



United States Department of Agriculture
Research, Education and Economics
Agricultural Research Service

March 25, 2009

Dr. Holly Stallworth
Designated Federal Officer CASAC
Environmental Protection Agency
1200 Pennsylvania Ave.
Washington, DC 20460

Dr. Stallworth:

Thank you for the additional information on the April, 2009 CASAC meeting and scheduling me for public comment. To supplement my public comment, I will be handing out the following documents:

1. **Buser, M.D.** PM sampler errors! Why should regulatory and agricultural industries care? Presentation given at the 2006 Beltwide Cotton Conferences.
2. **Buser, M.D.**, Parnell Jr., C.B., Shaw, B.W. and Lacey, R.E. Particulate matter sampler errors due to the interaction of particle size and sampler performance characteristics: background and theory. *Trans. ASABE*. 50(1): 221-228. 2007.
3. **Buser, M.D.**, Parnell Jr., C.B., Shaw, B.W. and Lacey, R.E. Particulate matter sampler errors due to the interaction of particle size and sampler performance characteristics: ambient PM10 samplers. *Trans. ASABE*. 50(1): 229-240. 2007.
4. **Buser, M.D.**, Parnell Jr., C.B., Shaw, B.W. and Lacey, R.E. Particulate matter sampler errors due to the interaction of particle size and sampler performance characteristics: ambient PM2.5 samplers. *Trans. ASABE*. 50(1): 241-254. 2007.
5. **Buser, M.D.**, Wanjura, J.D., Whitelock, D.P., Capareda, S.C., Shaw, B.W., and Lacey, R.E. Estimating FRM PM10 sampler performance characteristics using particle size analysis and collocated TSP and PM10 samplers: cotton gins. *Trans. ASABE*. 51(2): 695-702. 2008.
6. **Buser, M.D.** and Whitelock, D.P. Preliminary field evaluation of EPA Method CTM-039 (PM2.5 stack sampling method). *Proc. World Cotton Conference*. 2007.

Please feel free to post the documents on the CASAC web site.

Sincerely,

Michael Buser

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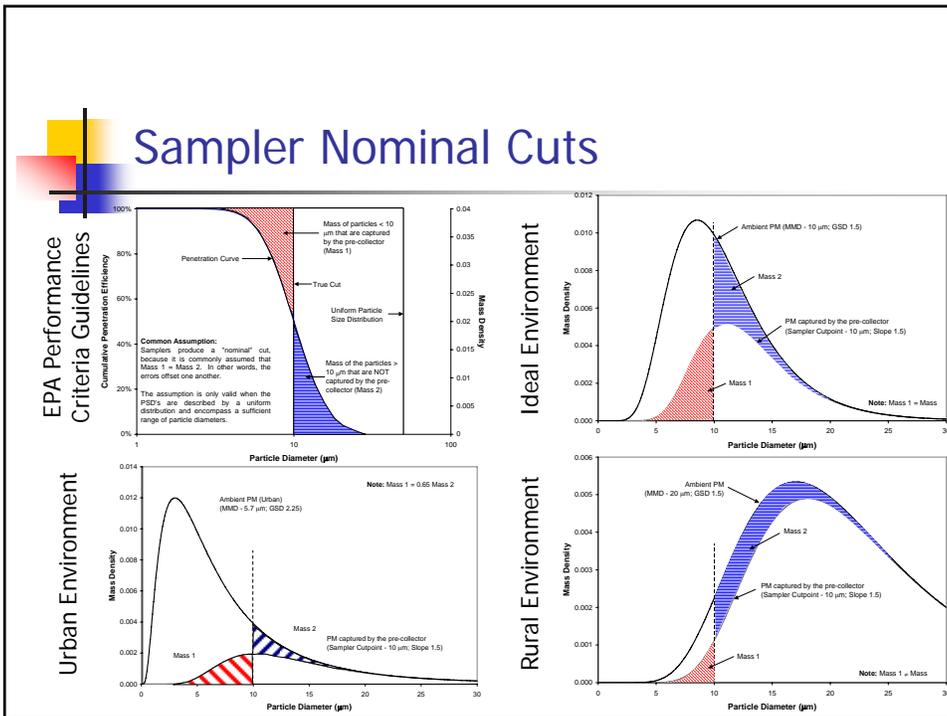
PM Sampler Errors! Why should Regulatory and Agricultural Industries Care?



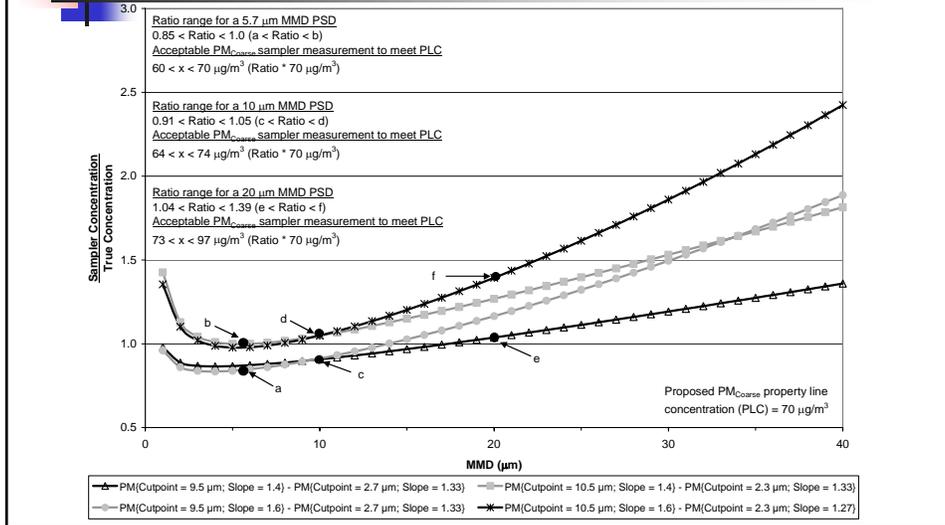
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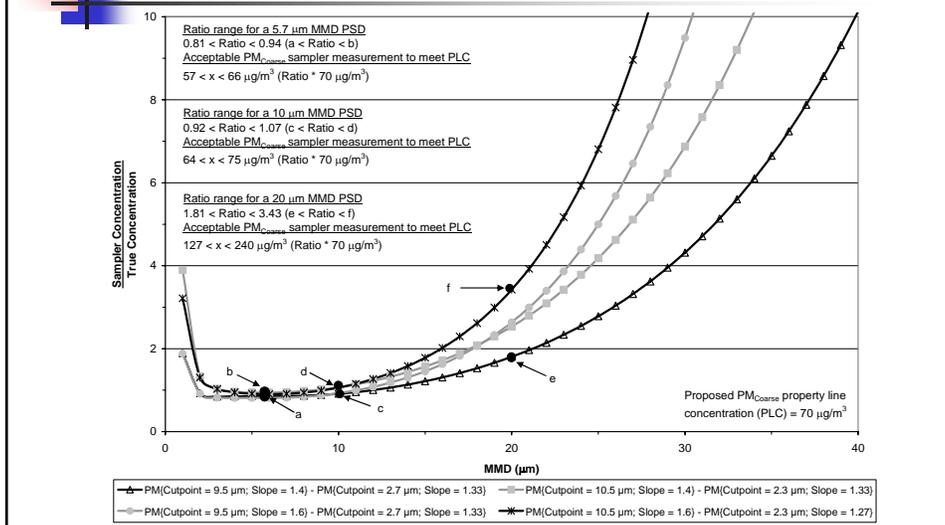
2006 Beltwide Cotton Conferences



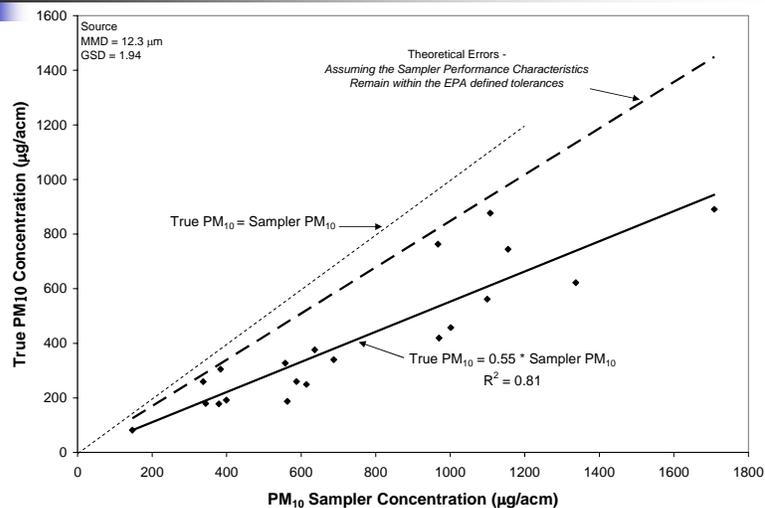
Theoretical PM_{coarse} to True PM_{coarse} (PSD – GSD = 2.0)



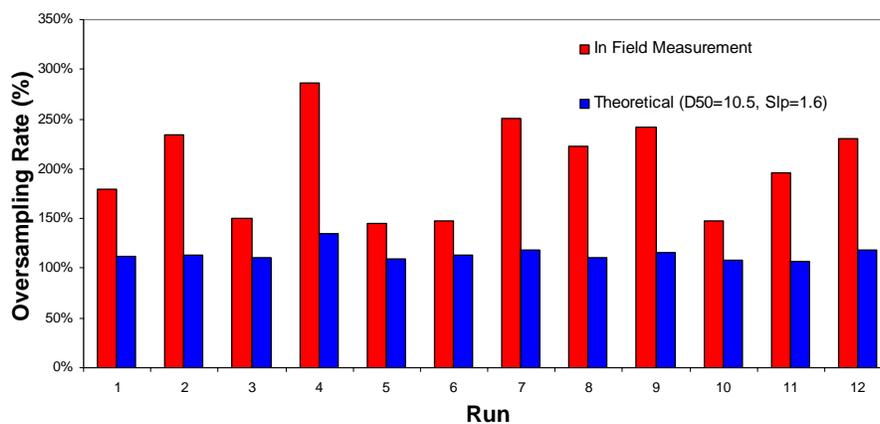
Theoretical PM_{coarse} to True PM_{coarse} (PSD – GSD = 1.5)



2004 Study of Co-Located PM₁₀ and TSP samplers



How the Theoretical Compares to the Real World!

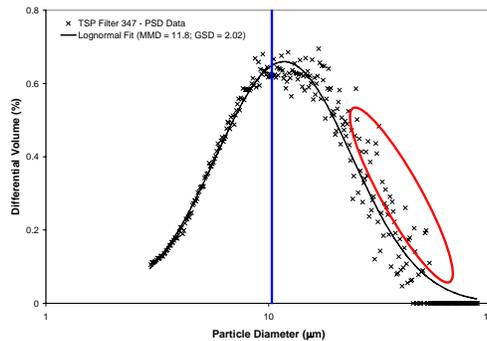


So What!

| | Concentration ($\mu\text{g}/\text{m}^3$) | MMD (μm) | GSD |
|------------------|--|-----------------------|-----|
| TSP | 1,207 | 13.4 | 2 |
| PM ₁₀ | 812 | 11.3 | 1.8 |

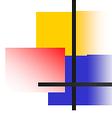
Bottom Line!

- Cutpoint = 24.1 μm
{compared to 10 μm }
- Slope = 2.9
{compared to 1.5}



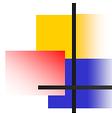
Scenario #1 Part A

- PM₁₀ & PM_{2.5} ambient air sampler are used in a PM_{coarse} (difference method) health effects study {will be considered in developing upcoming PM_{coarse} regulations}
 - PM₁₀ Cutpoint = 9.5 μm and a slope of 1.6
 - PM_{2.5} Cutpoint = 2.7 μm and a slope of 1.33
 - Samplers are placed in an urban environment
 - The samplers are exposed to a dust with a PSD characterized by a MMD of 5.7 μm and a 1.8
 - Let's say the study showed that a new standard should be set at 70 $\mu\text{g}/\text{m}^3$
 - So how do the sampling errors affect the basis for the new standard?



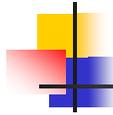
Scenario #1 Part A

- Measured PM_{coarse} concentration
 - 70 $\mu\text{g}/\text{m}^3$
- Under-sampling rate
 - 83%
- True PM_{coarse} concentration
 - 84 $\mu\text{g}/\text{m}^3$
- This means that the new standard would be 14 $\mu\text{g}/\text{m}^3$ lower than the levels causing any health effects (*as defined in this hypothetical study*).
 - The study's PM_{coarse} concentrations would be 17% lower than the levels causing the suggested health effects



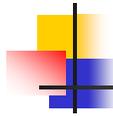
Scenario #1 Part B

- Let's say a new PM_{coarse} standard is passed (70 $\mu\text{g}/\text{m}^3$) and a state air pollution regulatory agency requires that a urban source's (say power plant) PM_{coarse} emissions be monitored.
 - Samplers with the same performance characteristics as Part A are used.
 - The samplers are exposed to a dust with a PSD characterized by a MMD of 5.7 μm and a 1.8
 - Based on the sampler measurements, the PM_{coarse} concentration was determined to be 69 $\mu\text{g}/\text{m}^3$ (*in compliance with the current hypothetical standard*).
 - How do the sampler errors affect the sources measurement concentrations?



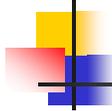
Scenario #1 Part B

- Measured PM_{coarse} concentration
 - $69 \mu\text{g}/\text{m}^3$
- Under-sampling rate
 - 83%
- True PM_{coarse} concentration
 - $83 \mu\text{g}/\text{m}^3$
- This means that this new standard, using EPA approved samplers, allows the urban source to emit $13 \mu\text{g}/\text{m}^3$ more true PM_{coarse} than the standard allows.
 - The regulatory agency is not accounting for 17% of the PM_{coarse} being emitted by the source.



Scenario #1 Part C

- Let's say a state air pollution regulatory agency requires an agricultural source's (say a cotton gin) PM_{coarse} emissions be monitored.
 - Samplers with the same performance characteristics as Part A are used, except that the PM_{10} sampler's cutpoint shifts to $10.5 \mu\text{m}$.
 - The samplers are exposed to a dust with a PSD characterized by a MMD of $20 \mu\text{m}$ and a 1.8
 - Based on the sampler measurements, the PM_{coarse} concentration was determined to be $71 \mu\text{g}/\text{m}^3$.
 - How do the sampler errors affect the sources measurement concentrations?



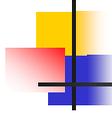
Scenario #1 Part C

- Measured $\text{PM}_{\text{coarse}}$ concentration
 - $71 \mu\text{g}/\text{m}^3$
- Over-sampling rate
 - 164%
- True $\text{PM}_{\text{coarse}}$ concentration
 - $43 \mu\text{g}/\text{m}^3$
- This means that if the cotton gin emits more than $43 \mu\text{g}/\text{m}^3$ of true $\text{PM}_{\text{coarse}}$ then it will not be able to comply with this $\text{PM}_{\text{coarse}}$ standard.
 - Regulating the $\text{PM}_{\text{coarse}}$ standard in this manner, applied under the scenario conditions, results in the power plant being able to emit 93% more $\text{PM}_{\text{coarse}}$ than the cotton gin is allowed to emit.



Scenario #1 Summary

- $\text{PM}_{\text{coarse}}$ concentrations from urban sources are most likely under-estimated.
- $\text{PM}_{\text{coarse}}$ concentrations from agricultural sources are most likely over-estimated.
- By not implementing this standard in terms of true $\text{PM}_{\text{coarse}}$, agricultural operations would be forced to comply with a standard that is twice as stringent as that for a urban source.



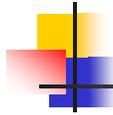
Scenario #2

- Let's say we keep everything the same as defined in Scenario #1, except that the sampler performance characteristics for the PM₁₀ sampler used in the agricultural source testing. Let's say these characteristics have shifted beyond the EPA defined regions (like the 2004 study).
 - Cutpoint = 24.1 μm
 - Slope = 2.9
- How do the sampler errors impact the way the power plant and the cotton gin are regulated?



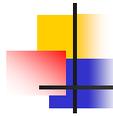
Scenario #2

- Power Plant
 - Measured PM_{coarse} concentration
 - 69 $\mu\text{g}/\text{m}^3$
 - Under-sampling rate
 - 83%
 - True PM_{coarse} concentration
 - 83 $\mu\text{g}/\text{m}^3$
- Cotton Gin
 - Measured PM_{coarse} concentration
 - 71 $\mu\text{g}/\text{m}^3$
 - Over-sampling rate
 - 470%
 - True PM_{coarse} concentration
 - 15 $\mu\text{g}/\text{m}^3$



Scenario Conclusions

- How did the sampler errors affect the development of the PM_{coarse} standard?
 - The study's PM_{coarse} concentrations would be 17% lower than the levels causing the suggested health effects.
 - The standard was set at $70 \mu g/m^3$ instead of $84 \mu g/m^3$.
- How did the sampler errors affect the way a urban source (power plant) is regulated?
 - The regulatory agency is not accounting for 17% of the PM_{coarse} being emitted by the source.
- How did the sampler errors affect the way a agricultural source (cotton gin) is regulated in comparison with the power plant, assuming the samplers worked as defined by EPA?
 - The power plant was allowed to emit 93% more PM_{coarse} than the cotton gin.
- How did the sampler errors affect the way a agricultural source (cotton gin) was regulated in comparison with the power plant, using the sampler performance characteristic shifts found in a real world study?
 - The power plant was allowed to emit 450% more PM_{coarse} than the cotton gin.



Why should Regulatory and Agricultural Industries Care about Sampler Errors?

- 1) Creating standards based on data containing sampler errors
 - a) Creates a huge demand for resources (time, money, and other resources) with no direct benefit or reduction of health effect risks.
- 2) By not accounting for the sampler errors in regulation of PM_{coarse} , regulatory agencies will end up focusing on the truly smaller PM_{coarse} emitters as opposed to the larger emitters (the regulatory agencies should be looking to get the biggest bang from your buck).
- 3) If regulatory agencies do not account for these sampler errors, agricultural sources are going to have a tough time complying with EPA's proposed $PM_{2.5}$ and PM_{coarse} standards.

PARTICULATE MATTER SAMPLER ERRORS DUE TO THE INTERACTION OF PARTICLE SIZE AND SAMPLER PERFORMANCE CHARACTERISTICS: BACKGROUND AND THEORY

M. D. Buser, C. B. Parnell, Jr., B. W. Shaw, R. E. Lacey

ABSTRACT. *The National Ambient Air Quality Standards (NAAQS) for particulate matter (PM), in terms of PM_{10} and $PM_{2.5}$, are ambient air concentration limits set by the EPA that should not be exceeded. Further, state air pollution regulatory agencies (SAPRAs) utilize the NAAQS to regulate criteria pollutants emitted by industries by applying the NAAQS as a property-line concentration limit. The primary NAAQS are health-based standards; therefore, an exceedance implies that it is likely that there will be adverse health effects for the public. Prior to and since the inclusion of PM_{10} and $PM_{2.5}$ into the EPA's regulation guidelines, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulations, methods of determining PM_{10} and $PM_{2.5}$, etc. A common trend among many of these publications is the use of samplers to collect information on PM_{10} and $PM_{2.5}$. Often, the sampler data are assumed to be an accurate measure of PM_{10} and $PM_{2.5}$. The fact is that issues such as sampler uncertainties, environmental conditions, and characteristics of the material that the sampler is measuring must be incorporated for accurate sampler measurements. The purpose of this article is to provide the background and theory associated with particle size distribution (PSD) characteristics of the material in the air that is being sampled, sampler performance characteristics, the interaction between these two characteristics, and the effect of this interaction on the regulatory process. The results show that if the mass median diameter (MMD) of the PM to which the sampler is exposed is smaller than the cutpoint of the sampler, then under-sampling occurs. If the MMD of the PM is greater than the cutpoint of the sampler, then over-sampling occurs. The information presented in this article will be utilized in a series of articles dealing with the errors associated with particulate matter measurements.*

Keywords. *Air, Air pollution, Environmental impact, Legislation, Mathematical models, Particle size distribution, PM, PM_{10} , Pollution, Sampler performance, Samplers, Sampling.*

The Federal Clean Air Act (CAA) of 1960, and subsequent amendments, established national goals for air quality and incorporated the use of standards for the control of pollutants in the environment. The 1970 CAA amendments provided the authority to create the Environmental Protection Agency (EPA) and required the EPA to establish National Ambient Air Quality Standards (NAAQS) (USEPA, 1996). The NAAQS are composed of primary standards (based on protecting against adverse health effects of listed criteria pollutants among sensitive population groups) and secondary standards (based on pro-

tecting public welfare, e.g., impacts on vegetation, crops, ecosystems, visibility, climate, and man-made materials). In 1971, the EPA promulgated the primary and secondary NAAQS as the maximum concentrations of selected pollutants (criteria pollutants) that, if exceeded, would lead to unacceptable air quality (Federal Register, 1971). The NAAQS for particulate matter (PM) was established in 1971, and total suspended particulate (TSP) was defined as the criteria pollutant. The CAA amendments of 1977 required the EPA to review and revise the ambient air quality standards every five years to ensure that the standards met all criteria based on the latest scientific developments. In 1987, the EPA modified the PM standards by replacing TSP with a new criteria pollutant that accounted for particles with an aerodynamic equivalent diameter (AED) less than or equal to a nominal 10 μm (PM_{10}) (Federal Register, 1987). On 16 July 1997, the EPA promulgated additional NAAQS for PM. This update incorporated an additional criteria pollutant for the ambient air standards that would account for particles with an AED less than or equal to a nominal 2.5 μm ($PM_{2.5}$) (Federal Register, 1997).

Health risks posed by inhaled particles are influenced by both the penetration and deposition of particles in the various regions of the respiratory tract and the biological responses to these deposited materials. The largest particles are deposited predominantly in the extrathoracic (head) region, with somewhat smaller particles deposited in the tracheobronchial region. Still smaller particles can reach the deepest

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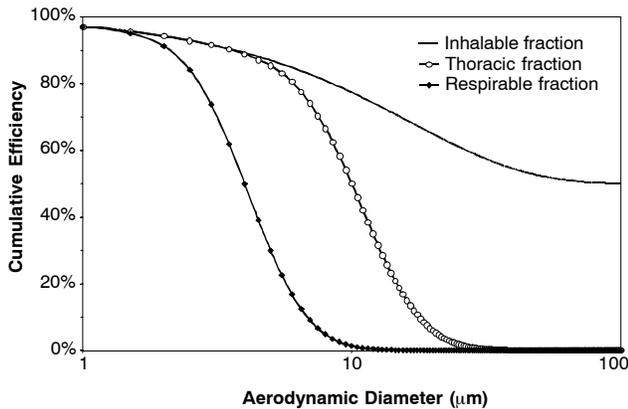


Figure 1. American Conference of Governmental Industrial Hygienists sampling criteria for inhalable, thoracic, and respirable fractions of PM (ACGIH, 1997).

portion of the lung, the pulmonary region. Risks of adverse health effects associated with the deposition of typical ambient fine and coarse particles in the thoracic region (tracheo-bronchial and pulmonary deposition) are much greater than those associated with deposition in the extrathoracic region. Further, extrathoracic deposition of typical ambient PM is sufficiently low, so particles depositing only in that region can safely be excluded from the indicator (USEPA, 1996). Figure 1 shows the ACGIH (1997) sampling criteria for the inhalable, thoracic, and respirable fractions of PM. Note that virtually no respirable PM (PM that can penetrate into the alveolar region of the human lung) is greater than 10 µm, whereas 50% of the 3.5 µm particles are considered respirable and can reach the alveolar region, as shown in figure 1.

In 1987, the EPA staff recommended that a PM₁₀ standard replace the TSP standard. Based on the literature, it was the EPA's intent for the PM₁₀ sampler to mimic the thoracic fraction of PM (Hinds, 1982). The original acceptable concentration range proposed by the EPA Administrator was 150 to 250 µg/m³ PM₁₀ 24-hour average, with no more than one expected exceedance per year (USEPA, 1996). The Administrator decided to set the final standard at the lower bound of the proposed range. The rationale behind this decision was that this standard would provide a substantial margin of safety below the levels at which there was a scientific consensus that PM caused premature mortality and aggravation of bronchitis, with a primary emphasis on children and the elderly.

In 1979, EPA scientists endorsed the need to measure fine and coarse particles separately (Miller et al. 1979). Fine particles are often associated with the respirable fraction of PM, with typical cutpoint values ranging from 3.5 to 5.0 µm for "healthy adults" (ISO, 1993). The EPA's emphasis on the 2.5 µm cutpoint was more closely associated with separating the fine and coarse atmospheric aerosol modes, rather than mimicking a respiratory deposition convention. Based on the availability of a dichotomous sampler with a separation size of 2.5 µm, the EPA recommended 2.5 µm as the cutpoint between fine and coarse particles (USEPA, 1996). Because of the wide use of this cutpoint, the PM_{2.5} fraction is frequently referred to as "fine" particles. It should be noted, however, that ISO (1993) defines a "high risk" respirable convention with a cutpoint of 2.4 µm, which is claimed to relate to the deposition of particles in the lungs of children and adults with certain lung diseases.

The NAAQS for PM₁₀ and PM_{2.5} are the ambient air concentration limits set by the EPA that should not be exceeded (USEPA 2001a). The regional or area consequences for multiple exceedances of the NAAQS are having an area designated as non-attainment, with a corresponding set of offset rules for any new or modified sources of PM in the area. Some state air pollution regulatory agencies (SAPRAs) are attempting to use the NAAQS as the property-line emission limit (standard). For example, if the property-line concentration is greater than the NAAQS, the facility is not in compliance. The current PM₁₀ primary 24-hour NAAQS is 150 micrograms per actual cubic meter (µg/acm). The secondary NAAQS for PM₁₀ is set at the same level as the respective primary NAAQS. The proposed PM_{2.5} primary 24-hour NAAQS is 65 µg/acm. The secondary NAAQS for PM_{2.5} is set at the same level as the primary NAAQS.

Prior to and since the inclusion of PM₁₀ and PM_{2.5} into the PM regulation, numerous journal articles and technical references have discussed epidemiological effects, trends, regulations, and methods of determining PM₁₀ and PM_{2.5}. A common trend among many of these publications is the use of size-selective samplers to collect information on PM₁₀ and PM_{2.5} concentrations. Size-selective sampler-based concentrations are commonly used in comparing PM₁₀ and PM_{2.5} emission concentrations from various sources. All too often, the sampler concentrations are assumed to be accurate measures of PM₁₀ and PM_{2.5}. However, issues such as airflow measurement uncertainties, weighing procedure uncertainties, sampler uncertainties, sampler biases, and environmental conditions used in reporting results (dry standard versus actual conditions) will impact the sampler concentration measurements and must be incorporated to obtain accurate PM₁₀ and PM_{2.5} concentrations.

The concentration obtained from a PM sampler is only an approximation or estimate of the true concentration and is complete only when accompanied by a quantitative statement of the measurements uncertainty (Taylor and Kuyatt, 1994). The difference between error and uncertainty is that a measured value can unknowingly be very close to the true value, resulting in a negligible error, even though the uncertainty associated with the measurement is relatively large. Accuracy is a qualitative term that corresponds to the degree of agreement between the measured concentration and the true concentration. Repeatability corresponds to the degree of agreement between the concentrations obtained from successive measurements carried out under the same conditions (e.g., same measurement procedure, same observer, same measuring instrument, same location, and repetition over a short period of time). Reproducibility corresponds to the degree of agreement between the concentrations obtained under changed measurement conditions (e.g., principle of measurement, method of measurement, observer, measuring instrument, reference standard, location, conditions of use, and time). Bias or systematic error corresponds to the mean that would result from an infinite number of measurements of the same concentration carried out under repeatability conditions minus the true value.

When air pollution compliance issues arise for a specific facility or operation, air pollution regulatory agencies generally conduct property-line sampling or dispersion modeling to determine if the facility or operation is in compliance with the corresponding regulations. Modeling

requires emission rates, which are determined either from the EPA list of emission factors (AP-42), from other published data, or from source sampling. Emission factors are industry specific and are generally based on source sampling studies; however, emission standards are part of a federal guidance and can be impacted by the political process. All property-line sampling for compliance purposes generally requires the use of EPA-approved samplers. Ideally, these samplers would produce an accurate measure of the pollutant indicator; for instance, a PM₁₀ sampler would produce an accurate measure of PM less than or equal to 10 μm AED (true PM₁₀). However, samplers are not perfect, and errors are introduced because of established tolerances for sampler performance characteristics, interaction of particle size and sampler performance characteristics, environmental conditions, and characteristics of the material that the sampler is measuring. The purpose of this series of articles is to illustrate the magnitude of the errors associated with current EPA-approved PM samplers and how these errors result in the unequal PM regulation between various industries at various physical locations.

PARTICLE SIZE DISTRIBUTIONS

The distribution of particles with respect to size is perhaps the most important physical parameter governing their behavior (Hinds, 1982). Aerosols containing only particles of a particular size are called mono-disperse, while those having a range or ranges of sizes are called poly-disperse. Hinds (1982) indicated that most aerosols in the ambient air are poly-disperse and that the lognormal distribution “is the most common distribution used for characterizing the particle sizes associated with the aerosol.” A lognormal distribution is a specific form of the size distribution function for which the population of particles follows a Gaussian distribution with respect to the natural log of the particle diameter, d_p . The significance of using a lognormal distribution is that the PSD can be described in terms of the mass median diameter (MMD) and the geometric standard deviation (GSD). The mathematical definition and manipulation of the lognormal distribution used herein was also described, in a similar fashion, by Hinds (1999) and Seinfeld and Pandis (1998). The lognormal mass density function is expressed as:

$$f(d_p, \text{MMD}, \text{GSD}) = \frac{1}{d_p \ln(\text{GSD}) \sqrt{2\pi}} \times \exp \left[-\frac{[\ln(d_p) - \ln(\text{MMD})]^2}{2[\ln(\text{GSD})]^2} \right] \quad (1)$$

for poly-disperse particles, where the GSD is greater than 1.0. For mono-disperse particles (i.e., GSD is equal to 1.0), the mass density function is equal to 1.0 when d_p is equal to the MMD and zero for all other d_p values. Mono-disperse particles are commonly used in evaluating samplers in a laboratory setting. During the PM sampler evaluation process, various mono-disperse particle sizes are commonly used. This range of particle sizes can be described as a uniform distribution assuming constant particle concentrations for each individual size. The uniform density function is expressed as:

$$f(d_p, n, R) = \begin{cases} \frac{1}{n} & \text{if } 0 < d_p < R \text{ and } n \geq 1 \\ 0 & \text{if } d_p \geq R \text{ and } d_p < 0 \end{cases} \quad (2)$$

where n is the number of mono-disperse particle sizes used, and R is the largest mono-disperse particle size.

For a lognormal distribution, the fraction of the total particles (df) having diameters between d_p and $d_p + dd_p$ is:

$$df = f(d_p, \text{MMD}, \text{GSD}) dd_p \quad (3)$$

where dd_p is a differential interval of particle size. The area under the density distribution curve is always:

$$\int_0^{\infty} f(d_p, \text{MMD}, \text{GSD}) dd_p = 1.0 \quad (4)$$

The area under the density function may be estimated for particle sizes ranging from zero to infinity, as in equation 4, between given sizes a and b , or it may be the small interval dd_p . The area under the density function curve between two sizes a and b equals the fraction of particles whose diameters fall within this interval, which can be expressed continuously as:

$$f_{ab}(a, b, \text{MMD}, \text{GSD}) = \int_a^b f(d_p, \text{MMD}, \text{GSD}) dd_p \quad (5)$$

Size distributions can also be presented as a cumulative distribution function, $F(a, \text{MMD}, \text{GSD})$, defined as:

$$F(a, \text{MMD}, \text{GSD}) = \int_0^a f(d_p, \text{MMD}, \text{GSD}) dd_p \quad (6)$$

where $F(a, \text{MMD}, \text{GSD})$ is the fraction of the particles having diameters less than a . The fraction of particles having diameters between sizes a and b , $f_{ab}(a, b, \text{MMD}, \text{GSD})$, can be determined directly by subtracting the cumulative fraction for size a from that for size b , as shown in equation 7:

$$f_{ab}(a, b, \text{MMD}, \text{GSD}) = F(b, \text{MMD}, \text{GSD}) - F(a, \text{MMD}, \text{GSD}) \quad (7)$$

The concentration of particles having diameters between sizes a and b , $C_{ab}(a, b, \text{MMD}, \text{GSD})$, can be expressed as:

$$C_{ab}(a, b, \text{MMD}, \text{GSD}) = C_T [F(b, \text{MMD}, \text{GSD}) - F(a, \text{MMD}, \text{GSD})] \quad (8)$$

where C_T is the total concentration of PM.

For a lognormal distribution, the mode < median < mean. Three important characteristics of lognormal distributions are: (1) the mode shifts significantly to the left as the GSD increases, (2) the median is not affected by the increase in GSD, and (3) the larger the GSD, the more closely the lognormal distribution is to a uniform distribution.

SAMPLER PERFORMANCE CHARACTERISTICS

A sampler's performance is generally described by either a cumulative collection or penetration efficiency curve. The

“sharpness of cut” of the sampler pre-separator or the “sharpness of slope” of the sampler penetration efficiency curve significantly impacts the accuracy of sampler measurements. Three terms are often used to describe the sharpness of the penetration curve and are frequently and inappropriately interchanged. These terms are ideal, true, and sampler. An ideal penetration curve corresponds to data provided in 40 CFR Part 53 (CFR, 2001). A true penetration curve can be described as a step function. In other words, all particles less than or equal to the size of interest are captured on the filter, and all particles greater than the particle size of interest are captured by the pre-separator. A sampler penetration curve refers to the actual penetration curve associated with a particular sampler.

A sampler penetration curve is defined by performance characteristics and based on these characteristics; a portion of PM less than the size of interest will not be collected on the filter (i.e., captured by the pre-separator), and a portion of the PM greater than the size of interest will be collected on the filter (i.e., should have been captured by the pre-separator). A common perception is that PM₁₀ and PM_{2.5} sampler-measured concentrations are true concentrations and that these concentrations relate to PM with particle sizes less than 10 and 2.5 μm, respectively; however, these measurement concentrations are actually based on the sampler performance characteristics.

A sampler’s pre-separator collection efficiency curve is most commonly represented by a cumulative lognormal distribution and characterized by a d_{50} (also referred to as cutpoint) and a slope. By definition, cutpoint is the particle size where 50% of the PM is captured by the pre-separator and 50% of the PM penetrates to the filter. Slope is defined as the ratio of particle sizes corresponding to cumulative collection efficiencies of 84.1% and 50% ($d_{84.1}/d_{50}$), 50% and 15.9% ($d_{50}/d_{15.9}$), or the square root of 84.1% and 15.9% ($\sqrt{d_{84.1}}/\sqrt{d_{15.9}}$) (Hinds, 1982).

Collection efficiency curves are usually assumed as constant and independent of particle size. In other words, it is assumed that a significant loading of large particles does not affect the pre-separator’s collection efficiency for smaller particles. Therefore, concentration data used to generate a sampler’s pre-separator collection efficiency curve is typically determined by conducting an array of tests over several mono-disperse particle sizes using known concentrations. The concentration data from each test is used to determine the collection efficiency (ϵ_m) associated with each particle size, using equation 9:

$$\epsilon_m = \frac{C_{pre-separator}}{C_{test}} \quad (9)$$

where $C_{pre-separator}$ is the concentration of particles captured by the pre-separator, and C_{test} is the concentration of particles used for the test. A smooth lognormal curve is fit to the calculated pre-separator collection efficiencies, and the sampler performance characteristics (d_{50} and slope) are determined from the fitted curve. The mathematical definition and manipulation of the lognormal collection efficiency curve used herein was also described, in a similar fashion, by Hinds (1999) and Seinfeld and Pandis (1998). The lognormal density distribution function for collection efficiency is defined as:

$$\epsilon_m(d_p, d_{50}, slope) = \frac{1}{d_p \ln(slope) \sqrt{2\pi}} \times \exp\left[\frac{-[\ln(d_p) - \ln(d_{50})]^2}{2[\ln(slope)]^2}\right] \quad (10)$$

Equation 10 applies to a sampler collection efficiency where the slope is greater than 1.0. An alternative equation is used to determine the true cut collection efficiency when the slope is equal to 1.0. Mathematical derivations for determining the cumulative distribution function for the collection efficiency can be achieved in the same manner as presented earlier in the “Particle Size Distribution” section.

The cumulative distribution function for the collection efficiency, $\psi(a, d_{50}, slope)$, is defined by:

$$\Psi_m(a, d_{50}, slope) = \int_0^a \epsilon_m(d_p, d_{50}, slope) dd_p \quad (11)$$

where $\psi(a, d_{50}, slope)$ gives the collection efficiency for particles having diameters less than a . The penetration efficiency, $P_m(a, d_{50}, slope)$, is defined as:

$$P_m(a, d_{50}, slope) = 1 - \Psi_m(a, d_{50}, slope) \quad (12)$$

Substituting equations 10 and 11 into equation 12 yields:

$$P_m(a, d_{50}, slope) = 1 - \int_0^a \left[\frac{1}{d_p \ln(slope) \sqrt{2\pi}} \times \exp\left(\frac{-[\ln(d_p) - \ln(d_{50})]^2}{2[\ln(slope)]^2}\right) \right] dd_p \quad (13)$$

where $P_m(a, d_{50}, slope)$ is the sampler penetration efficiency for particles having diameters less than a .

The true penetration curve is defined by a step function and defined as:

$$P_v(a, d_{50}, slope) = \begin{cases} 1 & \text{if } a \leq d_{50} \\ 0 & \text{if } a > d_{50} \end{cases} \quad (14)$$

In determining the errors associated with PM samplers, the most important question to ask is “What is the intent of the PM regulations?” It was previously established that the primary purpose of the regulations is to protect public health. It is quite clear in the literature that PM collected from a PM₁₀ sampler should mimic the fraction of PM that penetrates the thoracic region of the human respiratory system, which leads to the perception that the sampler must have a slope greater than 1 based on information presented in figure 1 (USEPA, 2001a). An assumption made in the PM₁₀ regulation is that it pertains to a measure of particles with an AED less than or equal to a nominal 10 μm. Unlike the published intent of the EPA in defining the performance criteria of the PM₁₀ sampler, the literature indicates that the EPA intended for the PM_{2.5} sampler to be a true measure of PM with a particle diameter less than or equal to 2.5 μm (USEPA, 1996). An assumption made in the PM_{2.5} regulation is that it pertains to a measure of particles with an AED less than or equal to a nominal 2.5 μm. The term “nominal” implies that the

measured PM described in the PM₁₀ or PM_{2.5} regulation does not account for all mass associated with particles less than or equal to 10 μm or 2.5 μm AED and does include some of the mass associated with particles larger than 10 μm or 2.5 μm AED.

The issue of nominal values leads to the primary focus of this series of articles and will be described and evaluated in general terms in this article. To evaluate the term nominal, the equations presented previously will need to be further expanded in order to calculate sampler and true concentrations.

METHODS AND PROCEDURES

ESTIMATING SAMPLER AND TRUE CUT CONCENTRATIONS

Sampler concentrations can be theoretically estimated using the PSD and sampler performance characteristics defined in equations 1 and 13, respectively, for particles described by a lognormal distribution. The method of determining sampler concentrations depends on whether the sampler uses a single-stage or multi-stage pre-separator. For instance, most PM₁₀ ambient air samplers are single stage; however, an EPA-approved PM_{2.5} ambient air sampler consists of a PM₁₀ pre-separator and a PM_{2.5} pre-separator. Some PM_{2.5} samplers do not include the PM₁₀ pre-separator. Sampler concentrations for single-stage samplers, $C_m(\text{MMD}, \text{GSD}, d_{50}, \text{slope})$, can be estimated by:

$$C_m(\text{MMD}, \text{GSD}, d_{50}, \text{slope}) = C_a \int_0^{\infty} f(d_p, \text{MMD}, \text{GSD}) P_m(d_p, d_{50}, \text{slope}) dd_p \quad (15)$$

Sampler concentrations for a two-stage sampler, $C_{m2}(\text{MMD}, \text{GSD}, d_{501}, \text{slope}_1, d_{502}, \text{slope}_2)$, can be estimated by:

$$C_{m2}(\text{MMD}, \text{GSD}, d_{501}, \text{slope}_1, d_{502}, \text{slope}_2) = C_a \int_0^{\infty} f(d_p, \text{MMD}, \text{GSD}) P_{m1}(d_p, d_{501}, \text{slope}_1) \times P_{m2}(d_p, d_{502}, \text{slope}_2) dd_p \quad (16)$$

where P_{m1} corresponds to the initial pre-separator, and P_{m2} corresponds to the secondary pre-separator.

For true concentrations, the cumulative penetration efficiency distribution function is assumed to be equal to 1 for all particle sizes less than or equal to the size of interest and zero for all other particle sizes. Therefore, the true concentration, $C_t(\text{MMD}, \text{GSD}, d_{50})$, can be estimated by:

$$C_t(\text{MMD}, \text{GSD}, d_{50}) = C_a \int_0^{d_{50}} f(d_p, \text{MMD}, \text{GSD}) dd_p \quad (17)$$

If the PSD is described by a uniform distribution, then equations 13, 16, and 17 will need to be further modified. For a uniformly distributed PSD, as described in equation 2, a single-stage sampler concentration, $C_m(n, R, d_{50}, \text{slope})$, can be estimated by:

$$C_m(n, R, d_{50}, \text{slope}) = C_a \int_0^{\infty} f(d_p, n, R) P_m(d_p, d_{50}, \text{slope}) dd_p \quad (18)$$

Likewise, a two-stage sampler concentration, $C_{m2}(n, R, d_{501}, \text{slope}_1, d_{502}, \text{slope}_2)$, can be estimated by:

$$C_{m2}(n, R, d_{501}, \text{slope}_1, d_{502}, \text{slope}_2) = C_a \int_0^{\infty} f(d_p, n, R) P_{m1}(d_p, d_{501}, \text{slope}_1) \times P_{m2}(d_p, d_{502}, \text{slope}_2) dd_p \quad (19)$$

For true concentrations, $C_t(n, R, d_{50})$, equation 17, is modified as follows using equation 2:

$$C_t(n, R, d_{50}) = C_a \int_0^{d_{50}} f(d_p, n, R) dd_p \quad (20)$$

In order to determine the generalized effects of the term “nominal” in the current PM regulations, equations 15, 17, 18, and 20 will be solved using generalized ambient PM₁₀ sampler performance characteristics and PSD characteristics. The EPA essentially defines the ambient PM₁₀ sampler performance characteristics in 40 CFR Part 53 in the discussion of tests required for a candidate sampler to receive EPA approval. The optimum d_{50} or cutpoint is explicitly stated in the regulations as 10 μm. No optimum slope value for the sampler is listed in 40 CFR Part 53 or in any other current EPA standard; however, penetration data are provided in 40 CFR Part 53. Hinds (1982) suggests that the optimum slope associated with the PM deposited in the thoracic region of the human respiratory system has an optimum slope of 1.5 and that this slope represents the optimum slope of the cumulative lognormal collection efficiency curve associated with the ambient PM₁₀ sampler.

Mathcad 2000 was used to evaluate equations 15, 17, 18, and 20 for various PSD and ambient PM₁₀ sampler performance characteristics previously defined in order to obtain a general concept of how the interaction of these characteristics impacts the current regulation of ambient PM₁₀. Four generalized PSDs will be used in solving equations 15, 17, 18, and 20. First, equations 18 and 20 will be solved using equation 2 and the particle diameters will range from 1 to 50 μm, representing a uniform PSD. Three generalized PSDs will be used in solving equations 15 and 17. The first PSD will be characterized by an MMD of 5.7 μm and a GSD of 2.25 (PSD characteristics of urban dust as defined by the EPA). The remaining two PSDs will be characterized by MMDs of 10 and 20 μm and a GSD of 1.5.

RESULTS AND DISCUSSION

The results of the evaluation of equations 15, 17, 18, and 20 for various PSD and ambient PM₁₀ sampler performance characteristics are illustrated in figures 2 through 5. Figure 2 illustrates the interaction associated with a uniformly distributed PSD and the optimum ambient PM₁₀ sampler performance characteristics. The two errors associated with the interaction are highlighted in the figure and labeled as

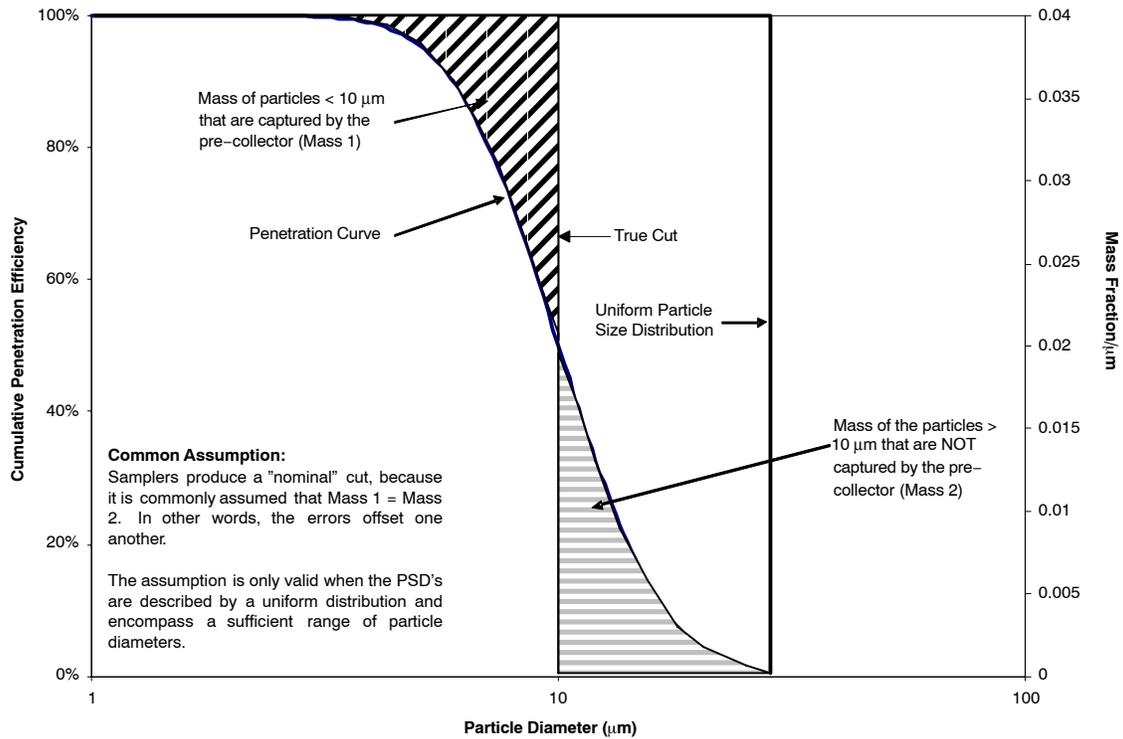


Figure 2. PM₁₀ sampler nominal cut for a uniform PSD.

mass 1 and mass 2. Mass 1 refers to an under-sampling error, while mass 2 corresponds to an over-sampling error. A common assumption made in the regulatory community to circumvent the problem associated with the two errors is that the mass of particles less than 10 μm and captured by the pre-separator (mass 1) is equal to the mass of particle greater than 10

μm and captured on the filter (mass 2). This assumption is valid when the density function of the PSD of the dust in the air being sampled is represented by a uniform distribution, i.e., mass 1 equals mass 2. When the under-sampling error is equal to the over-sampling error, the concentration measured by the sampler is equal to the true concentration.

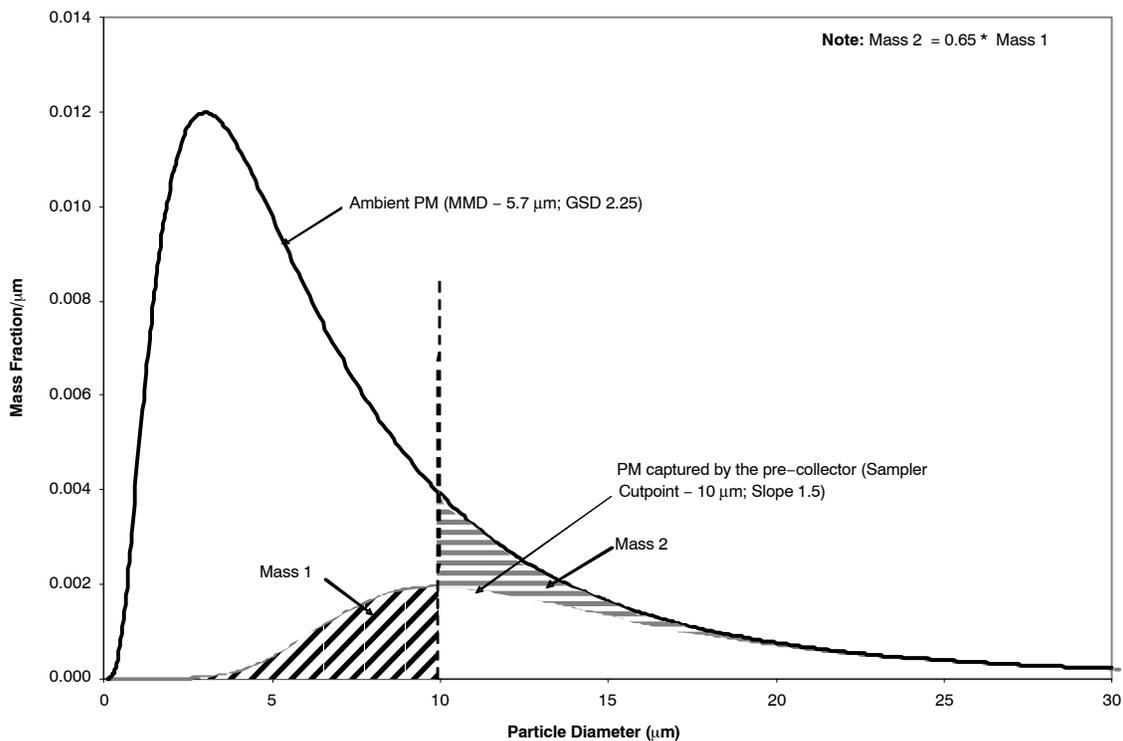


Figure 3. Sampler nominal cut for a lognormal PSD with an MMD = 5.7 μm and GSD = 2.25.

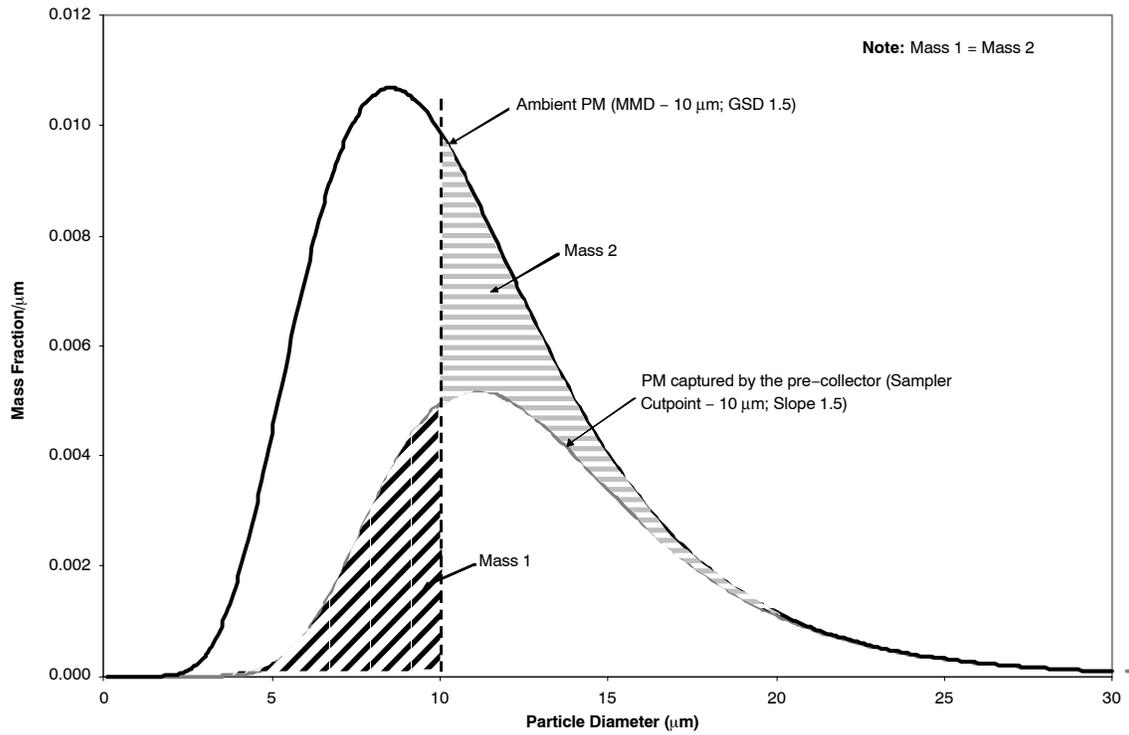


Figure 4. PM₁₀ sampler nominal cut for a lognormal PSD with an MMD = 10 µm and GSD = 1.5.

The outermost curve in figure 3 corresponds to a lognormal PSD with an MMD of 5.7 µm and a GSD of 2.25 (PSD characteristics associated with urban dust as defined by the EPA). The area below the innermost curve represents the mass of particles captured by the PM₁₀ pre-separator, and the area between the two curves represents the mass of particles that penetrated the pre-separator and were captured on the

filter. In this situation, mass 2, or the mass of particles associated with particle diameters greater than 10 µm that penetrate the pre-separator and are captured on the filter, is less than mass 1, or the mass of particles with diameters less than 10 µm that are captured by the pre-separator and are not captured on the filter. When mass 1 is greater than mass 2, the PM₁₀ sampler is under-estimating the PM₁₀ concentration.

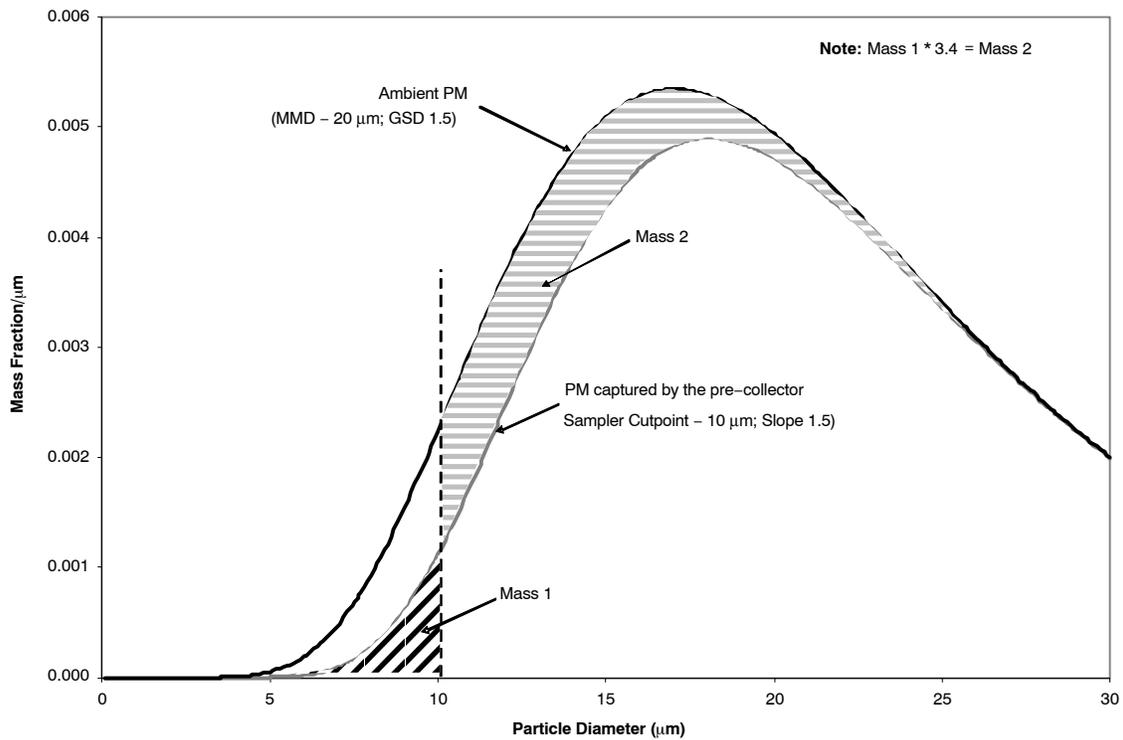


Figure 5. PM₁₀ sampler nominal cut for a lognormal PSD with an MMD = 20 µm and GSD = 1.5.

For an urban PSD, the over-sampling error is 0.65 times the under-sampling error.

Figure 4 is similar to figure 3, with the exception that the PSD characteristics are defined by an MMD of 10 μm and a GSD of 1.5. As in figure 3, the two errors associated with the interaction of the PSD and sampler performance characteristics are highlighted in figure 4 and labeled mass 1 and mass 2. In this situation where the MMD of the PSD is equal to the cutpoint of the pre-separator, mass 1 is equal to mass 2, the nominal assumption is valid, and the sampler concentration is equal to the true concentration.

Figure 5 is similar to figure 4, with the exception that the PSD characteristics are defined by an MMD of 20 μm and a GSD of 1.5. In this situation, mass 2, or the mass of particles associated with particle diameters greater than 10 μm that penetrate the pre-separator and are captured on the filter, is greater than mass 1, or the mass of particles with diameters less than 10 μm that are captured by the pre-separator and are not captured on the filter. For the given PSD characteristics, the concentration measured by this sampler is approximately 3.4 times the true PM_{10} concentration. When mass 2 is greater than mass 1, the PM_{10} sampler is over-estimating the PM_{10} concentration.

The over-sampling illustrated in figure 5 can significantly impact agricultural operations that typically generate dust with an MMD greater than 10 μm AED, forcing the operations to comply with more stringent regulations than urban-type sources that typically generate dust with an MMD less than 10 μm AED. For example, if the PM_{10} property-line sampler concentration measurements from two industries are exactly the same, and if 50% of industry A's total PM (characterized by an MMD of 10 μm and a GSD of 1.5) entering the sampler is less than 10 μm or true PM_{10} and 16% of industry B's PM (characterized by an MMD of 20 μm and a GSD of 2.0) entering the sampler is less than 10 μm , then, based on figure 1, 50% of industry A's PM can potentially reach the alveolar region of the lungs, as compared to 16% of industry B's PM. Therefore, under the current method of regulating PM_{10} , although both industries appear to be emitting the same levels of PM_{10} , in fact industry B is emitting 68%, i.e., $(50 - 16)/50$, less true PM_{10} than industry A.

SUMMARY AND CONCLUSIONS

Several errors are associated with the current air pollution rules and regulations established by the EPA, which should be minimized to ensure equal regulation of air pollutants between and within all industries. Potentially, one of the most significant errors is due to the interaction of the industry-specific PSD and sampler performance characteristics. Currently, the regulation of PM is based on sampler measurements and not true concentrations. The significance here is that sampler concentrations do not account for all the mass associated with the particle diameters less than the size of

interest, and further, sampler concentrations include a portion of the mass associated with particle diameters greater than the size of interest. The alternative to this method bases the regulations on a true concentration, which would account for all the mass associated with the particle diameters less than the size of interest and would not include mass associated with particle diameters greater than the size of interest.

Results of the analysis presented in this article show that not all industries are being equally regulated in terms of PM. This issue will be discussed in greater detail in the following articles of this series.

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PARTICULATE MATTER SAMPLER ERRORS DUE TO THE INTERACTION OF PARTICLE SIZE AND SAMPLER PERFORMANCE CHARACTERISTICS: AMBIENT PM₁₀ SAMPLERS

M. D. Buser, C. B. Parnell, Jr., B. W. Shaw, R. E. Lacey

ABSTRACT. *The National Ambient Air Quality Standards (NAAQS) for PM in terms of PM₁₀ are ambient air concentration limits set by the EPA that should not be exceeded. Further, some state air pollution regulatory agencies (SAPRAs) utilize the NAAQS to regulate criteria pollutants emitted by industries by applying the NAAQS as property-line concentration limits. Prior to and since the inclusion of the PM₁₀ standard, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulation, and methods of determining PM₁₀. A common trend among many of these publications is the use of samplers to collect information on PM₁₀. Often, the sampler data are assumed to be accurate measures of PM₁₀. The fact is that issues such as sampler uncertainties, environmental conditions, and the characteristics of the materials that the sampler is measuring must be incorporated for accurate sampler measurements. The focus of this article is on the errors associated with particle size distribution (PSD) characteristics of the material in the air that is being sampled, PM₁₀ sampler performance characteristics, the interaction between these two characteristics, and the effect of this interaction on the regulatory process. Theoretical simulations were conducted to determine the range of errors associated with this interaction for PM₁₀ ambient air samplers. Results from the PM₁₀ simulations indicated that a source emitting PM characterized by a mass median diameter (MMD) of 20 μm and a geometric standard deviation (GSD) of 1.5 could be forced to comply with a PM₁₀ standard that is 3.2 times more stringent than that required for a source emitting PM characterized by an MMD of 10 μm and a GSD of 1.5, and 3.6 times more stringent than that required for a source emitting PM characterized by an MMD of 5.7 μm and a GSD of 1.5. Therefore, in order to achieve equal regulation among differing industries, PM₁₀ and PM_{2.5} measurements must be based on true concentration measurements.*

Keywords. *Air, Air pollution, Environmental impact, Legislation, Mathematical models, Particle size distribution, PM, PM₁₀, pollution, Samplers, Sampling, Sampler performance, Sampler uncertainty.*

Particle measurements are needed to determine if a location is in compliance with air quality standards, to determine long-term trends in air quality patterns, and for epidemiological studies (USEPA, 2003). For these purposes, measurement accuracy is crucial. PM samplers, for the purposes of regulation, are classified as ambient or stack samplers. Ambient sampling refers to “the measurement of outdoor air pollutant levels, generally in attempts to characterize fairly broad area pollutant levels” (Wright, 1994). Quantifying pollutant emission rates can be accom-

plished by source sampling. According to Wright (1994), source sampling is the “measurement of gas flow rate, physical characteristics, composition, and pollutant concentration in exhaust gas streams leaving a process, factory, chimney, or ventilation system and entering the atmosphere.” No size-selective sampler is capable of passing 100% of the particles below a certain size and excluding 100% of the particles above that size (USEPA, 1999).

Not all countries categorize PM₁₀ samplers in the same manner. For instance, in the U.S., a PM₁₀ sampler is classified as having a penetration curve with a cutpoint of 10 μm , while other countries (e.g., Japan) classify a PM₁₀ sampler as rejecting (removing from the air stream) all particles greater than 10 μm (USEPA, 2003). A significant step in the standardization process of aerosol sampling was the EPA definition (USEPA, 1987) of the PM₁₀ size fraction, based on the AED of particles capable of penetrating to the thoracic region of the respiratory system. This definition was followed by the implementation of the EPA’s PM₁₀ Ambient Air Monitoring Reference and Equivalent Methods regulation (Federal Register, 1987). The Equivalent Method regulation format included the adoption of performance specifications for aerosol samplers based on controlled wind tunnel testing with mono-dispersed aerosols (USEPA, 1996).

PM₁₀ samplers are designated by the EPA as reference or equivalent methods under the provisions of 40 CFR Part 53 (CFR, 2001a). PM₁₀ reference methods must use the

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measurement principle and meet additional specifications set forth in 40 CFR Part 50, Appendix J (CFR, 2001c). Reference method PM₁₀ samplers must also meet the requirements specified in 40 CFR Part 53, Subpart D. Appendix J specifies a measurement principle based on extracting an air sample from the atmosphere with a sampler that incorporates inertial separation of the PM₁₀ size range particles followed by collection of the PM₁₀ particles on a filter over a 24-hour period. Alternatively, equivalent PM₁₀ methods are not required to conform to the measurement principle specified in Appendix J or meet the additional Appendix J requirements (USEPA, 1996). Instead, equivalent PM₁₀ methods must meet the performance specifications set forth in 40 CFR Part 53, Subpart D, and demonstrate comparability to a reference method as required by 40 CFR Part 53, Subpart C.

To determine the acceptability of the sampling effectiveness of the candidate sampler, the collection efficiency curve of the candidate sampler is compared to that of a specified "ideal" sampler. The model for this hypothetical "ideal" sampler, designed to mimic particle penetration to the thoracic region of the human respiratory tract, is based on Chan and Lippman's (1980) regression equation for extrathoracic deposition in the respiratory tract during mouth breathing. However, the "ideal" sampler's penetration curve is sharper than the thoracic penetration curve (ACGIH, 1994; ISO, 1993; CEN, 1993). According to the EPA (USEPA, 2003, 2001a), a PM₁₀ sampler with a penetration curve sharper than the thoracic curve has the advantage of reducing the problem of maintaining the finite collection efficiency specified by the thoracic curve for particles larger than 10 μm AED.

The procedures for testing the performance characteristics of candidate PM₁₀ ambient air samplers are described in 40 CFR Part 53, Subpart D. In the full wind tunnel test, the candidate sampler's collection efficiency is determined for several mono-disperse particle sizes (i.e., liquid particle target diameters of 3, 5, 7, 9, 10, 11, 13, 15, and 20 μm AED) at wind speeds of 2, 8, and 24 km/h (CFR, 2001a). A smoothed collection efficiency curve is generated using the individual collection efficiencies determined in the wind tunnel tests. The candidate sampler's collection efficiency curve, along with the idealized ambient particle size distribution, is then used to determine the expected mass concentration for the candidate sampler. The candidate sampler passes the liquid particle sampling effectiveness test if the expected mass concentration calculated for the candidate sampler, at each wind speed, differs by no more than $\pm 10\%$ from that predicted for the "ideal" sampler. The candidate method passes the 50% cutpoint test if the resulting cutpoint at each wind speed falls within $10 \pm 0.5 \mu\text{m}$. The candidate sampler must also pass other tests listed in 40 CFR Part 53, Subpart D; however, the full wind tunnel test is the primary test for evaluating the sampler collection efficiency curve. Additional information on conducting wind tunnel evaluations on PM₁₀ inlets was described by John and Wall (1983) and Ranade et al. (1990).

A number of samplers have been designated as PM₁₀ reference or equivalent method samplers (USEPA, 2001b). Mass concentration measurements with a reproducibility close to 10% have been obtained with collocated samplers of identical design (USEPA, 1996). However, field studies of collocated EPA-approved PM₁₀ samplers have shown substantial errors under certain conditions. These errors result

from: (1) allowing a tolerance of $\pm 0.5 \mu\text{m}$ for the 10 μm cutpoint; (2) cutpoint deviations, beyond the established tolerances, associated with various field application parameters; (3) inadequate restrictions on internal particle bounce; (4) surface overloading; (5) soiling of certain types of PM₁₀ inlets; and (6) losses of semivolatile components (USEPA, 1996). According to the EPA (USEPA, 1996), the most significant performance flaws have combined to produce excessive (up to 60%) mass concentration errors.

The ultimate goal of a PM sampler is to accurately measure the concentration of specific ranges of particle sizes that exist in the atmosphere. However, it is not currently possible to accurately characterize the material that exists as particles in the atmosphere because of difficulties in creating a reference standard for particles suspended in the atmosphere. No calibration standards for suspended particle mass exist. As a result, the EPA defines accuracy for PM measurements in terms of the agreement between a candidate sampler and a reference sampler under standardized conditions for sample collection, storage, and analysis (USEPA, 1996, 2001a). Therefore, sampler comparisons become very important in determining the reproducibility of sampler measurements (measurement precision, as defined by the EPA) and how sampler designs influences accuracy (USEPA, 2001a).

The NAAQS for PM, in terms of PM₁₀, are the concentration limits set by the EPA that should not be exceeded (CFR, 2001b). Further, some state air pollution regulatory agencies (SAPRAs) utilize the NAAQS to regulate criteria pollutants emitted by industries by applying the NAAQS as property-line concentration limits. The regional or area consequences for multiple exceedances of the NAAQS are having an area designated as non-attainment, with a corresponding reduction in the permit-allowable emission rates for all sources of PM in the area. The source-specific consequence of an exceedance of the NAAQS at the property line is the SAPRA denying an operating permit. The current PM₁₀ primary 24-hour NAAQS is 150 micrograms per actual cubic meter ($\mu\text{g}/\text{acm}$) (CFR, 2001b). The secondary NAAQS for PM₁₀ is set at the same levels as the primary NAAQS.

The evolution of the PM₁₀ regulation was briefly discussed by Buser et al. (2007). Prior to and since the inclusion of the PM₁₀ standard, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulation, and methods of determining PM₁₀. A common trend among many of these publications is the use of samplers to collect information on PM₁₀. The data collected from these samplers are commonly used in statistical correlations and statistical comparisons to draw conclusions about PM₁₀ emission concentrations. All too often, the sampler data are assumed to be accurate measures of PM₁₀. The fact is that issues such as sampler uncertainties, environmental conditions (dry standard versus actual conditions), and the characteristics of the material that the sampler is measuring must be incorporated for accurate sampler measurements.

The focus of this article is to determine the theoretical bias and uncertainty associated with the current ambient sampling methods used in regulating or estimating PM₁₀ emissions. The theoretical simulations will cover the effects of varying sampler performance characteristics, within EPA-defined guidelines, and the effects due to the interaction of the

sampler performance and particle size distribution characteristics.

LITERATURE REVIEW

Watson et al. (1983) affirmed that the EPA's PM₁₀ performance specifications allowed a cutpoint tolerance range that could allow inlets to be "fine tuned," suggesting that the cutpoint could be adjusted to the lower or upper end of the range to suit particular sampling needs. For example, a "reduction" in reported concentration could be achieved by simply using a lower (e.g., 9.5 µm) cutpoint inlet that is still within the acceptable cutpoint range. Errors between acceptable samplers have been apparent in the data from sampler comparison studies (e.g., Rodes et al., 1985; Purdue et al., 1986; Thanukos et al., 1992). Most of the reported errors between samplers were less than 10%, although some differences greater than 30% were reported. The collection efficiency of high-volume PM₁₀ sampler inlets based on cyclonic separation were consistently lower (Wedding, 1985), while those based on low-velocity impaction were consistently higher (McFarland, 1984).

Wang and John (1988) were critical of the EPA's PM₁₀ performance specification on allowable particle bounce (Federal Register, 1987), stating that the criteria can lead to a 30% overestimation of mass under worst-case conditions. In a related article, John et al. (1991) reported that although re-entrainment of particles deposited in a sampler inlet by airflow alone is typically negligible, re-entrainment caused from subsequent particle de-agglomeration caused by "bombardment" can be substantial. John and Wang (1991) suggested that particle loading on oiled deposition surfaces can affect particle collection and strongly suggested that periodic cleaning and re-oiling should be required for PM₁₀ inlets. Vanderpool et al. (2001) stated that "particle bounce at an impaction surface occurs when the collection surface is unable to completely absorb the kinetic energy of the incident particle." Vanderpool et al. (2001) further stated that "if this inelastic collision occurs, the particle is not retained by the surface and can bias the size distribution measurement towards smaller aerodynamic sizes." In addition, overloading can occur when the layers of previously collected particles adversely change the nature of the collection surface (Vanderpool et al., 2001).

Shifts in sampler cutpoints, attributed to soiling, have also been reported for cyclonic separators. Blachman and Lippmann (1974) reported that the performance of a 10 µm nylon cyclone was affected by loading, and the accumulation of particle deposits increased the collection efficiency (i.e., reduced the cutpoint). Tsai et al. (1999) determined that the penetration efficiency for a 10 µm cyclone was reduced from 97% to 71% for 3.06 µm diameter particles after a 0.4 mg loading.

Rodes et al. (1985) conducted a field comparison study and reported that the SA-321A PM₁₀ ambient air sampler collected an average of 0.3% less PM₁₀ and the WA-40CFM PM₁₀ ambient air sampler collected an average of 3.3 % more PM₁₀ than was present in the ambient air, as sampled by a wide-range aerosol classifier (WRAC). Rodes et al. (1985) stated that these estimates were more a measure of inlet performance "predictability" than measures of the error. Wedding (1985) stated that the WRAC system, as used in the

Rodes et al. (1985) field comparison study, was not satisfactory for obtaining particle size distributions. Rodes et al. (1985) also conducted wind tunnel studies and reported an average cutpoint of 6.6 µm AED for a dirty or used WA-40CFM sampler and an average cutpoint of 8.0 µm AED for a dirty or used SA-321A sampler.

Purdue et al. (1986) also compared the WA-40CFM and SA-321A samplers and reported variable concentration results between a new and used WA-40CFM sampler; similar results were reported for the SA-321A. The Andersen SA-321A PM₁₀ sampler was found to collect an average of 58% more mass than a collocated Wedding PM₁₀ sampler. This was partly attributed to the predicted error associated with cutpoint differences between the inlets. A more significant error (not predicted) was associated with degraded performances in opposite directions (Andersen over-sampling, Wedding under-sampling) because of soiling of the separators during extended sampling periods. Purdue et al. (1986) also observed variable results between the SA-321A and WA-40CFM samplers when both were tested at the same location. Purdue et al. (1986) did not measure the particle size distribution (PSD) of the dust being sampled, giving no indication of the samplers performance characteristics.

Sweitzer (1985) reported that there was a 15% variation between the SA-321A and WA-40CFM samplers, with the SA-321A sampler providing consistently higher values. Herber (1988) conducted a property-line sampling study at two stripper cotton gins in Texas using total suspended particulate (TSP) samplers and two PM₁₀ style samplers (WA-40CFM and SA1200 PM₁₀ inlets). Herber (1988) reported that the WA-40CFM sampler measured 62.4% of the actual PM₁₀ mass concentration and the SA-1200 sampler measured 1.1 times the actual PM₁₀ mass concentration.

Ranade et al. (1990) evaluated two high-volume PM₁₀ sampler inlets, the Sierra Andersen model 321A (SA-321A) and the Wedding IP10, using the EPA's sampler performance testing methods. Ranade et al. (1990) reported that SA-321A had a cutpoint of 10.5 µm and a slope of 1.4 (liquid particles) and a cutpoint of 11.1 µm and a slope of 1.46 (solid particles) at a wind speed of 8 km/h. The Wedding IP10 was reported to have a cutpoint of 9.5 µm and a slope of 1.32 (liquid particles) and a cutpoint of 9.6 µm and a slope of 1.35 (solid particles) at a wind speed of 8 km/h. Tests conducted at a wind speed at 2 km/h showed that the SA-321A sampler had a cutpoint of 10.7 µm and a slope of 1.42 (liquid particles) and a cutpoint of 10.6 µm and a slope of 1.49 (solid particles). The Wedding IP10 had a cutpoint of 9.6 µm and a slope of 1.27 (liquid particles) and a cutpoint of 9.65 µm and a slope of 1.33 (solid particles) at a wind speed of 2 km/h.

Ono et al. (2000) reported on a study using Partisol, TEOM, dichotomous, Wedding high-volume, and Graseby high-volume PM₁₀ samplers, which were collocated and operated at a location with high concentrations of coarse PM. Ono et al. (2000) reported that the TEOM and Partisol samplers agreed to within 6% on average; however, the dichotomous, Graseby, and Wedding samplers measured significantly lower PM₁₀ concentrations than the TEOM (on average 10%, 25%, and 35% lower, respectively). Ono et al. (2000) attributed these lower concentrations to a decrease in cutpoint caused by wind speeds and cleanliness of the inlet.

Wang et al. (2003) evaluated Graseby-Andersen FRM PM₁₀ samplers in a dust chamber where the samplers were

exposed to treatments of dispersed cornstarch, fly ash, and aluminum oxide. Wang et al. (2003) reported that the Graseby-Andersen FRM PM₁₀ sampler over-sampled the dispersed cornstarch, fly ash, and aluminum oxide by an average of 89%, 41%, and 14%, respectively. Wang et al. (2003) also reported that the average cutpoint and slope for the Graseby-Andersen sampler was 12.5 μm and 1.3 when sampling cornstarch, 17.7 μm and 1.5 when sampling fly ash, and 17 μm and 1.5 when sampling aluminum oxide. Wang et al. (2003) concluded that the Graseby-Andersen FRM PM₁₀ sampler's fractional efficiency curve shifted to the right when sampling dust with smaller mass median diameters (MMD).

METHODS AND PROCEDURES

The theoretical simulations were broken down into: (1) estimating particle size and sampler performance curves, (2) estimating sampler and true concentrations, and (3) determining the relative differences between the theoretical sampler and true concentrations.

ESTIMATING PARTICLE SIZE AND SAMPLER PERFORMANCE CURVES

Buser et al. (2007) provided background information on mathematically defining particle size distributions (PSDs) and sampler and true penetration curves. The equation for the lognormal mass density function most commonly used to describe dust particles in the ambient air or emitted from urban or agricultural operations, was defined as:

$$f(d_p, \text{MMD}, \text{GSD}) = \frac{1}{d_p \ln \text{GSD} \sqrt{2\pi}} \times \exp\left[\frac{-(\ln d_p - \ln \text{MMD})^2}{2(\ln \text{GSD})^2}\right] \quad (1)$$

where MMD, GSD, and d_p represent the mass median diameter, geometric standard deviation, and particle diameter of the distribution, respectively (Hinds, 1982). The cumulative sampler penetration efficiency was defined as:

$$P_m(d_{50}, \text{slope}) = 1 - \int_0^{\infty} \left[\frac{1}{d_p \ln(\text{slope}) \sqrt{2\pi}} \times \exp\left(\frac{-(\ln d_p - \ln d_{50})^2}{2[\ln(\text{slope})]^2}\right) \right] dd_p \quad (2)$$

where d_{50} represents the particle size where 50% of the particulate matter (PM) is captured by the pre-separator and 50% of the PM penetrates to the filter, and *slope* represents the slope of the cumulative penetration curve (Hinds, 1982). A more complete definition of slope is provided Buser et al. (2007). In addition, Buser et al. (2007) defined a true cumulative penetration curve or cut as a step function (slope = 1.0), which was defined as:

$$P_t(d_p, d_{50}) = \begin{cases} 1 & \text{if } d_p \leq d_{50} \\ 0 & \text{if } d_p > d_{50} \end{cases} \quad (3)$$

In order to solve equation 2, additional information is needed to define the d_{50} and slope associated with the PM₁₀ ambient air sampler. The EPA essentially defines the d_{50} and slope associated with the PM₁₀ ambient air sampler in 40 CFR Part 53 (CFR, 2001a) in the discussion of tests required for a candidate sampler to receive EPA approval. The d_{50} for the PM₁₀ sampler is explicitly stated in the EPA standards as 10.0 ± 0.5 μm AED. No slope values for the sampler are listed in 40 CFR Part 53 or in any other current EPA standard; however, penetration data are presented in 40 CFR Part 53. Ideally, the penetration data could be fit to a cumulative lognormal distribution to determine the characteristic d_{50} and slope for the PM₁₀ samplers; however, it was found that no single cumulative lognormal curve adequately represented the EPA data set in 40 CFR Part 53. It should be noted that this penetration data, along with EPA-defined interval mass concentrations and mass penetration tolerances, are used to determine if proposed samplers meet the EPA's PM₁₀ performance criteria.

Hinds (1982) suggested that the slope associated with PM deposited in the thoracic region of the human respiratory system was 1.5 ± 0.1 and that this slope represented the slope of the cumulative lognormal collection efficiency curve associated with the PM₁₀ ambient air sampler. The sampler performance characteristics for the PM₁₀ ambient air sampler as defined by Hinds (1982) (d_{50} of 10 ± 0.5 μm and slope of 1.5 ± 0.1) will be evaluated using the EPA criteria defined in 40 CFR Part 53 and will be the primary performance characteristics for ambient PM₁₀ sampler used throughout this article.

The performance characteristic ranges used to define the ambient PM₁₀ sampler performance characteristics in this research were divided into nine d_{50} and slope combinations: all combinations for d_{50} values of 9.5, 10.0, and 10.5 μm and slope values of 1.4, 1.5, and 1.6. These nine sampler performance criteria were evaluated using the EPA wind tunnel evaluation guidelines for ambient PM₁₀ samplers (CFR, 2001a). The procedure included: (1) the determination of penetration efficiency (referred to as "sampling effectiveness" by the EPA) for a specific set of sampler performance criteria for the particle sized defined by the EPA; (2) the penetration efficiency for each particle size was multiplied by the interval mass concentration defined by the EPA in order to determine an expected mass concentration; and (3) the expected mass concentration was summed for all particle sizes and compared to the ideal sampler expected mass concentration defined by the EPA. According to 40 CFR Part 53, a candidate sampler passes the sampling effectiveness test if the expected mass concentration calculated for the candidate sampler differs by no more than $\pm 10\%$ from that predicted for the ideal sampler (CFR, 2001b).

ESTIMATING SAMPLER AND TRUE CONCENTRATIONS

Sampler and true concentrations can be theoretically estimated using PSD and sampler performance characteristics defined in equations 1 through 3. According to Hinds (1982) and using equations 1 and 2, sampler concentrations, $C_m(\text{MMD}, \text{GSD}, d_{50}, \text{slope})$, can be estimated by:

$$C_m(\text{MMD}, \text{GSD}, d_{50}, \text{slope}) = C_a \int_0^{\infty} f(d_p, \text{MMD}, \text{GSD}) P_m(d_p, d_{50}, \text{slope}) dd_p \quad (4)$$

where C_m is the theoretical PM sampler concentration, and C_a is the ambient PM concentration.

For true concentrations, the cumulative penetration efficiency distribution function is assumed to be equal to 1 for all particle sizes less than or equal to the size of interest and zero for all other particle sizes, as defined in equation 3. Therefore, using equations 1 and 3, the true concentration, $C_t(\text{MMD, GSD, } d_{50})$, can be estimated by:

$$C_t(\text{MMD, GSD, } d_{50}) = C_a \int_0^{d_{50}} f(d_p, \text{MMD, GSD}) dd_p \quad (5)$$

RELATIVE DIFFERENCES BETWEEN SAMPLER AND TRUE CONCENTRATIONS

Sampler and true concentrations are not always equal. An estimate of the differences (E) between these two concentrations can be defined as:

$$E(x) = \frac{(\text{measured} - \text{true})}{\text{true}} = \left(\frac{\text{measured}}{\text{true}} \right) - 1 \quad (6)$$

where *measured* and *true* represent the estimated sampler and the true concentrations, respectively. For a sampler with a single pre-separator, substituting equations 4 and 5 into equation 6 and canceling like terms yields:

$$E(\text{MMD, GSD, } d_{50}, \text{slope}) + 1 = \frac{\int_0^{\infty} f(d_p, \text{MMD, GSD}) P_m(d_p, d_{50}, \text{slope}) dd_p}{\int_0^{d_{50}} f(d_p, \text{MMD, GSD}) dd_p} \quad (7)$$

Throughout the remaining sections of this article, $E(\text{MMD, GSD, } d_{50}, \text{slope}) + 1$ will be referred to as the ratio of the sampler concentration to true the concentration. Equation 7 will be solved for various PSD and sampler performance characteristics in order to estimate the errors associated with the interaction of these two characteristics.

Mathcad 2000 was used to solve equation 7 to determine the ratio and equation 6 to determine the estimated sampler concentration for various PSD and sampler performance characteristics in order to obtain an initial concept of how the interaction of these characteristics impacts the concentration ratio. The PSD characteristics included in the evaluation were MMDs of 5 and 10 μm with a GSD of 1.5, and MMDs of 15 and 20 μm with a GSD of 2.0. The sampler performance characteristics included the nine combinations of d_{50} and slope values for the ambient PM₁₀ sampler, as previously described.

In addition to ratios of sampler to true concentrations, sampler concentration estimates were made under the assumption that the current regulated limit is based on a sampler concentration and that the regulation should be based on a true concentration. In other words, the NAAQS are based on sampler concentrations; however, the NAAQS should be based on true concentrations so that all industries are equally regulated. The mathematical definition for this assumption is:

$$C_{\text{acceptable}} = \text{Ratio} * C_{\text{NAAQS}} \quad (8)$$

where C_{NAAQS} corresponds to the current concentrations associated with the NAAQS, and $C_{\text{acceptable}}$ corresponds to the acceptable concentrations if the NAAQS were based on true concentrations. In order to define the differences in the simulated sampler measurements and true PM₁₀ concentrations, equations 4 and 5 were solved using Mathcad for a d_{50} equal to 10.5 μm , slope of 1.6, GSD of 1.5, and MMDs ranging from 1 to 40 μm .

To further describe how the interaction of the PSD and sampler performance characteristics affect the acceptable PM concentrations, a series of calculations was performed in Mathcad 2000 to generate a data file containing the solutions to equation 7 over a range of parameters. These PSD parameters included MMD values ranging from 1 to 40 μm (in increments of 1 μm) and GSD values ranging from 1.3 to 2.5 (in increments of 0.1). The sampler performance characteristics were d_{50} values of 9.5 and 10.5 μm with slopes of 1.6 and 1.4. To illustrate the results of this simulation, several graphs were created to demonstrate how each of the parameters affects the sampler to true concentration ratio.

RESULTS AND DISCUSSION

According to the EPA (USEPA, 1996), the ideal ambient PM₁₀ sampler penetration curve should mimic the thoracic fraction of PM deposited in the human respiratory system. In figure 1, the EPA's ideal PM₁₀ ambient sampler penetration data (CFR, 2001a) are overlaid on the ACGIH (1994)

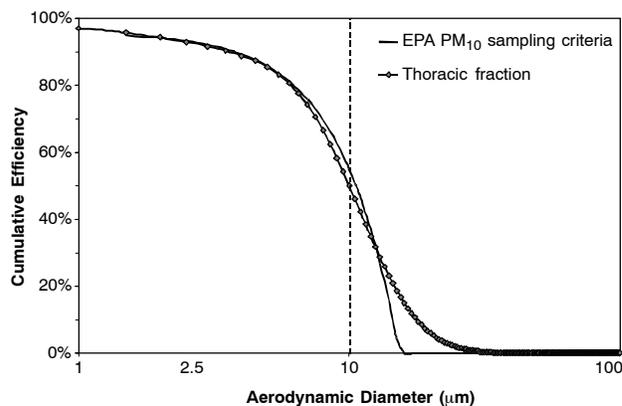


Figure 1. The EPA ideal PM₁₀ sampler penetration curve overlaid on the ACGIH sampling criteria for the thoracic fraction of PM (CFR, 2001c; ACGIH, 1994).

Table 1. PM₁₀ sampler effectiveness, as defined by the EPA, for nine d_{50} and slope combinations.

| d_{50} (μm) | Slope | Sampler Effectiveness (%) |
|----------------------------|-------|---------------------------|
| 9.5 | 1.4 | 100 |
| 9.5 | 1.5 | 101 |
| 9.5 | 1.6 | 102 |
| 10.0 | 1.4 | 104 |
| 10.0 | 1.5 | 105 |
| 10.0 | 1.6 | 106 |
| 10.5 | 1.4 | 107 |
| 10.5 | 1.5 | 108 |
| 10.5 | 1.6 | 109 |

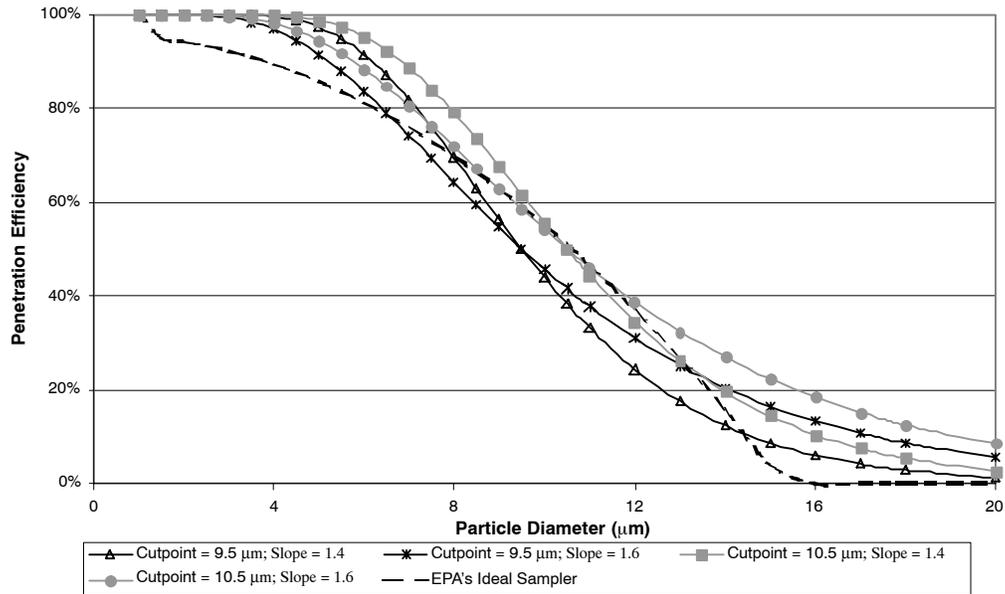


Figure 2. Comparison of the EPA (CFR, 2001a) ideal PM₁₀ sampler penetration data to the PM₁₀ sampler performance characteristics defined by Hinds (1982).

sampling criteria for the thoracic fraction of PM. Based on the curves in figure 1, the ambient PM₁₀ sampler penetration data appear to follow the thoracic convention fairly well for particle sizes less than about 13 μm AED. For particle diameters larger than 13 μm AED, the cumulative collection efficiency for the EPA's ambient PM₁₀ sampler penetration data moves towards zero much more rapidly than the thoracic penetration convention. The PM₁₀ cumulative penetration data

set produced a curve that appeared to have a larger slope for particle sizes less than 10 μm than for particle sizes greater than 10 μm, as shown in figure 1.

The results of the comparison on the nine sampler performance criteria to that of the EPA's ideal sampler are shown in table 1. Based on the EPA's criteria of acceptance, all nine sampler performance criteria used in this article meet the EPA's performance criteria for sampling effectiveness.

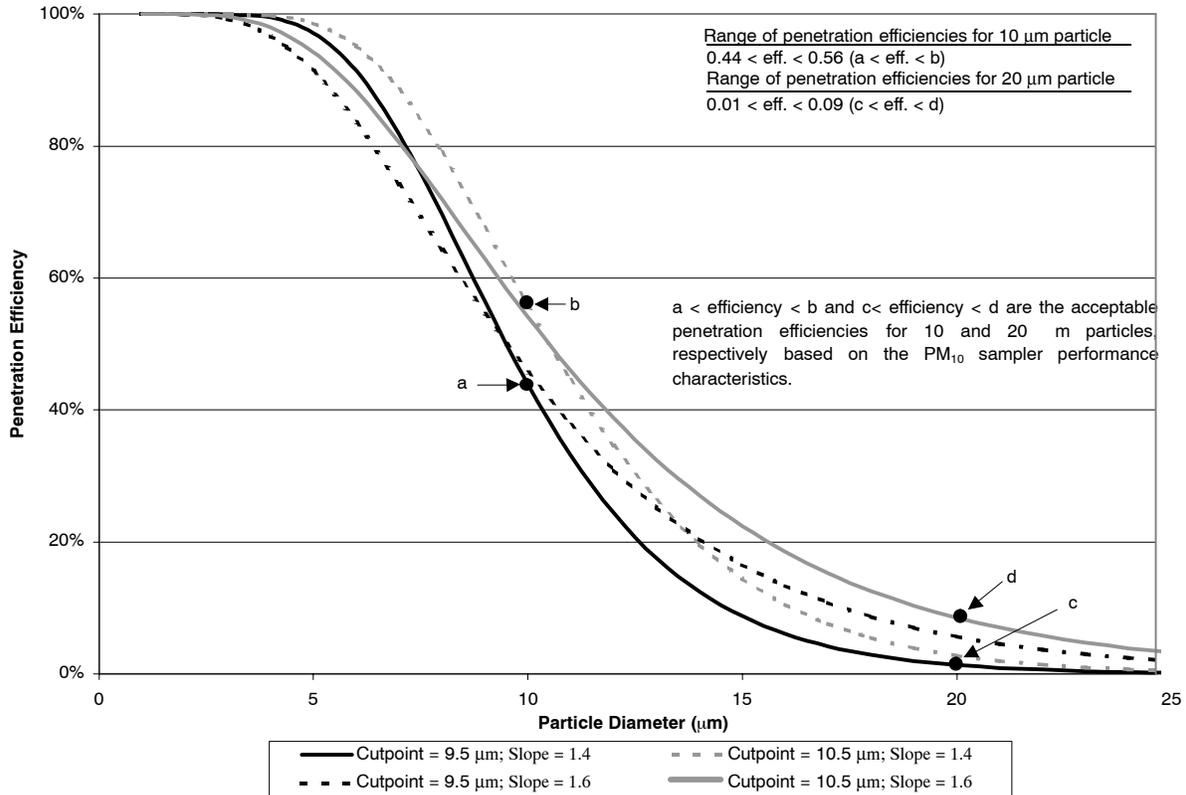


Figure 3. PM₁₀ sampler penetration curves based on the defining performance characteristics.

Based on the ambient PM₁₀ sampler performance criteria, four combinations of d_{50} and slope values were used to define boundary penetration efficiency curves. The boundary curves are defined as those curves that represent the minimum and maximum penetration efficiencies that can be obtained by using the sampler performance characteristics defined in table 1. These penetration curves were defined with d_{50} values of 9.5 and 10.5 μm and slope values of 1.4 and 1.6. Figure 2 illustrates the comparison of the boundary penetration curves, calculated using equation 2 and the above d_{50} and slope values, used in this research and the EPA's ideal PM₁₀ sampler penetration efficiency curve (CFR, 2001a). The ideal penetration curve is encompassed by the boundary penetration curves for particle diameters ranging from 6.5 to 14.5 μm .

When comparing the boundary penetration efficiency curves in figure 3, it is apparent that there is an acceptable range of penetration efficiencies for the PM₁₀ ambient air sampler. The acceptable range of penetration efficiencies for a particle size of 10 μm AED is 44% to 56%, whereas the acceptable range for a particle size of 20 μm AED is 1% to

9%. In other words, the uncertainty associated with the performance characteristics of a PM₁₀ sampler is $\pm 6\%$ when sampling 10 μm particles and $\pm 4\%$ when sampling 20 μm particles. These ranges are considered one form of inherent error associated with PM₁₀ ambient air samplers.

Results calculated using equation 7, to determine the ratio of sampler to true concentrations, and equation 6, to determine the estimated sampler concentration, for MMDs of 5 and 10 μm with a GSD of 1.5 and for MMDs of 15 and 20 μm with a GSD of 2.0 are shown in table 2. The following conclusions can be drawn from table 2: (1) the PM₁₀ sampler performance characteristics that define the range of acceptable concentrations are a d_{50} of 9.5 μm with slopes of 1.4 and 1.6 and a d_{50} of 10.5 μm with slopes of 1.4 and 1.6, (2) the ratios for PM₁₀ range from 89% to 139%, and (3) the ratio is equal to 100% only when the sampler d_{50} is equal to the PSD's MMD. This initial evaluation was expanded to incorporate a larger range of MMDs and GSDs for the PM₁₀ ambient air sampler.

Results of the simulation using d_{50} equal to 10.5 μm , slope of 1.6, GSD of 1.5, and MMDs ranging from 1 to 40 μm in

Table 2. Differences between theoretical sampler and true concentrations for various particle size and sampler performance characteristics.

| | | Particle Size Distribution (PSD) Characteristics | | | | | | | |
|----------------------------|-------|--|-----------------------|-------------------------------------|-----------------------|-------------------------------------|-----------------------|-------------------------------------|-----------------------|
| Cutpoint (μm) | Slope | MMD = 5 μm GSD = 1.5 | | MMD = 10 μm GSD = 1.5 | | MMD = 15 μm GSD = 2.0 | | MMD = 20 μm GSD = 2.0 | |
| | | Conc.[^a] | Ratio[^b] | Conc.[^a] | Ratio[^b] | Conc.[^a] | Ratio[^b] | Conc.[^a] | Ratio[^b] |
| 9.5 | 1.4 | 139.4 | 92.9% | 138.3 | 92.2% | 148.7 | 99.1% | 157.8 | 105.2% |
| 9.5 | 1.5 | 136.2 | 90.8% | 139.4 | 92.9% | 153.0 | 102.0% | 167.3 | 111.5% |
| 9.5 | 1.6 | 133.2 | 88.8% | 140.1 | 93.4% | 157.2 | 104.8% | 176.9 | 117.9% |
| 10.0 | 1.4 | 142.1 | 94.7% | 150.0 | 100.0% | 160.8 | 107.2% | 174.2 | 116.1% |
| 10.0 | 1.5 | 139.1 | 92.7% | 150.0 | 100.0% | 164.9 | 109.9% | 183.5 | 122.3% |
| 10.0 | 1.6 | 136.2 | 90.8% | 150.0 | 100.0% | 168.8 | 112.5% | 192.8 | 128.5% |
| 10.5 | 1.4 | 144.5 | 96.3% | 161.1 | 107.4% | 172.8 | 115.2% | 190.5 | 127.0% |
| 10.5 | 1.5 | 141.5 | 94.3% | 160.2 | 106.8% | 176.4 | 117.6% | 199.7 | 133.1% |
| 10.5 | 1.6 | 138.6 | 92.4% | 159.5 | 106.3% | 180.0 | 120.0% | 208.8 | 139.2% |

[^a] Values ($\mu\text{g}/\text{m}^3$) are based on the assumption that true concentrations are the correct estimates of the corresponding PM.

[^b] Concentrations are based on the corresponding regulations and adjusted by the ratio. Sampler concentrations for PM₁₀ are 150 $\mu\text{g}/\text{m}^3$.

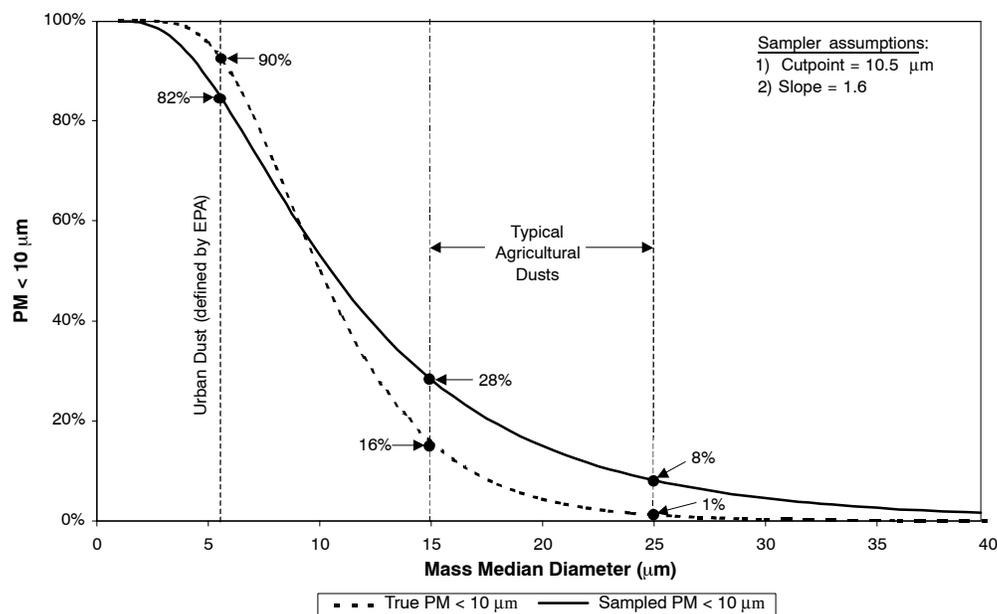


Figure 4. Comparison of true and sampled PM₁₀ percentages for a range of PSD mass median diameters and a GSD of 1.5.

equations 4 and 5 are illustrated in figure 4. In figure 4, three MMDs are highlighted. The first corresponds to 5.7 μm , an MMD associated with urban dust as defined by the EPA (USEPA, 1996), and the other two correspond to 15 and 25 μm , the range encompassing the MMDs expected from agricultural dusts. When comparing the sampled to true concentrations for the urban dust, the sampled concentration is about 9% [i.e., (true percent less than 5.7 μm – sampled percent less than 5.7 μm) / (true percent less than 5.7 μm)] lower than the true concentration. Further, when comparing the sampled to true concentrations for the range of agricultural dusts (Buser, 2004), the sampled concentrations were 75% to 700% higher than the true concentrations.

Figure 5 is similar to figure 4, and the data used in the graphs were generated in the same manner as for figure 4 except that the GSD is set to 2.0. When comparing the sampled to true concentrations for the urban dusts, the sampled concentration is about 3% lower than the true concentration. When comparing the sampled to true concentrations for the range of agricultural dusts, the sampled concentrations were 20% to 61% higher than the true concentrations.

In figure 6, the GSD is held constant at 2.0 for the four sets of PM_{10} sampler performance characteristics, which define the acceptable concentrations for PM_{10} , and the PSD MMDs range from 1 to 40 μm . To aid in the interpretation of the graph, an average concentration ratio is defined as the average of the largest and smallest ratio associated with the range of ratios defined by the sampler performance characteristics for a particular MMD. Conclusions that can be drawn from the information presented in figure 6 are: (1) the average ratio is less than 1.0 when the MMD is less than the d_{50} , (2) the average ratio is equal to 1.0 when the MMD is equal to the d_{50} , (3) the average ratio is greater than 1.0 when the MMD is greater than the d_{50} , and (4) the ratio range increases as the MMD increases. In general terms, when the ratio is less than 1.0, the current method of regulating PM_{10} underestimates the concentration of PM less than or equal to 10 μm AED; when the ratio is greater than 1.0, the current method

overestimates the concentration of PM less than or equal to 10 μm AED.

For example, if a PSD were characterized by an MMD of 5.7 μm AED and a GSD of 2.0, then the acceptable range of PM_{10} sampler concentrations would be 138 to 149 $\mu\text{g}/\text{m}^3$ (i.e., ratios of 0.92 and 0.99 obtained from figure 6 and multiplied by 150 $\mu\text{g}/\text{m}^3$, the current NAAQS for PM_{10}). In this scenario, the PM_{10} sampler uncertainty is $\pm 5.5 \mu\text{g}/\text{m}^3$ and the sampler bias is 0 $\mu\text{g}/\text{m}^3$ if the sampler concentration is assumed to be the standard and $-6.5 \mu\text{g}/\text{m}^3$ if the true concentration is assumed to be the standard. Likewise, if the PSD were characterized by an MMD of 10 μm and a GSD of 2.0, then the acceptable range of PM_{10} sampler concentrations would be 142 to 158 $\mu\text{g}/\text{m}^3$. This corresponds to a PM_{10} sampler uncertainty of $\pm 8.0 \mu\text{g}/\text{m}^3$ and a sampler bias of 0 $\mu\text{g}/\text{m}^3$ if the sampler concentration is assumed to be the standard and 0 $\mu\text{g}/\text{m}^3$ if the true concentration is assumed to be the standard. Further, if the PSD were characterized by an MMD of 20 μm and a GSD of 2.0, then the acceptable PM_{10} sampler concentrations would be 158 to 209 $\mu\text{g}/\text{m}^3$, corresponding to a PM_{10} sampler uncertainty of $\pm 25.5 \mu\text{g}/\text{m}^3$ and a sampler bias is 0 $\mu\text{g}/\text{m}^3$ if the sampler concentration is assumed to be the standard and 33.5 $\mu\text{g}/\text{m}^3$ if the true concentration is assumed to be the standard.

The data presented in figure 7 are based on the same assumptions as in figure 6, except the data are based on a GSD of 1.5. When comparing figures 6 and 7, it is obvious that the ratios increase much more rapidly as the MMD increases when the GSD is 1.5 as compared to a GSD of 2.0. For example, if a PSD were characterized by an MMD of 5.7 μm and a GSD of 1.5, then the acceptable range of PM_{10} sampler concentrations would be 131 to 144 $\mu\text{g}/\text{m}^3$. In this scenario, the PM_{10} sampler uncertainty is $\pm 6.5 \mu\text{g}/\text{m}^3$ and the sampler bias is 0 $\mu\text{g}/\text{m}^3$ if the sampler concentration is assumed to be the standard and $-12.5 \mu\text{g}/\text{m}^3$ if the true concentration is assumed to be the standard. If a PSD were characterized by an MMD of 10 μm and a GSD of 1.5, then the acceptable range of PM_{10} sampler concentrations would be 138 to 161 $\mu\text{g}/\text{m}^3$. This corresponds to a PM_{10} sampler uncertainty

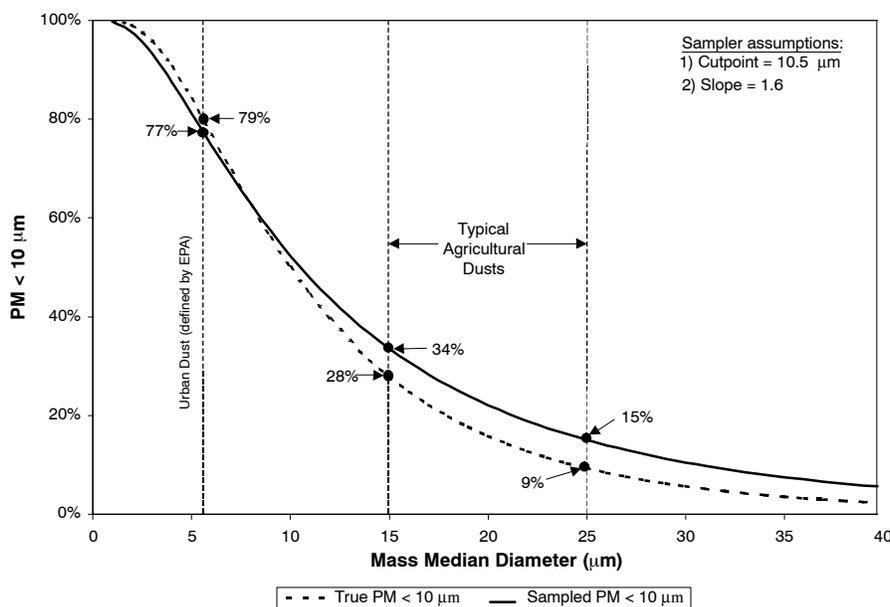


Figure 5. Comparison of true and sampled PM_{10} percentages for a range of PSD mass median diameters and a GSD of 2.0.

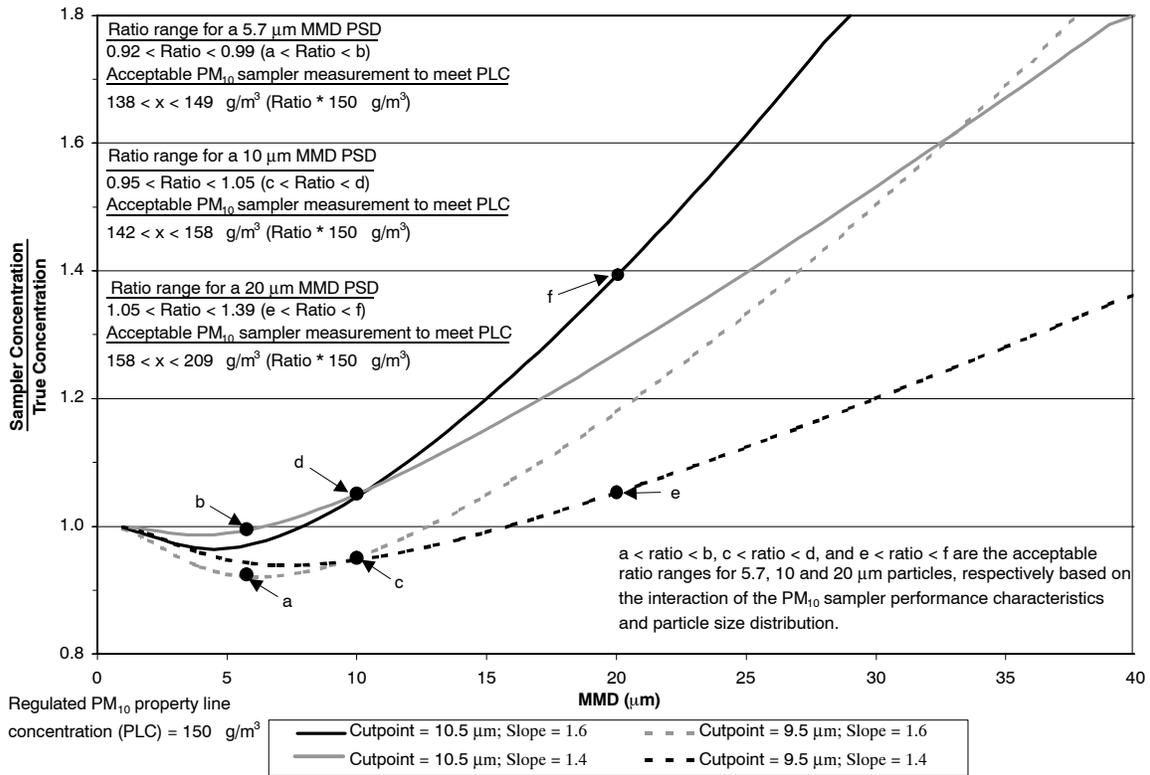


Figure 6. Theoretical ratios of PM_{10} sampler to true PSD concentrations (PSD – GSD = 2.0).

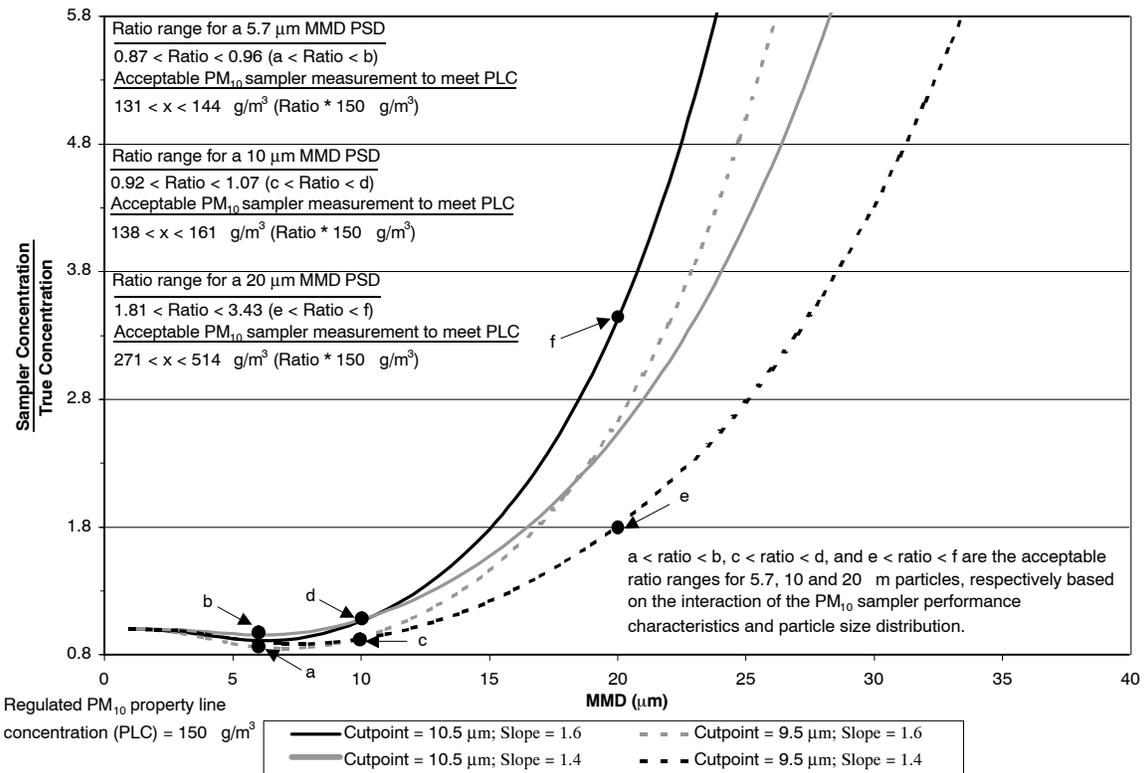


Figure 7. Theoretical ratios of PM_{10} sampler to true PSD concentrations (PSD – GSD = 1.5).

of $\pm 11.5 \mu\text{g/m}^3$ and a sampler bias of $0 \mu\text{g/m}^3$ if the sampler concentration is assumed to be the standard and $0 \mu\text{g/m}^3$ if the true concentration is assumed to be the standard. Further, if the PSD were characterized by an MMD of $20 \mu\text{m}$ and a GSD

of 1.5, then the acceptable range of PM_{10} sampler concentrations would be 271 to $514 \mu\text{g/m}^3$ (i.e., ratios of 1.81 and 3.43 obtained from figure 7 and multiplied by $150 \mu\text{g/m}^3$ the current NAAQS for PM_{10}), corresponding to a PM_{10} sampler un-

certainty of $\pm 121.5 \mu\text{g}/\text{m}^3$ and a sampler bias is $0 \mu\text{g}/\text{m}^3$ if the sampler concentration is assumed to be the standard and $242.5 \mu\text{g}/\text{m}^3$ if the true concentration is assumed to be the standard. Another conclusion that can be drawn from the data presented in figures 6 and 7 is that the range of acceptable concentrations increases as the GSD increases.

Figure 8 is a generalized graph to illustrate how MMDs and GSDs affect the concentration ratios for a PM_{10} sampler with a d_{50} of $10.0 \mu\text{m}$ and a slope of 1.5. The general observation that should be made from this graph is that the concentration ratios decrease (ratio approaches 1.0) as the GSD increases. Figure 9 further expands on how the concentration ratios are impacted by GSD. The data presented in figure 9 are based on MMDs of 10 and $20 \mu\text{m}$, sampler performance characteristics of $d_{50} = 9.5 \mu\text{m}$ with a slope of

1.4 and $d_{50} = 10.5 \mu\text{m}$ with a slope of 1.6, and variable GSDs ranging from 1.2 to 3.0. The general conclusions that should be drawn from this graph include: (1) when the MMD is equal to the d_{50} , the range of concentration ratios is centered around 1.0 for all GSDs; (2) as the GSD increases, the concentration ratio decreases and approaches 1.0; and (3) as the GSD decreases, the concentration ratio increases and approaches infinity for an MMD of $20 \mu\text{m}$ AED.

When the EPA implemented the PM_{10} NAAQS and approved the FRM ambient air sampler; the EPA's intent was for the performance characteristics of the PM_{10} sampler to mimic the thoracic penetration curve. This standard corresponds to PM in the ambient air (i.e., not impacted by only one source). Therefore, the question becomes: "Is it appropriate to use EPA-approved ambient PM_{10} samplers?" If the issue per-

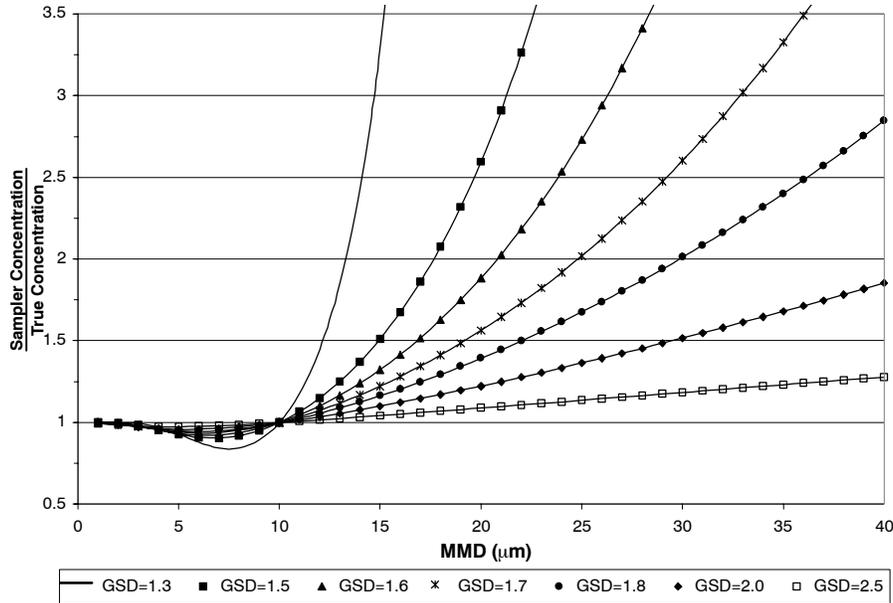


Figure 8. Theoretical ratios of PM_{10} sampler to true PSD concentrations (PM_{10} sampler characteristics; cutpoint = $10 \mu\text{m}$ and slope = 1.5).

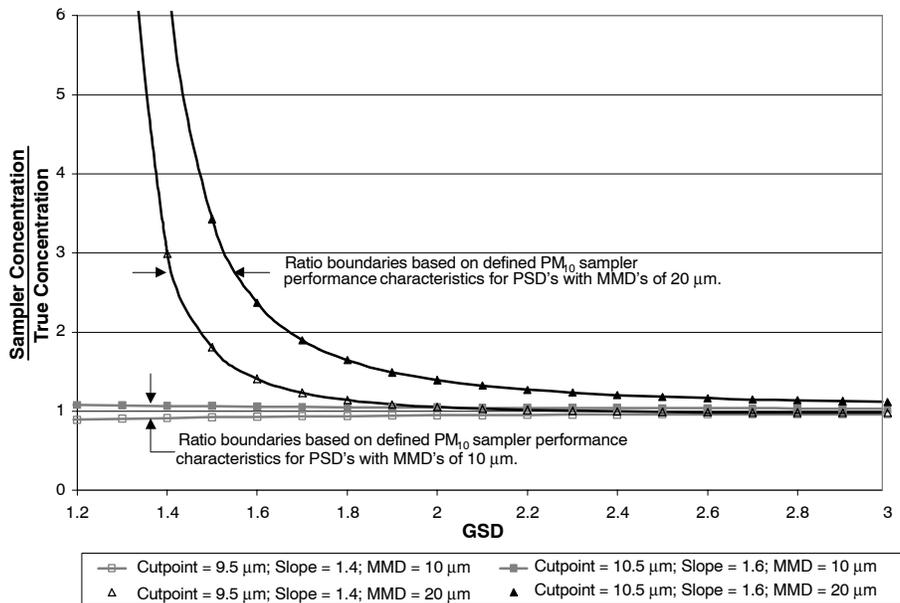


Figure 9. Theoretical PM_{10} sampler to true concentration ratio boundaries based on varying GSDs for PSDs with MMDs of 10 and $20 \mu\text{m}$.

tains to determining emission rates from cotton gin exhausts or from farming operations, then the answer is “absolutely not.” In general, these types of operations emit fairly large PM relatively close to the ground, which means that a large majority of the emitted PM will settle out of the air within a short time and within a short distance. As with any general statement, there will be exceptions, such as high wind events. Therefore, many of the ambient PM monitoring stations will never be exposed to the large particles emitted by these operations.

So how is this a problem? If a state or air district finds itself in non-attainment with the PM₁₀ NAAQS, then the corresponding agencies will, most likely, be required to reduce PM₁₀ emissions within the air shed. In order to reduce emissions from individual sources, the amount of PM emitted by the sources must be known or estimated. This is typically accomplished through source sampling or the use of emission factors, which may have been determined from source sampling or interrupted by some other means. In order to illustrate why it is crucial that emission factors, emission rates, and/or emission concentration from individual sources be based on true PM₁₀ and not PM₁₀ sampler measurements, the following example is provided.

Assume that EPA-approved PM₁₀ ambient air samplers are set up to monitor two commercial operations. Assume that the samplers have performance characteristics described by a d_{50} of 10.5 μm and a slope of 1.6 (both parameters are within the performance criteria defined by the EPA). Now assume that one operation is a power plant and is emitting PM (sampled by the PM₁₀ sampler) that can be described by a lognormal distribution with an MMD of 5 μm and a GSD of 1.5. Assume that the second operation is an agricultural operation and is emitting PM (sampled by the PM₁₀ sampler) that can be described by a lognormal distribution with an MMD of 20 μm and a GSD of 1.5. Further, assume that the PM₁₀ sampler used to monitor each of the operations measures 100 $\mu\text{g}/\text{m}^3$. Now, based on the methods laid out in this article, the true PM (PM less than 10 μm) emitted from each industry would be defined as follows:

Based on a PSD analysis, the percent of PM mass less than 10 μm being emitted from the power plant is 96%. Based on the PSD and sampler performance characteristics, the percent of TSP captured by the PM₁₀ sampler’s pre-separator is 88.4%. The TSP concentration emitted from the power plant is 113 $\mu\text{g}/\text{m}^3$ [i.e., 100 $\mu\text{g}/\text{m}^3$ (PM measured by the PM₁₀ sampler)/0.884 (% of TSP captured by the PM₁₀ sampler)]. Multiplying the TSP concentration by the true fraction of PM₁₀ (i.e., 113 $\mu\text{g}/\text{m}^3$ * 0.96), the true PM₁₀ concentration is determined to be 109 $\mu\text{g}/\text{m}^3$. Therefore, the PM₁₀ sampler underestimated the true PM₁₀ concentration by 8%.

For the agricultural operation, using the previous procedures, the true percent PM₁₀ is 4.37%, and based on the PSD and sampler performance characteristics, the percent of TSP captured by the PM₁₀ sampler is 15%. Therefore, the TSP concentration is 667 $\mu\text{g}/\text{m}^3$, resulting in the true PM₁₀ emitted from operation being equal to 29 $\mu\text{g}/\text{m}^3$. In this case, the PM₁₀ sampler overestimated the true PM₁₀ by 245%.

Based on this scenario, the two operations are not being equally regulated (i.e., 109% of the PM emitted from the power plant and measured by the PM₁₀ sampler corresponds

to PM less than 10 μm , whereas only 29% of the PM from the agricultural operation and measured by the PM₁₀ sampler corresponds to PM less than 10 μm).

Looking at the issue from another viewpoint, assume that the two operations described previously are emitting 100 $\mu\text{g}/\text{m}^3$ true PM₁₀. If the percent of TSP measured by the PM₁₀ sampler (defined as measured PM₁₀) is divided by the percent of true PM₁₀ and this ratio is multiplied by the true concentration of PM₁₀ being emitted, the PM₁₀ sampler concentrations can be determined. For the power plant, the PM₁₀ sampler could measure a concentration as high as 92 $\mu\text{g}/\text{m}^3$. For the agricultural operation, the PM₁₀ sampler could measure a concentration as high as 343 $\mu\text{g}/\text{m}^3$. What this means for the agricultural operation is that 100 $\mu\text{g}/\text{m}^3$ of the PM being sampled is less than 10 μm and 243 $\mu\text{g}/\text{m}^3$ of the PM being sampled is larger than 10 μm . Further, depending on the release height and meteorological conditions, the majority of this 243 $\mu\text{g}/\text{m}^3$ of particles larger than 10 μm will rapidly settle out of the air. Therefore, regarding the question, “Is it appropriate to use PM₁₀ samplers to determine PM₁₀ emission values for agricultural operations?” the answer is “absolutely not.”

SUMMARY AND CONCLUSIONS

There are several errors associated with the current air pollution rules and regulations established by the EPA that should be minimized to ensure equal regulation of air pollutants between and within all industries. Potentially, one of the most significant errors is attributed to the interaction of the industry-specific PSD and sampler performance characteristics. Currently, the regulation of PM is based on sampler measurements and not on true concentrations.

A sampler concentration corresponds to the concentration collected by a PM sampler. This concentration is dependent on the sampler’s performance characteristics (i.e., d_{50} and slope). Since the concentration is based on the sampler’s performance characteristics, there are two inherent errors associated with the measurement. For a PM₁₀ sampler, the first error corresponds to the mass of particles less than 10 μm that should have been captured on the filter but was removed from the air stream by the pre-separator. The second error (for a PM₁₀ sampler) corresponds to the mass of particles greater than 10 μm that should have been removed from the air stream by the pre-separator but was allowed to pass through the pre-separator and be collected on the filter. The following are generalized conclusions drawn from this research:

- If $\text{MMD} < d_{50}$, then $C_{\text{sampler}} < C_{\text{true}}$
- If $\text{MMD} = d_{50}$, then $C_{\text{sampler}} = C_{\text{true}}$
- If $\text{MMD} > d_{50}$, then $C_{\text{sampler}} > C_{\text{true}}$
- As GSD increases, the concentration ratio of C_{sampler} to C_{true} decreases.
- As sampler slope decreases, the concentration ratio of C_{sampler} to C_{true} decreases.

Results of the analysis presented in this research show that not all industries are being equally regulated in terms of PM and that all industries should be concerned with the current site-specific regulations implemented by the EPA and enforced by SAPRAs.

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PARTICULATE MATTER SAMPLER ERRORS DUE TO THE INTERACTION OF PARTICLE SIZE AND SAMPLER PERFORMANCE CHARACTERISTICS: AMBIENT PM_{2.5} SAMPLERS

M. D. Buser, C. B. Parnell, Jr., B. W. Shaw, R. E. Lacey

ABSTRACT. *The National Ambient Air Quality Standards (NAAQS) for particulate matter (PM) in terms of PM_{2.5} are ambient air concentration limits set by the EPA to protect public health and well-being. Further, some state air pollution regulatory agencies (SAPRAS) utilize the NAAQS to regulate criteria pollutants emitted by industries by applying the NAAQS as property-line concentration limits. Prior to and since the inclusion of the PM_{2.5} standard, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulation, and methods of determining PM_{2.5}. A common trend among many of these publications is the use of samplers to collect PM_{2.5} concentration data. Often, the sampler data are assumed to be accurate concentration measures of PM_{2.5}. The fact is that issues such as sampler uncertainties, environmental conditions, and characteristics of the material that the sampler is measuring must be incorporated for accurate sampler measurements. The focus of this article is on the errors associated with particle size distribution (PSD) characteristics of the material in the air that is being sampled, the PM_{2.5} sampler performance characteristics, the interaction between these two characteristics, and the effect of this interaction on the regulatory process. Theoretical simulations were conducted to determine the range of errors associated with this interaction for the PM_{2.5} ambient air samplers. Results from the PM_{2.5} simulations indicated that a source emitting PM characterized by a mass median diameter (MMD) of 20 μm and a geometric standard deviation (GSD) of 1.5 could be forced to comply with a PM_{2.5} standard that is 14 times more stringent than that required for a source emitting PM characterized by an MMD of 10 μm and a GSD of 1.5, and 59 times more stringent than that required for a source emitting PM characterized by an MMD of 5.7 μm and a GSD of 1.5. Therefore, in order to achieve equal regulation among differing industries, PM_{2.5} measurements must be based on true concentration measurements.*

Keywords. *Air, Environmental impact, Legislation, Mathematical models, Particle size distribution, PM, PM_{2.5}, PM₁₀, Pollution, Samplers.*

The Federal Reference Method (FRM) PM_{2.5} samplers are specified by design, unlike the performance-based FRM criteria for the PM₁₀ samplers. PM_{2.5} refers to particles with an aerodynamic equivalent diameter (AED) less than or equal to a nominal 2.5 μm . PM₁₀ refers to particles with an AED less than or equal to a nominal 10 μm . An update published by the EPA (USEPA, 2000) states: "The requirement that these instruments rely on specific design elements, rather than performance criteria alone, is structured to produce greater

measurement reproducibility and to avoid the data measurement uncertainties experienced in the PM₁₀ monitoring program."

In addition to the FRM PM_{2.5} sampler designation, the EPA also provides a Federal Equivalent Method (FEM) PM_{2.5} sampler designation. The EPA defined three FEM classes (Class I, Class II, and Class III) based on the degree of dissimilarity between a candidate sampler and the FRM requirements (CFR, 2001e). An increase in equivalency designation, from Class I to Class II to Class III, indicates a greater deviation from the FRM, requiring more extensive testing for equivalency verification. Class I equivalent methods correspond to candidate samplers that have only minor deviations from the reference method, usually relating to sample transmission component modifications incorporated to accommodate a sequential sampling mechanism. A Class I FEM candidate sampler must undergo the same testing as the FRM candidate sampler, with the addition of an internal aerosol transport test.

Class II equivalent methods are 24-hour integrated filter collection techniques that rely on gravimetric analysis, but have significant design or performance deviations from the reference method. For example, substituting a cyclone separator for the Well-Type Impactor Ninety Six (WINS) (Thermo Electron Corp., Waltham, Mass.) is a deviation from the FRM that could be designated as a Class II FEM. A

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Class II FEM candidate sampler must undergo more extensive testing than the FRM or Class I FEM, with the tests being specific to the nature of the modifications in the candidate method. Additional testing may include all, or some subset, of the following tests: full wind tunnel test, wind tunnel aspiration test, static fractionator test, loading test, and volatility test.

Class III equivalent methods do not fall under Class I or Class II designations because of further deviations from the FRM, but still provide mass concentration measurements of $PM_{2.5}$ comparable to the reference method. The two primary sampling categories that fall into this class are non-filter-based techniques and continuous (or semi-continuous) analyzers. Specific requirements for Class III FEM are not defined because of the wide range of technologies that might be employed for $PM_{2.5}$ mass measurement. As a result, the EPA develops specific Class III FEM testing and other requirements on a case-by-case basis. Class III FEMs may be required to undergo any or all of the testing required for validation as an FRM, Class I FEM, or Class II FEM, as well as additional testing specific to the sampling technology.

The basic design of the FRM $PM_{2.5}$ sampler is given in the Federal Register (1997) and 40 CFR Part 50, Appendix L (CFR, 2001e). Performance specifications for FRM $PM_{2.5}$ samplers are listed in 40 CFR Parts 53 and 58 (CFR, 2001a, 2001b). According to the EPA's criteria, the accuracy of FRM $PM_{2.5}$ samplers is determined through collocated sampler evaluation tests. The performance specifications for FEM $PM_{2.5}$ Class I samplers are very similar to those required for the FRM sampler. Detailed performance specifications are listed in 40 CFR Part 53.

A candidate $PM_{2.5}$ sampler classified as a Class II FEM is required to meet a more rigorous set of performance criteria, as defined in 40 CFR Part 53. Specifically, 40 CFR Part 53, Subpart F, describes the procedures for testing the performance characteristics of Class II FEM candidate $PM_{2.5}$ ambient air samplers. In the full wind tunnel test, the candidate sampler's collection efficiency is determined for several mono-disperse particle sizes (i.e., solid particle target diameters of 1.5, 2.0, 2.2, 2.5, 2.8, 3.5, and 4.0 μm AED) at wind speeds of 2 and 24 km/h (CFR, 2001a). A smooth collection efficiency curve is then generated using the individual collection efficiencies determined in the wind tunnel tests. The candidate sampler's collection efficiency curve, along with the three idealized ambient particle size distributions, i.e., coarse, "typical" coarse, and fine, as defined by the EPA (CFR, 2001e), is then used to determine the expected mass concentration for the candidate sampler. The candidate sampler passes the full wind tunnel evaluation if the expected mass concentration calculated for the candidate sampler, at each wind speed and for each idealized distribution, differs by no more than $\pm 5\%$ from that predicted for the "ideal" sampler. The candidate method passes the 50% cutpoint test if the test result at each wind speed falls within $2.5 \pm 0.2 \mu m$. The candidate sampler must also pass the wind tunnel aspiration, static fractionator, loading, and volatility tests listed in 40 CFR Part 53, Subpart F; however, the full wind tunnel test is the primary test for evaluating the samplers collection efficiency curve.

Vanderpool et al. (2001b) listed several factors that influence the mass concentration measured by the FRM WINS sampler including: PM concentration and size distribution; chemical composition of the collected aerosol;

sampler volumetric flow rate (affected by the accuracy of the sampler's ambient temperature, ambient pressure, and flow sensors); sampling time; sampler inlet geometry; performance of the sampler's internal size-selective separator; sampler internal particle losses; pre-sampling and post-sampling filter conditioning; and all other associated sampling and analysis procedures. In addition, relatively small changes in a sampler's cutpoint can produce significant and hard to predict mass concentration errors (USEPA, 1996a). Therefore, factors that affect sampler concentration errors should be identified and the corresponding influences determined as a function of particle size.

According to Vanderpool et al. (2001b), "Regardless of the inertial fractionation mechanism (conventional impaction, virtual impaction, or cyclonic separation) and the separator design, all separators overload to some degree if continuously exposed to particle-laden airstreams." One method of determining the sampler uncertainty attributed to overloading is to evaluate the elemental composition of $PM_{2.5}$ and PM_{10} , or the coarse fraction of PM_{10} (Vanderpool, 2001b). Using this method, elements relating to soil-type materials have been found in the $PM_{2.5}$ fraction. In a study using dichotomous samplers, the soil-type material found in the $PM_{2.5}$ fraction was equivalent to 5% of the coarse mode fraction of PM_{10} (Dzubay et al., 1988). Similar results were reported from the IMPROVE network, which suggested that the soil-derived material found in the $PM_{2.5}$ sample was equivalent to 20% of the coarse fraction of PM_{10} (Eldred et al., 1994).

Pitchford (1997) stated that an early concern with the WINS impactor was cleaning to avoid the possibility of having part of the impactor deposit break off and make its way to the filter, resulting in an over-sampling of $PM_{2.5}$. Pitchford (1997) also reported that sampling with a dirty WINS impactor could result in an under-sampling of $PM_{2.5}$. This under-sampling was attributed to deposits building up on the impaction surface, in effect changing the critical dimensions of the WINS, resulting in a low cutpoint. Vanderpool et al. (2001a) evaluated the loading characteristics of the WINS separator by monitoring the sampler's performance after repeated operation in an artificially generated, high concentration, coarse mode aerosol composed of Arizona Test Dust, as well as in field tests. In the wind tunnel experiments, the WINS performance was found to be a monotonic function of loading. A negative 5% error in the $PM_{2.5}$ measurement resulted from a coarse particulate loading of approximately 16 mg because of a slight reduction in the separator's cutpoint. It was also determined that the results from the laboratory experiments could not be extrapolated to the field settings and that the performance of the WINS was more sensitive to impactor loading in the field tests than in experiments with the single-component aerosol.

Kenny et al. (2000) evaluated a clean WINS Sharp-Cut Cyclone (SCC) (Thermo Electron Corp., Waltham, Mass.), GK cyclone (BGI, Inc., Waltham, Mass.), and University Research Glassware (URG) cyclone (University Research Glassware, Chapel Hill, N.C.) using EPA procedures for testing the performance characteristics of Class II equivalent $PM_{2.5}$ methods. They reported that the SCC could over-sample "coarse" aerosols by 4% to 5%. The URG cyclone could overestimate "coarse" aerosols by more than 13%, and the GK could overestimate "coarse" aerosols by more than 9%. The clean WINS impactor was within 1% of the ideal

concentration, which was expected since the ideal penetration curve is a sigmoid model fit to the WINS impactor data.

The WINS impactor was designed to be deployed downstream of the Graseby-Anderson 246A PM₁₀ inlet and operate at a flow rate of 16.7 L/min. Peters and Vanderpool (1996), under contract with the EPA to evaluate the WINS sampler, characterized the WINS penetration curve as a lognormal distribution with a cutpoint of 2.48 μm AED and a slope of 1.18. Peters et al. (2001b) evaluated the WINS using mono-disperse aerosols and reported that the WINS cutpoint ranged from 2.44 to 2.48 μm and the slope of the sampler's penetration curve ranged from 1.17 to 1.22. Vanderpool et al. (2001b) stated that "unlike conventional greased flat-plate impactors, the general effect of loading in the WINS separator is to reduce the cutpoint rather than to increase it." Vanderpool et al. (2001b) reported that the cutpoint for 13 archived WINS samplers from the various field sites after five days of loading ranged from 2.32 to 2.51 μm .

Kenny (1998) conducted an evaluation study on the WINS impactor, the SCC, the GK4.39 cyclone, and the URG. The SCC was based on the design of the SRI Cyclone III described by Smith et al. (1979) and the URG cyclone was based on the Stairmand design evaluated by Moore and McFarland (1993). Kenny (1998) reported cutpoints (slopes) of 2.44 μm (1.23), 2.46 μm (1.19), 2.37 μm (1.28), and 2.46 μm (1.45) for the WINS, SCC, GK4.39, and URG samplers, respectively, using mono-disperse particles. Kenny et al. (2000) evaluated the WINS and SCC when loaded with Aloxite dust (and no PM₁₀ inlet) and determined that the WINS cutpoint shifted steadily downwards to 2.15 μm , whereas the SCC cutpoint did not exhibit a significant downward shift.

Buch (1999) evaluated the WINS and the Interagency Monitoring of Protected Visual Environments (IMPROVE) PM_{2.5} samplers in a dust chamber using poly-disperse particles. Buch (1999) determined that the WINS cutpoint was $2.7 \pm 0.41 \mu\text{m}$ and the slope was 1.32 ± 0.03 when exposed to a dust consisting of 67% PM_{2.5}. The IMPROVE PM_{2.5} sampler was reported to have an average cutpoint of 3.8 μm and an average slope of 1.23 (Buch, 1999). Pargmann (2001) conducted a similar study that evaluated the WINS, the SCC, and the hi-vol PM_{2.5} sampler (Thermo Electron Corp., Waltham, Mass.) in a dust chamber using poly-disperse particles (i.e., alumina, corn starch, and wheat flour). No cutpoints or slopes were reported for the SCC or hi-vol PM_{2.5} samplers; however, the WINS fractional efficiency curve was defined by a cutpoint of $1.95 \pm 0.10 \mu\text{m}$ and a slope of 1.31 ± 0.04 when exposed to a dust consisting of 5.34% PM_{2.5}. Pargmann (2001) also reported the percent error between the sampler measurements and actual PM_{2.5} concentrations. The WINS sampler over-sampled by 51%, 211%, and 444% when sampling alumina, corn starch, and wheat flour, respectively. The SCC sampler over-sampled by 119%, 585%, and 1771% when sampling alumina, corn starch, and wheat flour, respectively. The hi-vol PM_{2.5} sampler over-sampled by 111%, 467%, and 632% when sampling alumina, corn starch, and wheat flour, respectively. Pargmann (2001) stated that over-sampling increased as the mass median diameter (MMD) of the dust being sampled increased.

BGI Incorporated (Waltham, Mass.) developed the Very Sharp-Cut Cyclone (VSCC), which was based on the design of the SCC described by Kenny et al. (2000). The VSCC

differs from the SCC in that it has a longer cone, wider base diameter, and decreased inlet and outlet tube diameters. The evaluation study conducted by Kenny (2000) consisted of testing the VSCC and the WINS impactor in a wind tunnel using solid, spherical glass microspheres (density = 2.45 g/cm³) with physical diameters up to 25 μm (MMD = 4 μm) at a loading rate of 100 to 200 particles/cm³. Kenny (2000) reported cutpoints (slopes) of 2.48 μm (1.22) and 2.5 μm (1.16) for the WINS impactor and VSCC (operated at 16.67 L/min), respectively.

Peters et al. (2001a) evaluated the SCC 1.829 (BGI, Inc., Waltham, Mass.), the SCC 2.141 (Met One Instruments, Inc., Grants Pass, Ore.), and the AN 3.68 (Andersen Instruments, Inc., Smyrna, Ga.) PM_{2.5} cyclones and a Spiral impactor using EPA procedures for testing the performance characteristics of Class II equivalent PM_{2.5} samplers. Each of these cyclone separators is based on the SRI designs described by Smith et al. (1979). Peters et al. (2001a) reported a cutpoint of 2.44 μm and a slope of 1.23 for the SCC 1.829. The SCC 2.141 was reported to have a cutpoint of 2.52 μm and 2.35 μm for flow rates of 6.7 and 7.0 L/min, respectively. The slope associated with the SCC 2.141 was reported as 1.24 for both flow rates tested. Peters et al. (2001a) reported that the SCC 2.141 overestimated the idealized "coarse" mass concentration by as much as 6.1% at a flow rate of 6.7 L/min. The AN 3.68 was reported to have a cutpoint of 2.72 μm and a slope of 1.15 when operated at the design flow rate of 24.0 L/min. Peters et al. (2001a) reported that the AN 3.68 overestimated the idealized "coarse" mass concentration by 7.4%, which was attributed to the sampler's larger cutpoint. Peters et al. (2001a) reported that the cutpoint associated with the Spiral impactor was highly variable and ranged from 1.9 to 2.7 μm for three separate tests when operated at the design flow rate of 7.0 L/min. Peters et al. (2001a) characterized the performance of the ungreased Spiral impactor by a cutpoint of 2.69 μm and a slope of 1.30. Kenny et al. (2000) concluded that cyclonic separators become more efficient with increased loading (i.e., the cutpoint shifts to the left with increased loading).

The MiniVol (Airmetrics, Eugene, Ore.), which is designed to have a 2.5 μm AED cutpoint at a flow rate of 5 L/min, does not meet the design specifications required for designation as a PM_{2.5} regulatory monitor (Hill et al., 1999). Based on the data provided by Hill et al. (1999) the MiniVol 2.5 μm impactor appeared to have a cutpoint of 2.7 μm and a slope of 1.4 when wind tunnel tested using mono-disperse particles. Hill et al. (1999) also evaluated a MiniVol PM_{2.5} impactor with various impactor plate grease loadings. The MiniVol impactor appeared to have a cutpoint ranging from 2.66 to 2.82 μm with a slope ranging from 1.25 to 1.37 based on data provided by Hill et al. (1999) for a wind tunnel study using mono-disperse particles and various application rates (defined as light, heavy, and very heavy) of grease on the impactor plate. Hill et al. (1999) also noted that recent modifications of the MiniVol PM_{2.5} impactor design required the use of a PM₁₀ impactor upstream of the PM_{2.5} impactor (i.e., cascade or tandem impactor configuration). Hill et al. (1999) provided data that were used to estimate the cutpoint (and slopes) associated with the MiniVol PM_{2.5} impactor using a flat plate, cup plate, flat plate following a PM₁₀ impactor, and a cup plate following a PM₁₀ impactor, which were determined to be 2.7 μm (1.48), 2.97 μm (1.29), 2.7 μm (1.65), and 3.1 μm (1.29), respectively.

The EPA recommended the use of a sharp 2.5 μm cutpoint for a fine-particle indicator (USEPA, 1996a). However, $\text{PM}_{2.5}$ samplers have some potential for an intrusion of the “tail” of the coarse mode during episodes of fugitive dust concentrations. The EPA recommends a sharp inlet for the FRM to minimize this potential intrusion of coarse-mode particles. According to the EPA, “Such intrusions into $\text{PM}_{2.5}$ measurement are not anticipated to be significant in most situations. Nevertheless, if subsequent data reveal problems in this regard, this issue can, and should be, addressed on a case-by-case basis in the monitoring and implementation programs. Because the purpose of a $\text{PM}_{2.5}$ standard is to direct controls toward sources of fine-mode particles, it would be appropriate to develop analytical procedures for identifying those cases where a $\text{PM}_{2.5}$ standard violation would not have occurred in the absence of coarse-mode particle intrusion. Consideration should be given to a policy similar to the natural events policy for addressing such cases” (USEPA, 1996a).

The available data show that typically only 5% to 15% (on the order of 1 to 5 $\mu\text{g}/\text{m}^3$) of the $\text{PM}_{2.5}$ mass is attributable to soil-type sources, even in dusty areas such as the San Joaquin Valley, California, and Phoenix, Arizona (USEPA, 1996a). However, this percentage may increase during events such as high winds. According to the EPA, “A sharper inlet for the Federal Reference Method may help to minimize the intrusion of coarse-mode particles into the $\text{PM}_{2.5}$ measurement” (USEPA, 1996a).

The ultimate goal of a PM sampler is to accurately measure the concentration of specific ranges of particle sizes that exist in the atmosphere. However, it is not currently possible to accurately characterize the material that exists as particles in the atmosphere because of difficulties in creating a reference standard for particles suspended in the atmosphere. No calibration standards for suspended particle mass exist. As a result, the EPA defines accuracy for PM measurements in terms of the agreement between a candidate sampler and a reference sampler under standardized conditions for sample collection, storage, and analysis (USEPA, 1996a, 2001). Therefore, sampler comparisons become very important in determining the reproducibility of sampler measurements (measurement precision, as defined by the EPA) and how the sampler design influences accuracy (USEPA, 2001).

The National Ambient Air Quality Standards (NAAQS) for PM, in terms of $\text{PM}_{2.5}$, are the concentration limits set by the EPA that should not be exceeded (CFR, 2001c). Further, some state air pollution regulatory agencies (SAPRAS) utilize the NAAQS to regulate criteria pollutants emitted by industries by applying the NAAQS as property-line concentration limits. The regional or area consequences for multiple exceedances of the NAAQS are having an area designated as non-attainment, with a corresponding reduction in the permit-allowable emission rates for all sources of PM in the area. The source-specific consequence of an exceedance of the NAAQS at the property line is the SAPRA denying an operating permit. The current $\text{PM}_{2.5}$ primary 24-hour NAAQS is 65 micrograms per actual cubic meter ($\mu\text{g}/\text{acm}$) (CFR, 2001c).

Buser et al. (2006a) briefly discussed the evolution of the $\text{PM}_{2.5}$ regulation. Prior to and since the inclusion of the $\text{PM}_{2.5}$ standard, numerous journal articles and technical references have been written to discuss the epidemiological effects,

trends, regulation, and methods of determining $\text{PM}_{2.5}$. A common trend among many of these publications is the use of samplers to collect information on $\text{PM}_{2.5}$. The data collected from these samplers are commonly used in statistical correlations and statistical comparisons to draw conclusions about $\text{PM}_{2.5}$ emission concentrations. All too often, the sampler data are assumed to be accurate measures of $\text{PM}_{2.5}$. The fact is that issues such as sampler uncertainties, concentration reporting basis (dry standard versus actual conditions), and characteristics of the material that the sampler is measuring must be incorporated for accurate sampler measurements. The focus of this article is on the particle size distribution (PSD) characteristics of the material in the air that is being sampled, the sampler performance characteristics, the interaction between these two characteristics for $\text{PM}_{2.5}$ ambient air samplers, and the effect of these interactions on the regulatory process.

METHODS AND PROCEDURES

Buser et al. (2006a) provided background information on mathematically defining PSDs and sampler and true penetration curves. The equation for the lognormal mass density function most commonly used to describe dust particles in the ambient air or emitted from urban or agricultural operations, was defined as:

$$f(d_p, MMD, GSD) = \frac{1}{d_p \ln GSD \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln MMD)^2}{2(\ln GSD)^2} \right] \quad (1)$$

where MMD, GSD, and d_p are the mass median diameter, geometric standard deviation, and particle diameter of the distribution, respectively (Hinds, 1982). The cumulative sampler penetration efficiency was defined as:

$$P_m(d_{50}, slope) = 1 - \int_0^{\infty} \left[\frac{1}{d_p \ln(slope) \sqrt{2\pi}} \times \exp \left[-\frac{(\ln d_p - \ln d_{50})^2}{2[\ln(slope)]^2} \right] \right] dd_p \quad (2)$$

where d_{50} is the particle size at which 50% of the particulate matter (PM) is captured by the pre-separator and 50% of the PM penetrates to the filter, and *slope* is the slope of the cumulative penetration curve. A complete definition of slope is provided by Buser et al. (2006a). In addition, Buser et al. (2006a) defined a true cumulative penetration curve or cut as a step function, which was defined as:

$$P_t(d_p, d_{50}) = \begin{cases} 1 & \text{if } d_p \leq d_{50} \\ 0 & \text{if } d_p > d_{50} \end{cases} \quad (3)$$

In order to solve equation 2, additional information is needed to define the d_{50} and slope associated with the $\text{PM}_{2.5}$ ambient air sampler's PM_{10} and $\text{PM}_{2.5}$ pre-separators. The $\text{PM}_{2.5}$

ambient air sampler's PM₁₀ pre-separator d_{50} and slope were defined as $10.0 \pm 0.5 \mu\text{m}$ and 1.5 ± 0.1 , respectively. Additional information on the selection of these PM₁₀ performance characteristics is discussed by Buser et al. (2006b). The EPA essentially defines the d_{50} and slope associated with the PM_{2.5} pre-separator in 40 CFR Part 53 in the discussion of tests required for a candidate sampler to receive EPA approval. The d_{50} for the PM_{2.5} pre-separator is explicitly stated in the EPA standards as $2.5 \pm 0.2 \mu\text{m AED}$. No slope values for the sampler are listed in 40 CFR Part 53, nor in any other current EPA standard; however, penetration data are presented in 40 CFR Part 53. Ideally, the penetration data could be fit to a cumulative lognormal distribution to determine the characteristic d_{50} and slope for the PM_{2.5} samplers; however, it was found that no single cumulative lognormal curve adequately represented the EPA dataset in 40 CFR Part 53. It should be noted that these penetration data, along with EPA-defined interval mass concentrations and mass penetration tolerances, are used to determine if proposed samplers meet the EPA's PM₁₀ performance criteria.

It appears from the literature that the EPA intended for the PM_{2.5} sampler to have a "sharp cut" or represent a true concentration of PM_{2.5}, which would mean that, ideally, the slope would be equal to 1.0 (USEPA, 1996b). However, from an engineering standpoint, it is not possible to design a sampler with a true cut. Work by Peters and Vanderpool (1996) suggested that a slope of 1.18 could be achieved with the WINS Impactor, an EPA-approved ambient air sampler. Further work by Buch (1999) suggested that the WINS Impactor slopes were not as sharp as previously reported and that a more appropriate estimation of the sampler slopes would be 1.3 ± 0.03 . Based on Buch's (1999) work, the primary performance characteristics for ambient PM_{2.5} sampler used in this research were a d_{50} of $2.5 \pm 0.2 \mu\text{m}$ and a slope of 1.3 ± 0.03 . These performance characteristic ranges were divided into nine d_{50} and slope combinations, i.e., all combinations for d_{50} values of 2.3, 2.5, and 2.7 μm and slope values of 1.27, 1.30, and 1.33. These sampler performance characteristics were evaluated using the EPA criteria defined in 40 CFR Part 53 to determine if these performance criteria fall within the EPA's ambient PM_{2.5} sampler criteria. Further, these performance criteria were evaluated to determine the uncertainty associated with these performance characteristic tolerances and were used to estimate sampler and true concentrations for an array of various PSD characteristics.

ESTIMATING SAMPLER AND TRUE CONCENTRATIONS

Sampler and true concentrations can be theoretically estimated using PSD and sampler performance characteristics defined in equations 1 through 3. The method of determining sampler concentrations depends on whether the sampler uses a single or multi-stage pre-separator. For instance, most PM₁₀ ambient air samplers are single stage; however, an EPA-approved PM_{2.5} ambient air sampler consists of a PM₁₀ pre-separator and a PM_{2.5} pre-separator. Some PM_{2.5} samplers do not include the PM₁₀ pre-separator. Sampler concentrations for single-stage samplers can be estimated by:

$$C_m(\text{MMD, GSD, } d_{50}, \text{ slope}) = C_a \int_0^{\infty} f(d_p, \text{MMD, GSD}) P_m(d_p, d_{50}, \text{ slope}) dd_p \quad (4)$$

Sampler concentrations for a two-stage sampler can be estimated by:

$$C_{m_2}(\text{MMD, GSD, } d_{50_1}, \text{ slope}_1, d_{50_2}, \text{ slope}_2) = C_a \int_0^{\infty} f(d_p, \text{MMD, GSD}) P_{m_1}(d_p, d_{50_1}, \text{ slope}_1) P_{m_2}(d_p, d_{50_2}, \text{ slope}_2) dd_p \quad (5)$$

For true concentrations, the cumulative penetration efficiency distribution function is assumed to be equal to 1 for all particle sizes less than or equal to the size of interest, and zero for all other particle sizes, as defined in equation 3. Therefore, using equations 1 and 3, the true concentration can be estimated by:

$$C_t(\text{MMD, GSD, } d_{50}) = C_a \int_0^{d_{50}} f(d_p, \text{MMD, GSD}) dd_p \quad (6)$$

RELATIVE DIFFERENCES BETWEEN SAMPLER AND TRUE CONCENTRATIONS

Sampler and true concentrations are not always equal. An estimate of the differences, $E(x)$, between these two concentrations can be defined as:

$$E(x) = \frac{(\text{Sampler} - \text{True})}{\text{True}} = \left(\frac{\text{Sampler}}{\text{True}} \right) - 1 \quad (7)$$

where *Sampler* and *True* are the estimated sampler and true concentrations, respectively. Substituting equations 4 and 6 into equation 7 and canceling like terms yields:

$$E(\text{MMD, GSD, } d_{50}, \text{ slope}) + 1 = \left[\frac{\int_0^{\infty} f(d_p, \text{MMD, GSD}) P_m(d_p, d_{50}, \text{ slope}) dd_p}{\int_0^{d_{50}} f(d_p, \text{MMD, GSD}) dd_p} \right] \quad (8)$$

for a sampler with a single pre-separator. Equation 8 can be further expanded for a multistage pre-separator. Throughout the remaining sections of this article, $E(\text{MMD, GSD, } d_{50}, \text{ slope}) + 1$ will be referred to as the ratio of the sampler to true concentration.

Mathcad 2000 (Mathsoft, Natick, Mass.) was used for the mathematical analyses. Equation 8 was solved for various PSD and sampler performance characteristics in order to obtain an initial concept of how the interaction of these characteristics impacts the concentration ratio. The PSD characteristics included in the evaluation were MMDs of 5 and 10 μm with a GSD of 1.5, and MMDs of 15 and 20 μm with a GSD of 2.0. The sampler performance characteristics included the nine combinations of d_{50} and slope values for the ambient PM_{2.5} sampler, as previously described. In order to further define the differences between the simulated sampler measurements and true PM₁₀ concentrations, equations 4 and 6 were solved for a d_{50} equal to 2.7 μm , slope of 1.33, GSD of 2.0, and MMDs ranging from 1 to 40 μm .

To further describe how the interaction of the PSD and sampler performance characteristics affects the acceptable PM concentrations, a series of calculations was performed to solve equation 8 over a range of parameters. These PSD parameters included MMD values ranging from 1 to 40 μm (in increments of 1 μm) and GSD values ranging from 1.3 to 2.5 (in increments of 0.1). The sampler performance characteristics corresponded to the $\text{PM}_{2.5}$ ambient air sampler with no PM_{10} inlet and the $\text{PM}_{2.5}$ ambient air sampler with a PM_{10} inlet. The sampler performance characteristics also corresponded to the parameters defining the boundary tolerance ranges for the individual samplers. For example, d_{50} values of 9.5 and 10.5 μm with slopes of 1.6 and 1.4 were used for the PM_{10} ambient air sampler, as specified by the EPA. Graphs of the results were created to demonstrate how each of the parameters affects the sampler to true concentration ratio.

RESULTS AND DISCUSSION

According to the literature, the EPA's emphasis on the 2.5 μm cutpoint was more closely associated with separating the fine and coarse atmospheric aerosol modes than mimicking a respiratory deposition convention (USEPA, 1996b). This emphasis is apparent when the penetration curve associated with the $\text{PM}_{2.5}$ ambient air sampler is compared to the American Conference of Governmental Industrial Hygienists (ACGIH) respirable fraction of PM, as shown in figure 1. The EPA's $\text{PM}_{2.5}$ cumulative penetration data set for Class II $\text{PM}_{2.5}$ candidate samplers produced a relatively smooth curve; however, the curve appeared to have a larger slope associated with particle sizes less than 2.5 μm AED than the slope associated with particle sizes larger than 2.5 μm AED.

According to 40 CFR Part 53, a candidate sampler passes the sampling effectiveness test if the expected mass concentration calculated for the candidate sampler differs by no more than $\pm 5\%$ from that predicted for the ideal sampler when using the idealized coarse aerosol, idealized "typical" coarse aerosol, and idealized fine coarse aerosol size distributions (CFR, 2001e). The results of the comparison of the nine sampler performance criteria used in this research to that of the EPA's ideal sampler are shown in table 1. All the penetration curves evaluated passed the sampler effectiveness tests for the "typical" coarse and fine coarse aerosol size distributions; however, not all curves passed the test for the coarse aerosol size distribution. The penetration curve defined by a d_{50} of 2.5 μm and a slope of 1.33 and all curves defined by a d_{50} of 2.7 μm failed the sampler effectiveness test for the coarse aerosol size distribution (i.e., deviated from the EPA idealized sampler by more than 5%). Although some of the penetration curves generated from d_{50} values of $2.5 \pm 0.2 \mu\text{m}$ and slope values of 1.3 ± 0.03 failed the sampler effectiveness tests, these performance criteria ranges were used throughout the remainder of this research effort since these ranges have been observed in the actual evaluation of EPA-approved $\text{PM}_{2.5}$ samplers.

Based on the ambient $\text{PM}_{2.5}$ sampler performance criteria used in this article, four combinations of d_{50} and slope values were used to define boundary penetration efficiency curves. These penetration curves were defined with d_{50} values of 2.3 and 2.7 μm and slope values of 1.27 and 1.33. Figure 2 illustrates the comparison of the boundary penetration curves and the EPA ideal $\text{PM}_{2.5}$ sampler penetration efficiency curve. The ideal penetration curve was encompassed by the boundary penetration curves for particle diameters less than about 2.7 μm and was outside of the boundary curves for particle diameters greater than 2.7 μm .

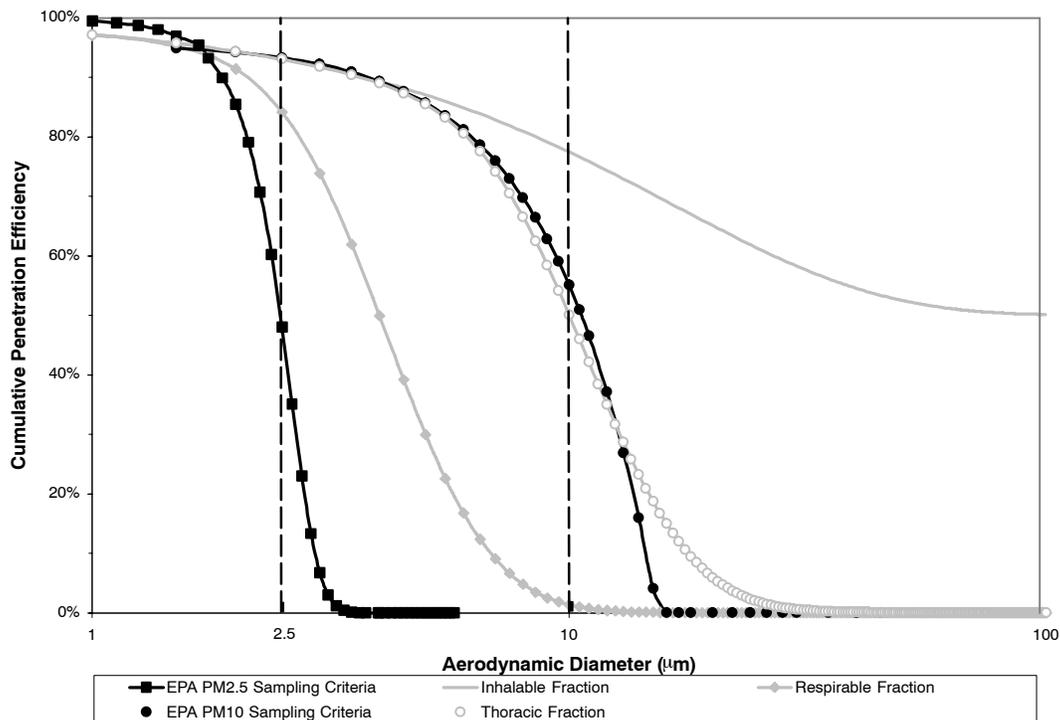


Figure 1. EPA ideal PM_{10} and $\text{PM}_{2.5}$ sampler penetration curves overlaid on the ACGIH sampling criteria for inhalable, thoracic, and respirable fractions of PM (ACGIH, 1997; CFR, 2001d, 2001e).

Table 1. Estimated PM_{2.5} mass concentration ratios between sampler performance characteristics and the EPA idealized sampler.

| Coarse Aerosol | | | "Typical" Coarse Aerosol | | | Fine Aerosol | | |
|----------------|-------|-----------|--------------------------|-------|-----------|---------------|-------|-----------|
| Cutpoint (μm) | Slope | Ratio (%) | Cutpoint (μm) | Slope | Ratio (%) | Cutpoint (μm) | Slope | Ratio (%) |
| 2.3 | 1.27 | 100 | 2.3 | 1.27 | 100 | 2.3 | 1.27 | 99 |
| 2.3 | 1.30 | 100 | 2.3 | 1.30 | 100 | 2.3 | 1.30 | 99 |
| 2.3 | 1.33 | 101 | 2.3 | 1.33 | 100 | 2.3 | 1.33 | 98 |
| 2.5 | 1.27 | 104 | 2.5 | 1.27 | 101 | 2.5 | 1.27 | 101 |
| 2.5 | 1.30 | 105 | 2.5 | 1.30 | 101 | 2.5 | 1.30 | 100 |
| 2.5 | 1.33 | 106 | 2.5 | 1.33 | 102 | 2.5 | 1.33 | 100 |
| 2.7 | 1.27 | 109 | 2.7 | 1.27 | 103 | 2.7 | 1.27 | 102 |
| 2.7 | 1.30 | 110 | 2.7 | 1.30 | 103 | 2.7 | 1.30 | 102 |
| 2.7 | 1.33 | 111 | 2.7 | 1.33 | 103 | 2.7 | 1.33 | 102 |

When comparing the boundary penetration efficiency curves in figure 2, it is apparent that there is an acceptable range of penetration efficiencies for the PM_{2.5} ambient air sampler. The acceptable range of penetration efficiencies for a particle size of 2.5 μm AED is 36% to 63%. In other words, the uncertainty associated with the performance characteristics of a PM_{2.5} ambient air sampler when sampling 2.5 μm particles is ±16.5%. These ranges are considered one form of inherent error associated with PM_{2.5} ambient air samplers.

Table 2 shows estimates of the ratios of sampler to true concentrations for the ambient PM_{2.5} sampler, based on equation 8. In addition, table 2 shows estimates for sampler concentrations under the assumption that the current regulated limit is based on a sampler concentration and that the regulation should be based on a true concentration. In other words, the NAAQS are based on sampler concentrations; however, the NAAQS should be based on true concentrations so that all industries are equally regulated. The mathematical definition for this assumption is:

$$C_{Acceptable} = Ratio * C_{NAAQS} \quad (9)$$

where C_{NAAQS} is the current concentrations associated with the NAAQS, and $C_{acceptable}$ is the acceptable concentrations if the NAAQS were based on true concentrations. Table 2

shows that: (1) the range of PM_{2.5} sampler performance characteristics used (from d_{50} of 2.3 μm with slope of 1.27 to d_{50} of 2.7 μm with slope of 1.33) define the range of acceptable concentrations for the PSDs characterized by MMDs greater than 2.5 μm, and (2) the ratios of sampler to true concentrations ranged from 108% to 1314%. This initial evaluation was expanded to incorporate a larger range of MMDs and GSDs for the PM_{2.5} ambient air sampler.

Results of the expanded simulation for the wider range of MMDs (ranging from 1 to 40 μm) are illustrated in figure 3. In figure 3, three MMDs are highlighted. The first (5.7 μm) corresponds to the MMD associated with urban dust as defined by the EPA, and the other two (15 to 25 μm) correspond to MMDs encompassing the range expected from agricultural-type dusts. When comparing the sampler to true concentrations for the urban dust, the sampler concentration is about 33% [i.e., (true percent less than 5.7 μm – sampler percent less than 5.7 μm) / (true percent less than 5.7 μm)] higher than the true concentration. Further, when comparing the sampler to true concentrations for the range of agricultural-type dusts, the sampler concentrations were 120% to 2400% higher than the true concentrations.

Figure 4 shows the sampler to true concentration ratios for the two sets of PM_{2.5} sampler (no PM₁₀ inlet) performance

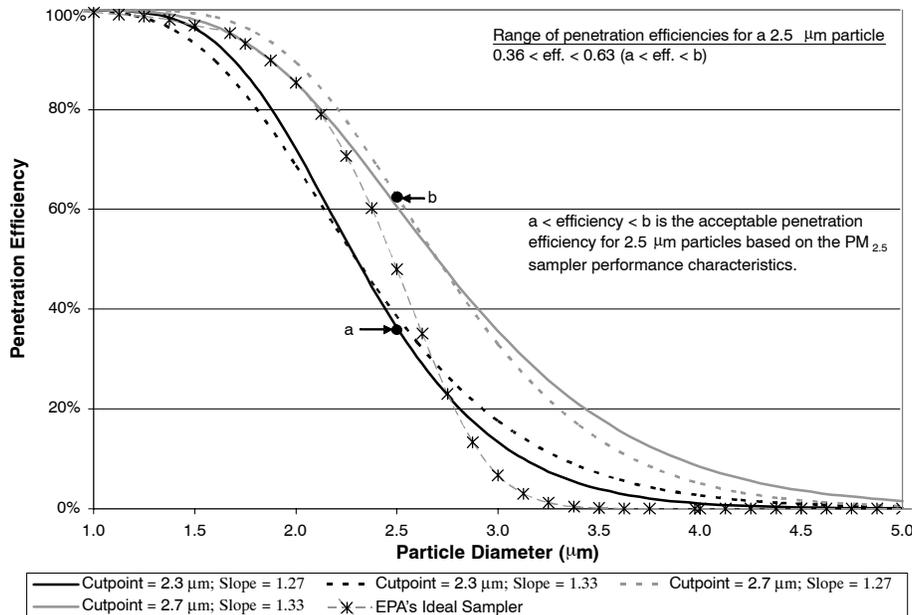


Figure 2. PM_{2.5} sampler penetration curves based on the defining performance characteristics.

Table 2. Concentration ratios of the theoretical sampler to true concentrations for various particle size distributions and sampler performance characteristics.

| Sampler Characteristics | | Particle Size Distribution Characteristics | | | | | | | |
|----------------------------|-------|--|---|--------------------------|---|--------------------------|---|--------------------------|---|
| | | GSD = 1.5 | | | | GSD = 2.0 | | | |
| | | MMD = 5 μm | | MMD = 10 μm | | MMD = 15 μm | | MMD = 20 μm | |
| Cutpoint (μm) | Slope | Ratio (%) ^[a] | PM _{2.5} Conc. ($\mu\text{g}/\text{m}^3$) ^[b] | Ratio (%) ^[a] | PM _{2.5} Conc. ($\mu\text{g}/\text{m}^3$) ^[b] | Ratio (%) ^[a] | PM _{2.5} Conc. ($\mu\text{g}/\text{m}^3$) ^[b] | Ratio (%) ^[a] | PM _{2.5} Conc. ($\mu\text{g}/\text{m}^3$) ^[b] |
| 2.3 | 1.27 | 113.3 | 73.65 | 285.3 | 185.45 | 108.3 | 70.40 | 117.8 | 76.57 |
| 2.3 | 1.30 | 123.5 | 80.28 | 372.6 | 242.19 | 117.1 | 76.12 | 130.4 | 84.76 |
| 2.3 | 1.33 | 134.2 | 87.23 | 482.0 | 313.30 | 126.9 | 82.49 | 144.7 | 94.06 |
| 2.5 | 1.27 | 161.2 | 104.78 | 531.3 | 345.35 | 149.3 | 97.05 | 169.1 | 109.92 |
| 2.5 | 1.30 | 173.1 | 112.52 | 652.1 | 423.87 | 160.4 | 104.26 | 186.0 | 120.90 |
| 2.5 | 1.33 | 185.5 | 120.58 | 821.8 | 534.17 | 172.7 | 112.26 | 204.9 | 133.19 |
| 2.7 | 1.27 | 218.1 | 141.77 | 860.1 | 559.07 | 198.7 | 129.16 | 233.8 | 151.97 |
| 2.7 | 1.30 | 231.2 | 150.28 | 1066.9 | 693.49 | 212.4 | 138.06 | 255.4 | 166.01 |
| 2.7 | 1.33 | 244.8 | 159.12 | 1314.0 | 854.10 | 227.4 | 147.81 | 279.6 | 181.74 |

[a] Values are based on the assumption that true concentrations are the correct estimates of the corresponding PM concentrations.

[b] Concentrations are based on the corresponding regulations and adjusted by the ratio. Sampler concentrations for PM_{2.5} are 65 $\mu\text{g}/\text{m}^3$.

characteristics that define the acceptable concentrations for PM_{2.5}, GSD = 2.0, and PSD MMDs ranging from 1 to 40 μm . To aid in the interpretation of the graph, an average concentration ratio is defined as the average of the largest and smallest ratios for a particular MMD. The information presented in figure 4 shows that: (1) the average ratio is equal to 1.0 when the MMD is equal to the d_{50} , (2) the average ratio is greater than 1.0 when the MMD is greater than the d_{50} , and (3) the ratio range increases as the MMD increases. In general terms, when the ratio is equal to 1.0, the current method of regulating PM_{2.5} results in an exact concentration measurement of PM less than or equal to 2.5 μm AED, and when the ratio is greater than 1.0, the current method overestimates the concentration of PM less than 2.5 μm AED. For example, if a PSD were characterized by an MMD of 5.7 μm and a GSD of 2.0, then the acceptable range of PM_{2.5} sampler concentrations to be in compliance with the property-line concentration limits would be 60 to 87 $\mu\text{g}/\text{m}^3$ (i.e., ratios of 0.92 and 1.34 obtained from figure 4 and multiplied by 65 $\mu\text{g}/\text{m}^3$, the proposed NAAQS for PM_{2.5}). In this scenario, the PM_{2.5} sampler uncertainty is $\pm 13.5 \mu\text{g}/\text{m}^3$, and since the EPA essentially states that the PM_{2.5} NAAQS should correspond to

a true concentration, the PM_{2.5} sampler bias is 8.5 $\mu\text{g}/\text{m}^3$. If the PSD were characterized by an MMD of 10 μm and a GSD of 2.0, then the acceptable range of PM_{2.5} sampler concentrations would be 64 to 115 $\mu\text{g}/\text{m}^3$, with a corresponding PM_{2.5} sampler uncertainty of $\pm 25.5 \mu\text{g}/\text{m}^3$ and a bias of 24.5 $\mu\text{g}/\text{m}^3$. Further, if the PSD were characterized by an MMD of 20 μm and a GSD of 2.0, then the acceptable range of PM_{2.5} sampler concentrations would be 77 to 182 $\mu\text{g}/\text{m}^3$, corresponding to a PM_{2.5} sampler uncertainty of $\pm 52.5 \mu\text{g}/\text{m}^3$ and a bias of 64.5 $\mu\text{g}/\text{m}^3$.

The data presented in figure 5 are based on the same assumptions as figure 4, except the data are based on a GSD of 1.5. When comparing figures 4 and 5, it is obvious that the ratios increase much more rapidly as the MMD increases when the GSD is 1.5 as compared to a GSD of 2.0. For example, if a PSD were characterized by an MMD of 5.7 μm AED and a GSD of 1.5, then the acceptable range of PM_{2.5} sampler concentrations would be 81 to 193 $\mu\text{g}/\text{m}^3$ (i.e., ratios of 1.24 and 2.96 obtained from figure 6 and multiplied by 65 $\mu\text{g}/\text{m}^3$, the proposed NAAQS for PM_{2.5}), corresponding to a PM_{2.5} sampler uncertainty of $\pm 56 \mu\text{g}/\text{m}^3$ and a bias of 72 $\mu\text{g}/\text{m}^3$. If the PSD were characterized by an MMD of

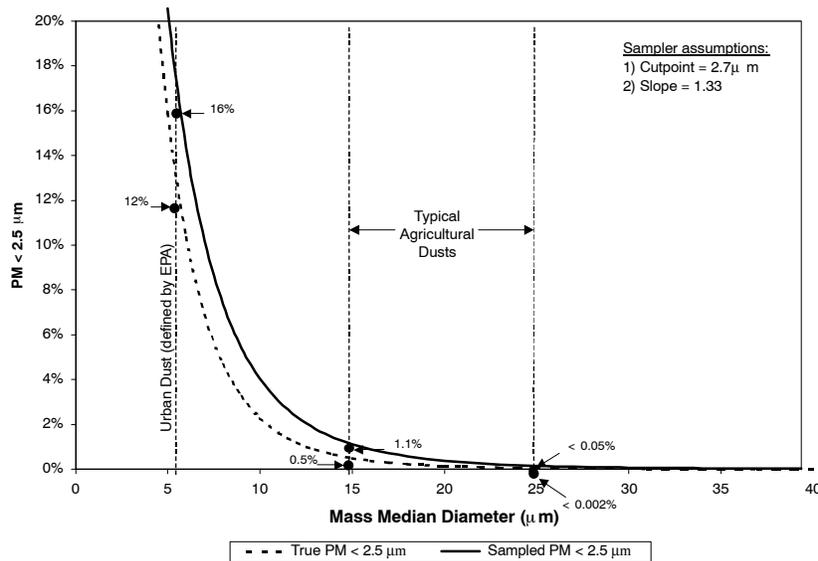


Figure 3. Comparison of sampler and true PM_{2.5} percentages for a range of PSD MMDs and GSD = 2.0.

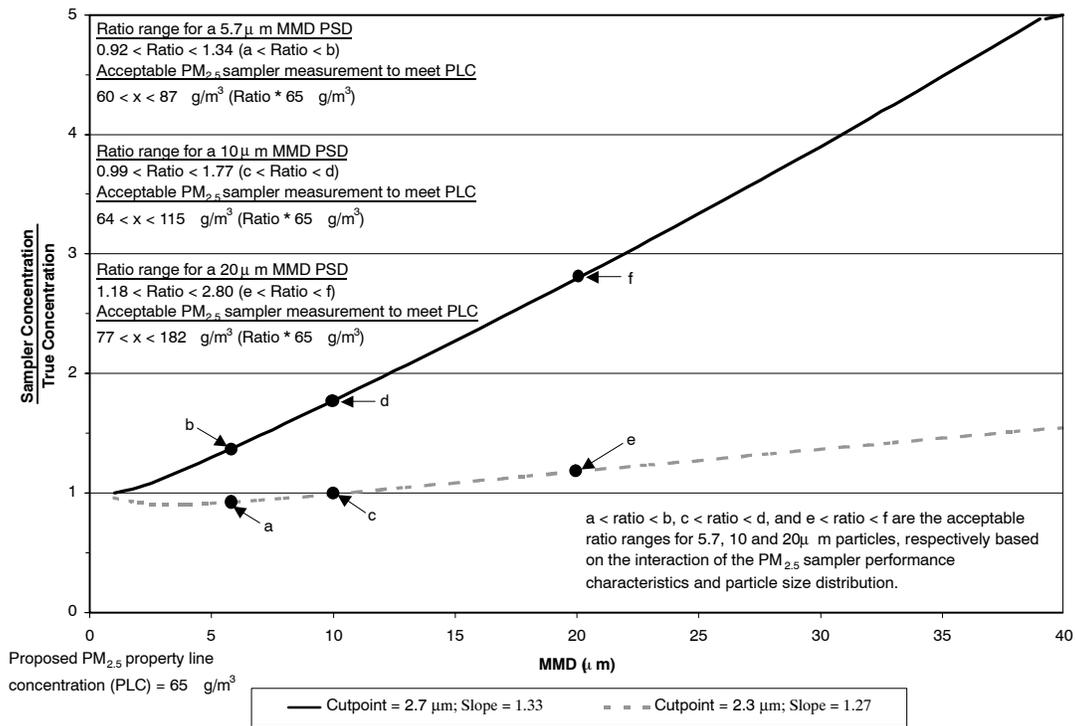


Figure 4. Theoretical ratios of $\text{PM}_{2.5}$ sampler to true PSD concentrations for a range of MMDs and a GSD = 2.0.

10 μm AED and a GSD of 1.5, then the acceptable range of $\text{PM}_{2.5}$ sampler concentrations would be 185 to 854 $\mu\text{g/m}^3$, corresponding to a $\text{PM}_{2.5}$ sampler uncertainty of $\pm 334.5 \mu\text{g/m}^3$ and a bias of 454.5 $\mu\text{g/m}^3$. Further, if the PSD were characterized by an MMD of 20 μm AED and a GSD of 1.5, then the acceptable range of $\text{PM}_{2.5}$ sampler concentrations would be 963 to 11,929 $\mu\text{g/m}^3$, corresponding to a

$\text{PM}_{2.5}$ sampler uncertainty of $\pm 5,483 \mu\text{g/m}^3$ and a bias of 6,381 $\mu\text{g/m}^3$. Thus, the data presented in figures 4 and 5 indicate that the range of acceptable concentrations increases as the GSD increases.

The data presented in figure 6 are based on the same assumptions as figure 4, except the sampler performance characteristics of a PM_{10} inlet are incorporated into the

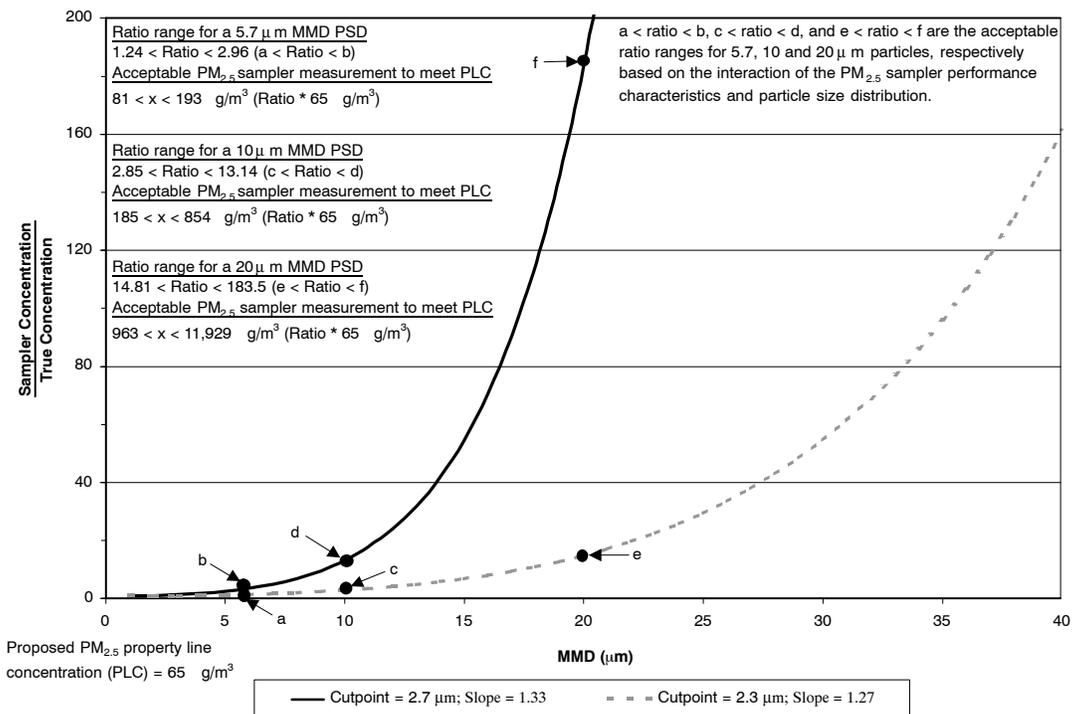


Figure 5. Theoretical ratios of $\text{PM}_{2.5}$ sampler to true PSD concentrations for a range of MMDs and a GSD = 1.5.

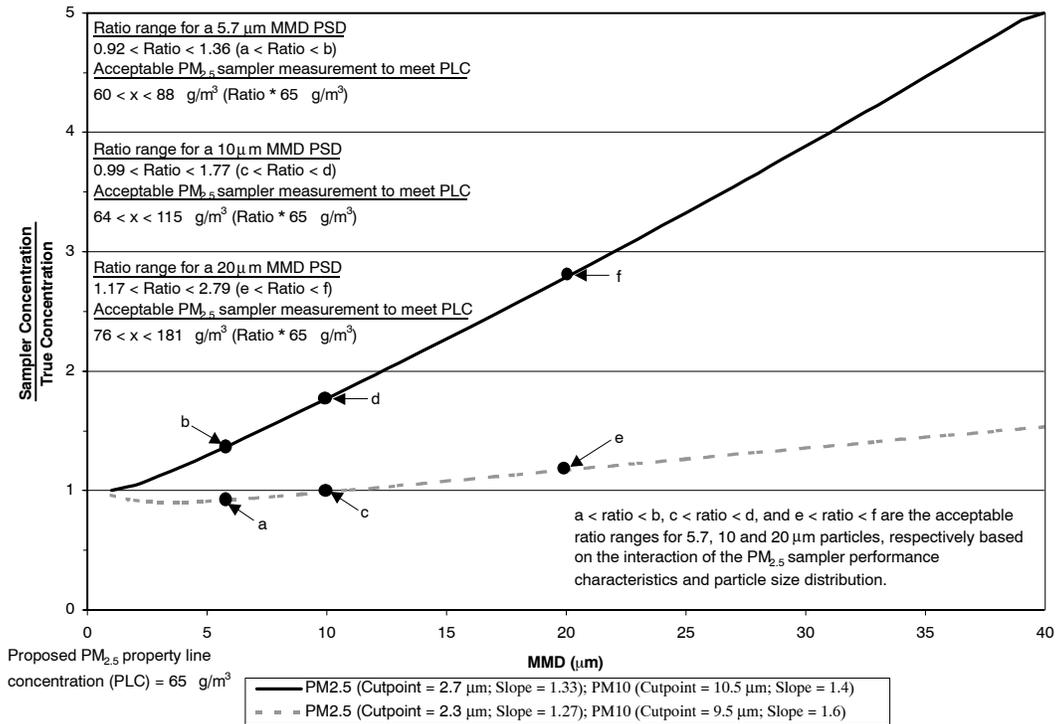


Figure 6. Theoretical ratios of $\text{PM}_{2.5}$ sampler, with PM_{10} inlet, to true PSD concentrations for a range of MMDs and a GSD = 2.0.

simulation. The d_{50} and slope values for the PM_{10} inlet used in the simulation were based on EPA guidelines and were refined through a trial and error process (i.e., determining which PM_{10} d_{50} and slope values coupled with the $\text{PM}_{2.5}$ boundary performance characteristic generated the $\text{PM}_{2.5}$ sampler with PM_{10} inlet boundary performance characteristics). The resulting PM_{10} performance characteristics were

defined as a d_{50} of 9.5 μm with a slope of 1.6, and a d_{50} of 10.5 μm with a slope of 1.4. In general, the inclusion of the PM_{10} inlet on the $\text{PM}_{2.5}$ sampler had very little effect on the sampler to true concentration ratio. For example, if the PSD were characterized by an MMD of 5.7 μm AED and a GSD of 2.0, then the acceptable concentration range for a $\text{PM}_{2.5}$ sampler with a PM_{10} inlet would be 60 to 88 $\mu\text{g/m}^3$ (fig. 6),

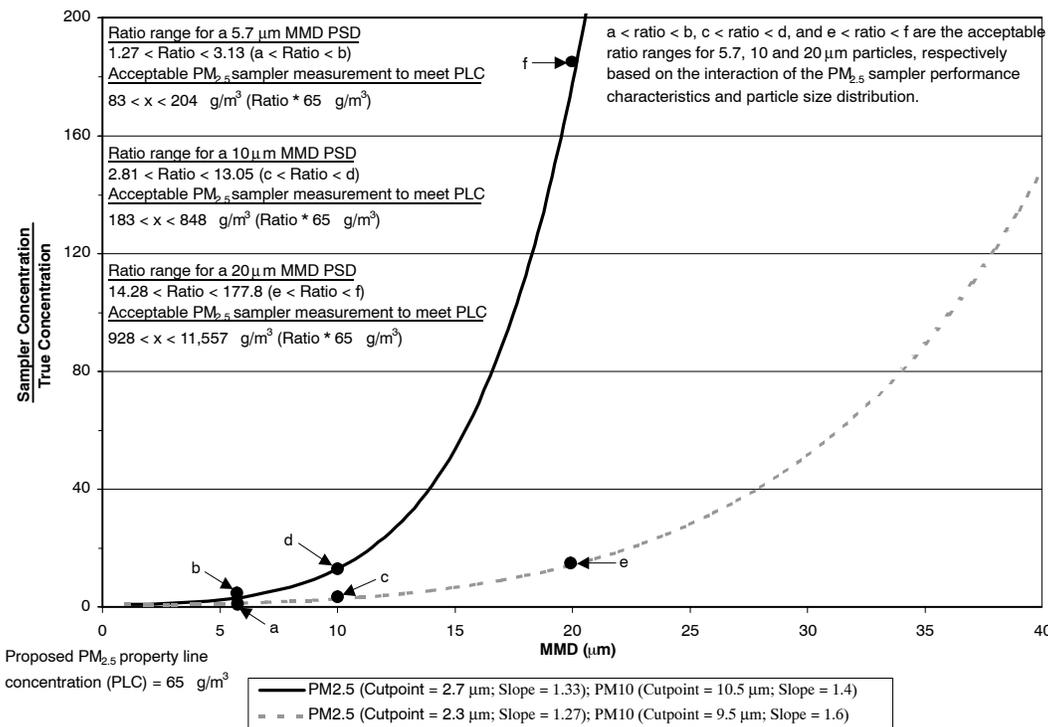


Figure 7. Theoretical ratios of $\text{PM}_{2.5}$ sampler, with PM_{10} inlet, to true PSD concentrations for a range of MMDs and a GSD = 1.5.

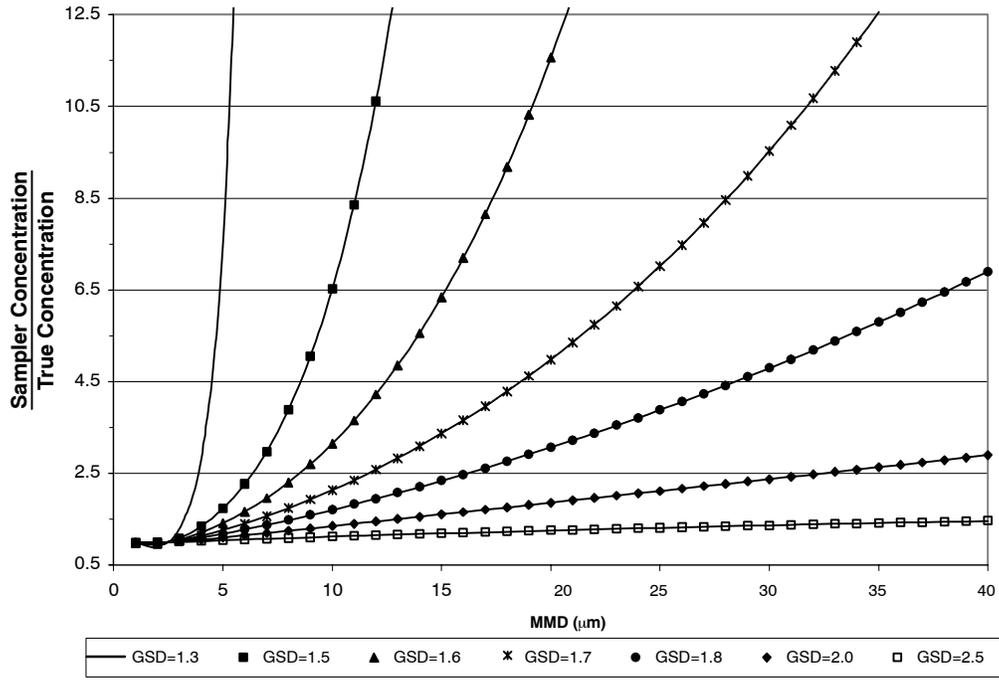


Figure 8. Theoretical ratios of PM_{2.5} sampler measured to true PSD concentrations (PM_{2.5} sampler characteristics: cutpoint = 2.5 μm and slope = 1.3).

as compared to 60 to 87 μg/m³ for a PM_{2.5} sampler with no PM₁₀ inlet (fig. 4). If the PSD were characterized by an MMD of 20 μm AED and a GSD of 2.0, then the acceptable concentration range for a PM_{2.5} sampler with a PM₁₀ inlet would be 76 to 181 μg/m³, as compared to 77 to 182 μg/m³ for a PM_{2.5} sampler with no PM₁₀ inlet.

The data presented in figure 7 are based on the same assumptions as figure 6, except the GSD = 1.5. Comparison of figures 4 and 6 shows that the inclusion of the PM₁₀ inlet

on the PM_{2.5} sampler had very little relative effect on the sampler to true concentration ratio. For example, if the PSD were characterized by an MMD of 5.7 μm AED and a GSD of 1.5, then the acceptable concentration range for a PM_{2.5} sampler with a PM₁₀ inlet would be 83 to 204 μg/m³ (fig. 7), as compared to 81 to 193 μg/m³ for a PM_{2.5} sampler with no PM₁₀ inlet (fig. 5). If the PSD were characterized by an MMD of 20 μm AED and a GSD of 1.5, then the acceptable concentration range for a PM_{2.5} sampler with a PM₁₀ inlet

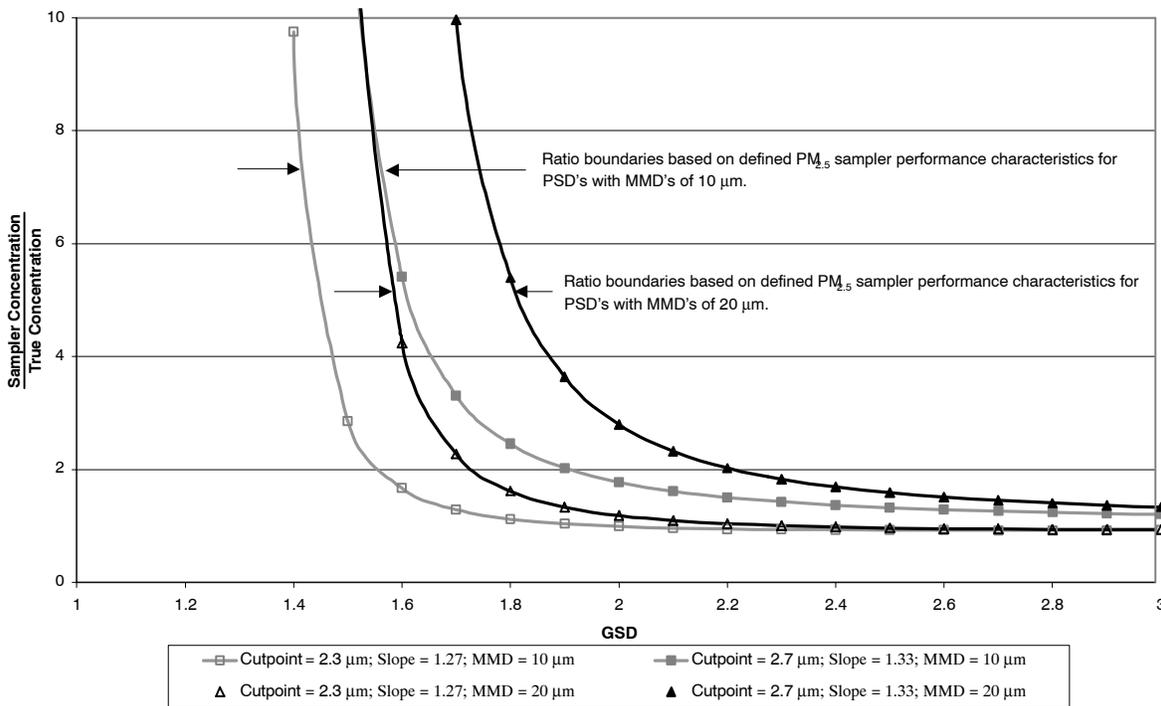


Figure 9. Theoretical PM_{2.5} sampler measured to true concentration ratio boundaries for varying GSDs with MMDs of 10 and 20 μm.

would be 928 to 11,557 $\mu\text{g}/\text{m}^3$, as compared to 963 to 11,929 $\mu\text{g}/\text{m}^3$ for a $\text{PM}_{2.5}$ sampler with no PM_{10} inlet. Although a decrease of 372 $\mu\text{g}/\text{m}^3$, when comparing the $\text{PM}_{2.5}$ sampler with and without a PM_{10} inlet for a PSD characterized by an MMD of 20 μm and a GSD of 1.5, would seem significant, the relative difference is negligible (i.e., only about a 3% decrease). Therefore, only the $\text{PM}_{2.5}$ sampler performance characteristics without the PM_{10} inlet performance characteristics are used in the remainder of the inherent sampler errors discussion.

Figure 8 further illustrates the effect of MMD and GSD on the concentration ratios for a $\text{PM}_{2.5}$ sampler with a d_{50} of 2.5 μm and a slope of 1.3. In general, the concentration ratios decrease (ratio approaches 1.0) as the GSD increases and as MMD decreases. Figure 9 further expands on how the concentration ratios are impacted by GSD. The data presented in figure 9 are based on MMDs of 10 and 20 μm , sampler performance characteristic of a d_{50} equal to 2.3 μm with a slope of 1.27 and a d_{50} of 2.7 μm with a slope of 1.33, and variable GSDs ranging from 1.2 to 3.0. The figure shows that: (1) as the GSD increases, the concentration ratio decreases and approaches 1.0, and (2) as the GSD decreases, the concentration ratio increases and approaches infinity.

SUMMARY AND CONCLUSION

Several errors are associated with the current air pollution rules and regulations established by the EPA that should be minimized to ensure equal regulation of air pollutants between and within all industries. Potentially one of the most significant errors is attributed to the interaction of the industry-specific PSD and sampler performance characteristics. Currently, the regulation of PM is based on sampler measurements and not on true concentrations.

Sampler concentration refers to the concentration collected by a PM sampler. This concentration is dependent on the sampler's performance characteristics (i.e., d_{50} and slope of the sampler penetration curve). Since the concentration is based on the sampler's performance characteristics, there are two inherent errors associated with the measurement. For a $\text{PM}_{2.5}$ sampler, the first error corresponds to the mass of particles less than 2.5 μm that should have been captured on the filter but was removed from the air stream by the pre-separator. The second error (for a $\text{PM}_{2.5}$ sampler) corresponds to the mass of particles greater than 2.5 μm that should have been removed from the air stream by the pre-separator but was allowed to pass through the pre-separator and was captured on the filter. When the MMD of the dust being sampled is less than the sampler d_{50} , under-sampling of the mass of particles less than 2.5 μm occurs. When the MMD of the dust being sampled is equal to the d_{50} of the sampler, the sampler provides a measurement equivalent to the true mass of particles less than 2.5 μm . When the MMD of the dust being sampled is greater than the d_{50} of the sampler, over-sampling of the mass of particles less than 2.5 μm occurs.

True concentration refers to the mass of particles less than or equal to the size of interest. In order for a sampler to provide a true concentration, independent of the MMD of the dust being sampled, the sampler would have to maintain a slope of 1.0 (i.e., the sampler's penetration curve would be represented by a step function).

According to the literature, the EPA decided to regulate $\text{PM}_{2.5}$ based on the availability of the dichotomous sample. The $\text{PM}_{2.5}$ regulation was not based on determining the respirable fraction of PM. ACGIH, ISO, and others have defined the respirable fraction of PM as having a d_{50} between 3.5 and 5 μm . The final justification for using true $\text{PM}_{2.5}$ values as opposed to sampler-based concentration comes from the literature in the following direct quotation:

"Staff also recommended the use of a sharp 2.5 micron cutpoint for a fine particle indicator. $\text{PM}_{2.5}$ does have some potential for intrusion of the tail of the coarse mode during episodes of fugitive dust concentrations. Staff recommends a sharp inlet for the FRM to minimize this potential intrusion of coarse-mode particles. Such intrusion into $\text{PM}_{2.5}$ measurement is not anticipated to be significant in most situations; nevertheless, if subsequent data reveal problems in this regard, this issue can and should be addressed on a case-by-case basis in the monitoring and implementation programs. Because the purpose of a $\text{PM}_{2.5}$ standard is to direct controls toward sources of fine-mode particles, it would be appropriate to develop analytical procedures for identifying those cases where a $\text{PM}_{2.5}$ standard violation would not have occurred in the absence of coarse-mode particle intrusion. Consideration should be given to a policy similar to the natural events policy for addressing such cases" (USEPA, 1996b).

The NAAQS standards correspond to PM in the ambient air (i.e., not impacted by only one source). Therefore, the question becomes, "Is it appropriate to use an EPA-approved ambient $\text{PM}_{2.5}$ sampler to determine emission values from individual sources?" In all situations when the source is emitting PM with an MMD larger than 2.5 μm , the answer is "absolutely not."

So how is this a problem? If a state or air district finds itself in non-attainment with the $\text{PM}_{2.5}$ NAAQS, then the corresponding agencies will, most likely, be required to reduce $\text{PM}_{2.5}$ emissions within the air shed. In order to reduce emissions from individual sources, the amount of PM emitted by the sources must be known or estimated. This is typically accomplished through source sampling or the use of emission factors, which may have been determined from source sampling or interpreted by some other means. In order to illustrate why it is crucial that emission factors, emission rates, and/or emission concentrations from individual sources be based on true $\text{PM}_{2.5}$ and not $\text{PM}_{2.5}$ sampler measurements, the following example is provided.

Assume that EPA-approved $\text{PM}_{2.5}$ ambient air samplers were set up to monitor two commercial operations. Assume also that the samplers have performance characteristics described by a d_{50} of 2.3 μm and a slope of 1.3 (both parameters are within the performance criteria defined by the EPA). Now assume that one operation is a power plant and is emitting PM (sampled by the $\text{PM}_{2.5}$ sampler) that can be described by a lognormal distribution with an MMD of 5 μm and a GSD of 1.8. Assume that the second operation is an agricultural operation and is emitting PM (sampled by the $\text{PM}_{2.5}$ sampler) that can be described by a lognormal distribution with an MMD of 20 μm and a GSD of 1.8. Further, assume that the $\text{PM}_{2.5}$ sampler used to monitor each of the operations measures 50 $\mu\text{g}/\text{m}^3$. Now, based on the methods laid out in this article, the true PM (PM less than 2.5 μm) emitted from each industry would be defined as follows:

Based on a PSD analysis, the percent of PM mass less than 2.5 μm being emitted by the power plant is 11.9%. Based on the PSD and sampler performance characteristics, the percent of total suspended particulate (TSP) captured by the PM_{2.5} sampler is 11.4%. The TSP concentration emitted by the power plant is 439 $\mu\text{g}/\text{m}^3$ (i.e., 50 $\mu\text{g}/\text{m}^3$ (PM measured by the PM_{2.5} sampler) / 0.114 (% of TSP captured by the PM_{2.5} sampler)). By multiplying the TSP concentration by the true fraction of PM_{2.5} (i.e., 439 $\mu\text{g}/\text{m}^3 \times 0.119$), the true PM_{2.5} concentration is determined to be 52 $\mu\text{g}/\text{m}^3$. Therefore, the PM_{2.5} sampler underestimated the true PM_{2.5} concentration by 3.8%.

For the agricultural operation, using the previous procedures, the true percent PM_{2.5} is 0.02%, and based on the PSD and sampler performance characteristics, the percent of TSP captured by the PM_{2.5} sampler is 0.039%. Therefore, the TSP concentration is 128,205 $\mu\text{g}/\text{m}^3$, resulting in the true PM_{2.5} emitted by the operation being equal to 25.6 $\mu\text{g}/\text{m}^3$. In this case, the PM_{2.5} sampler overestimated the true PM_{2.5} by 95%. Based on this scenario, the two operations are not being equally regulated, and the PM_{2.5} ambient air samplers are overestimating the concentration of particles less than 2.5 μm that are being emitted by the operations.

Looking at the issue from another viewpoint, assume that the two operations described previously are emitting 60 $\mu\text{g}/\text{m}^3$ true PM_{2.5}. If the percent of TSP measured by the PM_{2.5} sampler (defined as measured PM_{2.5}) is divided by the percent of true PM_{2.5}, and this ratio is then multiplied by the true concentration of PM_{2.5} being emitted, the PM_{2.5} sampler concentrations can be determined. For the power plant, the PM_{2.5} sampler would measure a concentration of 58 $\mu\text{g}/\text{m}^3$. For the agricultural operation, the PM₁₀ sampler would measure a concentration of 116 $\mu\text{g}/\text{m}^3$. What this means for the agricultural operation is that 60 $\mu\text{g}/\text{m}^3$ of the PM being sampled is less than 2.5 μm and 56 $\mu\text{g}/\text{m}^3$ of the PM being sampled is larger than 2.5 μm . Therefore, regarding the question, "Is it appropriate to use PM_{2.5} samplers to determine PM_{2.5} emission values from industries that are emitting PM with an MMD larger than 2.5 μm ?", the answer is "absolutely not."

Results of the analysis presented in this article show that all industries are not being equally regulated in terms of PM_{2.5} and that all industries should be concerned with the current site-specific regulations implemented by the EPA and enforced by SAPRAs.

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ESTIMATING FRM PM₁₀ SAMPLER PERFORMANCE CHARACTERISTICS USING PARTICLE SIZE ANALYSIS AND COLLOCATED TSP AND PM₁₀ SAMPLERS: COTTON GINS

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ABSTRACT. *In the U.S., regional air quality compliance with national ambient air quality standards (NAAQS) for particulate matter (PM) is based on concentration measurements taken by federal reference method (FRM) samplers. The EPA specifies the performance criteria for the FRM samplers. These criteria for the FRM PM₁₀ samplers are defined as a cutpoint and slope of $10 \pm 0.5 \mu\text{m}$ and 1.5 ± 0.1 , respectively. It is commonly assumed that the performance characteristics of the FRM PM₁₀ sampler do not vary and are independent of the PM characteristics. Several sources have observed errors in the concentrations measured by the FRM PM₁₀ samplers and have suggested that shifts in the sampler performance characteristics may lead to the observed concentration measurement errors. Limited work has been conducted on quantifying the shift in the performance characteristics of the FRM PM₁₀ sampler operating under field conditions. Recent work at a south Texas cotton gin showed that true PM₁₀ concentrations were 55% of the concentrations measured by the FRM PM₁₀ sampler. If the FRM PM₁₀ sampler were operating within the performance criteria range specified by the EPA, then the true concentrations would be within approximately 12% of the concentrations measured by the FRM PM₁₀ sampler. The focus of this work was to quantify the shifts in the cutpoint and slope of the penetration curve of the FRM PM₁₀ sampler. Results show that the cutpoint and slope of the FRM PM₁₀ sampler shifted substantially and ranged from 13.8 to 34.5 μm and from 1.7 to 5.6, respectively, when exposed to large PM as is characteristic of agricultural sources. These shifts in the cutpoint and slope of the FRM PM₁₀ sampler resulted in overestimation of true PM₁₀ concentrations by 145% to 287%.*

Keywords. *Cutpoint, Particulate matter, Penetration curve, PM₁₀ sampler, Slope, TSP sampler.*

In the U.S., a PM₁₀ sampler is classified as having a particulate matter (PM) penetration curve with a cutpoint of 10 μm (USEPA, 2003). The EPA defines the PM₁₀ size fraction based on the aerodynamic equivalent diameter (AED) of particles capable of penetrating to the thoracic region of the respiratory system (USEPA, 1987). This definition was followed by the implementation of EPA's PM₁₀ Ambient Air Monitoring Reference and Equivalent Methods regulation. The Equivalent Method regulation format included the adoption of performance specifications for aerosol samplers based on controlled wind tunnel testing with mono-dispersed aerosols (USEPA, 1996).

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PM₁₀ samplers are designated by the EPA as reference or equivalent methods under the provisions of Title 40 of the Code of Federal Regulations (40 CFR), Part 53 (CFR, 2001a). PM₁₀ federal reference method (FRM) samplers must use the measurement principle and meet additional specifications set forth in 40 CFR, Part 50, Appendix J (CFR, 2001b) and also meet the requirements specified in 40 CFR, Part 53, Subpart D. Appendix J specifies a measurement principle based on extracting an air sample from the atmosphere with a sampler that incorporates inertial separation of the PM₁₀ size range particles followed by collection of the PM₁₀ particles on a filter over a 24-hour period. Alternatively, equivalent PM₁₀ sampling methods are not required to conform to the measurement principle specified in Appendix J or meet the additional Appendix J requirements (USEPA, 1996). Instead, equivalent PM₁₀ sampling methods must meet the performance specifications set forth in 40 CFR, Part 53, Subpart D and demonstrate comparability to a reference method as required by 40 CFR, Part 53, Subpart C.

A number of samplers have been designated as PM₁₀ reference or equivalent method samplers (USEPA, 2001). Mass concentration measurements with reproducibility close to 10% have been obtained with collocated samplers of identical design (USEPA, 1996). However, field studies of collocated EPA-approved PM₁₀ samplers have shown substantial errors under certain conditions. These errors result from (1) allowing a tolerance of $\pm 0.5 \mu\text{m}$ for the 10 μm cutpoint; (2) cutpoint deviations, beyond the established tolerances, associated with various field application parameters; (3) inadequate restrictions on internal particle bounce; (4) surface

overloading; (5) soiling of certain types of PM₁₀ inlets; and (6) losses of semivolatile components. According to the USEPA (1996), the most significant performance flaws have combined to produce excessive (up to 60%) mass concentration errors.

Watson et al. (1983) affirmed that EPA's PM₁₀ performance specifications allowed a cutpoint tolerance range that could allow inlets to be "fine tuned," suggesting that the cutpoint could be adjusted to the lower or upper end of the range to suit particular sampling needs. For example, a reduction in reported concentration could be achieved by simply using a lower (e.g., 9.5 μm) cutpoint inlet that is still within the acceptable cutpoint range. Errors between acceptable samplers in the data from sampler comparison studies (Rodes et al., 1985; Purdue et al., 1986; Thanukos et al., 1992) were normally less than 10%, although some differences greater than 30% were reported. The reports suggest that the collection efficiency of high-volume PM₁₀ sampler inlets based on cyclonic separation (Wedding, 1985) were consistently lower than those based on low-velocity impaction (McFarland et al., 1984).

Wang and John (1988) were critical of the EPA's PM₁₀ performance specification on allowable particle bounce (Federal Register, 1987), stating that the criteria can lead to a 30% overestimation of mass under worst-case conditions. In a related article, John et al. (1991) reported that although re-entrainment of particles deposited in a sampler inlet by air-flow alone is typically negligible, re-entrainment caused from subsequent particle de-agglomeration caused by "bombardment" can be substantial. John and Wang (1991) suggested that particle loading on oiled deposition surfaces can affect particle collection and suggested that periodic cleaning and re-oiling should be required for PM₁₀ inlets. Vanderpool et al. (2001) reported that particle bounce at an impaction surface occurred when the collection surface was unable to completely absorb the kinetic energy of the incident particle and if this inelastic collision occurs, then the particle is not retained by the surface and can bias the size distribution measurement towards smaller aerodynamic sizes.

Shifts in sampler cutpoint, attributed to soiling, have also been reported for cyclonic separators. Blachman and Lippmann (1974) reported that the performance of a nylon cyclone with a reported cutpoint of 10 μm was affected by loading, and the accumulation of particle deposits increased the collection efficiency (i.e., reduced the cutpoint). Tsai et al. (1999) determined that the penetration efficiency for a cyclone with a reported cutpoint of 10 μm was reduced from 97% to 71% for 3.06 μm diameter particles after a 0.4 mg loading. Ono et al. (2000) reported that dichotomous, Graseby, and Wedding samplers measured significantly lower PM₁₀ concentrations than a TEOM (on average, 10%, 25%, and 35% lower, respectively) when operating in a location with high PM coarse concentration and attributed these lower concentrations to a decrease in cutpoint caused by wind speeds and cleanliness of the inlet.

FRM PM₁₀ samplers have been shown to produce concentration errors when sampling PM with mass median diameter (MMD) different from the sampler cutpoint. Wang et al. (2003) evaluated Graseby-Andersen FRM PM₁₀ samplers in a controlled chamber where the samplers were exposed to treatments of dispersed cornstarch, fly ash, and aluminum oxide. The Graseby-Andersen FRM PM₁₀ sampler oversampled the dispersed cornstarch, fly ash, and aluminum ox-

ide by an average of 89%, 41%, and 14%, respectively, and the average cutpoint and slope for the Graseby-Andersen sampler was 12.5 μm and 1.3 when sampling cornstarch, 17.7 μm and 1.5 when sampling fly ash, and 17 μm and 1.5 when sampling aluminum oxide. Wang et al. (2003) concluded that the sampler's fractional efficiency curve shifted to the right when sampling PM with smaller MMDs.

Buser (2004) conducted extensive mathematical simulations to illustrate the theoretical errors associated with EPA-approved ambient PM₁₀ samplers. Mathematical estimates showed that a sampler, described by a d_{50} of 10.5 μm and a slope of 1.6 (both parameters are within the performance criteria defined by EPA), monitoring a source emitting 100 μg m⁻³ of fine PM described by a lognormal distribution with a MMD of 5 μm and a geometric standard deviation (GSD) of 1.5 and another source emitting 100 μg m⁻³ of larger PM described by a lognormal distribution with a MMD of 20 μm and a GSD of 1.5 would underestimate the true PM₁₀ concentration of the fine PM by 8% and overestimate the true PM₁₀ concentration of the larger PM by 245%.

Capareda et al. (2005) reported that the true PM₁₀ concentrations measured downwind of a Texas cotton gin were 55% of the concentrations measured by an FRM PM₁₀ samplers. Further review of the particle density data indicated that the particle density was 2.62 g cm⁻³ instead of the reported 2.12 g cm⁻³. Corrections for particle density showed that the true PM₁₀ concentrations were actually 51% of the concentrations measured by the FRM PM₁₀ sampler. Figure 1 shows the relationship between the true and FRM PM₁₀ sampler concentrations as reported by Capareda et al. (2005) and the theoretical relationship between the true concentration and concentrations measured with an EPA FRM sampler operating according to design criteria (cutpoint of 10 ± 0.5 μm and slope of 1.5 ± 0.1). The shift of the regression line representing the relationship measured by Capareda et al. (2005) to the right of the theoretical relationship indicates that the performance characteristics of the FRM PM₁₀ sampler shifted, resulting in sampling errors larger than those expected from EPA-approved PM₁₀ samplers.

The purpose of an FRM PM sampler is to accurately measure the concentration of specific ranges of particle sizes that exist in the atmosphere. As no calibration standards for suspended particle mass exist, the EPA defines accuracy for PM measurements in terms of the agreement between a candidate sampler and a reference sampler under standardized conditions for sample collection, storage, and analysis (USEPA, 1996, 2001). Therefore, sampler comparisons become very important in determining the reproducibility of sampler measurements (measurement precision, as defined by EPA) and how sampler designs influences accuracy (USEPA, 2001). The objective of this research was to investigate the changes in performance criteria (cutpoint and slope) of an FRM PM₁₀ sampling inlet when sampling high concentrations of cotton gin PM.

METHODS

Concentration data used in this work were taken from the study conducted by Capareda et al. (2005). PM emitted from a Texas cotton gin was sampled using collocated low-volume (16.67 L min⁻¹ flow rate) total suspended particulate (TSP) and PM₁₀ samplers. The TSP sampler inlets were designed

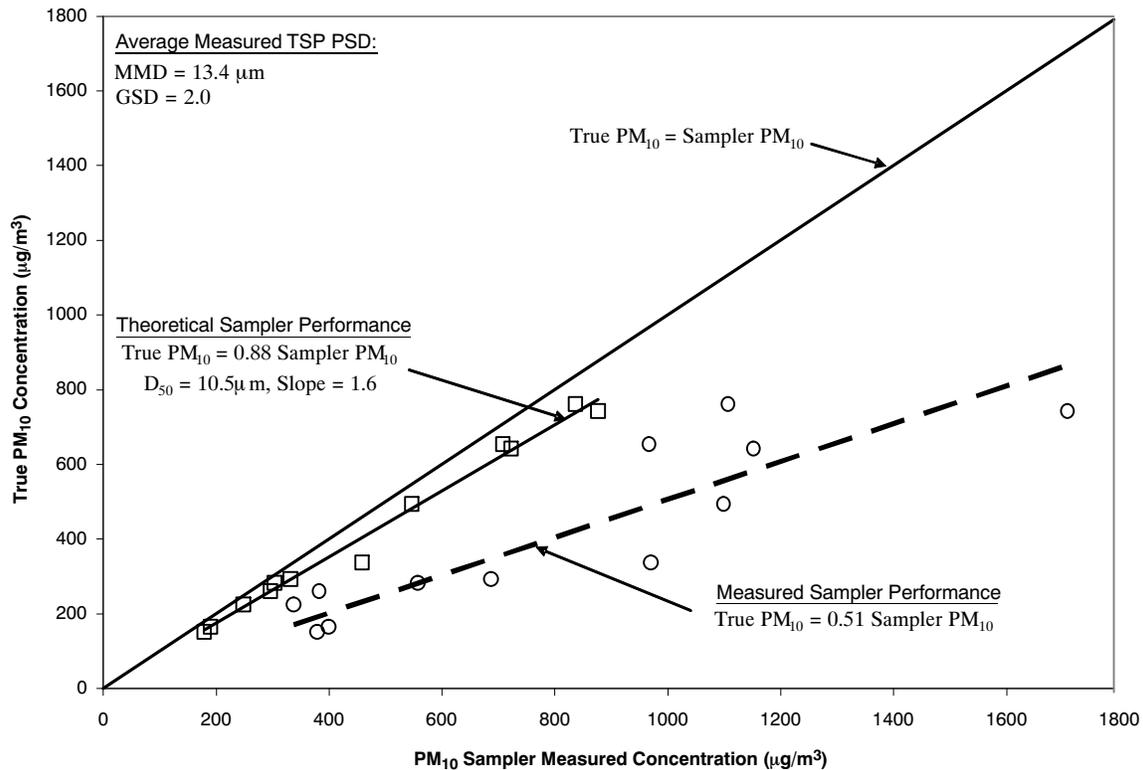


Figure 1. True PM₁₀ concentrations versus measured PM₁₀ sampler concentrations as determined by Capareda et al. (2005), corrected for particle density, and on a theoretical basis assuming the PM₁₀ sampler was operating with cutpoint = 10.5 µm and slope = 1.6 for PM with average measured MMD = 13.4 µm and GSD = 2.0.

by Texas A&M University (Wanjura et al., 2005) and the PM₁₀ samplers incorporated a Graseby-Andersen FRM PM₁₀ inlet. The systems used to establish and control the flow rate of the TSP and PM₁₀ samplers were identical. A 0.09 kW (1/8 hp) diaphragm pump was used to draw the 16.67 L min⁻¹ sample flow rate through the sampler inlet head. The airflow rate was indicated by a Magnehelic gauge (Dwyer Instruments, Michigan City, Ind.) measuring pressure drop across the sharp-edge orifice and recorded with a differential pressure transducer (PX274, Omega Engineering, Inc., Stamford, Conn.) and data logger (HOBO H8 RH/Temp/2x External, Onset Computer Corp, Pocasset, Mass).

The TSP and PM₁₀ samplers used 47 mm diameter Zeflur membrane filters (Pall Corporation, East Hills, N.Y.). The filters were conditioned prior to weighing before and after exposure in an environmental chamber for a minimum of 48 hours at 21 °C (70 °F) and 35% RH. The concentrations were calculated from the net filter mass and the measured airflow volume during the tests according to Capareda et al. (2005). A detailed description of the sampling locations and sampling protocol is given by Capareda et al. (2005).

Particle size distribution analyses were conducted on each of the TSP and PM₁₀ filters using the procedure described by Buser (2004). The results were reported in terms of percent volume versus equivalent spherical diameter (ESD). The PSD results were left in terms of ESD and not converted to AED because the effects of particle density and shape factor cancel out of the final equations used to determine the PM₁₀ sampler's cutpoint and slope.

The PSD of the data was expected to follow a lognormal distribution characterized by the MMD and the GSD (Hinds, 1999). The MMD is the particle diameter for which 50% of

the particle mass is comprised of particles with smaller diameter and the remaining 50% is comprised of particles with larger diameter. The GSD describes the spread of the distribution. For mono-disperse particles, the GSD is equal to 1 and for poly-disperse particles, the GSD is >1. The GSD is defined as:

$$GSD = \sqrt{\frac{d_{84.1}}{d_{15.9}}} \quad (1)$$

where $d_{15.9}$ and $d_{84.1}$ are the particle diameters (µm) corresponding to the 15.9% and 84.1% cumulative collection efficiencies obtained from the PSD.

The lognormal mass density function is defined as:

$$f(d_p, MMD, GSD) = \frac{1}{d_p \ln GSD \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln MMD)^2}{2(\ln GSD)^2} \right] \quad (2)$$

where d_p is particle diameter (µm).

The percent mass between two particle diameters can be found by integrating equation 2 between the two given particle diameters. Equation 3 gives the percent mass between particle diameters a and b :

$$f_{ab}(a, b, MMD, GSD) = \int_a^b f(d_p, MMD, GSD) dd_p \quad (3)$$

The true PM₁₀ concentration can be determined from a TSP sample by multiplying the TSP concentration by the percent mass less than 10 µm from the PSD (Buser et al.,

2002). The percent mass less than 10 μm can be found from equation 3 by setting $a = 0$ and $b = 10 \mu\text{m}$.

The efficiency of PM samplers is typically discussed in terms of collection efficiency or penetration efficiency, which are directly related. Collection efficiency refers to the sampler's ability to capture certain size particles, not allowing the particles to pass through to the sampler's filter media. Mathematically, collection efficiency is defined as:

$$CE(d_p, d_{50}, slope) = \frac{1}{d_p \ln(slope) \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln d_{50})^2}{2(\ln(slope))^2} \right] \quad (4)$$

where $CE(d_p, d_{50}, slope)$ is the collection efficiency of particle diameter d_p .

According to Hinds (1982), the collection efficiency curve for an FRM PM₁₀ sampler is described by a lognormal distribution with a cutpoint (d_{50}) of $10 \pm 0.5 \mu\text{m}$ and slope of 1.5 ± 0.1 .

Penetration efficiency refers to the efficiency of particles to pass through the sampler's collection mechanism (e.g., impactor or cyclone) and be deposited on the filter media. Penetration efficiency is defined as:

$$PE(a, d_{50}, slope) = 1 - \int_0^a fec(d_p, d_{50}, slope) dd_p \quad (5)$$

where $PE(a, d_{50}, slope)$ is the penetration efficiency for particles with a diameter of d_p .

The particulate mass concentration on a PM₁₀ sampler filter can be calculated by combining equations 2 and 5 such that:

$$C_{PM10} = C_{TSP} \int_0^\infty (f_{TSP}(d_p, MMD, GSD) \times (PE_{PM10}(d_p, d_{50}, slope))) dd_p \quad (6)$$

where

- C_{PM10} = mass concentration of PM that penetrated the PM₁₀ sampler and was deposited on the filter
- C_{TSP} = TSP filter concentration
- $f_{TSP}(d_p, MMD, GSD)$ = PSD of the PM on the TSP filter
- PE_{PM10} = penetration efficiency of the PM₁₀ sampler.

The mass density function of the PM on a PM₁₀ sampler filter (f_{PM10}) is related to the ambient PSD and the PM₁₀ sampler penetration efficiency curve as:

$$\int_0^\infty f_{PM10}(d_p, MMD, GSD) dd_p = \int_0^\infty (f_{TSP}(d_p, MMD, GSD) \times (PE_{PM10}(d_p, d_{50}, slope))) dd_p \quad (7)$$

Equation 8 and 9 were developed from the relationships shown in equations 6 and 7.

$$J = \int_0^\infty (f_{TSP}(d_p, MMD, GSD) \times (PE_{PM10}(d_p, d_{50}, slope)) - f_{PM10}(d_p, MMD, GSD)) dd_p \quad (8)$$

$$K = \frac{C_{PM10}}{C_{TSP}} - \int_0^\infty (f_{TSP}(d_p, MMD, GSD) \times PE_{PM10}(d_p, d_{50}, slope)) dd_p \quad (9)$$

When the concentration and PSD of the collocated TSP and PM₁₀ samplers are known, the PM₁₀ sampler d_{50} and slope can be determined by simultaneously solving equations 8 and 9 such that J and K are minimized. The mass concentration of the TSP and PM₁₀ samples (C_{TSP} and C_{PM10} , respectively) and MMD and GSD defining the lognormal PSDs of the PM on the TSP and PM₁₀ sampler filters (f_{TSP} and f_{PM10} , respectively) were determined by Capareda et al. (2005). The two remaining unknown parameters in equations 8 and 9, d_{50} and slope of the PM₁₀ sampler performance characteristics, were determined using the measured data from Capareda et al. (2005) and minimizing J and K . This process was used to estimate the PM₁₀ sampler performance characteristics for 12 sets of filters from the collocated PM₁₀ and TSP samplers from the Texas gin sampling campaign conducted by Capareda et al. (2005).

RESULTS

The results of the concentration analysis, PSD analysis, and the PM₁₀ sampler performance characteristic estimation process for the 12 collocated PM₁₀/TSP samples are shown in table 1. The concentrations listed in table 1 were taken at locations well within the property line boundaries of the cotton gin and should not be considered to be property line concentrations. The samplers were placed close to an emission point at the gin to ensure that the samplers were well within the emitted plume throughout the sampling period.

The MMD and GSD of the PM collected on the TSP samples were $13.4 \pm 1.51 \mu\text{m}$ and 2.0 ± 0.11 , respectively. The concentrations measured by the PM₁₀ samplers were significantly higher than the true PM₁₀ concentrations ($p = 0.01$) using an analysis of variance (SPSS 12.0.1, SPSS, Inc., Chicago, Ill.). However, the estimated PM₁₀ concentrations based on the calculated PM₁₀ sampler performance characteristics (using eqs. 8 and 9 and the process previously described) were not significantly different from the measured PM₁₀ sampler concentrations at the 0.05 level ($p = 0.992$). A one-sample T-test indicated that the estimated cutpoint and slope values for each test are significantly greater than the upper limit of the cutpoint ($p < 0.001$) and slope ($p = 0.005$) ranges specified by EPA for an FRM PM₁₀ sampler. A comparison of the measured concentrations from the 12 samples with the theoretical concentrations estimated for

Table 1. Concentration, PSD, and PM₁₀ sampler characteristic estimation results for 12 collocated PM₁₀ and TSP samples taken downwind of a Texas cotton gin.

| Sample No. | TSP Sampler Data | | | | PM ₁₀ Sampler Data | | | Estimated PM ₁₀ Sampler Performance Characteristics | | |
|------------|-------------------------|-----|---------------------------------|---|-------------------------------|-----|--|--|-------|--|
| | MMD ^[a] (μm) | GSD | TSP Conc. (μg m ⁻³) | True PM ₁₀ Conc. (μg m ⁻³) | MMD ^[a] (μm) | GSD | PM ₁₀ Sampler Conc. (μg m ⁻³) | Cutpoint ^[a] (μm) | Slope | PM ₁₀ Conc. (μg m ⁻³) |
| 1 | 12.8 | 2 | 1770 | 642 | 11.5 | 1.8 | 1152 | 23.1 | 3.8 | 1140 |
| 2 | 13.4 | 2.1 | 852 | 294 | 11.4 | 1.8 | 687 | 29.6 | 1.7 | 683 |
| 3 | 12 | 2 | 567 | 225 | 10.7 | 1.8 | 337 | 18.9 | 5.6 | 333 |
| 4 | 18.9 | 2 | 1913 | 338 | 14.3 | 1.8 | 970 | 19.5 | 2.7 | 994 |
| 5 | 11.7 | 2 | 1873 | 762 | 10.4 | 1.7 | 1107 | 17.1 | 4.3 | 1087 |
| 6 | 12.7 | 1.9 | 727 | 260 | 9.5 | 1.8 | 383 | 13.8 | 2.6 | 381 |
| 7 | 15.8 | 2.2 | 551 | 151 | 12.9 | 1.9 | 379 | 28 | 2.4 | 383 |
| 8 | 13.6 | 2.3 | 1385 | 494 | 12.1 | 1.9 | 1099 | 32.6 | 1.9 | 1089 |
| 9 | 15.3 | 2.2 | 556 | 165 | 11.9 | 1.9 | 399 | 27.6 | 1.9 | 402 |
| 10 | 10.6 | 1.7 | 1434 | 654 | 9.7 | 1.7 | 967 | 21.2 | 4.1 | 966 |
| 11 | 10.4 | 1.8 | 603 | 284 | 10.2 | 1.7 | 557 | 34.5 | 1.8 | 550 |
| 12 | 13 | 1.8 | 2254 | 743 | 10.6 | 1.7 | 1708 | 22.9 | 1.7 | 1716 |

^[a] Equivalent spherical diameter.

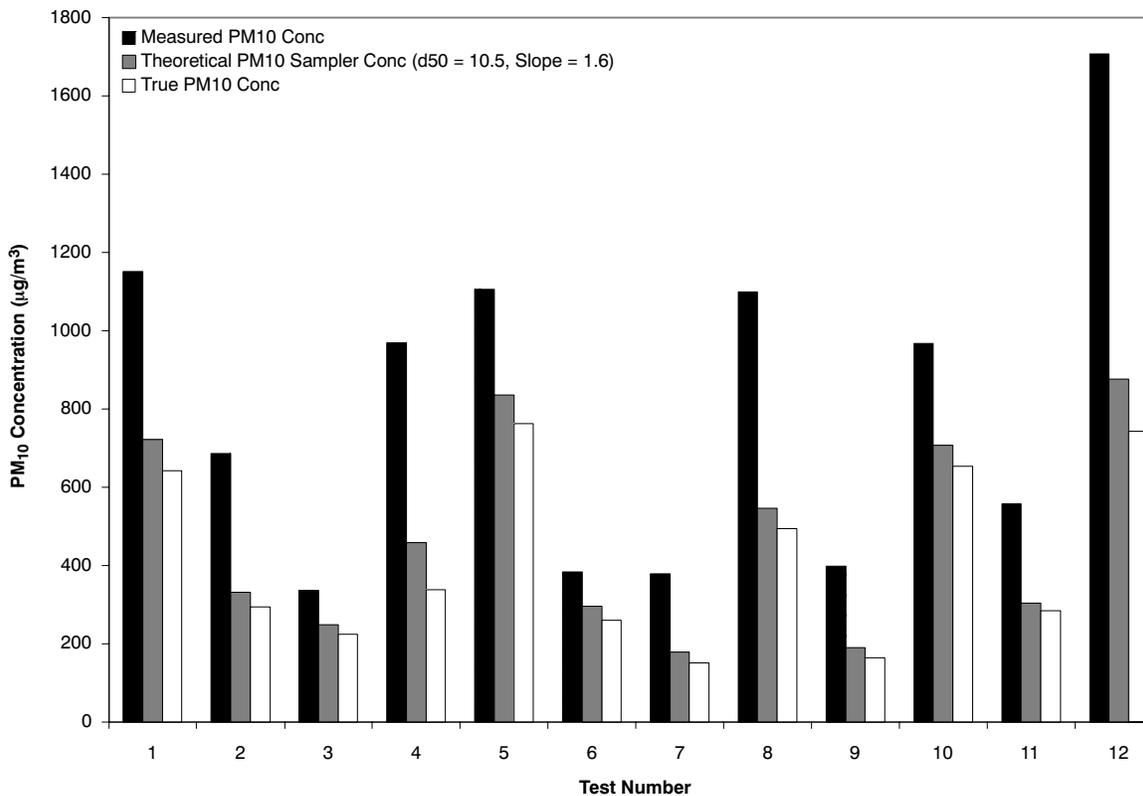


Figure 2. PM₁₀ concentrations as measured by the FRM PM₁₀ sampler, the concentration that the FRM PM₁₀ sampler would measure if it were operating with a cutpoint of 10.5 μm and slope of 1.6, and the true PM₁₀ concentrations.

an FRM PM₁₀ sampler operating with a cutpoint of 10.5 μm and slope of 1.6 is shown in figure 2.

The results shown in figure 2 indicate that there was a shift in the performance characteristics of the FRM PM₁₀ sampler as indicated by the fact that the concentrations measured by the PM₁₀ sampler were higher than the concentrations that the PM₁₀ sampler theoretically should measure if it were operating with a cutpoint of 10.5 μm and slope of 1.6. The concentrations shown for the theoretical PM₁₀ sampler represent the maximum concentrations that an FRM PM₁₀ sampler should measure if it were truly operating within the specified EPA performance criteria. The measured PM₁₀

concentrations ranged from 129% to 212% higher than the theoretical FRM PM₁₀ concentrations. The measured PM₁₀ concentrations ranged from 145% to 287% higher than the true PM₁₀ concentrations.

The oversampling error observed with the FRM PM₁₀ samplers refers to the difference between the measured concentrations of the FRM PM₁₀ sampler and the true PM₁₀ concentrations. The measured and estimated oversampling errors of the FRM PM₁₀ samplers are shown in figure 3 along with the theoretical oversampling error for the PM₁₀ sampler operating with a cutpoint of 10.5 μm and a slope of 1.6. A significant positive correlation (R = 0.82) was observed

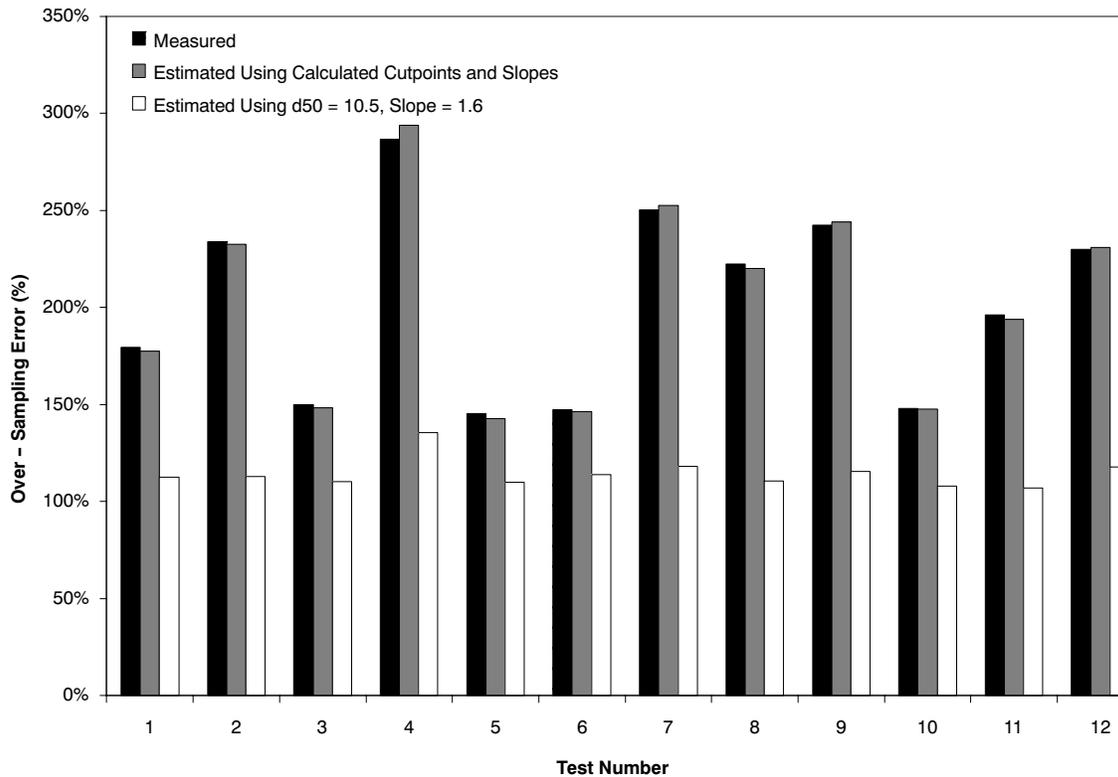


Figure 3. Measured and estimated (using the individual cutpoints and slopes calculated from the sample data in table 1) oversampling error of the FRM PM₁₀ sampler and the theoretical oversampling error of the PM₁₀ sampler operating with a cutpoint of 10.5 μm and slope of 1.6.

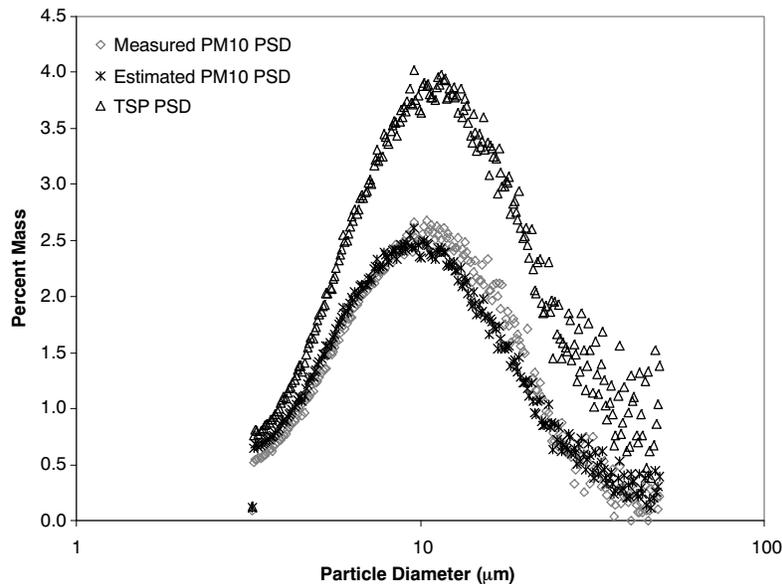


Figure 4. TSP, PM₁₀ sampler measured, and PM₁₀ sampler estimated PSDs from test 3.

($P = 0.001$) between the measured oversampling error and the MMD of the TSP sampler. This result was expected, as Buser et al. (2002) observed that the oversampling error of an FRM PM₁₀ sampler increases as the MMD of the sampled dust increases. A positive correlation was observed between the GSD of the TSP sample and the oversampling error of the FRM PM₁₀ sampler ($R = 0.452$). However, this correlation was not significant at the 0.05 level ($P = 0.14$). The magnitude of the true PM₁₀ concentration was found to be negatively correlated (not significant) with the oversampling

error of the FRM PM₁₀ sampler ($R = -0.339$, $P = 0.281$), indicating that the magnitude of the true PM₁₀ concentration does not affect the performance of the FRM PM₁₀ sampler.

The estimated cutpoints and slopes for the FRM PM₁₀ samplers (table 1) were substantially different from the range specified by the EPA. The cutpoints ranged from 13.8 to 34.5 μm with a standard deviation of 6.4 μm, and the slopes ranged from 1.7 to 5.6 with a standard deviation of 1.3. There were no significant correlations found between the estimated cutpoint of the FRM PM₁₀ sampler and any of the measured

parameters, including the TSP MMD, TSP GSD, TSP concentration, PM₁₀ MMD, PM₁₀ GSD, or the PM₁₀ sampler measured concentration. Similarly, the estimated PM₁₀ sampler penetration curve slopes were not significantly correlated with any of the measured parameters. These results indicate that the performance characteristics of the FRM PM₁₀ sampler are highly unpredictable.

The PM₁₀ sampler performance characteristic estimation process yielded estimated PM₁₀ sampler filter PSDs that were almost identical to those measured. No significant differences were found between the measured PM₁₀ PSD MMDs and estimated PM₁₀ PSD MMDs at the 0.05 level ($p = 0.399$) using an analysis of variance. Similarly, no significant differences were found between the measured PM₁₀ PSD GSDs and the estimated PM₁₀ PSD GSDs at the 0.05 level ($p = 0.419$). Figure 4 illustrates the similarity between the measured PM₁₀ sampler PSD and estimated PM₁₀ PSD typical of the samples.

CONCLUSIONS

The process described in this article to estimate the performance characteristics of the FRM PM₁₀ sampler yielded estimated PM₁₀ PSDs that were almost identical to the PSDs measured by the FRM PM₁₀ samplers. The performance characteristics of the FRM PM₁₀ samplers were highly variable and were not correlated to any of the parameters measured in this study. The cutpoints of the estimated penetration curves for the FRM PM₁₀ samplers ranged from 13.8 to 34.5 μm , with the estimated slopes ranging from 1.7 to 5.6. The estimated ranges for the cutpoints and slopes of the FRM PM₁₀ sampler are substantially different from the performance characteristics specified by the EPA.

The oversampling errors measured downwind of the Texas cotton gin ranged from 145% to 287%. The results of this work show that the true PM₁₀ concentrations should be 88.2% of the PM₁₀ concentrations measured by the FRM PM₁₀ samplers if the PM₁₀ performance characteristics were within the limits specified by EPA. However, shifts in the performance characteristics of the FRM PM₁₀ sampler resulted in the true PM₁₀ concentrations being 50.6% of the PM₁₀ concentrations measured by the FRM PM₁₀ sampler. The findings of this work indicate that the FRM PM₁₀ sampler does not operate according to the performance characteristics specified by the EPA when exposed to agricultural dust.

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**Preliminary Field Evaluation of EPA Method CTM-039
(PM_{2.5} Stack Sampling Method)**

Michael D. Buser and Derek P. Whitelock

ABSTRACT

Agricultural operations are encountering difficulties complying with current air pollution regulations for particulate matter (PM). These regulations are based on the National Ambient Air Quality Standards, which set maximum concentration limits for ambient air PM. Source sampling for compliance purposes require the use of U.S. Environmental Protection Agency (EPA) approved samplers. Ideally, these samplers would produce accurate measures of the pollutant; for instance, PM_{2.5} samplers would produce accurate measures of PM less than or equal to 2.5 μ m (true PM_{2.5}). However, samplers are not perfect and errors are introduced due to established tolerances for sampler performance characteristics and the interaction of particle size and sampler performance characteristics. A performance evaluation of the stack sampler referenced in EPA Method CTM-039 was conducted at a commercial roller cotton gin. EPA Methods CTM-039 and 5 were used to sample the PM emissions being emitted from the gin's No. 1 stick machine system, the overflow and seed-cotton carryover reclaiming system, and the feeder dust system. Total suspended particulate (TSP), PM₁₀, and PM_{2.5} concentrations were obtained according to EPA defined methodology. A particle size analysis was conducted on the filter and wash from the Method 5 sampler. These particle size distributions and the TSP concentrations were used to determine the true PM₁₀ and PM_{2.5} concentrations for comparison with the Method CTM-039 concentrations. Based on a preliminary data analysis, the CTM-039 PM₁₀ concentrations were similar to the true PM₁₀ concentrations. However, the CTM-039 PM_{2.5} concentrations were 5.8, 11, and 13 times greater than the true PM_{2.5} concentrations for the stick machine, feeder, and overflow systems, respectively.

INTRODUCTION

The original EPA method for determining PM stack emission rates was Method 5 (*Federal Register*, 1977). This method was used to determine TSP emission rates through isokinetic stack sampling (USEPA, 1996a). In response to the 1987 National Ambient Air Quality Standards (NAAQS) changes, EPA approved Method 201a. Method 201a is a constant

sampling rate procedure (isokinetic) that utilizes a stainless steel cyclone to determine PM_{10} emission rates from exhaust stacks. EPA has developed a new method (titled ctm-039) that uses a cyclone with a nominal cutpoint of $2.5 \mu m$ in series with the Method 201a cyclone. This sampling system consists of a nozzle (matched with the air velocity in the stack to provide isokinetic sampling), PM_{10} cyclone with a grit pot, $PM_{2.5}$ cyclone with a grit pot, and a filter holder that attaches to the Method 5 sampling train. A picture of the combination PM_{10} and $PM_{2.5}$ stack sampler is shown in Figure 1.

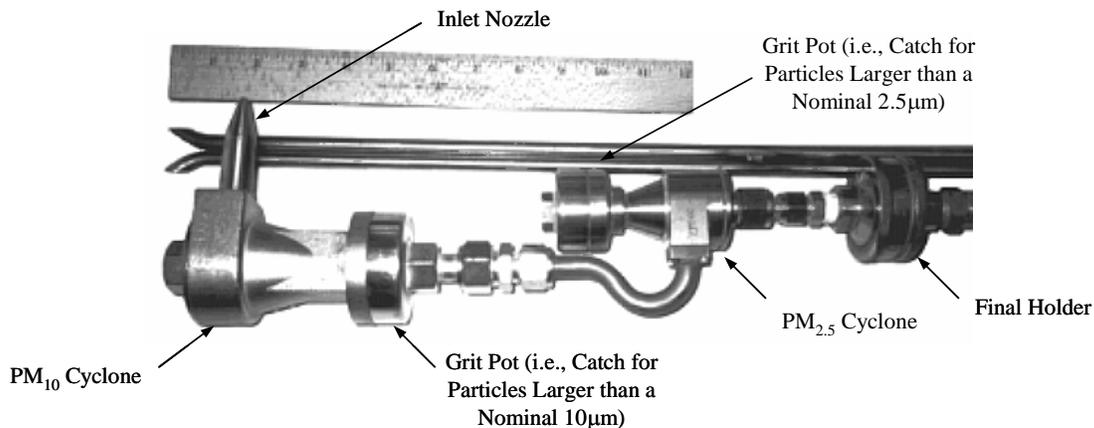


Figure 1. PM_{10} and $PM_{2.5}$ cyclone combination sampler.

USEPA (2002) describes the validation methods and procedures and the criteria of acceptance for in-stack PM_{10} samplers. The operating principle of this in-stack sampler requires that isokinetic sampling be maintained within the well-defined limits, as deviations in the sampling flow rate can distort the flow pattern in the stack resulting in PM_{10} measurement errors. The validation methods call for the in-stack sampler to be tested in a wind tunnel at target gas velocities of 7 ± 1.0 , 15 ± 1.5 , and 25 ± 2.5 m/s. The sampler's collection efficiency is evaluated by exposing the sampler to dispersed concentrations of mono-disperse particles. The various mono-disperse particle size used in the wind tunnel validation studies include: 5, 7, 10, 14, and $20 \mu m$. A smooth curve is drawn through the reported collection efficiencies, associated with the various mono-disperse particle sizes, and compared to the curves shown in Figure 2. According to the USEPA (2002), the in-stack sampler's performance is acceptable if the reported fraction efficiency curve falls within the banded region for all particle sizes tested (shown in Figure 9) and the sampler's cutpoint is $10.0 \pm 1.0 \mu m$ AED.

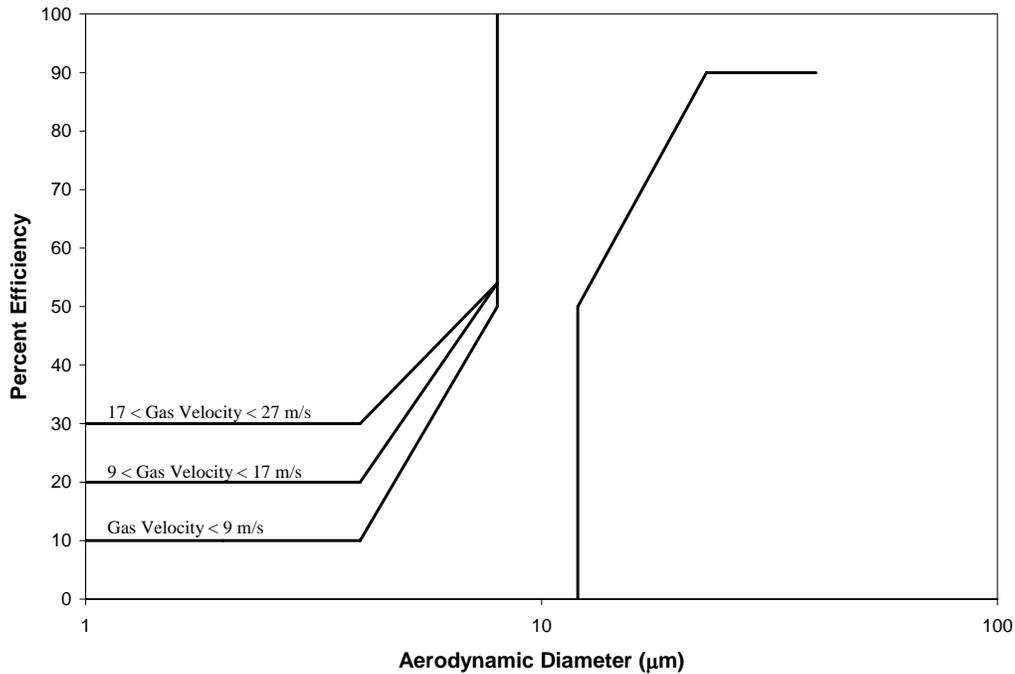


Figure 2. Efficiency envelope for the PM₁₀ cyclone (USEPA, 2002).

The cutpoint (d_{50}) of the PM₁₀ stack sampler is explicitly defined as 10.0 +/-1.0 μm AED. Using the following equation with a equal to infinity slopes were determined for d_{50} 's of 9.0, 10.0, and 11.0 μm that fall within the EPA acceptable Method 201a PM₁₀ cyclone efficiency envelope.

$$P_m(a, d_{50}, slope) = 1 - \int_0^a \left[\frac{1}{d_p \ln(slope) \sqrt{2\pi}} \exp \left[\frac{-[\ln(d_p) - \ln(d_{50})]^2}{2(\ln(slope))^2} \right] \right] dd_p \quad (1)$$

where $P_m(a, d_{50}, slope)$ is the sampler penetration efficiency for particles having diameters less than a . The resulting collection efficiency curves are shown in Figure 3 along with the EPA collection efficiency envelope. It was determined that collection efficiency curve of PM₁₀ stack sampling cyclone could be described by a d_{50} of 9 μm and a slope of 1.87, a d_{50} of 10 μm and a slope of 1.90, or a d_{50} of 11 μm and a slope of 1.76 and still meet the EPA performance requirements.

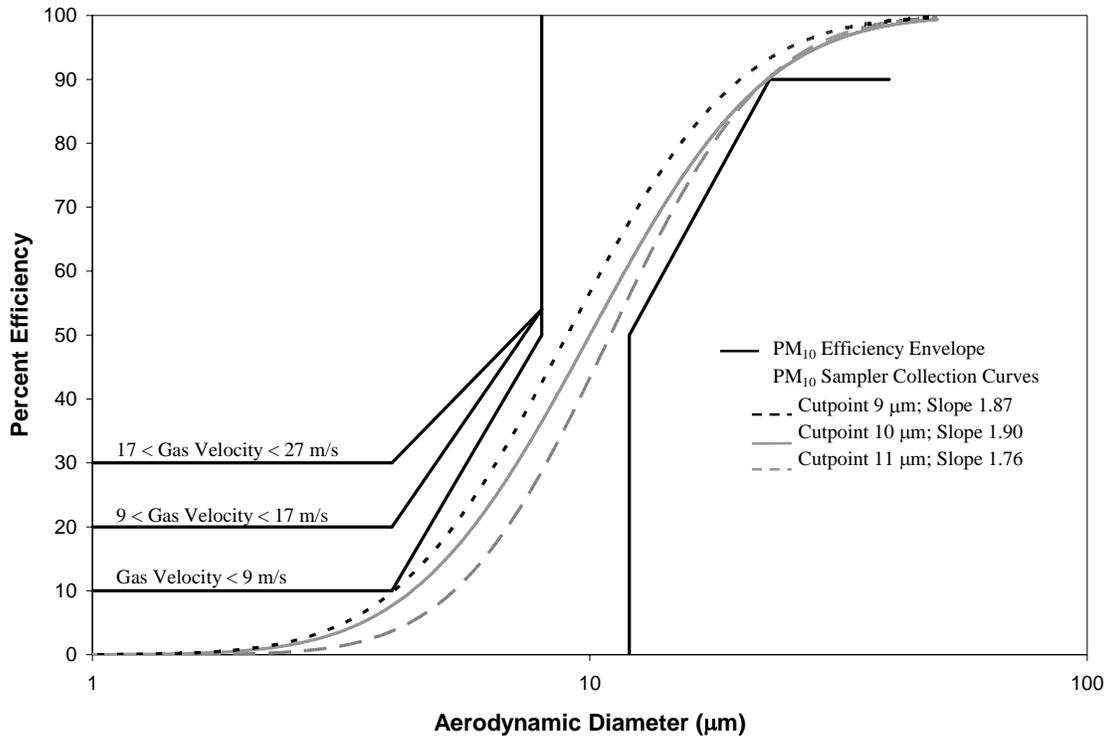


Figure 3. Method 201a PM₁₀ cyclone efficiency envelope and theoretical PM₁₀ cyclone collection efficiency curves.

Using the methodology described by Buser et al. (2007), theoretical simulations of the errors associated with EPA approved PM₁₀ stack samplers were conducted to determine the expected range of errors associated with these samplers. Using the EPA defined performance criteria, it was theoretically determined that concentrations from the Method 201a stack samplers could be 87 to 100%, 91 to 108%, and 100 to 160% of the true PM₁₀ concentration when the samplers are exposed to particulate matter characterized by a mass median diameters (MMD) of 5.7, 10, and 20 microns, respectively with a geometric standard deviation (GSD) of 2.0, as shown in Figure 4. These ranges of uncertainty increase as the GSD decreases. For example, the theoretical Method 201a stack sampler concentration is 80 to 100%, 89 to 111%, and 100 to 457% of the true concentration when the samplers are exposed to a MMD of 5.7, 10, and 20 microns, respectively with a GSD of 1.5, as shown in Figure 5. Due to the extremely limited information describing the performance characteristics of the PM_{2.5} stack sampler, similar simulations could not be performed for the EPA approved PM_{2.5} stack sampler.

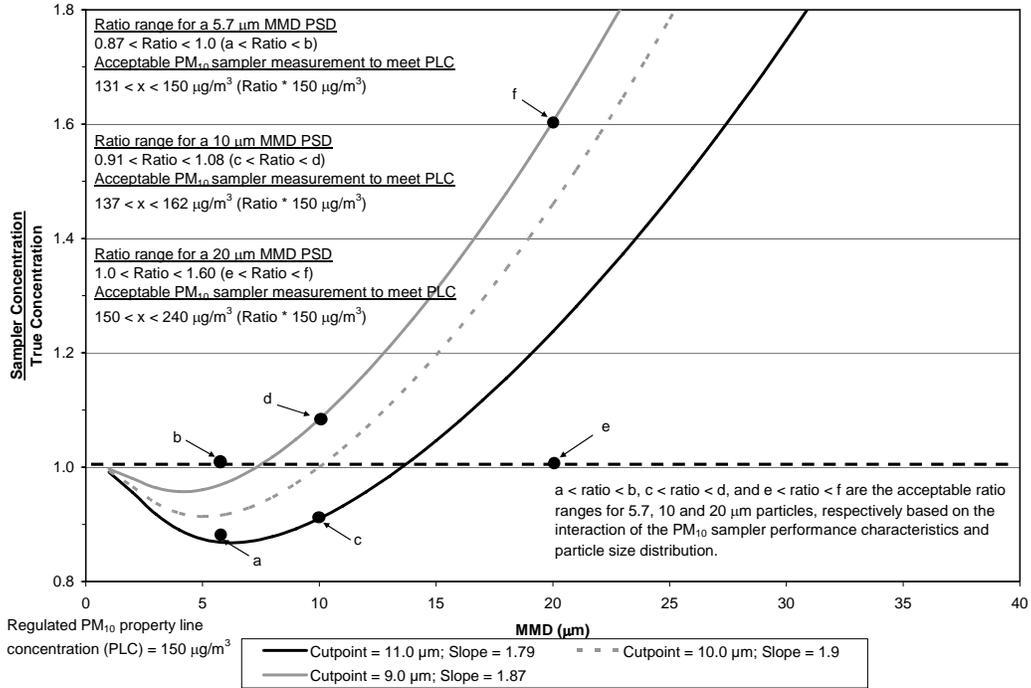


Figure 4. Theoretical ratios of PM_{10} stack sampler to true PSD concentrations (PSD – GSD = 2.0).

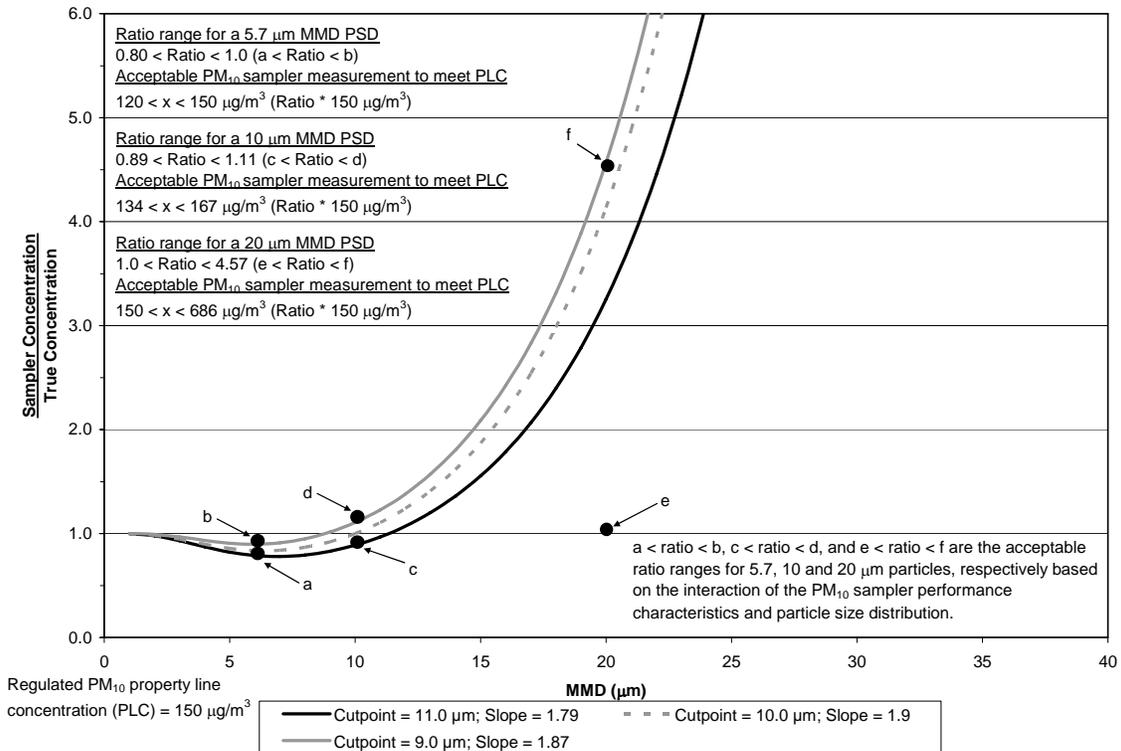


Figure 5. Theoretical ratios of PM_{10} stack sampler to true PSD concentrations (PSD – GSD = 1.5).

In 2006, laboratory tests were conducted to determine the actual errors associated with EPA's Method 201a and CTM-039. The first experimental test consisted of exposing the samplers to particulate matter with known characteristics, conducting isokinetic sampling, maintaining a constant loading rate, and evaluating only Method 201a. The test dusts were Micro Alumina #3 characterized by a MMD of 10.0 microns and a GSD of 1.5 and a starch characterized by a MMD of 19.4 microns and a GSD of 1.34 (should resulting in over-sampling). Based on the results of the study the Method 201a stack sampler under-sampled the true PM10 concentration by 17% when exposed to the Micro Alumina #3 and over-sampled the true PM10 concentration by 143% when exposed to the starch. A second round of testing focused on two test dusts, two loading rates, and Method 201a and CTM-039 sampling methods. Results for the Method 201 and CTM-039 tests are shown in Table 1 and Table 2, respectively. These results indicate that the sampler performance characteristics can vary beyond the EPA defined tolerances; therefore, predicting over or under-sampling based simply on the characteristics of the particulate matter being sampled becomes complicated as it is dependent on the large shifts in the sampler performance characteristics.

Table 1. 2006 experimental test results for EPA's Method 201a.

| | True PM ₁₀ | Sampler PM ₁₀ | Sampler PM ₁₀ /True PM ₁₀ |
|-----------------------------------|-----------------------|--------------------------|---|
| Limestone {MMD = 14.8; GSD = 1.8} | | | |
| Rate = 32 g/m ³ | 27% | 23% | 86% |
| Rate = 148 g/m ³ | 27% | 31% | 113% |
| Starch {MMD = 19.5; GSD = 1.3} | | | |
| Rate = 32 g/m ³ | 5% | 12% | 250% |
| Rate = 148 g/m ³ | 5% | 11% | 228% |

Table 2. 2006 experimental test results for EPA's Method CTM-039.

| | PM ₁₀ | | | PM _{2.5} | | |
|-----------------------------------|------------------|---------|--------------|-------------------|---------|--------------|
| | True | Sampler | Sampler/True | True | Sampler | Sampler/True |
| Limestone {MMD = 14.8; GSD = 1.8} | | | | | | |
| Rate = 32 g/m ³ | 27% | 33% | 123% | 1% | 9% | 700% |
| Rate = 148 g/m ³ | 27% | 36% | 133% | 1% | 8% | 606% |
| Starch {MMD = 19.5; GSD = 1.3} | | | | | | |
| Rate = 32 g/m ³ | 5% | 22% | 477% | 0.02% | 6% | 30000% |
| Rate = 148 g/m ³ | 5% | 21% | 444% | 0.02% | 5% | 25316% |

METHODS AND PROCEDURES

The field evaluation was conducted at a California roller gin. The sampling was conducted on December 12 & 13, 2006. The gin's No. 1 stick machine, feeder dust, and the overflow/seed reclaimer systems were evaluated. Both the No. 1 stick machine and feed dust system exhausts were equipped with two 38 inch 1D-3D cyclones. The overflow/seed reclaimer system was equipped with four 38 inch 1D-3D cyclones. The gin's production data (bales of cotton ginned per hour) was collected from the gin's management by the Environmental Services and Testing company and was provided to the USDA-ARS through the source testing companies official report.

The CTM-039 and Method 5 stack sampling performed by the USDA-ARS was conducted in conjunction with Method 201a and Method 202 stack sampling that was performed by Environmental Services and Testing. Method 5 sampling was conducted to quantify the total suspended particulate (TSP) being emitted from the stacks. Method 201a was used to quantify the solid PM10 being emitted from the stacks. Method 202 is an analytical procedure that was used to quantify the organic and water soluble PM10 that penetrated the filter and condensed in the impingement train. Method CTM-039 was used to quantify both the PM10 and PM2.5 solid particulates being emitted for the stacks. The sampling ports used in the tests were positioned in accordance with EPA Method 1 to accommodate a 12-point traverse. The volumetric airflow was determined in accordance with EPA Methods 2 through 4. Stack gas O₂ and CO₂ levels were ambient (O₂ = 20.9%, CO₂ = 0.1%) and were not measured. All volumetric airflow rates were corrected to dry standard conditions (T = 68 °F, P = 29.92 in. Hg). All airflow rate measurements were conducted by Environmental Services and Testing and were provided to the USDA-ARS.

Three replications of each test method were performed on one of the cyclone exhausts from each of the systems. A candy cane equipped with two ports was attached to the cyclone exhaust. Each Method 201a run lasted approximately 60 minutes and were performed in accordance to EPA's defined protocol. The protocols used for Methods 5 and CTM-039 were modified versions of EPA's defined protocol. Each of the Method 5 and CTM-039 runs lasted 30 minutes. No Method 5 or CTM-039 traverse sampling was conducted, as only center point measurements were collected. These modifications were made so that the Method 5 and CTM-039 sampling could be conducted in conjunction with the Method 201a sampling without

interfering with Method 201a sampling protocol. Therefore, the results from the Method 5 and Method CTM-039 tests should only be used to compare the various methods and should not be used to quantify the total PM emissions being emitted from the exhausts.

Sampler preparation, operation, and wash and filter sample collections were conducted in accordance to EPA's defined protocols. All Method 201a washes and filter media collections and gravimetric analysis of these samples were conducted by Environmental Services and Testing personnel. Arrangements were established for the samples to be shipped to the USDA-ARS Cotton Production and Processing Research Unit's Air Quality Laboratory for particle size analyses to be conducted on the wash and filter samples. All Method 5 and CTM-039 washes and filter media collections and gravimetric and particle size analysis of these samples were conducted by USDA-ARS personnel. Particle size analysis is above and beyond the scoped defined by the various EPA protocols. The particle size procedures defined by Buser (2004) were used to generate all the particle size distributions for the PM wash and filter samples.

RESULTS AND DISCUSSION

To date, all the gravimetric analyses have been completed. The USDA-ARS has received Environmental Services and Testing's official source sampling report but have not included the results in this discussion. The Method 201a wash and filter samples have not been received by the USDA-ARS and therefore, the subsequent particle size analysis has not been completed. The particle size analyses for the Method 5 samples have been completed; however, the particle size analyses for the CTM-039 samples have not been completed. The comparative results reported in this manuscript are based on the gravimetric analyses of the Method 5 and CTM-039 samples and the particle size analyses of the Method 5 samples.

The particle size distributions for the No. 1 Stick Machine, Overflow/Seed Reclaimer, and Feeder Dust systems are shown in Figures 6, 7, and 8, respectively. The PM captured on the Method 5 filters from the No. 1 Stick Machine and the Feeder Dust systems were similar size. The MMD, GSD, percent PM₁₀, and percent PM_{2.5} for the No. 1 Stick Machine was 6.4 μm , 1.8, 78.3%, and 4.89%, respectively. The MMD, GSD, percent PM₁₀, and percent PM_{2.5} for the Feeder Dust system was 6.0 μm , 1.6, 86.3%, and 3.29%, respectively. The particle size distribution of the PM captured on the Method 5 filters from the Overflow/Seed Reclaimer system was shifted slightly to the right resulting in a larger MMD and smaller PM₁₀ and PM_{2.5}

percentages. The MMD, GSD, percent PM10, and percent PM2.5 for the Overflow/Seed Reclaimer system was 8.0 μm, 1.7, 66.9%, and 1.26%, respectively.

The percent PM10 and PM2.5 based on the CTM-039 gravimetric analyses and the ratios of the sampler (CTM-039 sampler) to the true (based on particle size distribution analyses of the Method 5 filters), also referred to as the over- or under-sampling rate, are shown in Table 3. The PM10 percentages as determine by the CTM-039 method and Method 5/particle size analyses method produced similar results. For the PM10 analyses, the CTM-039 concentrations were 93% to 100% (exactly matching) of the true concentrations. For the PM2.5 percentages, the CTM-039 method produced PM2.5 concentrations higher than the true PM2.5 concentrations. The percent PM2.5 for the No. 1 Stick Machine was 28.3 and 4.9% based on the CTM-039 and Method 5/particle size analyses methods, respectively. In other words, the CTM-039 concentration estimates were 5.79 times higher than the true concentrations. The percent PM2.5 for the Overflow/Seed Reclaimer system was 16.8 and 1.30% based on the CTM-039 and Method 5/particle size analyses methods, respectively. Based on these results the CTM-039 concentration estimates were 13.35 times higher than the true concentrations. The percent PM2.5 for the Feeder Dust system was 36.0 and 3.30% based on the CTM-039 and Method 5/particle size analyses methods. Based on these results the CTM-039 concentration estimates were 10.95 times higher than the true concentrations.

Table 3. 2007 Field evaluation results for the CTM-039 stack sampler.

| Exhaust | <u>CTM-039 Results</u> | | <u>PSD Analysis of Method 5 Filter</u> | | <u>Sampler/True</u> | |
|---------------|------------------------|-----------|--|-----------|---------------------|-----------|
| | % < 10μm | % < 2.5μm | % < 10μm | % < 2.5μm | % < 10μm | % < 2.5μm |
| Stick Machine | 73% | 28.3% | 78% | 4.90% | 93% | 579% |
| Overflow | 67% | 16.8% | 67% | 1.30% | 100% | 1335% |
| Feeder | 81% | 36.0% | 86% | 3.30% | 93% | 1095% |

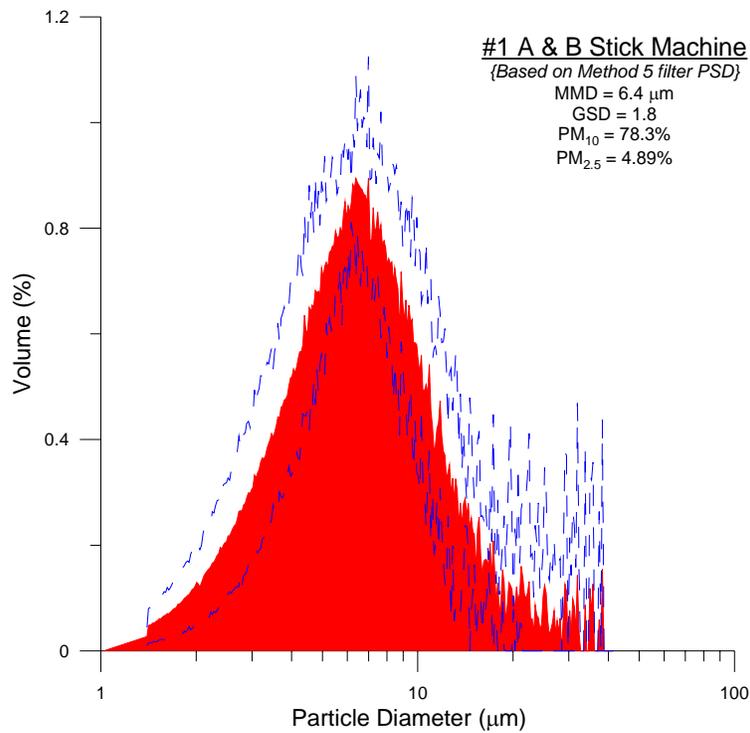


Figure 6. Average particle size distribution for the No. 1 Stick Machine as determined from the Method 5 filter.

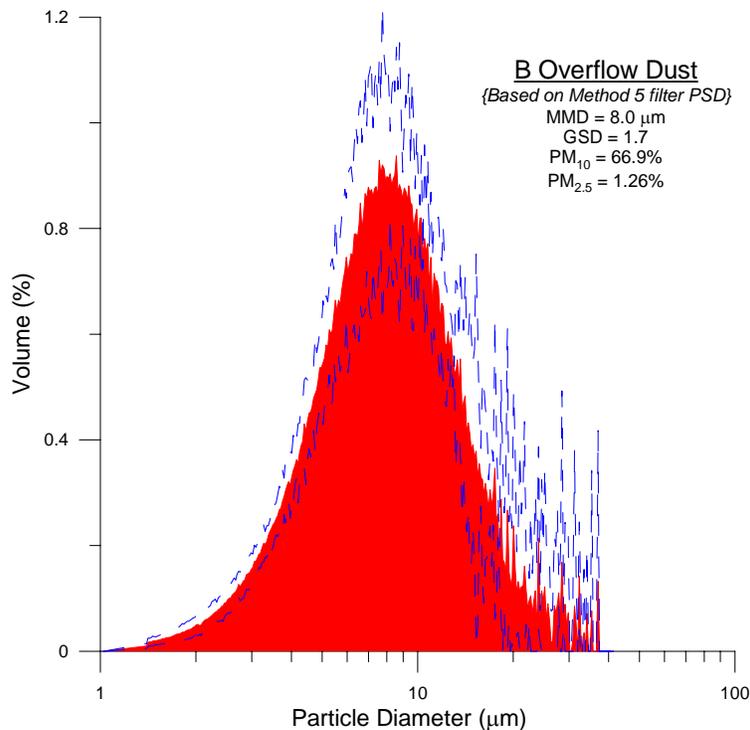


Figure 7. Average particle size distribution for the Overflow/Seed Reclaimer system as determined from the Method 5 filter.

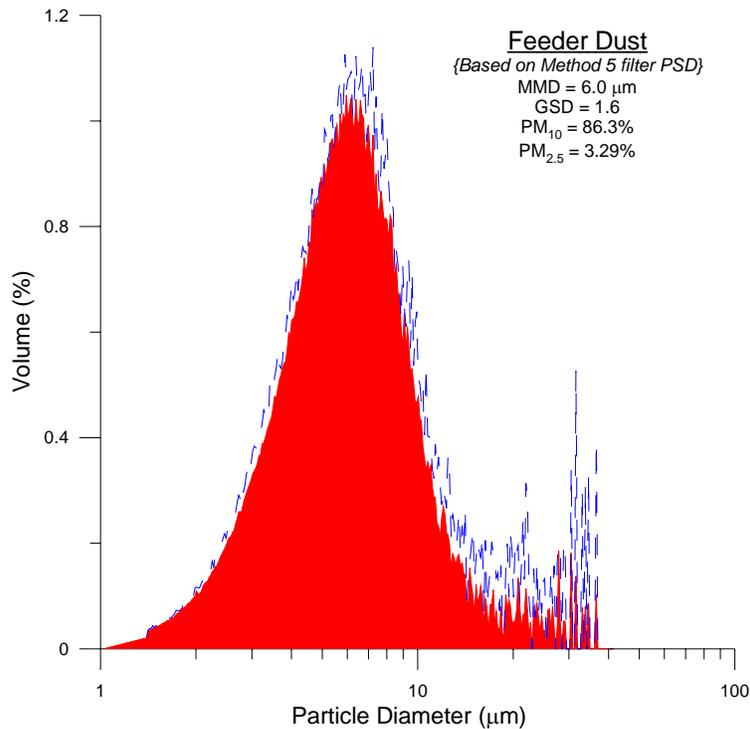


Figure 8. Average particle size distribution for the Feeder Dust system as determined from the Method 5 filter.

CONCLUSION

These types of samplers are currently being used to monitor and/or evaluate emissions emitted by agricultural point source exhausts. Theoretical estimates indicate that the PM₁₀ stack samplers could be producing concentrations that are 4.5 times higher than the true PM₁₀ concentrations for certain PM. The experimental data collected to date also indicates that the sampler's performance characteristics could be shifting beyond the EPA defined criteria even when the sampler is operated in accordance to EPA protocol. The experimental data on EPA CTM-039 method (PM_{2.5} stack sampling) indicates dramatic over-sampling when used to sample certain PM.

Why should regulatory and agricultural industries care about these sampler errors?

- 1) Creating standards based on data containing sampler errors creates a huge demand for resources (time, money, and other resources) with no direct benefit or reduction of health effect risks.

- 2) By not accounting for these errors, regulatory agencies will end up focusing on the truly smaller PM_{2.5} emitters as opposed to the larger emitters (the regulatory agencies should be looking to get the biggest bang for your buck).
- 3) If regulatory agencies do not account for these sampler errors, agricultural sources are going to have a tough time complying with EPA's PM_{2.5} standards.

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DISCLAIMER

Mention of a trade name, propriety product or specific equipment does not constitute a guarantee or warranty by the United States Department of Agriculture and does not imply approval of a product to the exclusion of others that may be suitable.

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