PARTICULATE MATTER SAMPLER ERRORS DUE TO THE INTERACTION OF PARTICLE SIZE AND SAMPLER PERFORMANCE CHARACTERISTICS: AMBIENT PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ standard, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulation, and methods of determining PM$_{10}$. A common trend among many of these publications is the use of samplers to collect information on PM$_{10}$. Often, the sampler data are assumed to be accurate measures of PM$_{10}$. 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, PM$_{10}$ 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 PM$_{10}$ ambient air samplers. Results from the PM$_{10}$ simulations indicated that a source emitting PM characterized by a mass median diameter (MMD) of 20 $\mu$m and a geometric standard deviation (GSD) of 1.5 could be forced to comply with a PM$_{10}$ standard that is 3.2 times more stringent than that required for a source emitting PM characterized by an MMD of 10 $\mu$m 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 $\mu$m and a GSD of 1.5. Therefore, in order to achieve equal regulation among differing industries, PM$_{10}$ 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, PM$_{10}$, 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 accomplished 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 PM$_{10}$ samplers in the same manner. For instance, in the U.S., a PM$_{10}$ sampler is classified as having a penetration curve with a cutpoint of 10 $\mu$m, while other countries (e.g., Japan) classify a PM$_{10}$ sampler as rejecting (removing from the air stream) all particles greater than 10 $\mu$m (USEPA, 2003). A significant step in the standardization process of aerosol sampling was the EPA definition (USEPA, 1987) of the PM$_{10}$ 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 PM$_{10}$ 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).

PM$_{10}$ samplers are designated by the EPA as reference or equivalent methods under the provisions of 40 CFR Part 53 (CFR, 2001a). PM$_{10}$ reference methods must use the...
measurement principle and meet additional specifications set forth in 40 CFR Part 50, Appendix J (CFR, 2001c). Reference method PM$_{10}$ 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 PM$_{10}$ size range particles followed by collection of the PM$_{10}$ particles on a filter over a 24-hour period. Alternatively, equivalent PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 ±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 ±0.5 µm. 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 PM$_{10}$ inlets was described by John and Wall (1983) and Ranade et al. (1990).

A number of samplers have been designated as PM$_{10}$ 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 PM$_{10}$ samplers have shown substantial errors under certain conditions. These errors result from: (1) allowing a tolerance of ±0.5 µm 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 PM$_{10}$ 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 PM$_{10}$, 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 PM$_{10}$ primary 24-hour NAAQS is 150 micrograms per actual cubic meter (µg/acm) (CFR, 2001b). The secondary NAAQS for PM$_{10}$ is set at the same levels as the primary NAAQS.

The evolution of the PM$_{10}$ regulation was briefly discussed by Buser et al. (2007). Prior to and since the inclusion of the PM$_{10}$ standard, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulation, and methods of determining PM$_{10}$. A common trend among many of these publications is the use of samplers to collect information on PM$_{10}$. The data collected from these samplers are commonly used in statistical correlations and statistical comparisons to draw conclusions about PM$_{10}$ emission concentrations. All too often, the sampler data are assumed to be accurate measures of PM$_{10}$. 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ ambient air sampler collected an average of 0.3% less PM$_{10}$ and the WA-40CFM PM$_{10}$ ambient air sampler collected an average of 3.3% more PM$_{10}$ 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 PM$_{10}$ sampler was found to collect an average of 58% more mass than a collocated Wedding PM$_{10}$ 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 PM$_{10}$ style samplers (WA-40CFM and SA1200 PM$_{10}$ inlets). Herber (1988) reported that the WA-40CFM sampler measured 62.4% of the actual PM$_{10}$ mass concentration and the SA-1200 sampler measured 1.1 times the actual PM$_{10}$ mass concentration.

Ranade et al. (1990) evaluated two high-volume PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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:

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

(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:

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

(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:

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

(3)

In order to solve equation 2, additional information is needed to define the $d_{50}$ and slope associated with the PM$_{10}$ ambient air sampler. The EPA essentially defines the $d_{50}$ and slope associated with the PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ 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 PM$_{10}$ ambient air sampler. The sampler performance characteristics for the PM$_{10}$ 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 PM$_{10}$ sampler used throughout this article.

The performance characteristic ranges used to define the ambient PM$_{10}$ 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 PM$_{10}$ 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 ±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, $C_m$(MMD, GSD, $d_{50}$, slope), can be estimated by:

\[
C_m(\text{MMD, GSD, } d_{50}, \text{slope}) = \int_0^{\infty} f(d_p, \text{MMD, GSD}) P_m(d_p, d_{50}, \text{slope}) dd_p
\]

(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, \( C_t(MMD, \text{GSD}, d_{50}) \), can be estimated by:

\[
C_t(MMD, \text{GSD}, d_{50}) = \frac{d_{50}}{C_m} \int_0^{d_{50}} f(d_p, MMD, \text{GSD}) dd_p
\]

**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:

\[
E(x) = \frac{(\text{measured} - \text{true})}{\text{true}} = \frac{\text{measured}}{\text{true}} - 1
\]

where \( \text{measured} \) and \( \text{true} \) 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:

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

Throughout the remaining sections of this article, \( E(MMD, \text{GSD}, d_{50}, \text{slope}) + 1 \) 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 \( \mu m \) with a GSD of 1.5, and MMDs of 15 and 20 \( \mu m \) with a GSD of 2.0. The sampler performance characteristics included the nine combinations of \( d_{50} \) and slope values for the ambient PM\textsubscript{10} 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:

\[
C_{\text{acceptable}} = \text{Ratio} \times C_{\text{NAAQS}}
\]

where \( C_{\text{NAAQS}} \) 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 PM\textsubscript{10} concentrations, equations 4 and 5 were solved using Mathcad for a \( d_{50} \) equal to 10.5 \( \mu m \), slope of 1.6, GSD of 1.5, and MMDs ranging from 1 to 40 \( \mu m \).

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 \( \mu m \) (in increments of 1 \( \mu m \)) 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 \( \mu m \) 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 PM\textsubscript{10} sampler penetration curve should mimic the thoracic fraction of PM deposited in the human respiratory system. In figure 1, the EPA’s ideal PM\textsubscript{10} ambient sampler penetration data (CFR, 2001a) are overlaid on the ACGIH (1994)

Figure 1. The EPA ideal PM\textsubscript{10} sampler penetration curve overlaid on the ACGIH sampling criteria for the thoracic fraction of PM (CFR, 2001c; ACGIH, 1994).

<table>
<thead>
<tr>
<th>( d_{50} ) (( \mu m ))</th>
<th>Slope</th>
<th>Sampler Effectiveness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5</td>
<td>1.4</td>
<td>100</td>
</tr>
<tr>
<td>9.5</td>
<td>1.5</td>
<td>101</td>
</tr>
<tr>
<td>9.5</td>
<td>1.6</td>
<td>102</td>
</tr>
<tr>
<td>10.0</td>
<td>1.4</td>
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<td>1.6</td>
<td>106</td>
</tr>
<tr>
<td>10.5</td>
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<td>10.5</td>
<td>1.5</td>
<td>108</td>
</tr>
<tr>
<td>10.5</td>
<td>1.6</td>
<td>109</td>
</tr>
</tbody>
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sampling criteria for the thoracic fraction of PM. Based on the curves in figure 1, the ambient PM$_{10}$ 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 PM$_{10}$ sampler penetration data moves towards zero much more rapidly than the thoracic penetration convention. The PM$_{10}$ 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.
Based on the ambient PM$_{10}$ 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 $\mu$m 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 PM$_{10}$ 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 $\mu$m.

When comparing the boundary penetration efficiency curves in figure 3, it is apparent that there is an acceptable range of penetration efficiencies for the PM$_{10}$ ambient air sampler. The acceptable range of penetration efficiencies for a particle size of 10 $\mu$m AED is 44% to 56%, whereas the acceptable range for a particle size of 20 $\mu$m AED is 1% to 9%. In other words, the uncertainty associated with the performance characteristics of a PM$_{10}$ sampler is ±6% when sampling 10 $\mu$m particles and ±4% when sampling 20 $\mu$m particles. These ranges are considered one form of inherent error associated with PM$_{10}$ 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 $\mu$m with a GSD of 1.5 and for MMDs of 15 and 20 $\mu$m with a GSD of 2.0 are shown in table 2.

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

<table>
<thead>
<tr>
<th>Cutpoint (µm)</th>
<th>Slope</th>
<th>MMD = 5 µm GSD = 1.5</th>
<th>MMD = 10 µm GSD = 1.5</th>
<th>MMD = 15 µm GSD = 2.0</th>
<th>MMD = 20 µm GSD = 2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5</td>
<td>1.4</td>
<td>139.4 92.9%</td>
<td>138.3 92.2%</td>
<td>148.7 99.1%</td>
<td>157.8 105.2%</td>
</tr>
<tr>
<td>9.5</td>
<td>1.5</td>
<td>136.2 90.8%</td>
<td>139.4 92.9%</td>
<td>153.0 102.0%</td>
<td>167.3 111.5%</td>
</tr>
<tr>
<td>9.5</td>
<td>1.6</td>
<td><strong>133.2</strong> 88.8%</td>
<td>140.1 93.4%</td>
<td>157.2 104.8%</td>
<td>176.9 117.9%</td>
</tr>
<tr>
<td>10.0</td>
<td>1.4</td>
<td>142.1 94.7%</td>
<td>150.0 100.0%</td>
<td>160.8 107.2%</td>
<td>174.2 116.1%</td>
</tr>
<tr>
<td>10.0</td>
<td>1.5</td>
<td>139.1 92.7%</td>
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<td>183.5 122.3%</td>
</tr>
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<tr>
<td>10.5</td>
<td>1.6</td>
<td>138.6 92.4%</td>
<td>159.5 106.3%</td>
<td><strong>180.0</strong> 120.0%</td>
<td><strong>208.8</strong> 139.2%</td>
</tr>
</tbody>
</table>

[a] Values (µg/m³) 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 PM$_{10}$ are 150 µg/m³.

Figure 4. Comparison of true and sampled PM$_{10}$ percentages for a range of PSD mass median diameters and a GSD of 1.5.
of PM10 sampler performance characteristics, which define concentrations. When comparing the sampled to true concentrations for the urban dust, the sampled concentration is about 3% 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 PM10 sampler performance characteristics, which define the acceptable concentrations for PM10, 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 d50, (2) the average ratio is equal to 1.0 when the MMD is equal to the d50, (3) the average ratio is greater than 1.0 when the MMD is greater than the d50, 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 PM10 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 PM10 sampler concentrations would be 138 to 149 µg/m³ (i.e., ratios of 0.92 and 0.99 obtained from figure 6 and multiplied by 150 µg/m³, the current NAAQS for PM10). In this scenario, the PM10 sampler uncertainty is ±5.5 µg/m³ and the sampler bias is 0 µg/m³ if the sampler concentration is assumed to be the standard and −6.5 µg/m³ 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 PM10 sampler concentrations would be 142 to 158 µg/m³. This corresponds to a PM10 sampler uncertainty of ±8.0 µg/m³ and a sampler bias of 0 µg/m³ if the sampler concentration is assumed to be the standard and 0 µg/m³ 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 PM10 sampler concentrations would be 158 to 209 µg/m³, corresponding to a PM10 sampler uncertainty of ±25.5 µg/m³ and a sampler bias is 0 µg/m³ if the sampler concentration is assumed to be the standard and 33.5 µg/m³ 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 PM10 sampler concentrations would be 131 to 144 µg/m³. In this scenario, the PM10 sampler uncertainty is ±6.5 µg/m³ and the sampler bias is 0 µg/m³ if the sampler concentration is assumed to be the standard and −12.5 µg/m³ 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 PM10 sampler concentrations would be 138 to 161 µg/m³. This corresponds to a PM10 sampler uncertainty

![Figure 5. Comparison of true and sampled PM10 percentages for a range of PSD mass median diameters and a GSD of 2.0.](image-url)
of $\pm 11.5 \, \mu g/m^3$ and a sampler bias of $0 \, \mu g/m^3$ if the sampler concentration is assumed to be the standard and $0 \, \mu g/m^3$ if the true concentration is assumed to be the standard. Further, if the PSD were characterized by an MMD of $20 \, \mu m$ and a GSD of 1.5, then the acceptable range of PM$_{10}$ sampler concentrations would be $271$ to $514 \, \mu g/m^3$ (i.e., ratios of $1.81$ and $3.43$ obtained from figure 7 and multiplied by $150 \, \mu g/m^3$ the current NAAQS for PM$_{10}$), corresponding to a PM$_{10}$ sampler un-
certainty of ±121.5 µg/m³ and a sampler bias is 0 µg/m³ if the sampler concentration is assumed to be the standard and 242.5 µg/m³ 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 PM₁₀ sampler with a d₅₀ of 10.0 µm 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 µm, sampler performance characteristics of d₅₀ = 9.5 µm with a slope of 1.4 and d₅₀ = 10.5 µm 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 d₅₀, 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 µm AED.

When the EPA implemented the PM₁₀ NAAQS and approved the FRM ambient air sampler; the EPA's intent was for the performance characteristics of the PM₁₀ 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 PM₁₀ samplers?” If the issue per-

![Figure 8](image1.png)

**Figure 8.** Theoretical ratios of PM₁₀ sampler to true PSD concentrations (PM₁₀ sampler characteristics; cutpoint = 10 µm and slope = 1.5).

![Figure 9](image2.png)

**Figure 9.** Theoretical PM₁₀ sampler to true concentration ratio boundaries based on varying GSDs for PSDs with MMDs of 10 and 20 µm.
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 PM$_{10}$ NAAQS, then the corresponding agencies will, most likely, be required to reduce PM$_{10}$ emissions within the air shed. In order to determine PM$_{10}$ 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 PM$_{10}$ and not PM$_{10}$ sampler measurements, the following example is provided.

Assume that EPA-approved PM$_{10}$ 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 $\mu$m 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 PM$_{10}$ sampler) that can be described by a lognormal distribution with an MMD of 5 $\mu$m and a GSD of 1.5. Assume that the second operation is an agricultural operation and is emitting PM (sampled by the PM$_{10}$ sampler) that can be described by a lognormal distribution with an MMD of 20 $\mu$m and a GSD of 1.5. Further, assume that the PM$_{10}$ sampler used to monitor each of the operations measures 100 $\mu$g/m$^3$. Now, based on the methods laid out in this article, the true PM (PM less than 10 $\mu$m) emitted from each industry would be defined as follows:

- **Power Plant Operation**
  - Assumes that one operation is a power plant and is emitting PM (sampled by the PM$_{10}$ sampler) that can be described by a lognormal distribution with an MMD of 5 $\mu$m and a GSD of 1.5.
  - The second error (for the agricultural operation) corresponds to the mass of particles less than 10 $\mu$m emitted from the air stream by the pre-separator. The second error (for the agricultural operation) corresponds to the mass of particles less than 10 $\mu$m emitted 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 general conclusions drawn from this research:

  - If MMD < $d_{50}$, then $C_{\text{sampler}} < C_{\text{true}}$
  - If MMD = $d_{50}$, then $C_{\text{sampler}} = C_{\text{true}}$
  - If MMD > $d_{50}$, then $C_{\text{sampler}} > C_{\text{true}}$

  - As GSD increases, the concentration ratio of $C_{\text{sampler}}$ to $C_{\text{true}}$ decreases.
  - As sampler slope decreases, the concentration ratio of $C_{\text{sampler}}$ to $C_{\text{true}}$ 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.
REFERENCES


Buser, M. D. 2004. Errors associated with particulate matter measurements on rural sources: Appropriate basis for regulating cotton gins. PhD diss. College Station, Texas: Texas A&M University, Department of Agricultural and Biological Engineering.


