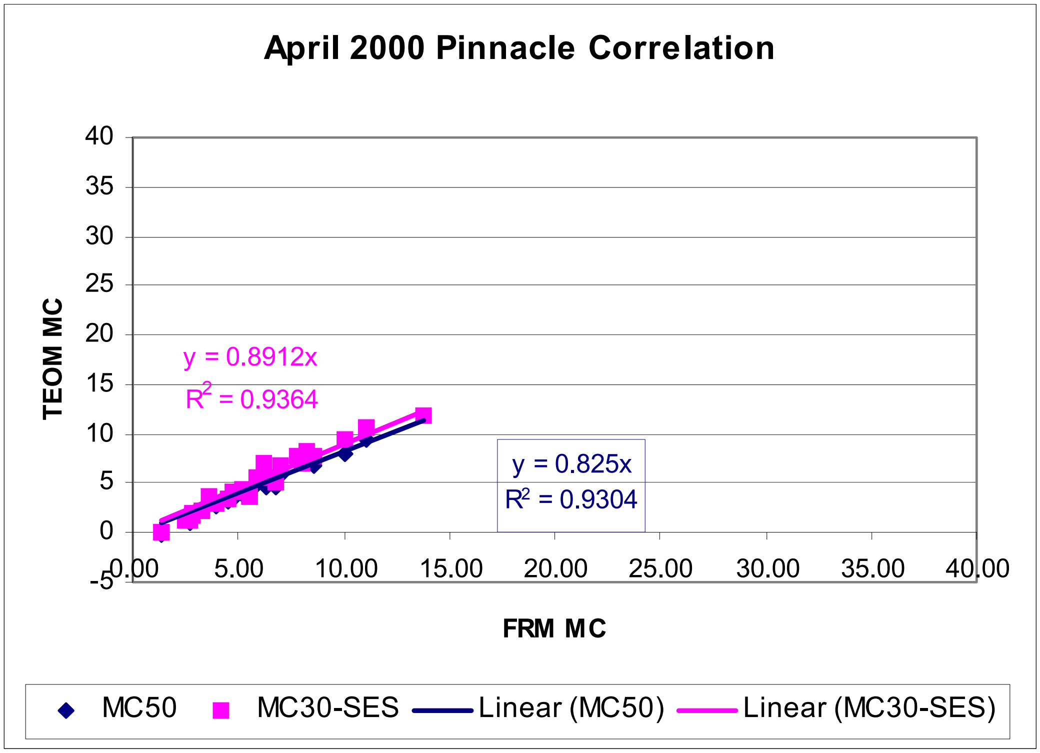

March 2001 Pinnacle Correlation
TEOM MC
FRM MC
y = 0.7931x + 2.6383
R2 = 0.9081
y = 0.661x + 2.8846
R2 = 0.9143
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

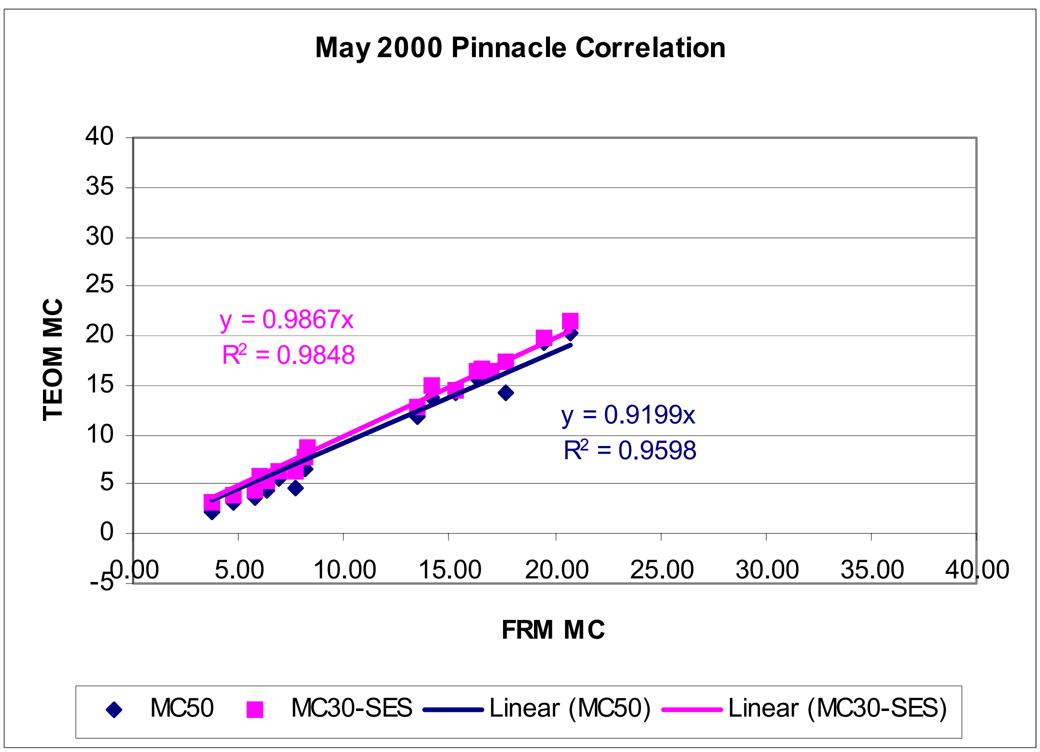

April 2001 Pinnacle Correlation
40
35
30
25
20
15
10
5
0
-5
0
5
10
15
20
25
30
35
40
TEOM MC
FRM MC
y = 1.0941x + 1.6479
R² = 0.8124
y = 1.2441x + 0.0661
R² = 0.8092
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

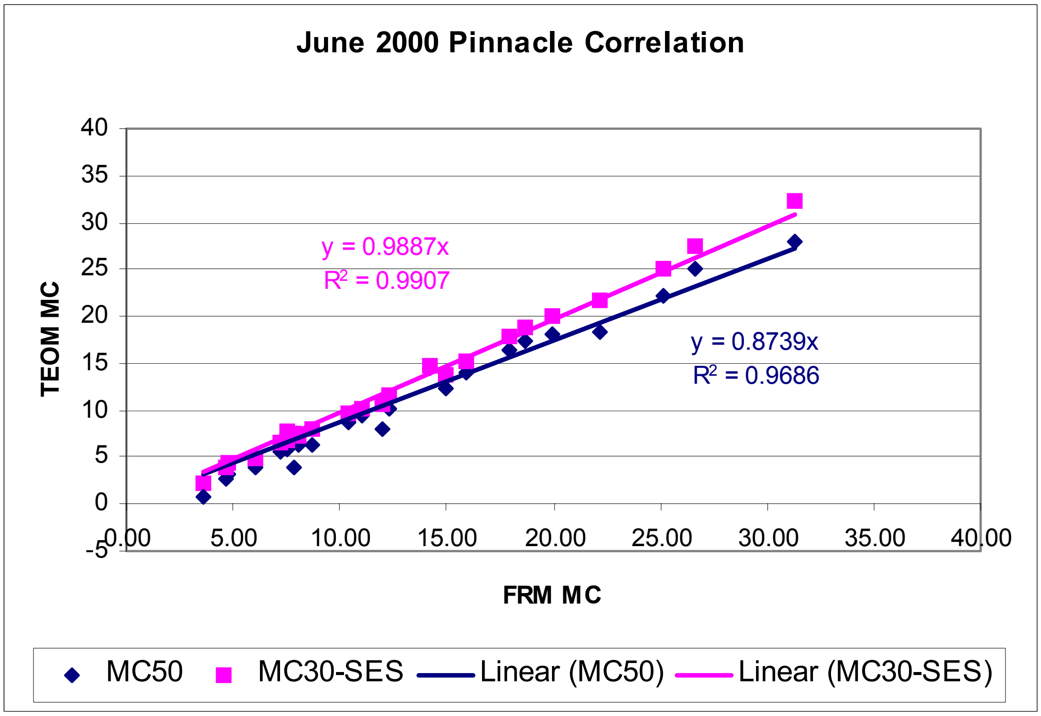

May 2001 Pinnacle Correlation
40
35
30
25
20
15
10
5
0
-5
0
5
10
15
20
25
30
35
40
TEOM MC
FRM MC
y = 0.9621x + 2.458
R² = 0.9752
y = 1.1775x + 0.4027
R² = 0.9828
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

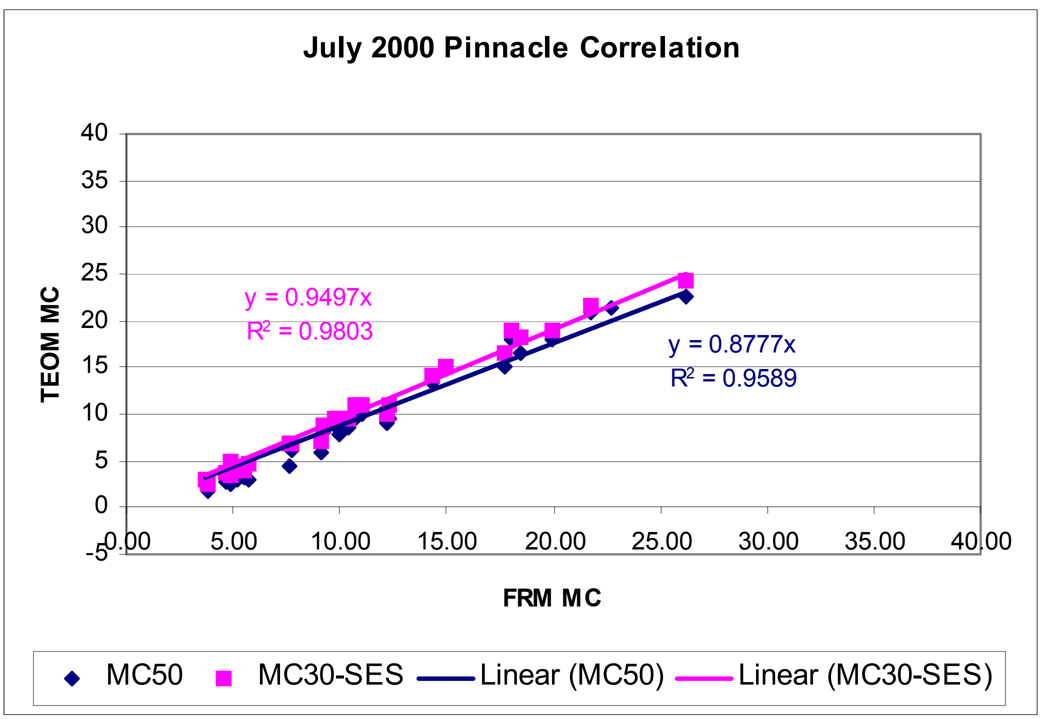


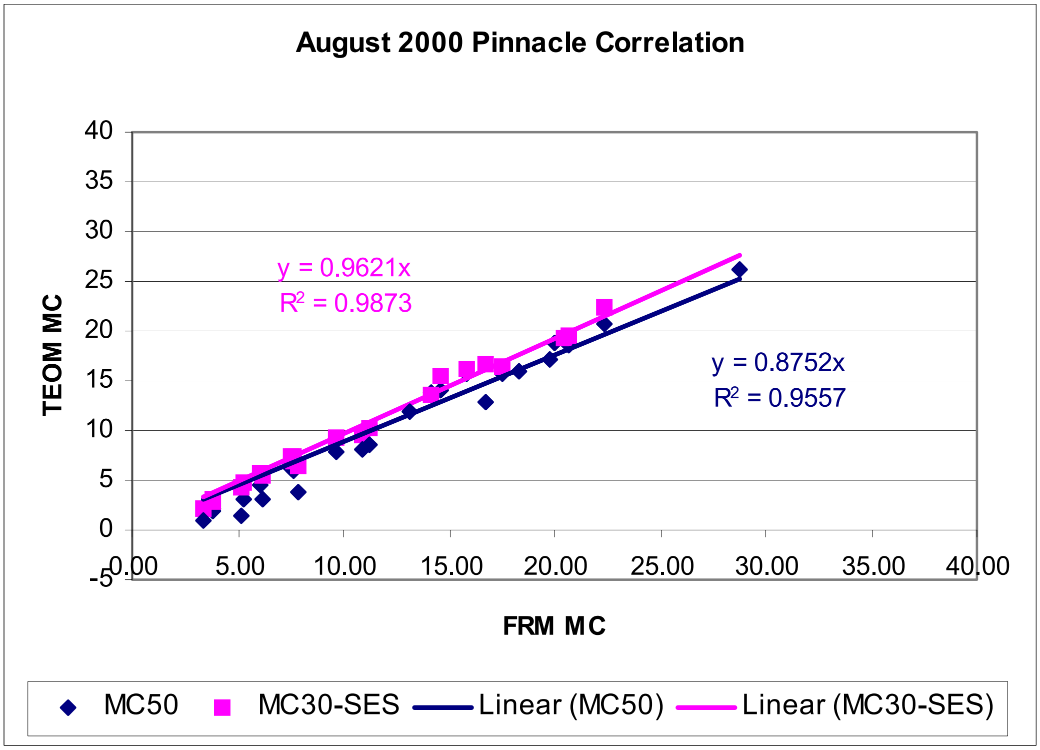
June2001 Pinnacle Correlation
y = 0.9665x + 2.3366
R2 = 0.98
y = 1.0131x + 1.8623
R2 = 0.9739
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0
5
10
15
20
25
30
35
40
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)


April 2000 Pinnacle Correlation
40
35
30
25
20
15
10
5
0
-5
TEOM MC
y = 0.8912x
R2 = 0.9364
y = 0.825x
R2 = 0.9304
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
FRM MC
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

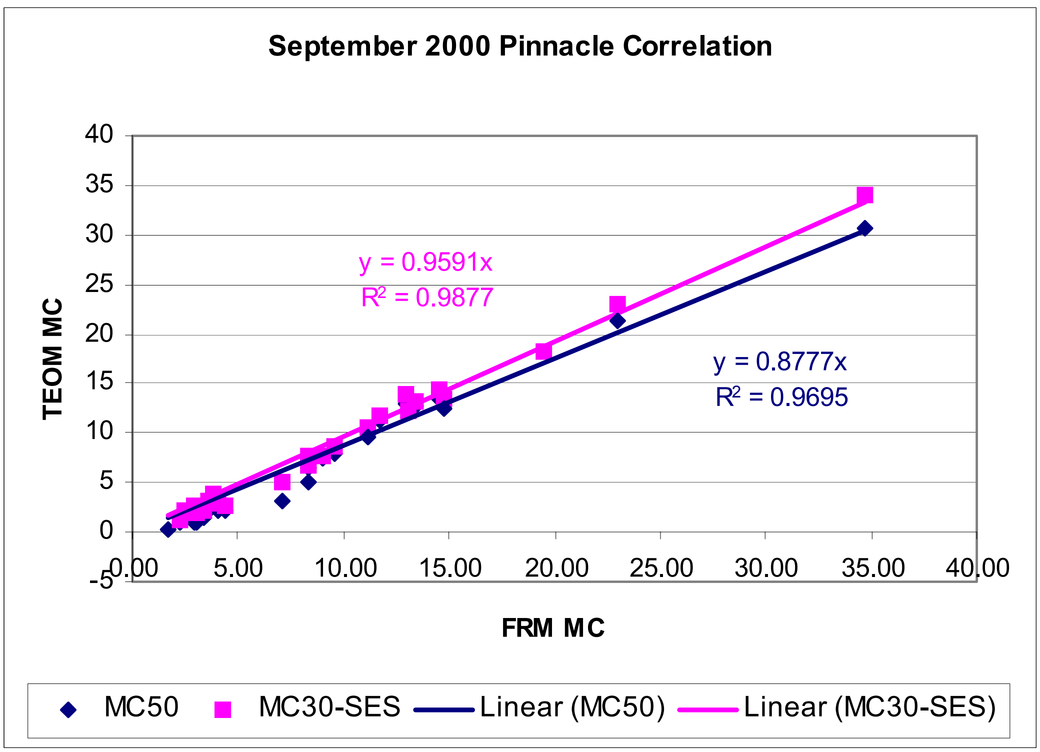

May 2000 Pinnacle Correlation
40
35
30
25
20
15
10
5
0
-5
TEOM MC
y = 0.9867x
R2 = 0.9848
y = 0.9199x
R2 = 0.9598
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
FRM MC
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)


June 2000 Pinnacle Correlation
y = 0.9887x
R² = 0.9907
y = 0.8739x
R² = 0.9686
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

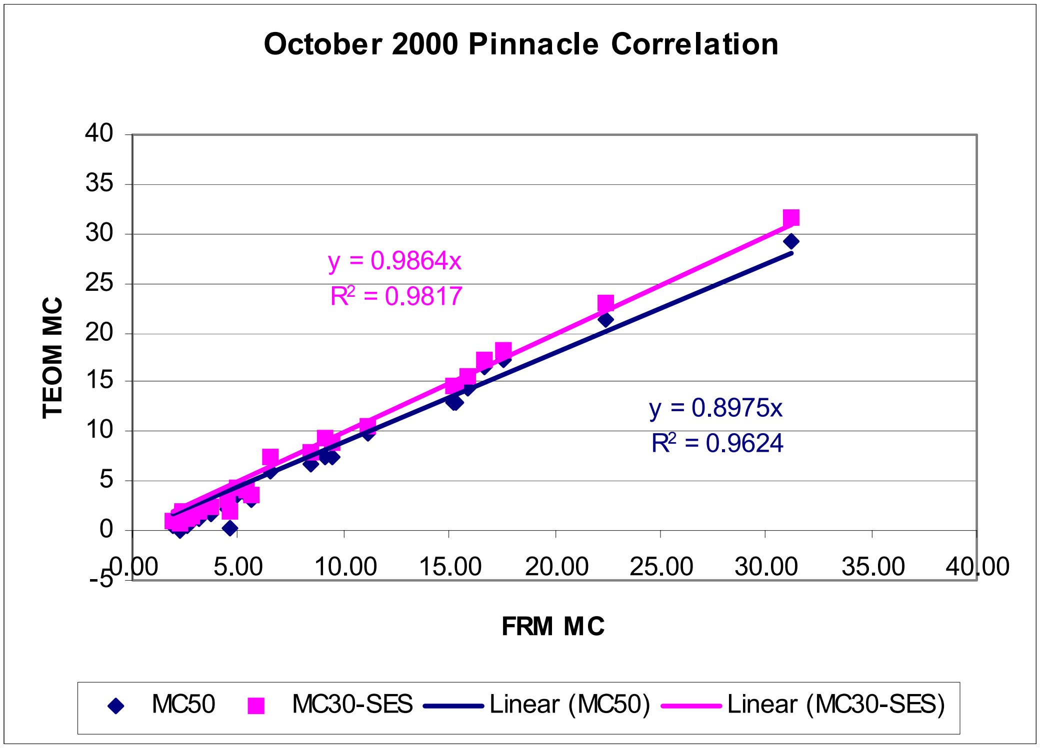

July 2000 Pinnacle Correlation
y = 0.9497x
R² = 0.9803
y = 0.8777x
R² = 0.9589
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

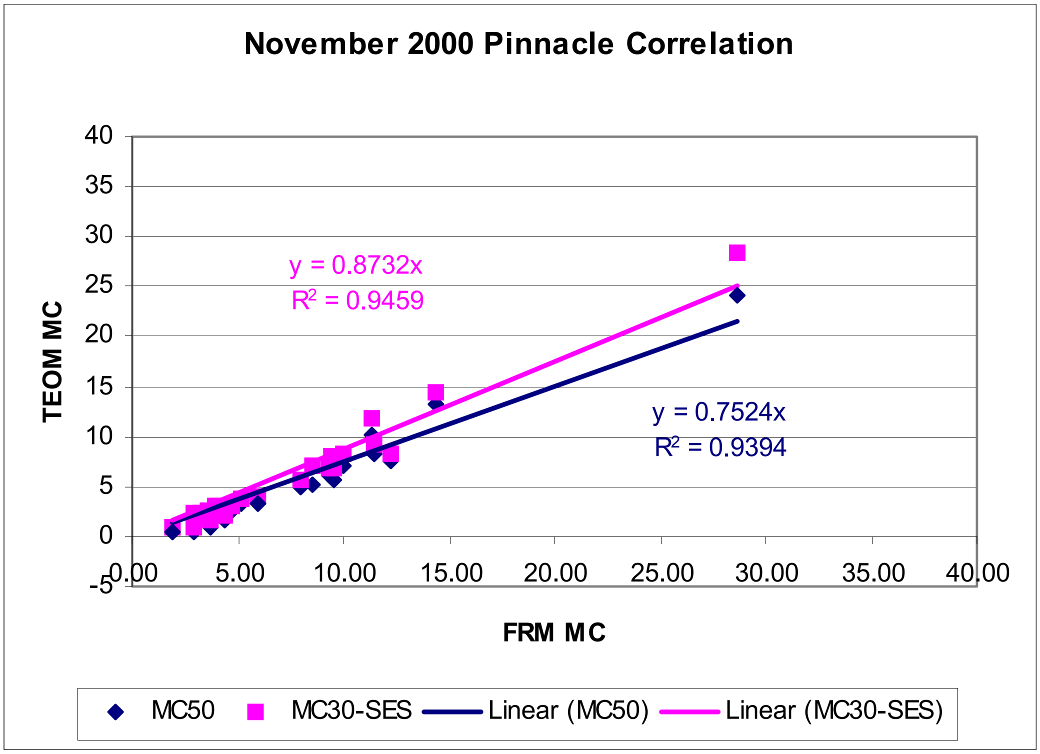


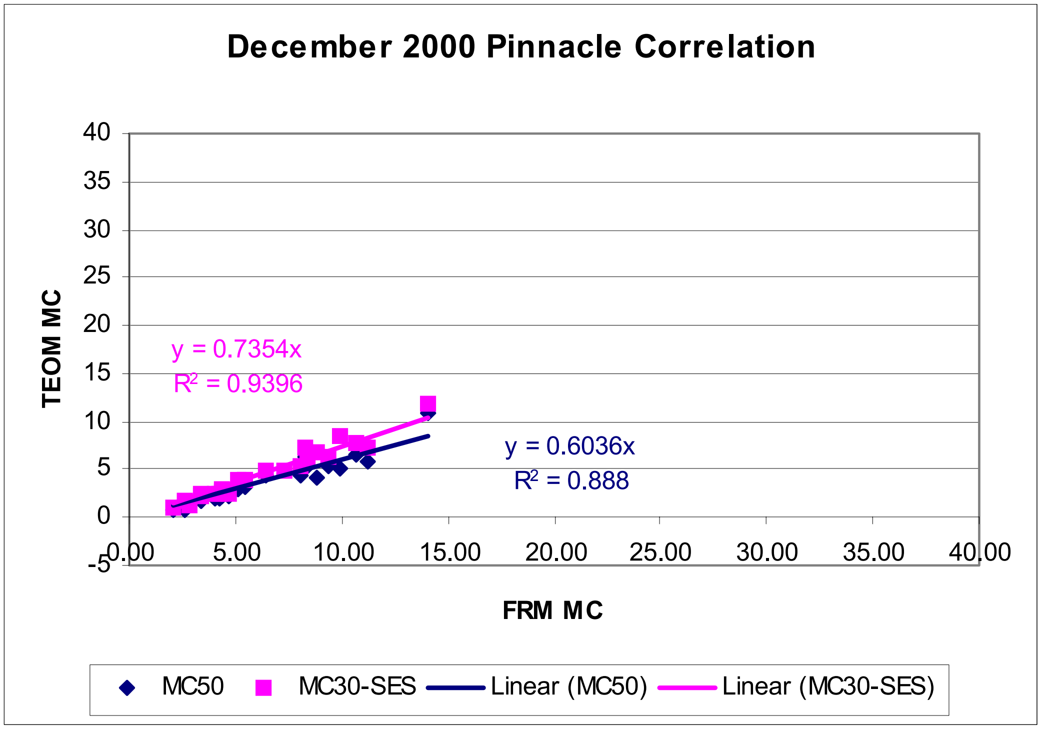
August 2000 Pinnacle Correlation
y = 0.9621x
R2 = 0.9873
y = 0.8752x
R2 = 0.9557
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

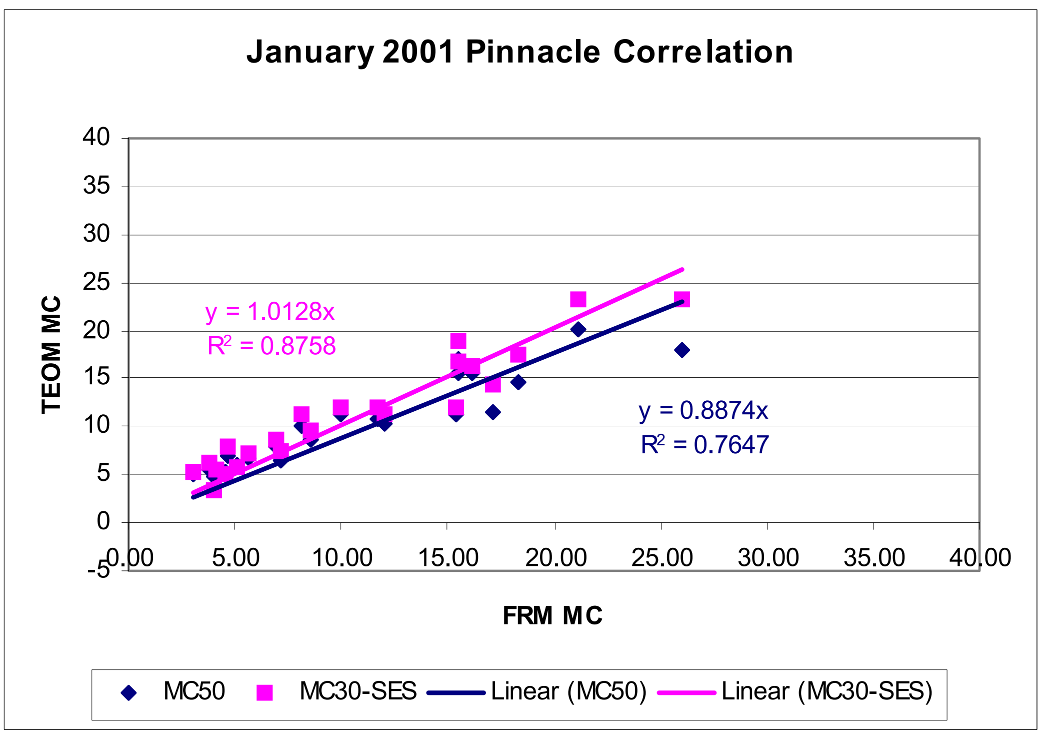


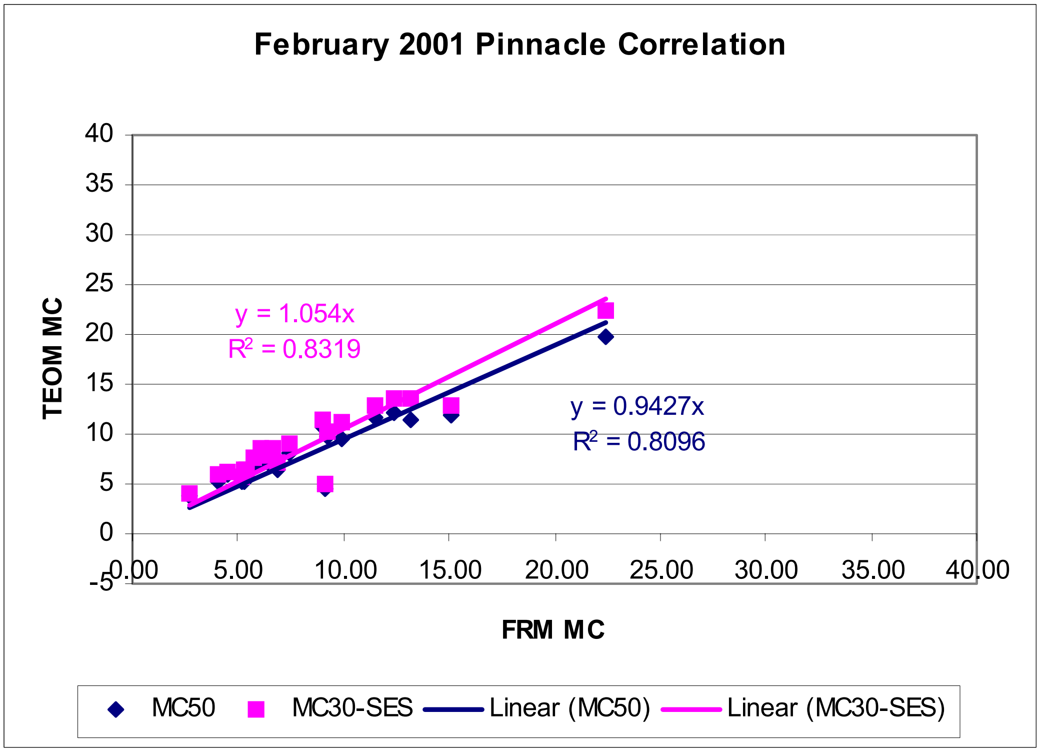
September 2000 Pinnacle Correlation
y = 0.9591x
R2 = 0.9877
y = 0.8777x
R2 = 0.9695
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

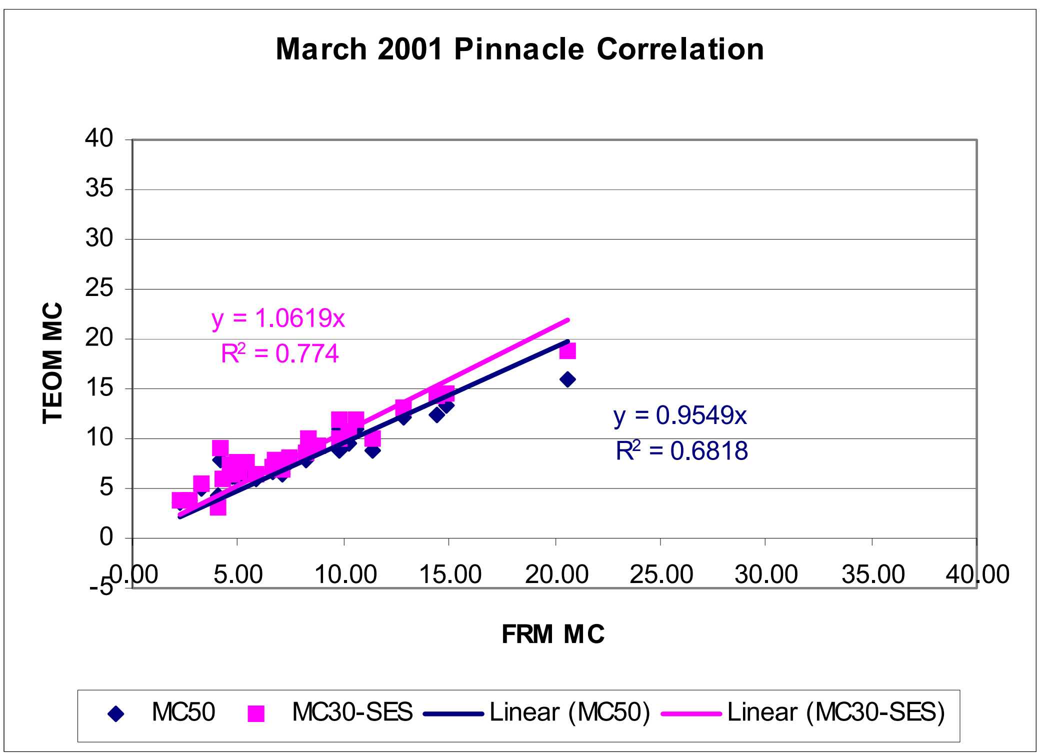

October 2000 Pinnacle Correlation
TEOM MC
FRM MC
y = 0.9864x
R2 = 0.9817
y = 0.8975x
R2 = 0.9624
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

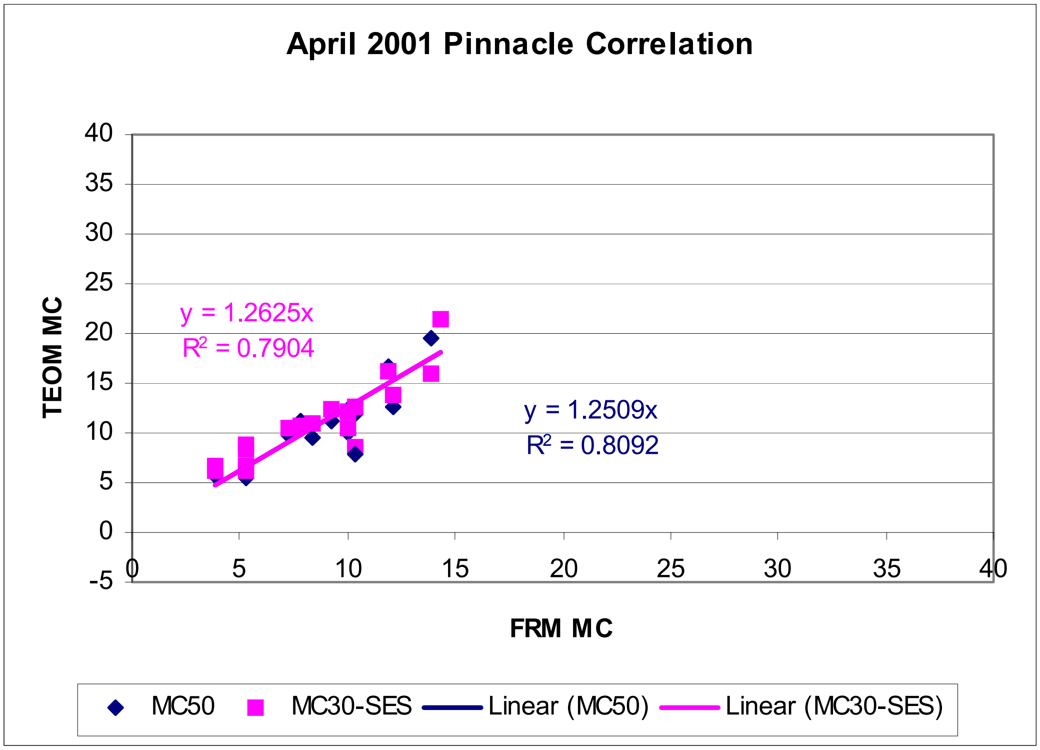

November 2000 Pinnacle Correlation
TEOM MC
FRM MC
y = 0.8732x
R2 = 0.9459
y = 0.7524x
R2 = 0.9394
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

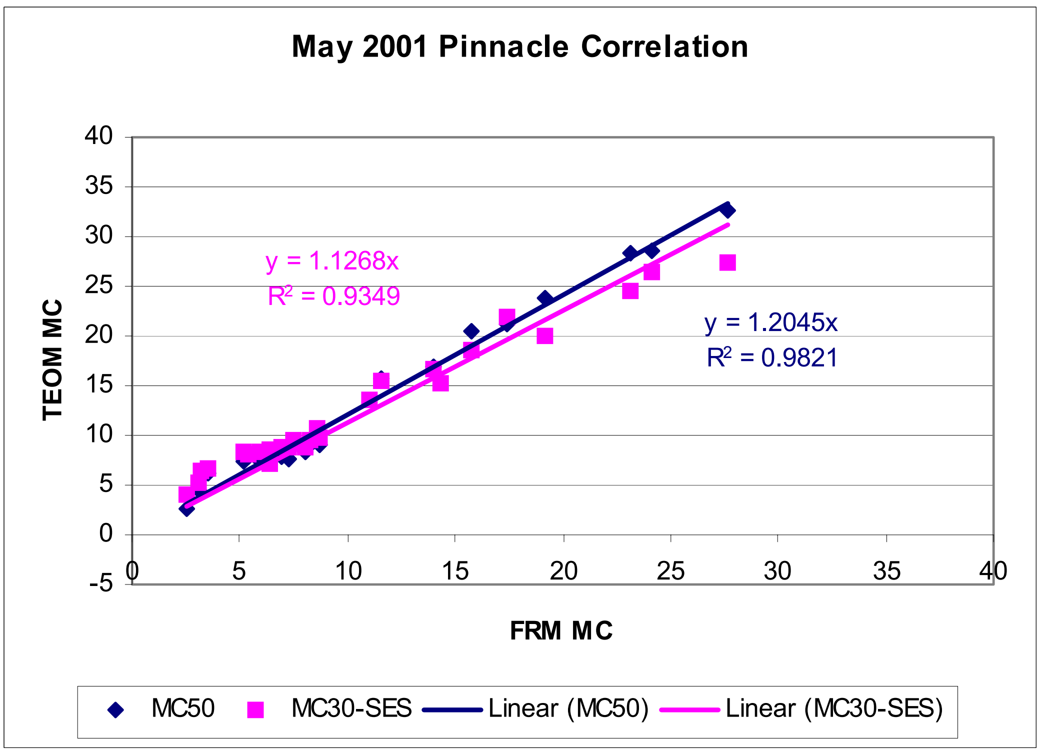

December 2000 Pinnacle Correlation
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
TEOM MC
FRM MC
y = 0.7354x
R² = 0.9396
y = 0.6036x
R² = 0.888
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

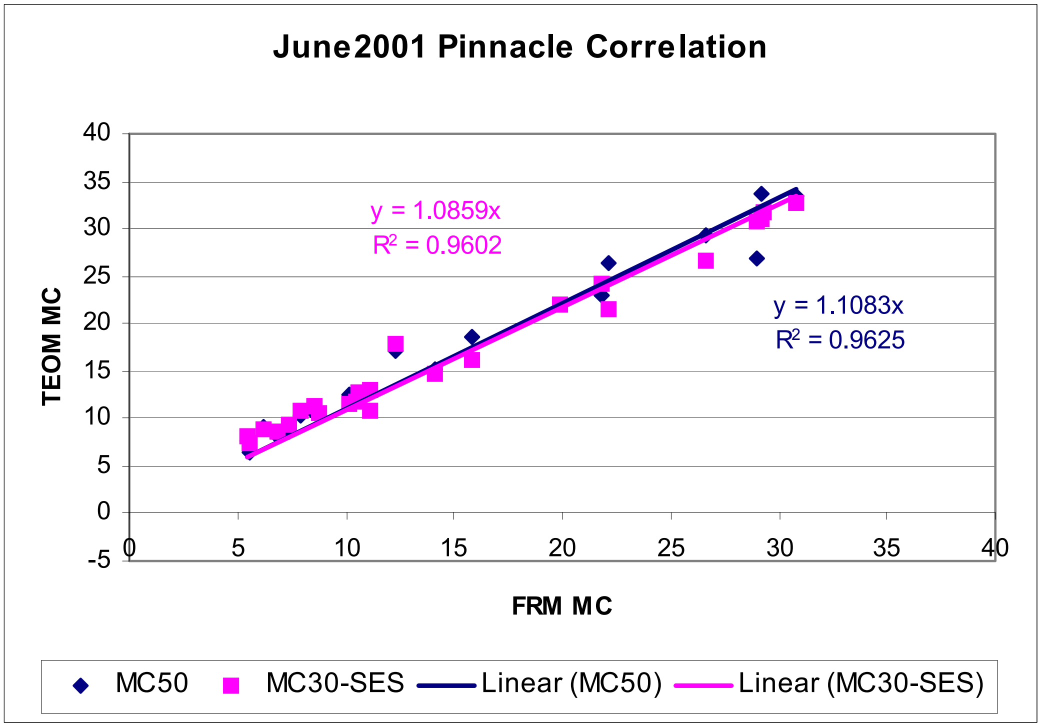

January 2001 Pinnacle Correlation
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
TEOM MC
FRM MC
y = 1.0128x
R² = 0.8758
y = 0.8874x
R² = 0.7647
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)


February 2001 Pinnacle Correlation
y = 1.054x
R^2 = 0.8319
y = 0.9427x
R^2 = 0.8096
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)


March 2001 Pinnacle Correlation
y = 1.0619x
R^2 = 0.774
y = 0.9549x
R^2 = 0.6818
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)


April 2001 Pinnacle Correlation
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0
5
10
15
20
25
30
35
40
y = 1.2625x
R2 = 0.7904
y = 1.2509x
R2 = 0.8092
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

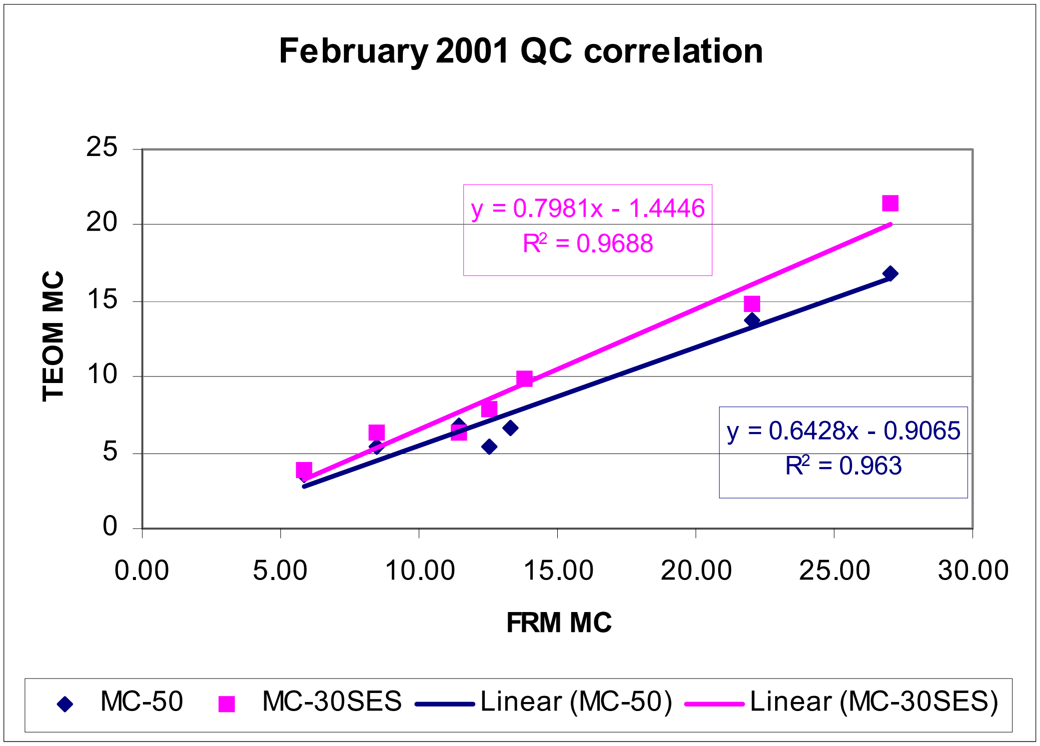

May 2001 Pinnacle Correlation
TEOM MC
FRM MC
40
35
30
25
20
15
10
5
0
-5
0
5
10
15
20
25
30
35
40
y = 1.1268x
R2 = 0.9349
y = 1.2045x
R2 = 0.9821
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

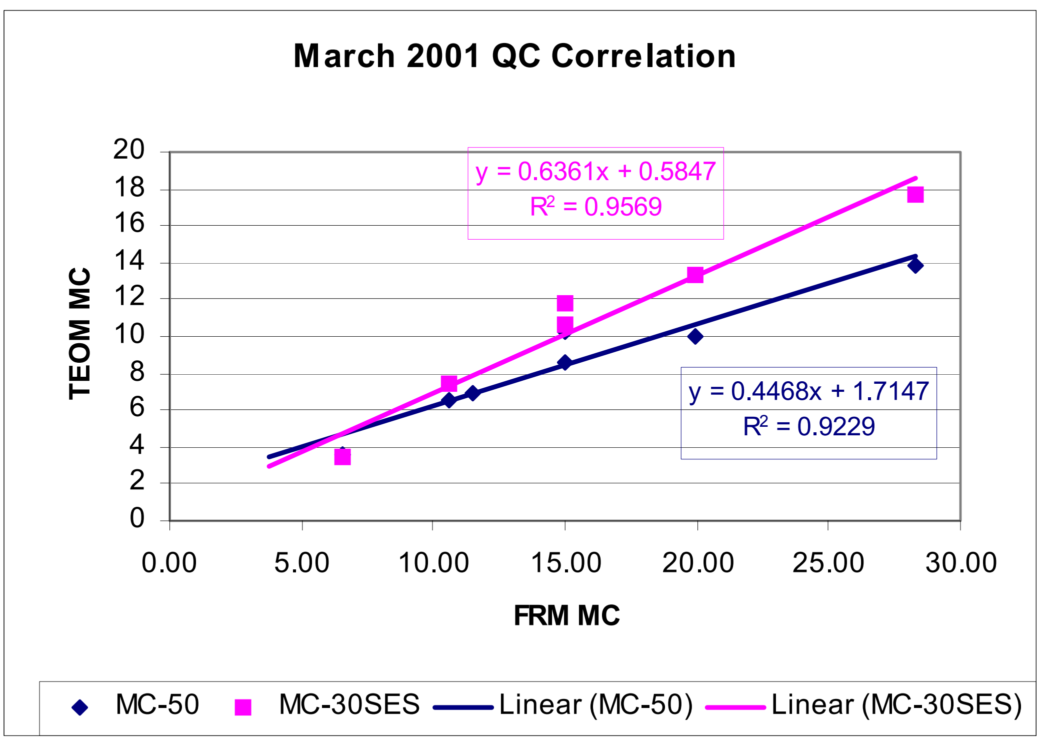

June2001 Pinnacle Correlation
TEOM MC
FRM MC
y = 1.0859x
R2 = 0.9602
y = 1.1083x
R2 = 0.9625
40
35
30
25
20
15
10
5
0
-5
0
5
10
15
20
25
30
35
40
MC50
MC30-SES
Linear (MC50)
Linear (MC30-SES)

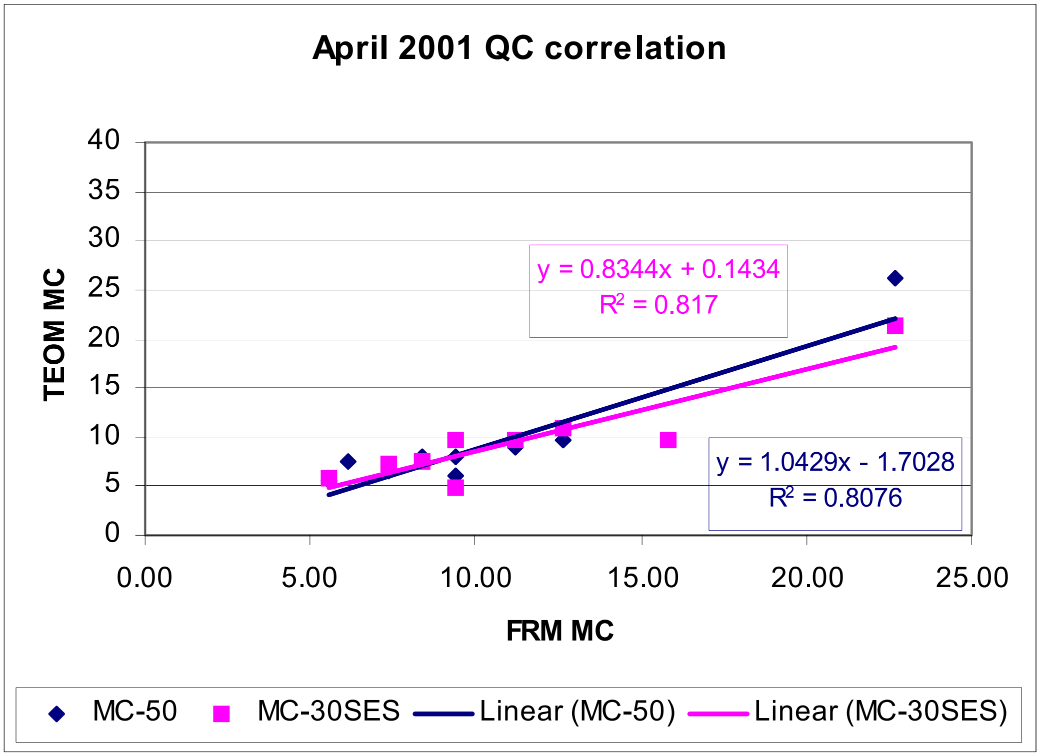
APPENDIX D

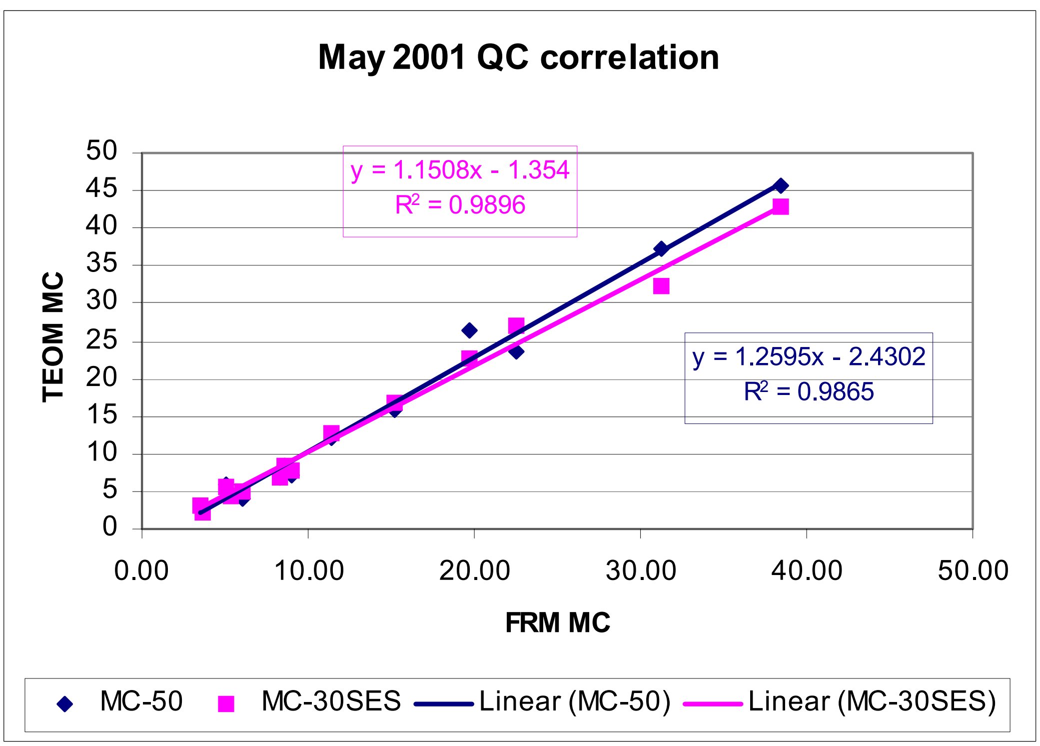
Detailed Results - SES Equipped TEOM Monitor Study - Urban New York State Sampling Location

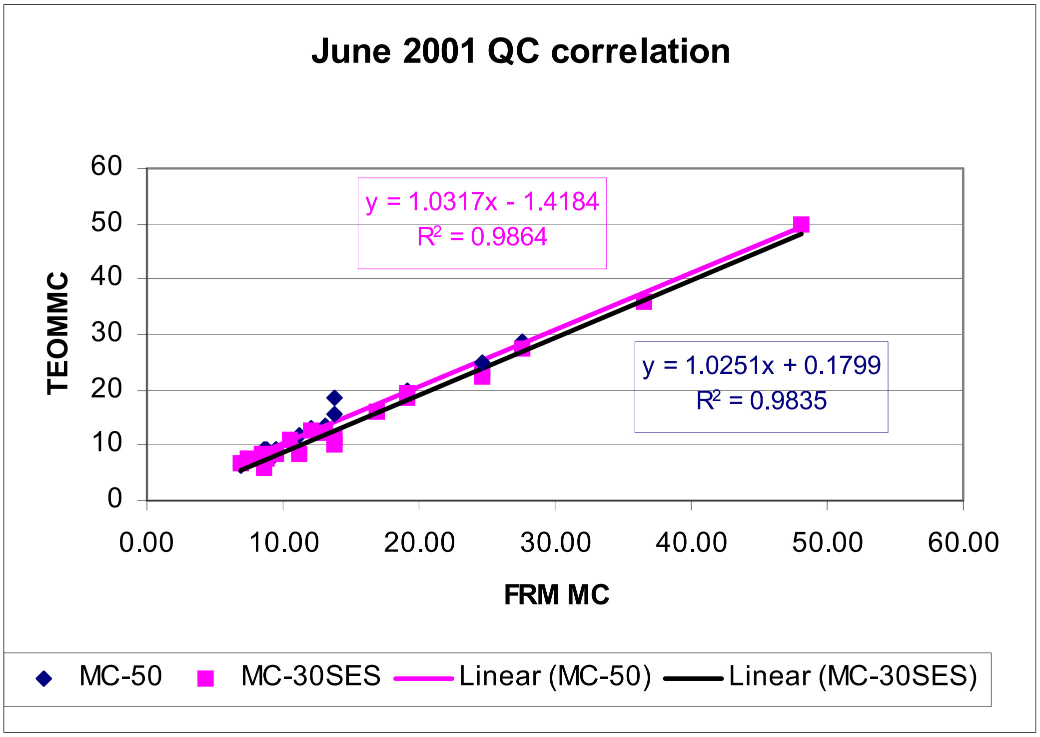
Appendix D contains all of the monthly correlations between the SES equipped TEOM monitor and the standard 50ºC TEOM monitor compared with the FRM samples over the entire sampling period at the PS219 sampling location in Queens, NY. The first set of figures include the correlations where the intercept of the correlation curve is determined by the data. If the resulting intercept is significantly different than zero, then there is a potential bias between the two sampling techniques. The second set of figures includes the correlations where the intercept is constrained to pass through the origin of the graph. If there is no bias between the different sampling methods, then the two sets of figures will be identical.

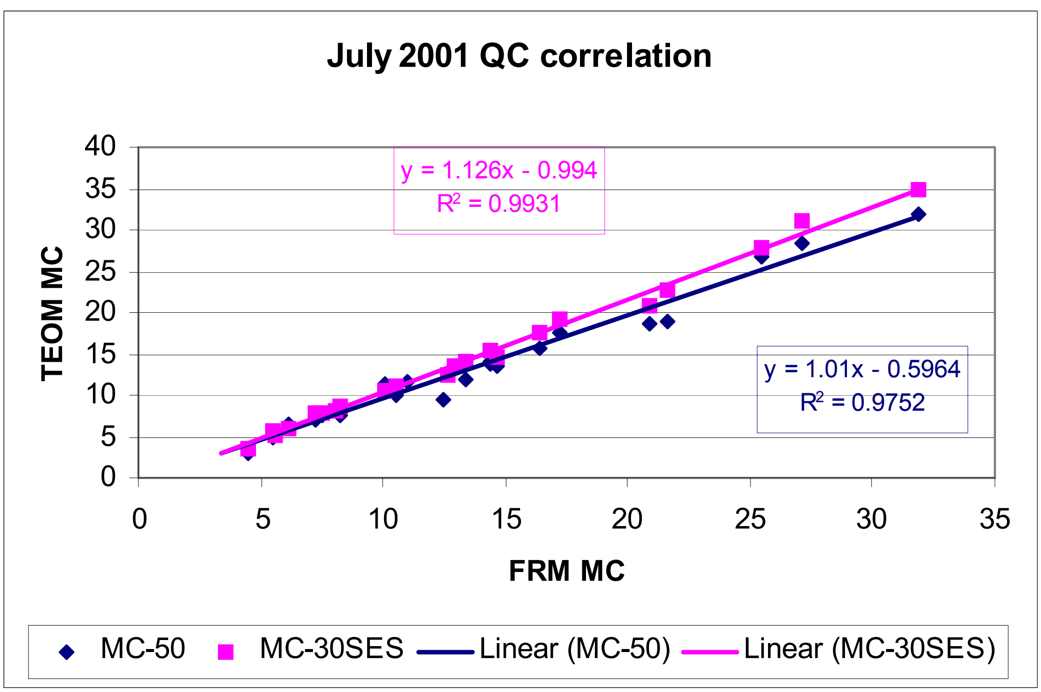

February 2001 QC correlation
y = 0.7981x - 1.4446
R2 = 0.9688
y = 0.6428x - 0.9065
R2 = 0.963
TEOM MC
FRM MC
25
20
15
10
5
0
0.00
5.00
10.00
15.00
20.00
25.00
30.00
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)

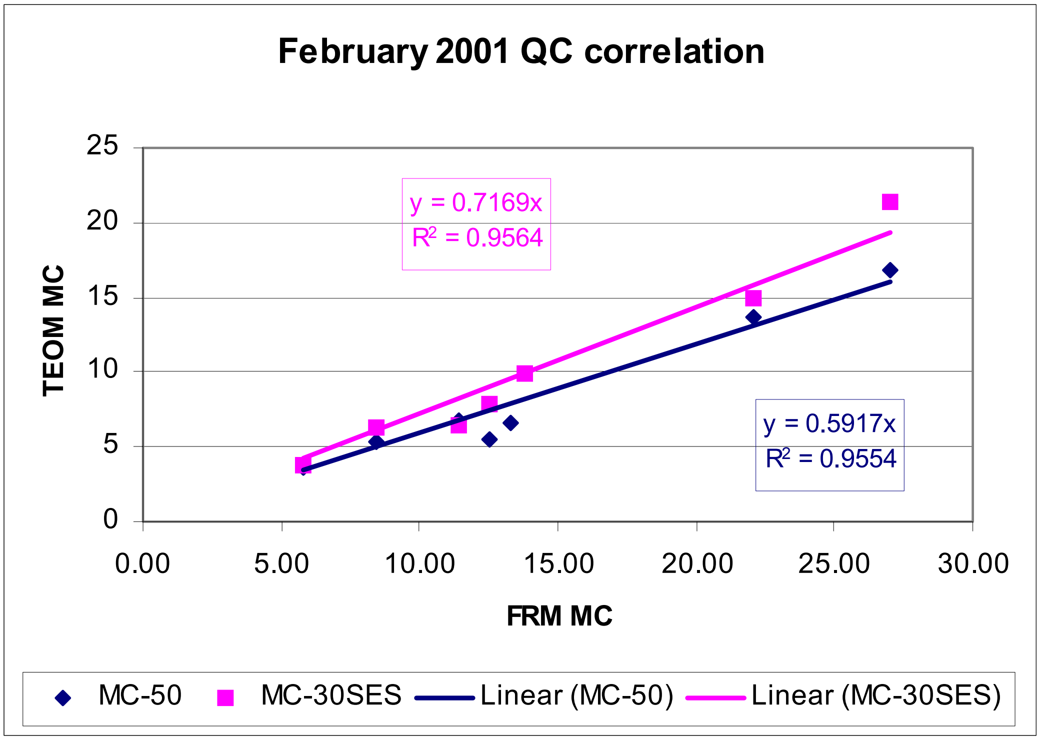

March 2001 QC Correlation
y = 0.6361x + 0.5847
R2 = 0.9569
y = 0.4468x + 1.7147
R2 = 0.9229
TEOM MC
FRM MC
20
18
16
14
12
10
8
6
4
2
0
0.00
5.00
10.00
15.00
20.00
25.00
30.00
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)

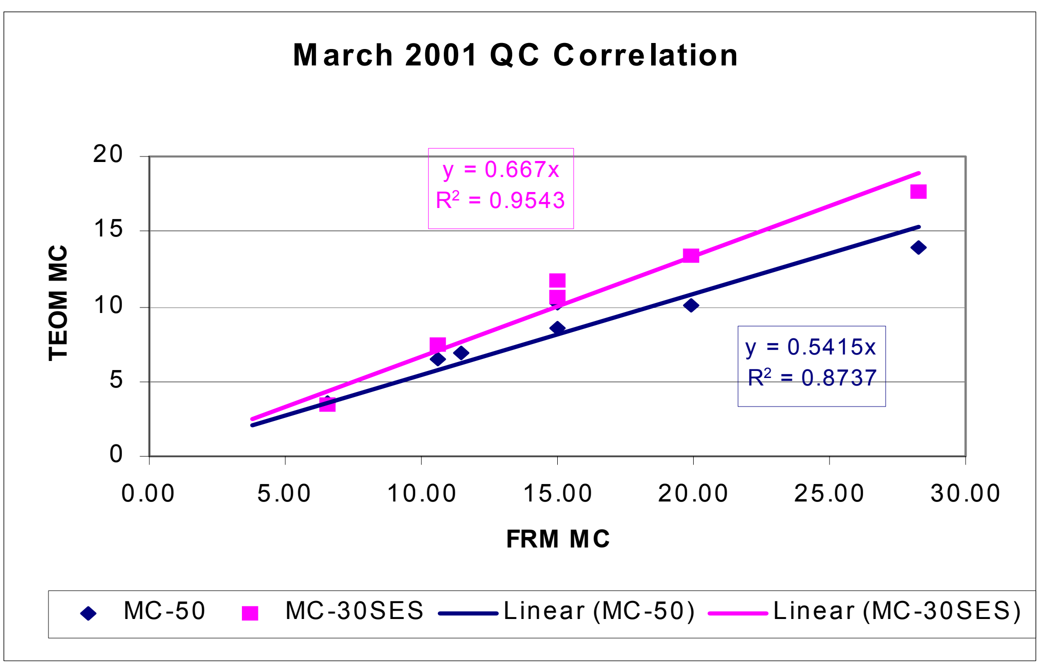

April 2001 QC correlation
TEOM MC
40
35
30
25
20
15
10
5
0
0.00
5.00
10.00
15.00
20.00
25.00
FRM MC
y = 0.8344x + 0.1434
R² = 0.817
y = 1.0429x - 1.7028
R² = 0.8076
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)

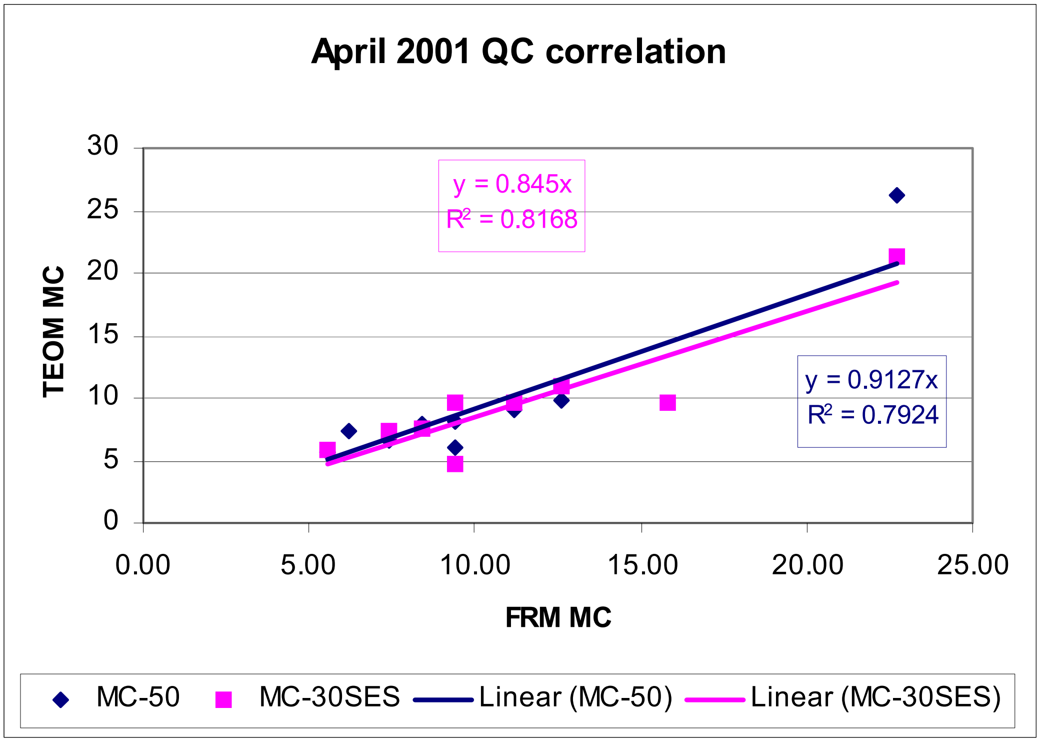

May 2001 QC correlation
TEOM MC
50
45
40
35
30
25
20
15
10
5
0
0.00
10.00
20.00
30.00
40.00
50.00
FRM MC
y = 1.1508x - 1.354
R² = 0.9896
y = 1.2595x - 2.4302
R² = 0.9865
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)


June 2001 QC correlation
y = 1.0317x - 1.4184
R² = 0.9864
y = 1.0251x + 0.1799
R² = 0.9835
TEOMMC
60
50
40
30
20
10
0
0.00
10.00
20.00
30.00
40.00
50.00
60.00
FRM MC
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)

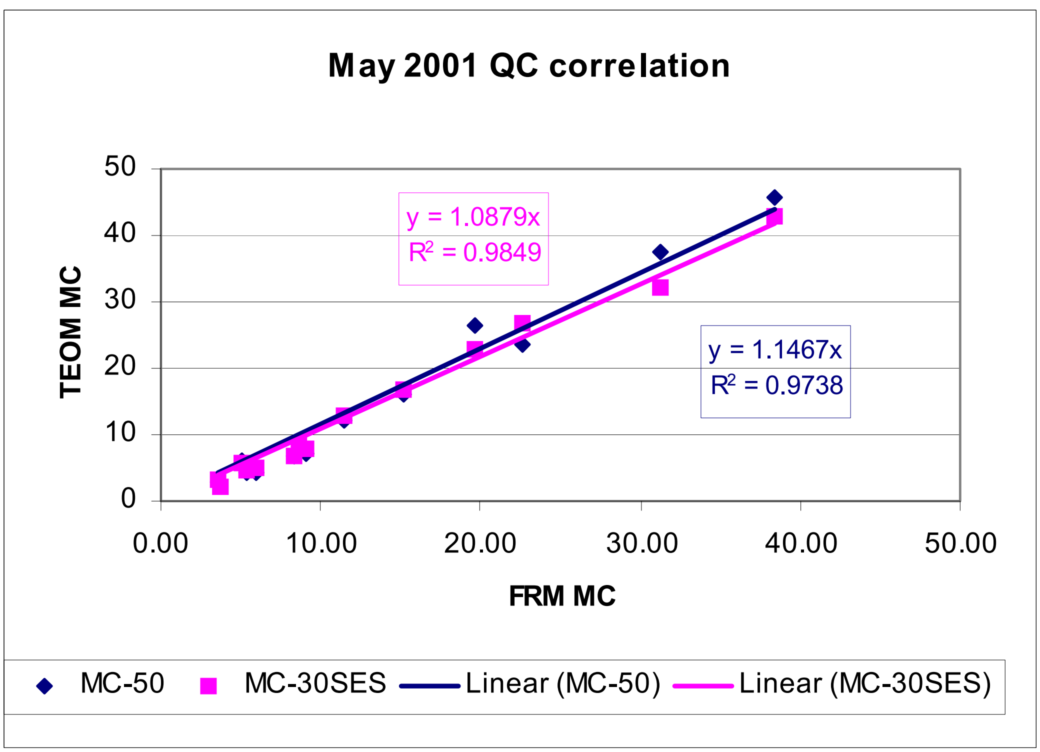

July 2001 QC correlation
y = 1.126x - 0.994
R² = 0.9931
y = 1.01x - 0.5964
R² = 0.9752
TEOM MC
40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
30
35
FRM MC
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)


February 2001 QC correlation
y = 0.7169x
R² = 0.9564
y = 0.5917x
R² = 0.9554
TEOM MC
FRM MC
0
5
10
15
20
25
0.00
5.00
10.00
15.00
20.00
25.00
30.00
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)

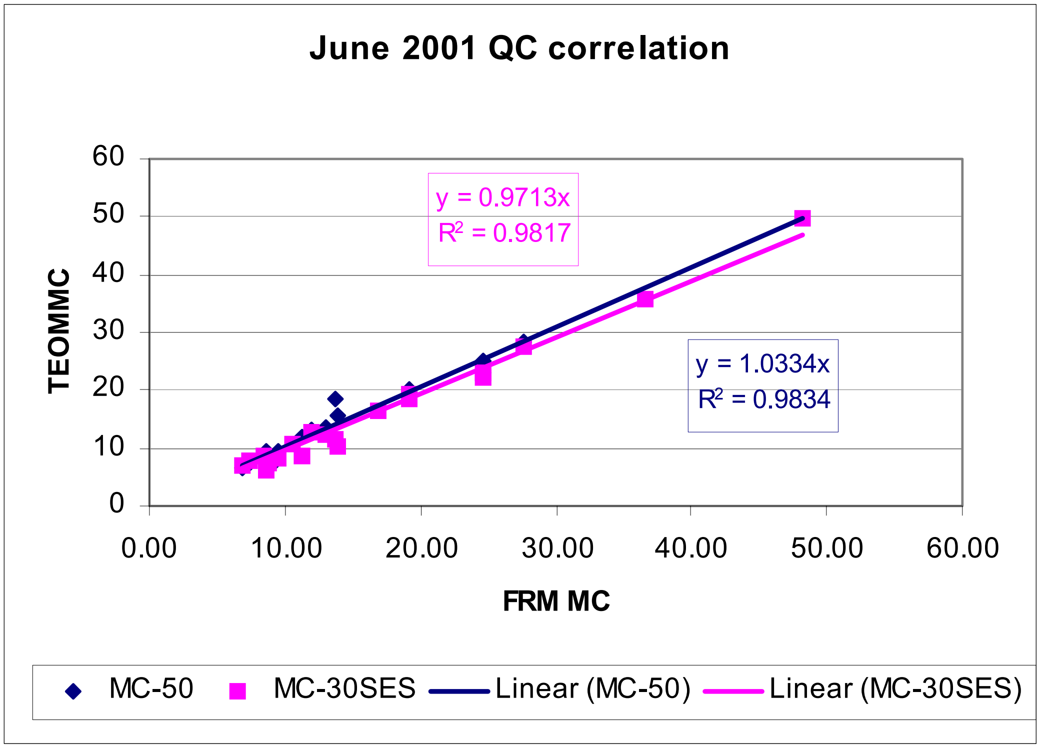

March 2001 QC Correlation
y = 0.667x
R² = 0.9543
y = 0.5415x
R² = 0.8737
TEOM MC
FRM MC
0
5
10
15
20
0.00
5.00
10.00
15.00
20.00
25.00
30.00
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)

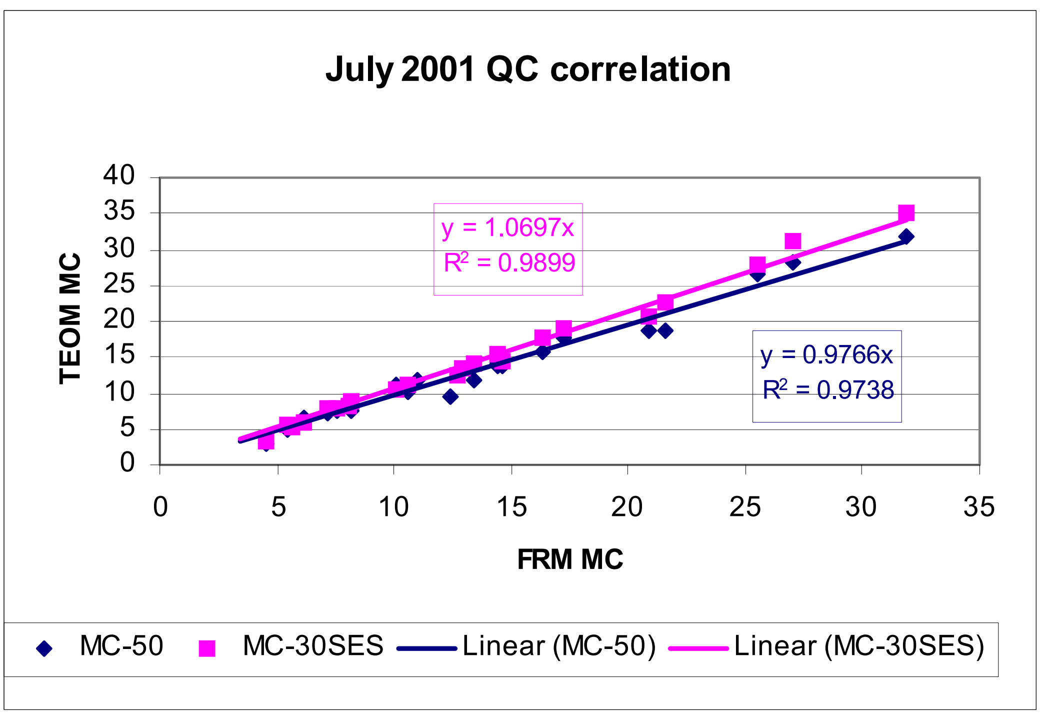


April 2001 QC correlation
30
25
20
15
10
5
0
TEOM MC
y = 0.845x
R2 = 0.8168
y = 0.9127x
R2 = 0.7924
0.00
5.00
10.00
15.00
20.00
25.00
FRM MC
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)



May 2001 QC correlation
50
40
30
20
10
0
TEOM MC
y = 1.0879x
R2 = 0.9849
y = 1.1467x
R2 = 0.9738
0.00
10.00
20.00
30.00
40.00
50.00
FRM MC
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)


June 2001 QC correlation
60
50
40
30
20
10
0
TEOMMC
y = 0.9713x
R² = 0.9817
y = 1.0334x
R² = 0.9834
0.00
10.00
20.00
30.00
40.00
50.00
60.00
FRM MC
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)


July 2001 QC correlation
40
35
30
25
20
15
10
5
0
TEOM MC
y = 1.0697x
R² = 0.9899
y = 0.9766x
R² = 0.9738
0
5
10
15
20
25
30
35
FRM MC
MC-50
MC-30SES
Linear (MC-50)
Linear (MC-30SES)

For information on other
NYSERDA reports, contact:

New York State Energy Research
and Development Authority
17 Columbia Circle
Albany, New York 12203-6399

toll free: 1 (866) NYSERDA
local: (518) 862-1090
fax: (518) 862-1091

info@nyserda.org
www.nyserda.org

Develop and Field Test Rupprecht & Patashnick (R&P) Series-6400 Controlled Sampling Continuous Particulate Monitor

Final Report 03-06

NYSERDA