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Comparison of Continuous Monitor (TEOM) vs. Gravimetric Sampler Particulate Matter Concentrations

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Abstract. *The Tapered Element Oscillating Microbalance (TEOM) sampler is an EPA designated equivalent method sampler for measuring PM₁₀ concentrations. Many state air pollution regulatory agencies have implemented TEOM samplers in monitoring PM₁₀ concentrations for regulatory purposes. Previous research has shown that TEOM samplers may over state the concentration of PM₁₀ when compared to concentrations measured by collocated FRM gravimetric PM₁₀ samplers. Previous research has shown that the FRM PM₁₀ samplers may report concentrations in excess of true PM₁₀ concentrations by as much as 400%. Recent work has shown that more accurate measurements of PM₁₀ concentrations can be achieved by measuring TSP concentrations and multiplying by the corresponding mass fraction = 10 μm from a particle size distribution analysis. This manuscript presents the results of collocated TEOM and gravimetric samplers configured to measure total suspended particulate (TSP) matter concentrations. The results show that there is a significant positive linear correlation between the concentrations measured by the TEOM and gravimetric TSP samplers. It was observed that in general, the TEOM samplers will report lower TSP concentrations than the collocated gravimetric TSP sampler. Further investigation into these results indicated that the difference in the concentration measured by the TEOM sampler versus the gravimetric TSP sampler (known as the TEOM measurement error) is not significantly correlated with the concentration measured by the gravimetric TSP sampler. However, significant linear relationships were observed between the measurement error of the TEOM samplers and the mass median diameter and geometric standard deviation of the collocated gravimetric TSP sample.*

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Keywords. TEOM, TSP, Air Sampler, Measurement Error, Particle Size Distribution

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Introduction

The particle size indicator on which particulate matter (PM) air quality regulations in the US is based has changed over the years from a total suspended particulate (TSP) basis to the current PM10 and PM2.5 basis. The national ambient air quality standards (NAAQS) for PM are ambient concentration limits established to protect public health (primary standards) and public well being (secondary standards). The original NAAQS for TSP was 260 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) based on a 24 hour average. This standard was changed in 1987 to regulate the concentration of particles less than or equal to 10 micrometers (μm) in aerodynamic equivalent diameter (AED) (PM10). The primary and secondary PM10 NAAQS is $150\mu\text{g}/\text{m}^3$ (24 hour average) and $50\mu\text{g}/\text{m}^3$ (annual average) (Federal Register, 1987). In 1997, the NAAQS was further modified to include a standard for regulating particles less than or equal to 2.5 μm AED (PM2.5) (Federal Register, 1997). The primary and secondary NAAQS for PM2.5 is $15\mu\text{g}/\text{m}^3$ (annual average) and $65\mu\text{g}/\text{m}^3$ (24 hour average). Today, only PM10 and PM2.5 are regulated by the NAAQS.

Ambient PM2.5 and PM10 (and formerly TSP) concentration monitoring for regulatory purposes must be conducted in accordance with federal guidelines. The EPA publishes a list of approved sampling devices that may be used to measure ambient PM concentrations for regulatory purposes (EPA, 2005). All of the samplers approved by the EPA have been designated as federal reference method (FRM) or federal equivalent method (FEM) samplers according to 40 CFR Part 53. Work by Buser et al. (2004) shows that FRM PM10 and PM2.5 samplers overstate the true concentrations of PM10 and PM2.5 respectively, when sampling dusts with mass median diameters (MMD) larger than the cutpoint of the sampler. Agricultural operations (including feedyard, cotton gin, and grain processing facilities) emit dusts with MMDs larger than 10 μm (Capareda et al. 2005). Consequently, PM10 and PM2.5 samplers may overstate the true concentration of PM10 and PM2.5 respectively, when sampling agricultural dusts. Field work by Capareda et al. (2005) at a Texas cotton gin indicates that PM10 samplers overstate true PM10 concentrations by 181%. A protocol described by Wanjura et al. (2004) uses TSP concentration measurements along with particle size distribution analysis to obtain more accurate measurements of PM10 concentrations from agricultural operations.

Included in the list of EPA approved PM10 samplers is the Rupprecht and Patashnick (R&P) Series 1400a Ambient PM10 monitor. This R&P monitor obtained its status as an Automated Equivalent Method for PM10 in 1990 (Federal Register, 1990) and has since become a popular device used by state air pollution regulatory agencies (SAPRA) to continuously monitor PM10 concentrations. When configured as designated for its PM10 federal equivalence method status, the R&P Series 1400a monitor uses the same PM10 inlet as the FRM PM10 sampler identified by Buser et al. (2004) to exhibit over-sampling errors.

The R&P Series 1400a monitor uses the tapered element oscillating microbalance (TEOM) method to measure PM10 concentrations on a real-time basis. When the R&P Series 1400a monitor is configured as it was approved as an Equivalent Method PM10 sampler, it consists essentially of a sample inlet head that allows particles less than 10 μm to pass into the instrument, the TEOM sensor unit with mass transducer, and the control unit. The monitor can be configured to measure TSP or PM2.5 concentrations as well, but has not been designated as an Equivalent or Reference Method by EPA for these configurations.

Several sources have indicated that the Series 1400a monitor, when configured to measure PM2.5 or PM10 concentrations, tends to report different concentrations than measured by gravimetric samplers. Hitzenberger et al. (2004) concluded that PM2.5 concentration measurements made by the R&P Series 1400a monitor could be as much as 18% lower than

comparable gravimetric measurements. Hitzemberger et al. (2004) further conclude that these differences in PM_{2.5} concentration may be partially attributable to the evaporation of volatile materials in the sample stream due to the heating of the sample stream. The sample stream is heated to 50°C before entering the sensor unit to remove particle bound water that may affect mass measurements. Similarly, Eatough et al. (2003) found that volatile particulate matter makes up a considerable portion of urban fine particulate matter (PM_{2.5}) and will not be measured if the sample stream is heated such that these materials volatilize and subsequently are not deposited on the sampler filter media.

The opposite result was observed by Vega et al. (2003) in a study comparing TEOM PM₁₀ concentrations to US FRM gravimetric PM₁₀ concentrations taken at five sites near Mexico City, Mexico. Over the two month testing period, it was concluded that the TEOM concentration measurements were consistently higher than the FRM gravimetric PM₁₀ concentrations. The degree to which concentration values were overstated varied with the PM₁₀ concentration level. Vega et al. (2003) go on to say that statistical tests showed that the TEOM and FRM gravimetric samplers did not yield equivalent measurements and that they should not be used interchangeably.

A successful method to correct continuous beta-attenuation monitor concentrations to gravimetric PM₁₀ concentrations taken every fourth day was developed by Gehrig et al. (2005). Gehrig et al. (2005) conclude that this same method would be successful if used to correct real time concentrations measured by TEOM monitors to concentrations measured by FRM gravimetric samplers. The implications of this work are that continuous TEOM monitors can be used with collocated gravimetric samplers that take concentration measurements on a less frequent basis (approximately every four days) to give accurate PM₁₀ concentration monitoring results with increased time resolution. Decreasing the number of gravimetric samples taken significantly reduces monitoring costs as gravimetric measurements are time and labor intensive to obtain.

The Center for Agricultural Air Quality Engineering and Science (CAAQES) at Texas A&M University has collected several data sets from collocated TEOM samplers (configured to measure TSP concentrations) and low volume TSP samplers from agricultural operations. The main objective of this work is to define the relationship between PM concentrations measured by the TEOM and gravimetric samplers and characterize the influence of concentration intensity and particle size on that relationship. It is hypothesized that differences in TSP concentrations measured by the TEOM sampler versus the gravimetric TSP sampler are attributable to the characteristics defining the particle size distribution (mass median diameter and geometric standard deviation) of the sampled dust. If the relationship between TEOM and FRM TSP concentrations is determined, it may be possible to develop a methodology similar that used by Wanjura et al. (2004) to monitor PM₁₀ and PM_{2.5} concentrations on a near real-time basis.

TEOM Sampler Principles and Operation

The R&P Series 1400a monitor essentially consists of three main components including:

1. The sample inlet designed to allow the TSP, PM₁₀, or PM_{2.5} fraction of the PM concentration in the ambient air to pass into the instrument for concentration analysis,
2. The TEOM sensor unit containing the microbalance and filter chamber, and
3. The system control module to monitor and record sampling flow rate data, filter mass measurements, and ambient temperature and barometric pressure measurements.

Figure 1 shows the layout of the R&P Series 1400a sampler configured to measure TSP concentrations. Initially, the 16.67 l/min sampling flow rate is drawn through the inlet head from the outside. The sampling flow rate is isokinetically split into a 3 l/min sample flow rate that is passed to the TEOM sensor unit and the remaining 13.67 l/min bypass flow (auxiliary flow) is exhausted to the outside. The 3 l/min sample flow is drawn through a replaceable cartridge containing a filter made of Teflon coated borosilicate (glass fiber). Air flow through the sampler is monitored and controlled by two mass flow controllers that maintain the total flow at 16.67 ± 1 l/min and the sample flow rate at 3 ± 0.2 l/min (Rupprecht and Patashnick, 2002).

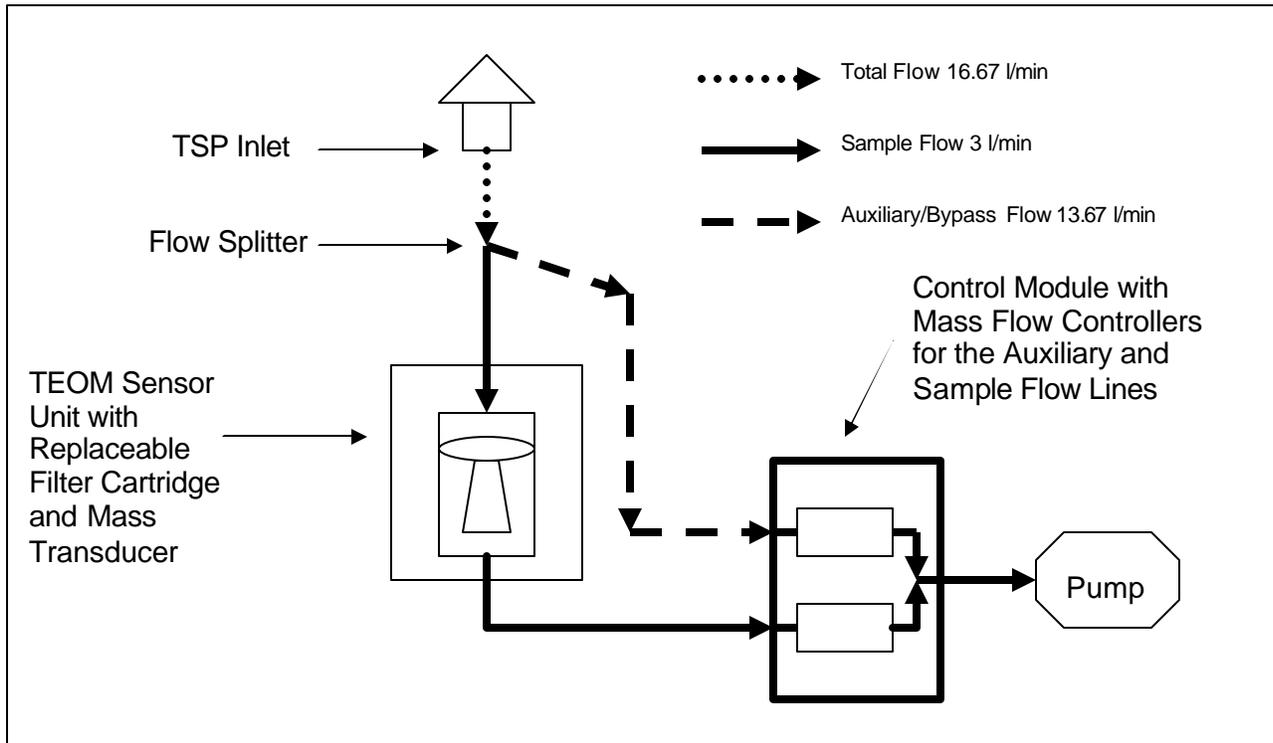


Figure 1. Schematic diagram of the R&P Series 1400a monitor configured to sample TSP concentrations.

The TEOM measures the change in oscillation frequency of a hollow tapered element to determine the change in total mass of the replaceable filter cartridge that is used to collect the particulate matter from the sample air stream. The hollow tapered element, replaceable filter cartridge, and the captured particulate mass can be modeled as a spring-mass system by equation 1.

$$F = \sqrt{\frac{K_0}{M}} \quad (1)$$

where:

F = frequency of oscillation (1/sec),

K_0 = spring rate (N/m), and

M = total mass of hollow tapered element, replaceable filter cartridge, and captured particulate matter (kg).

The relationship in equation 1 holds for any unit system as long as consistent units are used. As the mass of collected particulate matter increases on the filter, the oscillation frequency of the system decreases. Equation 1 may be modified to give equation 2 there by determining the change in total system mass by a measured change in oscillation frequency.

$$\Delta M = K_0 \left(\frac{1}{F_1^2} - \frac{1}{F_2^2} \right) \quad (2)$$

where:

ΔM = change in total system mass (kg), and

$F_{1,2}$ = initial and final measured oscillation frequency (1/sec).

The K_0 value is specific for each TEOM unit and is determined by the manufacturer. This value can be determined by solving equation 2 for K_0 and measuring the change in frequency of the tapered element with a known change in filter mass (i.e. two pre-weighed filters with different masses).

In practice, the R&P 1400a monitor evaluates equation 1 to determine the initial total system mass at the beginning of the sampling period and then once every two seconds afterwards. Subtracting the initial total system mass from the total system mass measured every 2 seconds gives the total mass of PM accumulated on the filter cartridge. This is shown by equation 3.

$$TPM = TSM_i - TSM_0 \quad (3)$$

where:

TPM = total particulate mass accumulated on the filter in a 2 second period (g), and

$TSM_{i,0}$ = total system mass at the end of the 2 second period (i) and the initial system mass (0) calculated initially at the beginning of the sampling period (g).

The TPM masses are smoothed by an exponential smoothing routine before being recorded by the internal data buffer. Equations 4 and 5 show the smoothing routine used by the R&P Series 1400a monitor to determine the smoothed total particulate mass accumulated on the filter.

$$a = \left(\frac{2GT}{TPM_{avg}} \right) \quad (4)$$

$$STPM_i = a(TPM_i) + (1 - a)STPM_{i-1} \quad (5)$$

where:

a = constant used in the exponential smoothing routine to calculate the smoothed total particulate mass,

GT = frequency sampling gate time (2 seconds),

TPM_{avg} = time period over which total particulate mass values are averaged (300 seconds), and

STPM = smoothed total particulate mass from the i^{th} 2 second period (g).

The STPM values are used to determine the change in mass for a 2 second time period by equation 6.

$$MC = STPM_i - STPM_{i-1} \quad (6)$$

where:

MC = change in smoothed particulate mass for a 2 second time period (g).

The MC values are then smoothed using equations 7 and 8 before being recorded by the internal data buffer for later use in calculating mass concentrations.

$$b = \left(\frac{2GT}{MC_{avg}} \right) \quad (7)$$

$$SMC_i = b(MC_i) + (1 - b)MC_{i-1} \quad (8)$$

where:

β = constant used in the exponential smoothing routine to calculate the smoothed mass change over a two second period, and

SMC = smoothed particulate mass change on the filter during the i^{th} 2 second period (g).

The SMC values for each two second period are used to calculate mass concentrations for the corresponding 2 second time period using equation 9.

$$SCONC_i = \frac{SMC_i}{V} 10^6 \quad (9)$$

where:

SCONC = smoothed mass concentration from the i^{th} 2 second time period ($\mu\text{g}/\text{m}^3$),

V = sample air volume calculated from the flow rate measured by the sample flow mass flow controller multiplied by the 2 second sampling time period (m^3), and

10^6 = unit conversion constant to convert g to μg .

The 4 line display on the TEOM monitor control unit displays a 10 minute sliding concentration that is updated every two seconds from the concentrations calculated using equation 9. The TEOM monitor also calculates 30 minute, 60 minute, and 24 hour concentrations using the STPM values calculated above and equation 10.

$$STAC = \frac{STPM_b - STPM_a}{V_T} 10^6 \quad (10)$$

where:

STAC = smoothed time average concentration for a 30 minute, 60 minute, or 24 hour time period ($\mu\text{g}/\text{m}^3$),

STPM_{b,a} = smoothed total particulate mass at the end and beginning of the time period (g), and

V_T = Total volume of air drawn through the filter during the averaging period (m^3).

Mass concentrations measured by the TEOM monitors can be reported in units of μg per actual or standard m^3 . The temperature and barometric pressure values used to calculate the actual air density (used to calculate concentrations based on actual conditions) are supplied with the TEOM monitor. The standard air temperature and pressure used by the instrument is the EPA standard of 25°C and 1 atm respectively.

Sampling Methodology

R&P Series 1400a TEOM monitors were collocated with low volume TSP samplers (LVTSP) at a Texas cattle feedyard in the summer of 2003, spring of 2004, and spring of 2005. The sampling sites located to the north and east of the feedyard were downwind sampling locations as indicated by the meteorological data taken during each sampling event. The placement of the samplers during the sampling conducted during the summer of 2003 was chosen so that the samplers would both measure PM emissions downwind from the feeding pens. The particle size distribution of the PM measured was expected to be considerably larger than that of the upwind or background PM based on previous studies. In the spring of 2004, one of the TEOM samplers was placed again at the northern edge of the feedyard and the second was placed at the southern edge of the feed yard to measure background concentrations. During the spring of 2005, the samplers were placed on the eastern and western edges of the feedyard. It was expected that the eastern sampler would measure predominately downwind concentrations from the feeding pens and from the unpaved road located between the sampling station and the feeding pens. The second TEOM sampler was placed on the western edge of the yard during the spring 2005 sampling event to measure predominately upwind concentrations with smaller particle size distributions than the samplers located on the eastern edge.

Equipment failures during the summer of 2003 and spring of 2005 caused problems in the data collection process. As a result, only data from the northwestern sampler is available from the sampling conducted during the summer of 2003. Similarly, only data from the eastern sampler is available from the sampling conducted during the spring of 2005 leaving a total of 4 datasets for comparison purposes. The sampling locations from which data is available are shown in figure 2 by the colored icons (summer 2003 – red, spring 2004 – blue, spring 2005 – green).

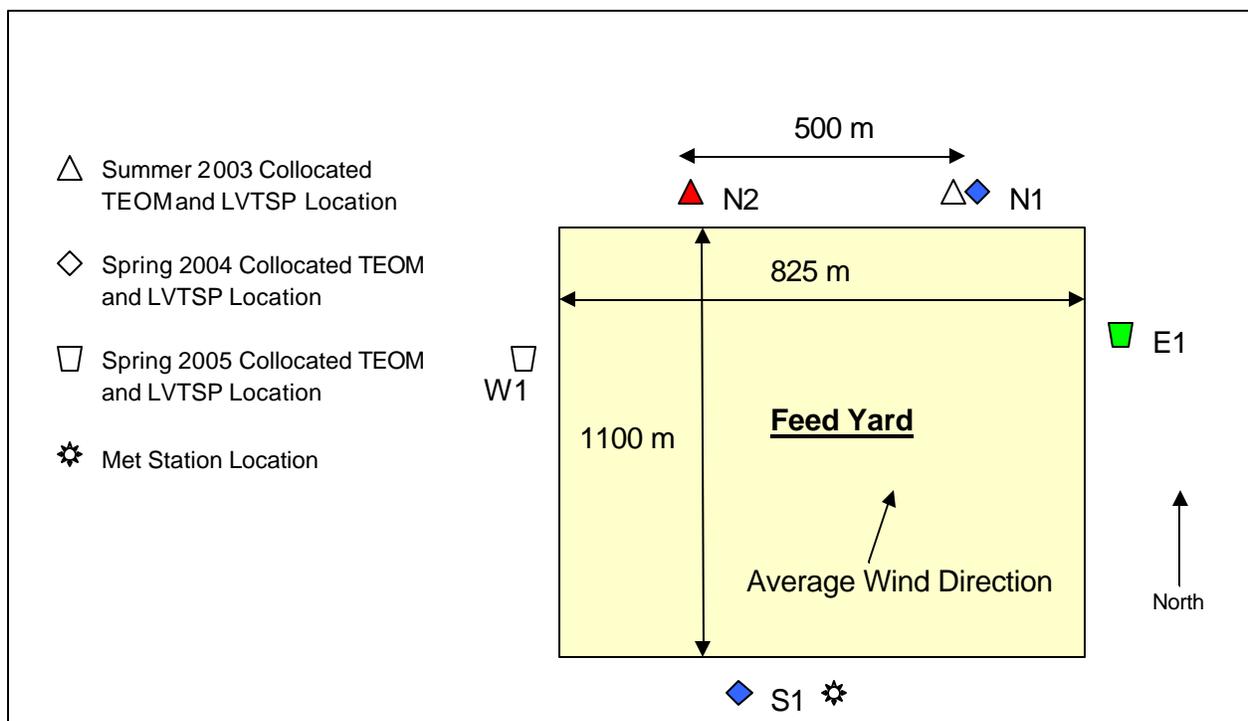


Figure 2. Feedyard schematic showing the location of the collocated TEOM and low volume TSP (LVTSP) samplers during sampling events during the summer of 2003, spring of 2004, and

the spring of 2005. The sampling locations from which data is available are shown by the colored icons, summer 2003 – red, spring 2004 – blue, spring 2005 – green.

Each of the TEOM samplers were configured to measure TSP concentrations with a flow rate of 16.7 l/min. The TSP inlets used on the TEOM instruments were the same as those designed for the low volume TSP samplers designed by CAAQES. The design of these TSP inlets is detailed by Wanjura et al. (2003). The sample flow rate of particle laden air drawn through the mass transducer was 3 LPM. The remaining 13.67 l/min was exhausted to the outside of the instrument. The TEOM monitors were setup to report 10 minute, 30 minute, 1 hour, and 24 hour average concentrations.

The low volume TSP samplers used to obtain the gravimetric TSP concentrations for this study were the same as those described by Wanjura et al. (2003). The low volume TSP samplers used a 16.67 l/min sampling flow rate. The sampled air was drawn through a 47mm diameter polytetrafluoroethylene (PTFE) filter (2 µm pore size Zefluor Membrane Filter, Pall Corp., East Hills, NY). All of the filters used were conditioned before and after exposure according to the protocol outlined by Wanjura (2003) before being weighed on a Mettler – Toledo AG245 balance (AG245, Mettler Toledo, Greifensee Switzerland) (range: 0-41g, accuracy: ±0.01mg). Test durations for the gravimetric TSP samples ranged from 3 to 9 hours.

Particle size distribution (PSD) analyses were performed on the filters collected from the LVTSP samplers using the Coulter Multisizer3 (Beckman – Coulter, Coulter Multisizer3, Miami, FL). The filter media were placed in a 5% lithium chloride – methanol solution prior to being subjected to an ultrasonic bath for 5 minutes to remove the PM from the filter media. The Multisizer3 was configured with a 100µm aperture tube to measure particles in the range from 2 – 60µm. The protocol used to analyze the PSDs is described by Simpson et al. (2003). Previous work by Sweeten and Parnell (1989) indicate that PSD analyses results of filters used to measure PM concentrations from a feedyard follow the lognormal distribution relating percent mass to aerodynamic equivalent particle diameter. Thus it was expected that the relationship between percent mass and aerodynamic equivalent diameter (AED) from the PSDs was expected to follow a lognormal distribution described by the mass median diameter (MMD) and geometric standard deviation (GSD).

Results

The overall trend seen in the comparison of the gravimetric sampler concentrations versus the TEOM sampler concentrations from all datasets indicated that the TEOM samplers measured lower concentrations than the gravimetric samplers. Figures 3 – 6 show the plots of the gravimetric sampler concentration versus the collocated TEOM concentrations for all four datasets.

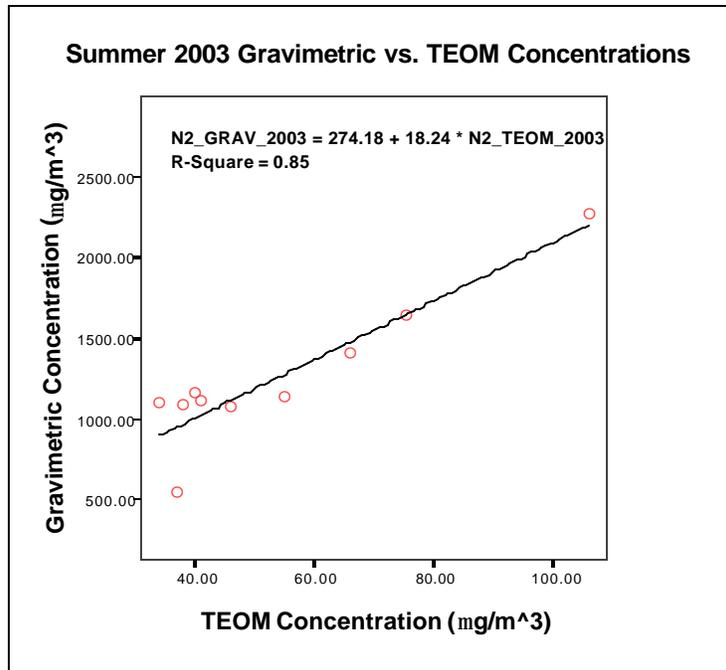


Figure 3. Plot of gravimetric sampler concentrations versus TEOM sampler concentrations for the N2 location (see figure 2) during the summer of 2003.

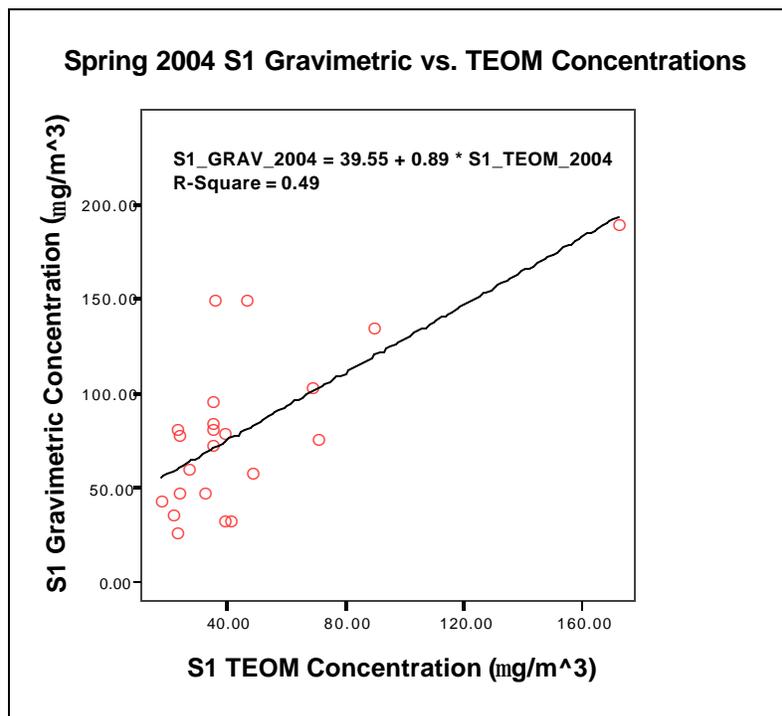


Figure 4. Plot of gravimetric sampler concentrations versus TEOM sampler concentrations for the S1 location (see figure 2) during the spring of 2004.

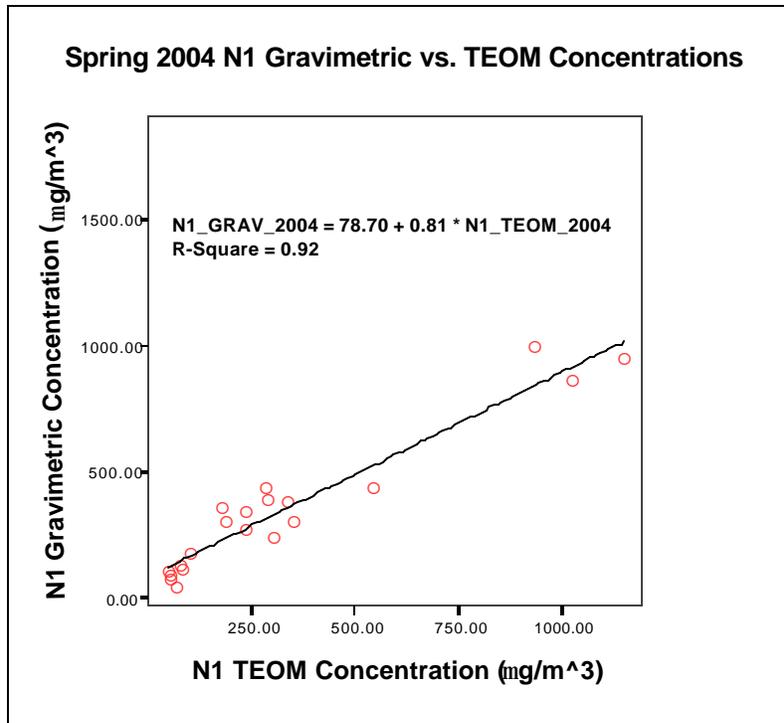


Figure 5. Plot of gravimetric sampler concentrations versus TEOM sampler concentrations for the N1 location (see figure 2) during the spring of 2004.

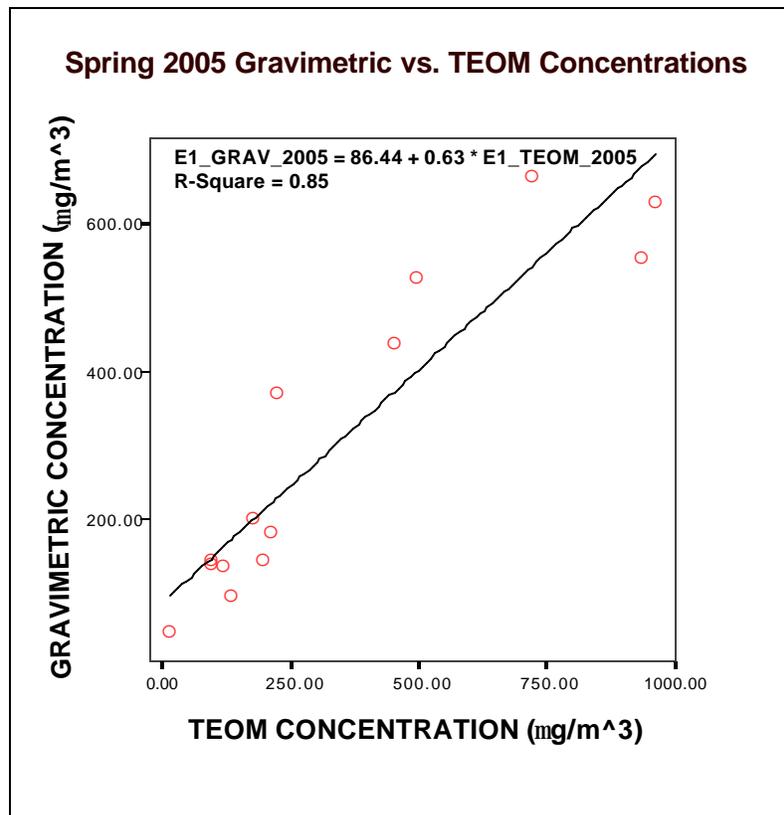


Figure 6. Plot of gravimetric sampler concentrations versus TEOM sampler concentrations for the E1 location (see figure 2) during the spring of 2005.

The results of the linear regression analysis relating gravimetric concentrations to TEOM concentrations for each of the datasets is shown in table 1. All of the data follow a linear pattern indicating the relationship between the gravimetric and TEOM sampler measured concentrations. However, the data from location S1 taken during the spring of 2004 is more scattered than the other datasets and as a result has a lower coefficient of determination (R^2) value than the other data.

Table 1. Linear regression analysis results of the gravimetric vs. TEOM concentration data taken during the summer of 2003, spring of 2004, and spring of 2005. For each case, the measured TEOM concentration is multiplied by the slope and added to the constant to determine the expected gravimetric concentration.

| Dataset | Location | R^2 | Regression Equation Coefficients | | Slope 95% Confidence Interval | | Slope P-Value |
|-------------|----------|-------|----------------------------------|-------|-------------------------------|-------------|---------------|
| | | | Constant | Slope | Lower Limit | Upper Limit | |
| Summer 2003 | N2 | 0.85 | 274.18 | 18.24 | 11.94 | 24.54 | 0.00 |
| Spring 2004 | S1 | 0.49 | 39.55 | 0.89 | 0.47 | 1.32 | 0.00 |
| | N1 | 0.92 | 78.70 | 0.81 | 0.70 | 0.93 | 0.00 |
| Spring 2005 | E1 | 0.85 | 86.44 | 0.63 | 0.47 | 0.80 | 0.00 |

The P-values given in table 1 test the null hypothesis that the corresponding slope is equal to zero, thus testing the predictive value of the regression model. In each case the null hypothesis is rejected because the P-values are not significant at the 0.05 level ($\alpha = 0.05$). This indicates that there is a linear relationship between the gravimetric and TEOM concentrations and that the model has predictive value. This same result can be determined by observing that zero is not contained within any of the confidence intervals given for the slopes.

The concentration data measured during the summer of 2003 present a much different relationship between the concentrations measured by the collocated TEOM and low volume TSP samplers from the other datasets. The reason for this difference is unknown. High concentrations downwind of the feedyard were measured by the gravimetric TSP samplers due to hot and dry conditions. In order to determine if there is a relationship between the measurement error associated with the TEOM samplers and the magnitude of the TSP concentration (as measured by the low volume TSP samplers), linear regression analyses were performed. In this case, the measurement error was determined as a percentage of the gravimetric TSP concentration as shown by equation 11.

$$E_M = \frac{C_G - C_T}{C_G} \quad (11)$$

where:

E_M = measurement error of the TEOM sampler,

C_G = concentration measured by the gravimetric low volume TSP sampler, and

C_T = concentration measured by the TEOM sampler.

The regression analyses yielded no linear relationship between the measurement error of the TEOM samplers and the gravimetric TSP concentrations. Table 2 shows the results of these analyses.

Table 2. Linear regression analysis results relating the measurement error of the TEOM samplers to the measured low volume TSP sampler concentration. In each case the low volume TSP sampler concentration is multiplied by the slope and added to the constant to determine the expected measurement error.

| Dataset | Location | R ² | Regression Equation Coefficients | | Slope 95% Confidence Interval | | Slope P-Value |
|-------------|----------|----------------|----------------------------------|----------|-------------------------------|-------------|---------------|
| | | | Constant | Slope | Lower Limit | Upper Limit | |
| Summer 2003 | N2 | 0.31 | 0.95 | 1.7E-06 | -9.6E-08 | 3.5E-06 | 0.06 |
| Spring 2004 | S1 | 0.09 | 0.24 | 2.0E-03 | -1.0E-03 | 0.0E+00 | 0.18 |
| | N1 | 0.06 | 0.21 | -2.8E-04 | -8.5E-04 | 0.0E+00 | 0.32 |
| Spring 2005 | E1 | 0.20 | 0.22 | -7.9E-04 | -1.8E-03 | 0.0E+00 | 0.11 |

The slope 95% confidence intervals and the P-values for the test for predictive value indicate that there is no linear relationship between the measurement error of the TEOM samplers and the low volume TSP sampler concentrations for any of the datasets. In general, the measurement error of the TEOM samplers did not change as a function of measured TSP concentration.

Linear regression analyses were performed on the data from the N1 sampling location (spring 2004) and the E1 sampling location (spring 2005) relating MMD and measurement error as well as GSD and measurement error. PSD data were not available from the other datasets. A significant correlation at the 0.05 level was found between the measurement error of the TEOM sampler and the MMDs of the gravimetric TSP samples from the N1 location during the spring of 2004 ($r = 0.706$). Similarly, significant correlations ($\alpha = 0.05$) were found between the TEOM measurement error and the MMD and GSD of the TSP samples from the E1 location of the data collected during the spring of 2005 ($r = 0.606$ and 0.707 respectively). Linear regression analyses were performed on the data showing significant correlations. The results of these analyses are shown in tables 3 and 4.

Table 3. Linear regression results relating the measurement error of the TEOM sampler to the MMD of the collocated gravimetric TSP sampler from the spring of 2004 and 2005. The independent variable in each case is the MMD of the gravimetric sample with the measurement error of the TEOM being the dependent variable.

| Dataset | Location | R ² | Regression Equation Coefficients | | Slope 95% Confidence Interval | | Slope P-Value |
|-------------|----------|----------------|----------------------------------|-------|-------------------------------|-------------|---------------|
| | | | Constant | Slope | Lower Limit | Upper Limit | |
| Spring 2004 | N1 | 0.50 | -0.974 | 0.053 | 0.016 | 0.091 | 0.01 |
| Spring 2005 | E1 | 0.367 | -1.122 | 0.093 | 0.007 | 0.180 | 0.037 |

Table 4. Linear regression results relating the measurement error of the TEOM sampler to the GSD of the collocated gravimetric TSP sampler from the spring of 2004 and 2005. The independent variable in each case is the GSD of the gravimetric sample. The dependent

variable is the TEOM sampler measurement error. The P-value of the N1 location is not significant indicating that there is no linear relationship.

| Dataset | Location | R ² | Regression Equation Coefficients | | Slope 95% Confidence Interval | | Slope P-Value |
|-------------|----------|----------------|----------------------------------|-------|-------------------------------|-------------|---------------|
| | | | Constant | Slope | Lower Limit | Upper Limit | |
| Spring 2004 | N1 | 0.02 | -0.333 | 0.210 | -0.946 | 1.366 | 0.694* |
| Spring 2005 | E1 | 0.50 | -1.838 | 0.792 | 0.234 | 1.349 | 0.01 |

The positive correlation coefficient and significant slope P-value from the data collected during the spring of 2005 indicate a positive linear relationship between the TEOM measurement error and the GSD of the collocated gravimetric TSP sample. However, the GSD data from the spring of 2004 did not yield a significant correlation. It is likely that increasing the number of data points may help to strengthen the significance of this correlation.

Both the positive correlation coefficient and the significant slope coefficient values from the regression analyses relating the measurement error of the TEOM sampler to the MMD of the gravimetric sampler indicate a positive linear relationship between the two variables.

An analysis of variance procedure to test the null hypothesis that the MMDs measured by the N1 and E1 locations were equal yielded a P-value of 0.228. It was concluded that the MMDs from the two locations were not different and that the two datasets could be combined to further analyze the relationship between the measurement error of the TEOM sampler and the MMD of corresponding gravimetric TSP sample. The results of the linear regression performed on the combined datasets is shown in figure 5.

Table 5. Linear regression results from the combined 2004 and 2005 datasets comparing TEOM measurement error to the MMD of the collocated gravimetric TSP sampler. The dependent variable is the TEOM measurement error and the independent variable is the MMD of the gravimetric TSP sampler.

| Dataset | R ² | Regression Equation Coefficients | | Slope 95% Confidence Interval | | Slope P-Value |
|--|----------------|----------------------------------|-------|-------------------------------|-------------|---------------|
| | | Constant | Slope | Lower Limit | Upper Limit | |
| Combined Data From 2004 (N1) and 2005 (E1) | 0.46 | -1.039 | 0.056 | 0.030 | 0.083 | 0.000 |

Combining the two datasets results in a lower slope P-value indicating a stronger linear relationship between the two variables. In general, as the MMD of the gravimetric TSP sample increases, so does the measurement error of the TEOM sampler.

Summary and Conclusions

The major findings of the work presented in this manuscript are:

- There is a significant positive linear correlation between TSP concentrations measured by collocated TEOM and gravimetric samplers. In general the TEOM sampler measured lower concentrations than the collocated gravimetric TSP sampler.
- The measurement error of the TEOM sampler did not show a significant correlation with the concentrations measured by the gravimetric TSP sampler.

- The measurement error of the TEOM has a positive correlation with the MMD and GSD of the collocated gravimetric TSP sampler.
- There is a stronger positive linear relationship between the measurement error of the TEOM sampler and the MMD of the collocated gravimetric TSP sampler than with the GSD.

It was expected that the relationship between TSP measurements made by collocated TEOM and gravimetric TSP samplers would follow a similar pattern to that seen by Vega et al. (2003). The results presented by Vega et al. (2003) indicated that the TEOM sampler would report higher concentrations of PM₁₀ than a collocated gravimetric PM₁₀ sampler. These samplers were sampling in an urban environment near Mexico City, Mexico. The EPA (1996) characterizes the particle size distribution typical of urban environments as having an MMD of approximately 6 μ m with a GSD of approximately 2.25.

The results presented here for TSP concentration sampling indicate that in general the TEOM sampler will measure lower concentrations than a collocated gravimetric TSP sampler. At first glance, these results seem to counter to the trends presented by Vega et al. (2003). However, the linear regression analyses relating the measurement error of the TEOM sampler and the MMD of the gravimetric TSP sampler indicate that for MMDs lower than 18.5 μ m, the measurement error of the TEOM sampler (as defined by equation 11) is negative. A negative measurement error indicates that the TEOM sampler is reporting larger concentrations than the gravimetric sampler. The converse is true for MMDs over 18.6 μ m.

Several factors could have lead to these results including:

- The operating characteristics of the TSP inlets allow a much broader range of particle diameters to enter the sample stream of the TEOM than PM₁₀ inlets. In general, this causes the percentage of smaller particles (particle diameter = 10 μ m) to be lower for a TSP sample than the percentage of smaller particles for a PM₁₀ sample. As a result, the isokinetic sampling point in the flow splitter of the TEOM may influence the sample flow such that more of the smaller diameter particles are pulled into the sample stream that is sent to the TEOM sensor unit. This possibility is indicated in the relationship between the TEOM measurement error and the MMD of the gravimetric TSP sampler. As the MMD increases, the measurement error of the TEOM moves from a negative value (indicating that the TEOM concentrations are higher than the gravimetric TSP sampler concentrations) to a positive value when the MMD is higher.
- The deposition of particles on the TEOM filter may influence the mass concentrations in some way. If the PM mass is deposited on the filter in a concentrated location, the physical parameters of the TEOM mass-spring system could be influenced such that the K_0 value changes. However, this is highly unlikely as the TEOM units have been repeatedly shown to have a linear decrease in oscillation frequency with increasing system mass.

These factors are not presented as definitive answers to explain the differences in the concentrations measured by the TEOM samplers compared to that of the gravimetric TSP sampler, but only perhaps as suggestions for future work in this area.

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