Inherent biases of PM$_{10}$ and PM$_{2.5}$ samplers based on the interaction of particle size and sampler performance characteristics

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Abstract. *Agricultural operations across the United States are encountering difficulties in complying with the current air pollution regulations for particulate matter (PM). The National Ambient Air Quality Standards (NAAQS) for PM in terms of PM$_{10}$ and PM$_{2.5}$, are the property line concentration limits set by EPA that should not be exceeded. The primary NAAQS are health-based standards and an exceedance of the NAAQS implies that it is likely that there will be adverse health effects for the public. The current PM$_{10}$ and PM$_{2.5}$ primary 24-hour NAAQS are 150 and 65 micrograms per actual cubic meter (mg/acm), respectively. Prior to and since the inclusion of the PM$_{10}$ and PM$_{2.5}$ indicators into the PM regulation, numerous journal articles and technical references have been written to discuss the epidemiological effects of PM, trends*

*of PM, regulation of PM, 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. All to often, the sampler data are assumed to be an accurate measure of PM, when in fact issues such as; sampler uncertainties, environmental conditions, and material characteristics for which the sampler is measuring must be incorporated for accurate sampler measurements. The focus of this manuscript is on the biases associated with material characteristics or particle size distributions (PSD) of the material in the air that is being sampled, the assumptions associated with PSD's and sampler performance characteristics, and the interaction between these two characteristics. The perception of the public is that PM_{10} and $PM_{2.5}$ measurement concentrations relate to virtual cut concentrations or PM with particle sizes less than 10 and 2.5 mm aerodynamic equivalent diameter (AED), respectively; however, these measurement concentrations are actually based on sampler measurements. PM_{10} and $PM_{2.5}$ samplers bias the concentration measurements, since a portion of the PM less than the size of interest will not be collected on the filter and a portion of the PM greater than the size of interest will be collected on the filter. A common assumption made in the regulatory community to circumvent this problem is that mass of particles less than the size of interest captured by the pre-separator are <u>equal</u> to the mass of particles greater than the size of interest that are captured on the filter. This issue leads to a primary focus of this manuscript, that is, that industries that emit PM with an mass median diameter (MMD) less than 10 µm are not regulated at the same level as agricultural operations, which typically emit PM with an MMD greater than 10 µm. This unequal regulation is primarily due to the interaction of the sampler performance and PSD characteristics. For example, if property line sampler concentration measurements from two industries are exactly the same and if 100% of industry ones PM is less than 10 µm and 38% of industry twos PM is less than 10 µm; then 100% industry ones PM can potentially reach the alveolar region of the lungs as compared to 38% of industry twos PM. Since the emphasis of the primary NAAQS is to protect public health; then in the previous example the two industries are not equally regulated. Therefore, in order to achieve equal regulation among differing industries, PM_{10} and $PM_{2.5}$ measurements <u>**MUST**</u> be based on virtual-cut measurements.*

Introduction

The Federal Clean Air Act (FCAA) and subsequent amendments have established national goals for air quality and have incorporated the use of standards for the control of pollutants in the environment since 1960. The 1970 FCAA Amendments (FCAAA) provided the authority to create the Environmental Protection Agency (EPA) and required the EPA to establish National Ambient Air Quality Standards (NAAQS). The NAAQS are composed of primary (based on protecting against adverse health effects of listed criteria pollutants among sensitive population groups) and secondary standards (based on protecting public welfare e.g., impacts on vegetation, crops, ecosystems, visibility, climate, man-made materials, etc). In 1971, 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. The NAAQS for particulate matter (PM) was established and the indicator of PM was defined as total suspended particulate (TSP). The FCAAA of 1977 required 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 EPA modified the PM standard by replacing the TSP indicator with a new indicator that accounts for particles with an aerodynamic equivalent diameter (AED) less than or equal to a nominal 10 μm (PM_{10}). On July 16, 1997, the EPA promulgated additional NAAQS for PM. This update would incorporate an additional indicator for the ambient air standards that would account for particles with an AED less than or equal to a nominal 2.5 μm ($PM_{2.5}$).[1]

It should be emphasized that PM is the pollutant and TSP, PM_{10}, and $PM_{2.5}$ are indicators of the pollutant. Further, based on the indicator definitions, TSP represents a greater than or equal to indicator of PM than the PM_{10} indicator, and PM_{10} represents a greater than or equal to indicator of PM than the $PM_{2.5}$ indicator. Although this comparison appears relatively trivial, several SAPRAs currently utilize the TSP and PM_{10} indicators and regulate these indicators at exactly the same level. The NAAQS for PM (40CFR50.6), in terms of PM_{10} and $PM_{2.5}$, are the concentration limits set by EPA that should not be exceeded. The regional or area consequences for multiple exceedances of the NAAQS are having an area designated as nonattainment 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. Since the primary NAAQS are health-based standards, an exceedance of the NAAQS implies that it is likely that there will be adverse health effects for the public. The current PM_{10} and $PM_{2.5}$ primary 24-hour NAAQS are 150 and 65 micrograms per actual cubic meter (μg/acm), respectively (40CFR50.7). The secondary NAAQS for PM_{10} and $PM_{2.5}$ are set at the same levels as the respective primary NAAQS.

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 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 (tracheobronchial 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 that particles depositing only in that region can safely be excluded from the indicator. Figure 1 shows the American Conference of Governmental Hygienists (ACGIH, 1997) sampling criteria for the inhalable, thoracic, and respirable

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[1] Disclaimer – Mention of a trade name, proprietary product, or specific machinery does not constitute a guarantee or warranty by the U.S. Department of Agriculture and does not imply approval of the product to the exclusion of others that may be available.

fraction of PM. Note that virtually all respirable PM (PM that can penetrate into the alveolar region of the human lung) is less than 10 μm, whereas 50% of the 3.5 μm particles are respirable and can reach the alveolar region.
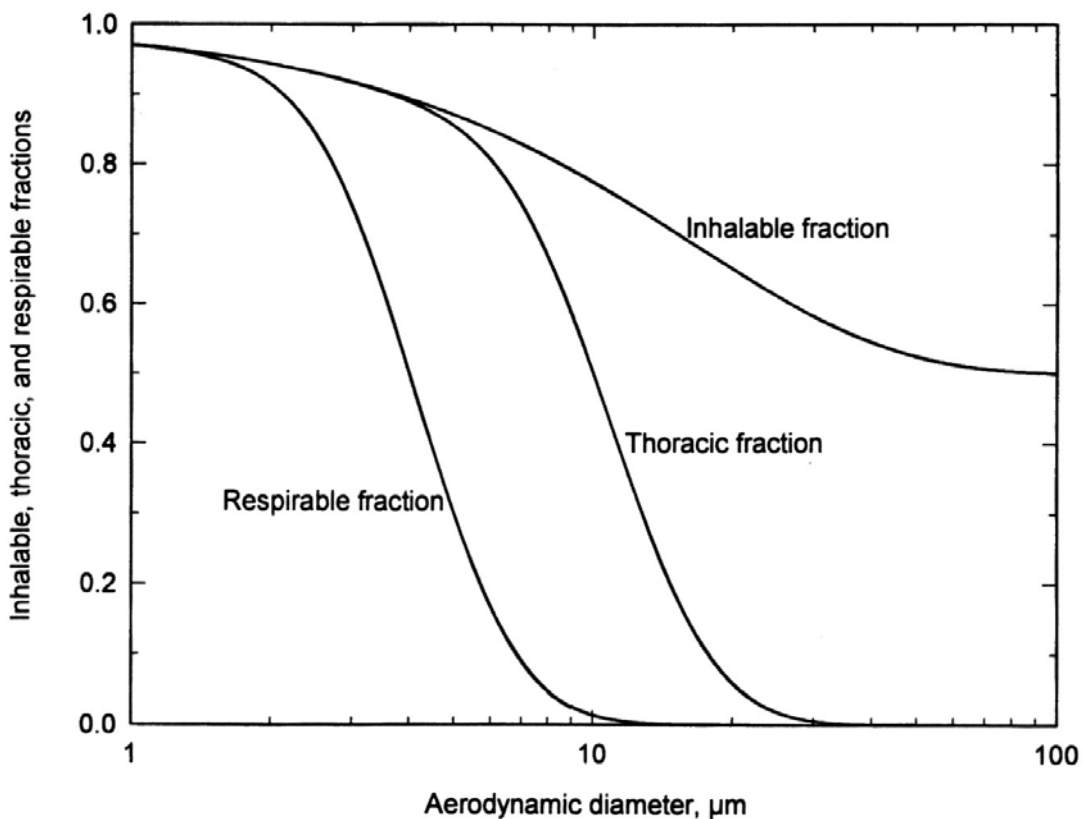

Figure 1. ACGIH sampling criteria for inhalable, thoracic, and respirable fraction of PM.

In 1987, the EPA staff recommended that a PM_{10} indicator replace the TSP indicator for the PM standard. Based on the information in the literature, it was EPA's intent for the PM_{10} sampler to mimic the thoracic fraction of PM, which is shown in Figure 1. The original acceptable concentration range proposed by the EPA Administrator, drawn from the 1984 staff analysis, was 150 to 250 $\mu g/m^3$ PM_{10} 24-hour average, with no more than one expected exceedance per year. 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 provided 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 an analysis reported 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 d_{50} values ranging from 3.5 to 5.0 μm for "healthy adults". EPA's emphasis on the 2.5 μm cut-point 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, EPA recommended 2.5 μm as the cut-point between fine and coarse particles. Because of the wide use of this cut-point, 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 d_{50} of 2.4 μm, which is claimed to relate to the deposition of particles in the lungs of children and

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adults with certain lung diseases. A $PM_{10-2.5}$ size fraction may be obtained from a dichotomous sampler or by subtracting the mass on a $PM_{2.5}$ sampler from the mass on a PM_{10} sampler. The resulting $PM_{10-2.5}$ mass is often referred to as "coarse-mode" particles.

Prior to and since the inclusion of the PM_{10} and $PM_{2.5}$ indicators into the PM regulation, numerous journal articles and technical references have been written to discuss the epidemiological effects of PM, trends of PM, regulation of PM, 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. The data collected from the samplers are commonly used in statistical correlations and statistical comparisons to draw conclusions about PM emission concentrations. All to often, the sampler data are assumed to be an accurate measure of PM, when in fact issues such as; sampler uncertainties, environmental conditions (dry standard versus actual conditions), and material characteristics for which the sampler is measuring must be incorporated for accurate sampler measurements. The focus of this manuscript is on the material characteristics or particle size distributions (PSD) of the material in the air that is being sampled, the assumptions associated with PSD's and sampler performance characteristics, and the interaction between these two characteristics.

Particle Size Distributions

The distribution of particles with respect to size is perhaps the most important physical parameter governing their behavior. Aerosols containing only particles of a particular size are called monodisperse while those having a range or ranges of sizes are called polydisperse. Hinds (1982) indicated that most aerosols in the ambient air are polydisperse 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 lognormal mass density function is expressed as

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

For monodisperse particles GSD=1 and for polydisperse particles GSD>1. The fraction of the total number of particles *df* having diameters between d_p and $d_p + dd_p$ is

$$df = f\left(d_p, MMD, GSD\right)dd_p \tag{2}$$

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

$$\int_0^\infty f\left(d_p, MMD, GSD\right)dd_p = 1.0 \tag{3}$$

This area can be estimated by the following discrete summation

$$\sum f_i = \sum_i (h_i \Delta d_i) = 1.0 \tag{4}$$

where $h_i\Delta d_i$ is equal to the fraction f_i of particles in the size range Δd_i. The area under the density function may be estimated for particle sizes ranging from zero to infinity, as in equation 3, 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

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

or discretely as

$$f_i = \frac{n_i}{N} = (h_i\Delta d_i) \tag{6}$$

where

$$N = \sum_i \left(h_i'\Delta d_i\right) \tag{7}$$

and N is used to standardize for sample size. When using the discrete summation, Δd_i should be relatively small to minimize the error associated with this estimation method. The size distribution information can also be presented as a cumulative distribution function, $F(a,MMD,GSD)$, which is defined by

$$F(a,MMD,GSD) = \int_0^a f(d_p,MMD,GSD)dd_p \tag{8}$$

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

$$f_{ab}(a,b,MMD,GSD) = F(b,MMD,GSD) - F(a,MMD,GSD) \tag{9}$$

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

$$C_{ab}(a,b,MMD,GSD) = C_T\left(F(b,MMD,GSD) - F(a,MMD,GSD)\right) \tag{10}$$

where C_T is the total concentration of PM in the ambient air.

For a lognormal distribution, the mode < median < mean. A lognormal density distribution defined by a MMD of 20 μm and a GSD of 3.0 is shown in Figure 2 to illustrate the differences between the mode, median, and mean of a lognormal distribution. Typically, the x-axis of a lognormal distribution is displayed on a log scale; however, the x-axis in Figure 2 is not displayed on a log scale, to graphically show the effects MMD and GSD on lognormal PSD's. Three important observations should be noted for lognormal distributions: (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.
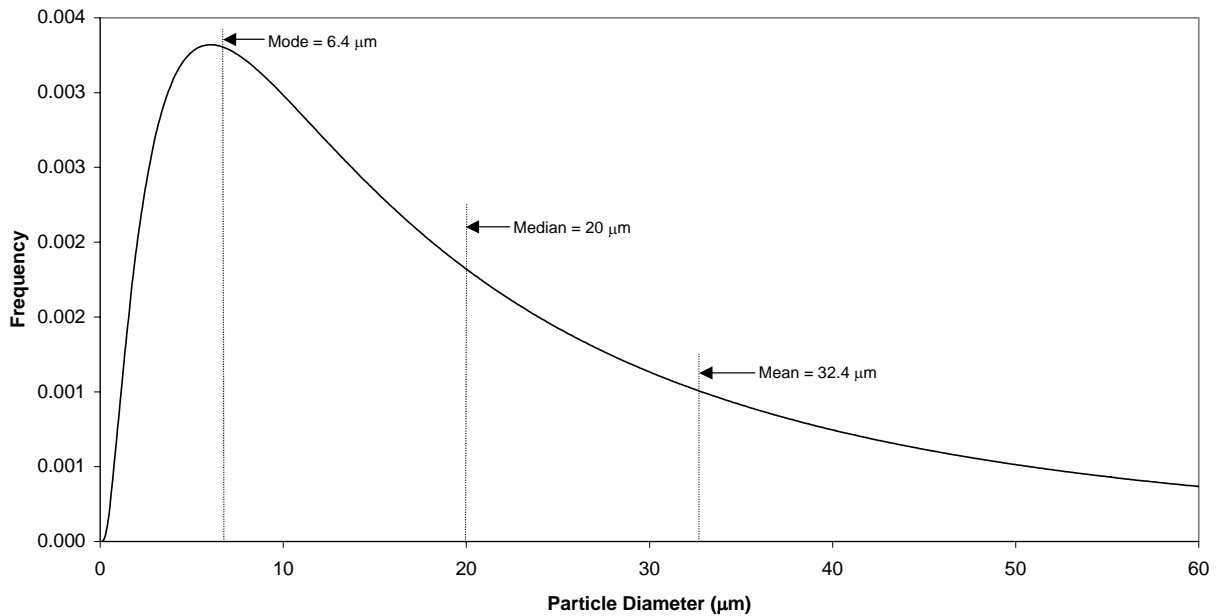
Figure 2. Lognormal particle size distribution defined by a MMD of 20 μm and a GSD of 3.0.

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 on the 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, virtual, and sampler cut. An ideal cut corresponds to the penetration curves provided by EPA in 40CFR53. A virtual cut penetration curve can be described as a step function; in other words, all the 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 cut refers to the actual penetration curve associated with a particular sampler. A sampler cut is defined by a sampler's performance characteristics and based on these characteristics, a portion of the PM less than the size of interest will not be collected on the filter and a portion of the PM greater than the size of interest will be collected on the filter. The perception of the public is that PM_{10} and $PM_{2.5}$ measurement concentrations are virtual cut concentrations and that the concentrations relate to PM with particle sizes less than 10 and 2.5 μm, respectively; however, these measurement concentrations are actually based on a sampler cut.

A sampler's pre-separator collection efficiency curve is most commonly represented by a lognormal distribution, which is characterized by the d_{50} (also referred to as cut-point) and slope of the collection efficiency curve. The cut-point is the particle size where 50% of the PM is captured by the pre-separator and 50% of the PM penetrates to the filter. The slope is the ratio of the particle sizes corresponding to cumulative collection efficiencies of 84.1% and 50% ($d_{84.1}/d_{50}$) or 50% and 15.9% ($d_{50}/d_{15.9}$). 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-separators 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 monodisperse particle sizes using known ambient concentrations. The concentration data from each test is used to determine the collection efficiency, ε_m, associated with each particle size, using the following equation.

$$\varepsilon_m = \frac{C_{\Pr e-Separator}}{C_{ambient}} \tag{11}$$

In equation 11, $C_{Pre-Separato}$ is the concentration of particles captured by the pre-separator $C_{ambient}$ 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 lognormal density distribution function for collection efficiency is defined as

$$\varepsilon_m(d_p, d_{50}, slope) = \left[\frac{1}{d_p \ln(slope)\sqrt{2\pi}} \exp\left[\frac{-(\ln d_p - \ln d_{50})^2}{2(\ln(slope))^2} \right] \right] \tag{12}$$

For a virtual cut sampler the slope is equal to 1 and for all other samplers the slope is greater than 1. Mathematical derivations for determining the cumulative distribution function for the collection efficiency can be achieved in the same manner presented in the particle size distribution section of this manuscript. The cumulative distribution function for the collection efficiency, $\psi(a, d_{50}, slope)$, is defined by

$$\psi_m(a, d_{50}, slope) = \int_0^a \varepsilon_m(d_p, d_{50}, slope) dd_p \tag{13}$$

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

$$P_m(a, d_{50}, slope) = 1 - \psi_m(a, d_{50}, slope) \tag{14}$$

Substituting equations 12 and 13 into equation 14 yields

$$P_m(a, d_{50}, slope) = 1 - \int_0^a \left[\frac{1}{d_p \ln(slope)\sqrt{2\pi}} \exp\left[\frac{-(\ln d_p - \ln d_{50})^2}{2(\ln(slope))^2} \right] \right] dd_p \tag{15}$$

where $P_m(a, d_{50}, slope)$ is the sampler penetration efficiency for particles having diameters less than a. Since a virtual cut penetration curve is defined by a step function, equation 15 can be simplified so that the virtual cut penetration efficiency can be defined as

$$P_v(a, d_{50}, slope) = \begin{cases} 1 & if\ a \le d_{50} \\ 0 & if\ a > d_{50} \end{cases} \tag{16}$$

Now that the penetration function has been defined, the sampler performance characteristics for the PM$_{10}$ and PM$_{2.5}$ samplers need to be defined in terms of d_{50} and slope. EPA essentially defines these parameters in 40CFR53 in the discussion of tests required for a candidate sampler to receive EPA approval. The d_{50} for both the PM$_{10}$ and PM$_{2.5}$ samplers are explicitly stated in the EPA standards as 10.0

± 0.5 µm and 2.5 ± 0.2 µm, respectively. No slope values for either sampler are listed in EPA's 40CFR53 or any other current EPA standard; however, penetration data is presented 40CFR53. Ideally, the penetration data could be fit to a cumulative lognormal distribution to determine the characteristic d_{50} and slope for each of the samplers; however, it was found that no single cumulative lognormal curve adequately represented the data sets.

The PM_{10} cumulative penetration data set produced a rough curve, which appeared to have a larger slope for the particle sizes less than 10 µm than the slope for the particle sizes greater than 10 µm. Hinds (1982) suggested that the slope associated PM deposited in the thoracic region of the human respiratory system had a slope of 1.5 ± 0.1 and that this slope represented the slope of the cumulative lognormal collection efficiency curve associated with the PM_{10} sampler. When comparing the nine curves produced by these sampler performance characteristics (d_{50} equal to 9.5, 10.0, and 10.5 µm and slopes equal to 1.4, 1.5, and 1.6) to the penetration data presented in 40CFR53, it was found that a combination of the nine curves produced a fairly good estimate of EPA's penetration data. Therefore, for the remaining sections of this manuscript the PM_{10} performance specifications will be assumed to be a d_{50} of 10 ± 0.5 µm and a slope of 1.5 ± 0.1.

Figure 3 illustrates the boundary penetration efficiency curves for the PM_{10} sampler, based the previously defined sampler performance characteristics. 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} 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%. These ranges are considered to be one form of inherent biases associated with PM_{10} samplers.
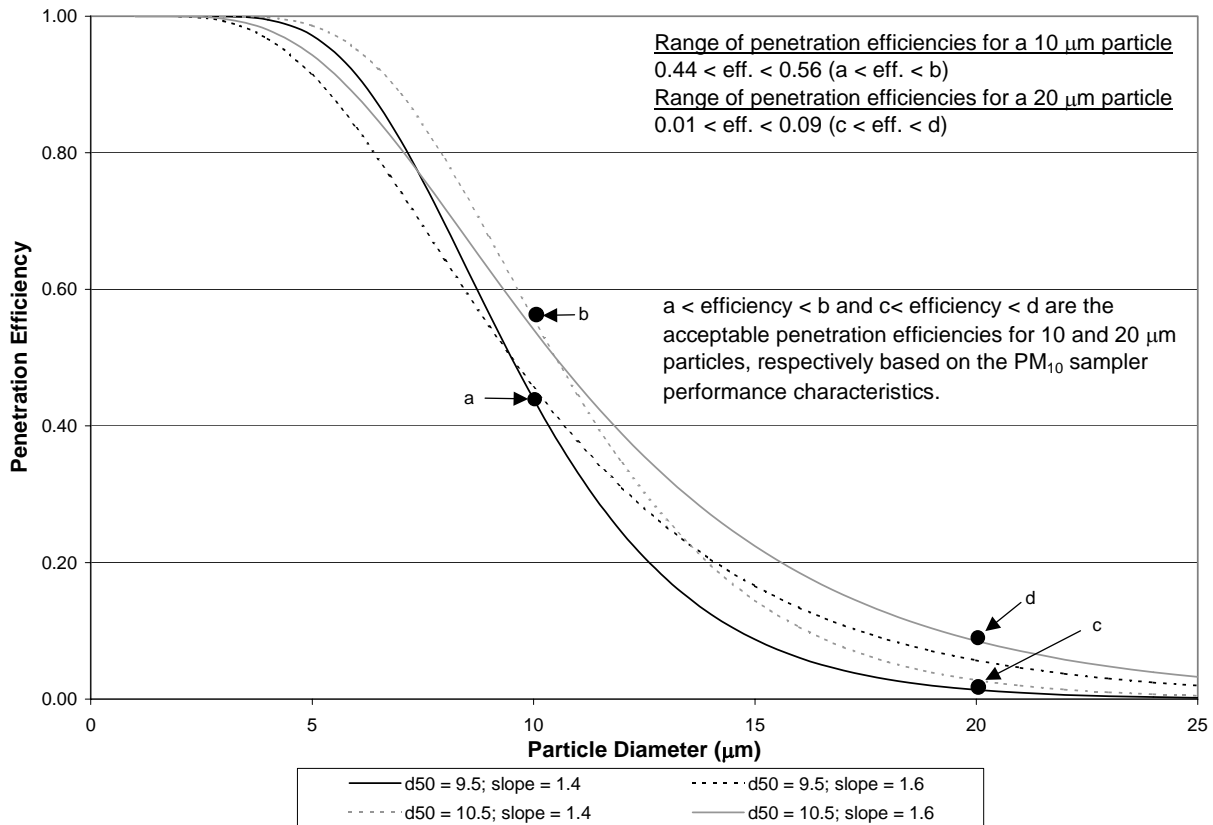

Figure 3. PM_{10} sampler penetration curves based on the defining performance characteristics.

EPA's PM$_{2.5}$ cumulative penetration data set produced a relatively smooth curve; however, the curve appeared to have a larger slope associated with particle sizes less than 2.5 μm than the slope associated with the particle sizes larger than 2.5 μm. It appears from the literature, that EPA intended for the PM$_{2.5}$ sampler to have a "sharp cut" or represent a virtual cut concentration of PM$_{2.5}$, which would mean that, ideally, the slope would be equal to 1. However, from an engineering standpoint, it is not possible to design a sampler with a virtual cut. Work by Peters and Vanderpool (1996) suggested that the slope of 1.18 could be achieved with the WINS Impator an EPA approved sampler. Further work by Buch (1999) suggested that the slopes were not as sharp as previously reported and that a more appropriate estimation of the sampler slopes would be 1.3 ± 0.03. For the purposes of this manuscript, the PM$_{2.5}$ sampler performance characteristics will be defined as having a d$_{50}$ equal to 2.5 ± 0.2 μm and a slope equal to 1.3 ± 0.03.

Figure 4 illustrates the boundary penetration efficiency curves for the PM$_{2.5}$ sampler, based the previously defined sampler performance characteristics. When comparing the boundary penetration efficiency curves in Figure 4, it is apparent that there is an acceptable range of penetration efficiencies for the PM$_{2.5}$ sampler. The acceptable range of penetration efficiencies for a particle size of 2.5 μm AED is 36 to 63%. These ranges are considered to be one form of inherent biases associated with PM$_{2.5}$ samplers. Figure 5 graphically illustrates the differences between a PM$_{2.5}$ sampler-cut, PM$_{10}$ sampler-cut, TSP-cut, PM$_{2.5}$ virtual-cut, and a PM$_{10}$ virtual-cut in relationship to a PSD characterized by an MMD of 20 μm and a GSD of 2.0.
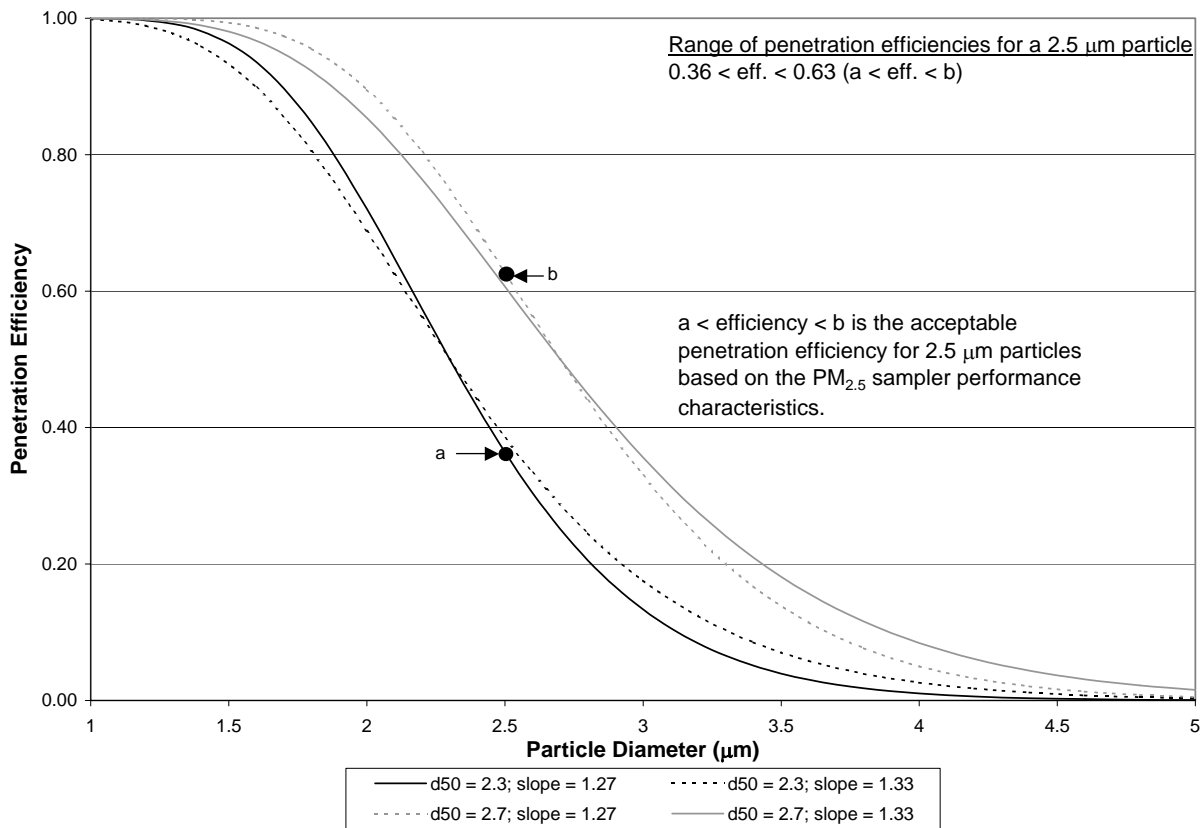

Figure 4. PM$_{2.5}$ sampler penetration curves based on the defining performance characteristics.
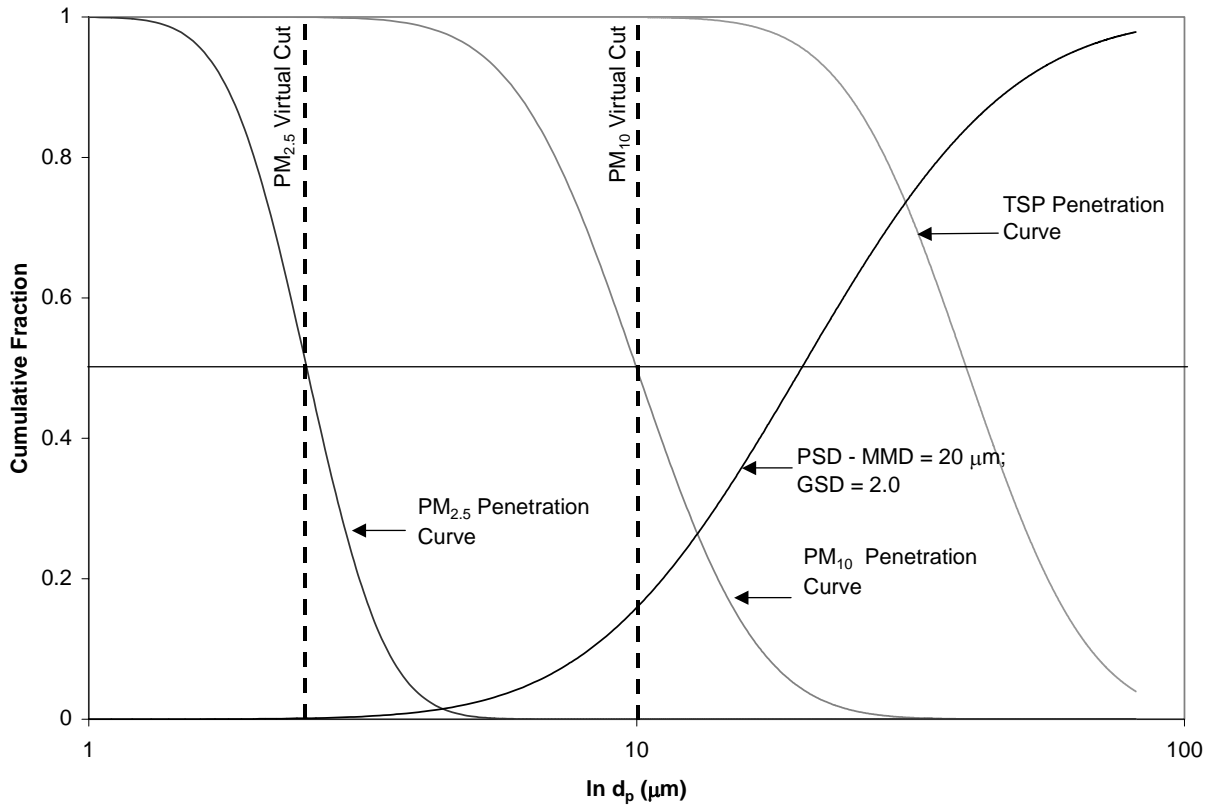
Figure 5. PM$_{2.5}$, PM$_{10}$, and TSP Penetration curves.

The issue of which sampler performance characteristics are correct is a valid concern; however, the most important question 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. According to the literature, it was EPA's intent for the PM$_{2.5}$ indicator to be a "true" (virtual cut) measure of PM with a particle diameter less than or equal to 2.5 μm. The intent of the PM$_{10}$ regulation is somewhat more complicated that the PM$_{2.5}$ regulation. First, it is quite clear in the literature that PM collected from a PM$_{10}$ 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. Another assumption made in the PM$_{10}$ regulation is that it pertains to a measure of particles with an AED less than or equal to a <u>nominal</u> 10 μm. The term nominal implies that the measured PM does not account for all mass associated with particles less than or equal to 10 μm and does include some of the mass associated with particles larger than 10 μm.

This issue of nominal values leads to a primary focus of this manuscript, that is, that industries that emit PM with an MMD less than 10 μm are not regulated at the same level as agricultural operations, which typically emit PM with an MMD greater than 10 μm. This unequal regulation is primarily due to the interaction of the sampler performance and PSD characteristics. A common assumption made in the regulatory community to circumvent this problem is that mass of particles less than the size of interest captured by the pre-separator are <u>equal</u> to the mass of particles greater than the size of interest that are captured on the filter. Figure 6 graphically illustrates this assumption. This assumption is only valid when the density function of the particle size distribution of the ambient air can be represented by a uniform distribution. Further, this assumption introduces a major source of error when the particle size

density distribution function is represented by a lognormal distribution; as is the case in virtually all situations involving ambient air. In simplistic terms, if property line sampler concentration measurements from two industries are exactly the same and if 100% of industry ones PM is less than 10 μm and 38% of industry twos PM is less than 10 μm; then based on Figure 1 100% industry ones PM can potentially reach the alveolar region of the lungs as compared to 38% of industry twos PM. Since the emphasis of the primary NAAQS is to protect public health; then in the previous scenario the two industries are not equally regulated. Therefore, in order to achieve equal regulation among differing industries, PM_{10} and $PM_{2.5}$ measurements **MUST** be based on virtual-cut measurements. A more in-depth discussion of this issue will be addressed herein.
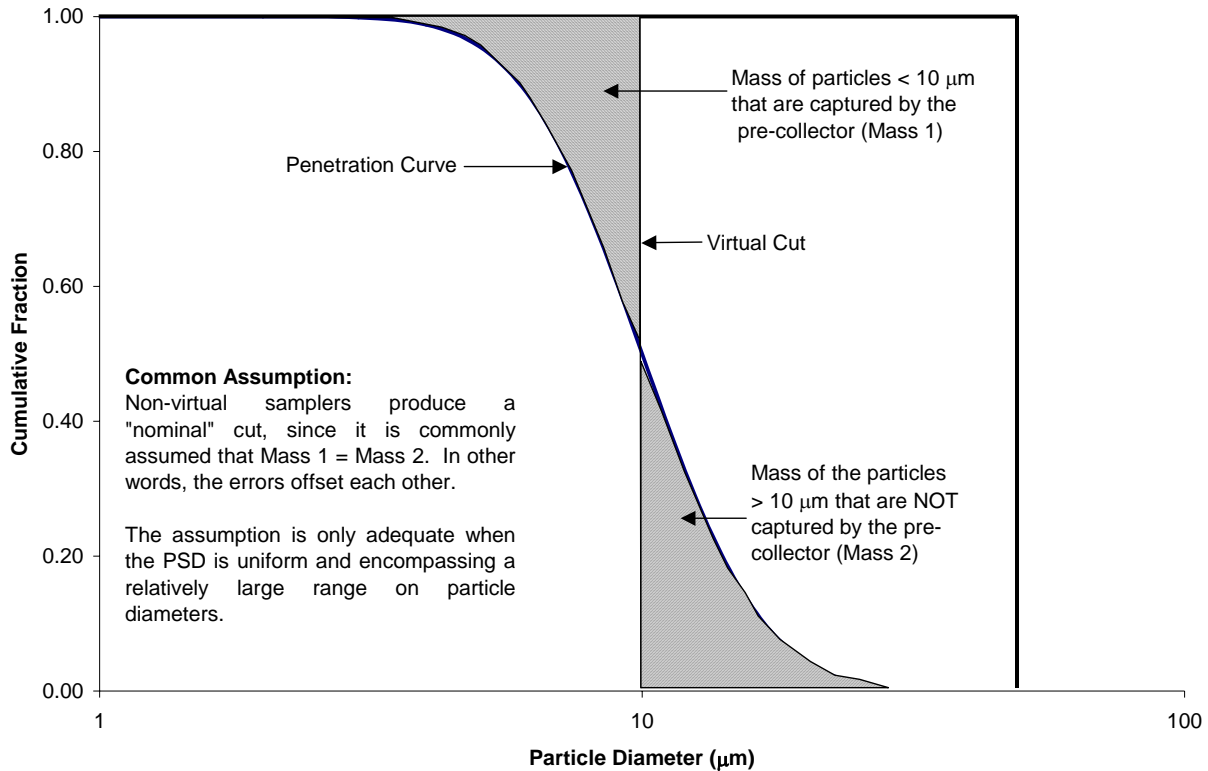

Figure 6. Sampler nominal cuts.

Estimating sampler and virtual cut concentrations

Sampler and virtual cut concentrations can be theoretically estimated using PSD and sampler performance characteristics. Sampler concentrations, $C_m(MMD,GSD,d_{50},slope)$, can be estimated by

$$C_m\left(MMD, GSD, d_{50}, slope\right) = C_a \int_0^\infty f(d_p, MMD, GSD) P_m(d_p, d_{50}, slope) dd_p \qquad (17)$$

For virtual-cut 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 virtual-cut concentration, $C_v(MMD,GSD,d_{50})$, can be estimated by

$$C_v\left(MMD, GSD, d_{50}\right) = C_a \int_0^{d_{50}} f(d_p, MMD, GSD) dd_p \qquad (18)$$

Relative differences between sampler and virtual-cut concentrations

As previously stated, sampler and virtual-cut concentrations do not always produce equal values. An estimate of the differences, $E(x)$, between these two concentrations can be estimated by

$$E(x) = \frac{(Measured - VirtualCut)}{VirtualCut} = \left(\frac{Measured}{VirtualCut}\right) - 1 \qquad (19)$$

where *Measured* and *VirtualCut* represent the estimated sampler and the virtual-cut concentrations, respectively. Substituting equations 17 and 18 into equation 19 and canceling like terms, yields

$$E(MMD, GSD, d_{50}, slope) + 1 = \left[\frac{\int_0^{\infty} f(d_p, MMD, GSD) P_m(d_p, d_{50}, slope) dd_p}{\int_0^{d_{50}} f(d_p, MMD, GSD) dd_p}\right] \qquad (20)$$

Throughout the remaining sections of this manuscript, *E(MMD, GSD, d₅₀, slope)+1* will be referred to as the ratio of the sampler concentration to the virtual-cut concentration.

Evaluation of concentration ratio

Mathcad 2000 was used to evaluate equation 20 for various PSD and sampler performance characteristics in order to obtain a general concept of how the interaction of these characteristics impacts the concentration ratio. The PSD characteristics included in the evaluation were MMD's of 5 and 10 μm with a GSD of 1.5 and MMD's of 15 and 20 μm with a GSD of 2.0. The sampler performance characteristics included the nine combinations of d_{50} and slope for both the PM_{10} and $PM_{2.5}$ samplers as described previously. Table 1 lists the results of this evaluation. In addition, Table 1 contains estimates for property line concentrations, under the assumption that the current regulated limit is based on a sampler concentration, and the regulation should be based on a virtual-cut concentration. In other words the NAAQS are based on sampler concentrations; however the NAAQS should be based on virtual-cut concentrations so that all industries are equally regulated. The mathematical definition for this assumption is

$$C_{Acceptable} = Ratio * C_{NAAQS} \qquad (21)$$

where C_{NAAQS} corresponds to the current concentrations associated with the NAAQS and $C_{acceptable}$ corresponds to the acceptable concentrations *if* the NAAQS were based on virtual-cut concentrations. The NAAQS for PM_{10} and $PM_{2.5}$ are 150 and 65 μg/acm, respectively. The following conclusions can be drawn from Table 1: (1) the PM_{10} sampler performance characteristics that define the range of acceptable concentrations are a d_{50} of 9.5 μm with a slope of 1.4 and 1.6 and a d_{50} of 10.5 μm with a slope of 1.4 and 1.6, (2) the $PM_{2.5}$ sampler performance characteristics that define the range of acceptable concentrations are a d_{50} of 2.3 μm with a slope of 1.27 and a d_{50} of 2.7 with a slope of 1.33 for PSD's with a MMD greater than 2.5 μm, (3) the ratios for PM_{10} range from 89 to 139%, (4) the ratios for $PM_{2.5}$ range from 108 to 1,314%, and (5) the ratio is equal to 100% only when the sampler d_{50} is equal to the PSD's MMD.

Table 1. Percent differences between theoretical sampler concentrations and virtual cut concentrations for various particle size and sampler performance characteristics.

| | Particle Size distribution (PSD) Characteristics | | | | | | | |
| | MMD = 5 μm GSD = 1.5 | | MMD = 10 μm GSD = 1.5 | | MMD = 15 μm GSD = 2.0 | | MMD = 20 μm GSD = 2.0 | |
PM_{10} sampler characteristics	Conc. (μg/m³)[ζ]	Ratio[γ]	Conc. (μg/m³)[ζ]	Ratio[γ]	Conc. (μg/m³)[ζ]	Ratio[γ]	Conc. (μg/m³)[ζ]	Ratio[γ]
d_{50} = 9.5 μm; slope = 1.4	139.4	92.9%	*138.3*	92.2%	*148.7*	99.1%	*157.8*	105.2%
d_{50} = 9.5 μm; slope = 1.5	136.2	90.8%	139.4	92.9%	153.0	102.0%	167.3	111.5%
d_{50} = 9.5 μm; slope = 1.6	*133.2*	88.8%	140.1	93.4%	157.2	104.8%	176.9	117.9%
d_{50} = 10.0 μm; slope = 1.4	142.1	94.7%	150.0	100.0%	160.8	107.2%	174.2	116.1%
d_{50} = 10.0 μm; slope = 1.5	139.1	92.7%	150.0	100.0%	164.9	109.9%	183.5	122.3%
d_{50} = 10.0 μm; slope = 1.6	136.2	90.8%	150.0	100.0%	168.8	112.5%	192.8	128.5%
d_{50} = 10.5 μm; slope = 1.4	*144.5*	96.3%	*161.1*	107.4%	172.8	115.2%	190.5	127.0%
d_{50} = 10.5 μm; slope = 1.5	141.5	94.3%	160.2	106.8%	176.4	117.6%	199.7	133.1%
d_{50} = 10.5 μm; slope = 1.6	138.6	92.4%	159.5	106.3%	*180.0*	120.0%	*208.8*	139.2%
$PM_{2.5}$ sampler characteristics								
d_{50} = 2.3 μm; slope = 1.27	*73.65*	113.3%	*185.45*	285.3%	*70.40*	108.3%	*76.57*	117.8%
d_{50} = 2.3 μm; slope = 1.3	80.28	123.5%	242.19	372.6%	76.12	117.1%	84.76	130.4%
d_{50} = 2.3 μm; slope = 1.33	87.23	134.2%	313.30	482.0%	82.49	126.9%	94.06	144.7%
d_{50} = 2.5 μm; slope = 1.27	104.78	161.2%	345.35	531.3%	97.05	149.3%	109.92	169.1%
d_{50} = 2.5 μm; slope = 1.3	112.52	173.1%	423.87	652.1%	104.26	160.4%	120.90	186.0%
d_{50} = 2.5 μm; slope = 1.33	120.58	185.5%	534.17	821.8%	112.26	172.7%	133.19	204.9%
d_{50} = 2.7 μm; slope = 1.27	141.77	218.1%	559.07	860.1%	129.16	198.7%	151.97	233.8%
d_{50} = 2.7 μm; slope = 1.3	150.28	231.2%	693.49	1066.9%	138.06	212.4%	166.01	255.4%
d_{50} = 2.7 μm; slope = 1.33	*159.12*	244.8%	*854.10*	1314.0%	*147.81*	227.4%	*181.74*	279.6%

[γ] Values are based on the assumption that virtual-cut concentrations are the correct estimates of the corresponding PM.
[ζ] Concentrations are based on the corresponding regulations and adjusted for the ratio. Property line concentrations for PM_{10}

and $PM_{2.5}$ are 150 and 65 μ g/m³, respectively.

To further describe how the interaction of the PSD and sampler characteristics affect the acceptable PM concentrations, a series of macros were created in Microsoft Excel to generate a data file containing the solutions to equations 20 and 21 over a range of parameters. These parameters included MMD values ranging from 1 to 40 μm (in increments of 1 μm), GSD values ranging from 1.1 to 3.0 (in increments of 0.1), d_{50} values ranging from 1 to 13 μm (in increments of 1 μm), and slope values ranging from 1.1 to 3.0 (in increments of 0.1). To illustrate the results of this simulation, several graphs were created to demonstrate how each of the parameters affects the concentration ratio.

In Figure 7, 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 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 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 this figure are: (1) the average ratio is less than 1 when MMD<d_{50}, (2) the average ratio is equal to 1 when MMD=d_{50}, (3) the average ratio is greater than 1 when MMD>d_{50}, and (4) the ratio range increases as the MMD increases. In general terms, when the ratio is less than 1 the current method of regulating PM_{10} underestimates the concentration of PM less than or equal to 10 μm AED and when the ratio is greater than 1 the current method overestimates the concentration of PM less than or equal to 10 μm AED. For example, if a PSD were characterized by a MMD of 10 μm AED and a GSD of 2.0 then the acceptable range of PM_{10} concentrations would be 143 to 158 μg/acm. However, if a PSD were characterized by a

MMD of 20 μm AED and a GSD of 2.0 then the acceptable range of PM_{10} concentrations would be 158 to 209 μg/acm.
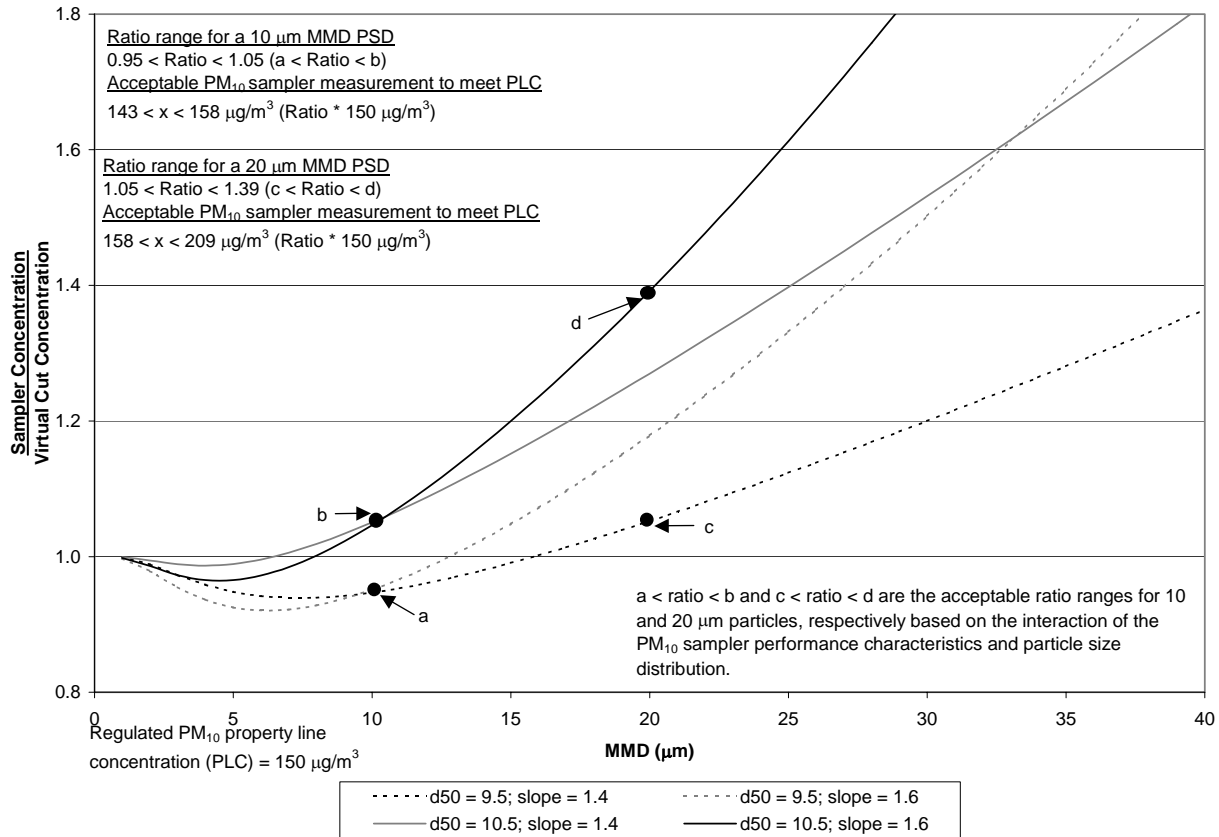

Figure 7. Ratios of the theoretical PM_{10} sampler concentrations to PM_{10} concentrations based on a PSD virtual cut (PSD – GSD = 2.0)

The data presented in Figure 8 are based on the same assumptions as Figure 7, except the data are based on a GSD of 1.5. When comparing Figures 7 and 8, 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 a MMD of 10 μm AED and a GSD of 1.5 then the acceptable range of PM_{10} concentrations would be 138 to 159 μg/acm. However, if a PSD were characterized by a MMD of 20 μm AED and a GSD of 1.5 then the acceptable range of PM_{10} concentrations would be 272 to 515 μg/acm. Another conclusion that can be drawn from the data presented in Figure 8 is that the range of acceptable concentration increases as the GSD increases.

In Figure 9 the GSD is held constant at 2.0 for the two sets of $PM_{2.5}$ sampler performance characteristics (which define the acceptable concentrations for $PM_{2.5}$), and the PSD MMDs range from 1 to 40 μm. A conclusion that can be drawn from this graph is that the concentration ratios are always greater than 1 when MMD is greater than 10 μm AED. For example, if a PSD were characterized by a MMD of 10 μm AED and a GSD of 2.0 then the acceptable range of $PM_{2.5}$ concentrations would be 65 to 117 μg/acm. However, if a PSD were characterized by a MMD of 20 μm AED and a GSD of 1.5 then the acceptable range of $PM_{2.5}$ concentrations would be 78 to 182 μg/acm.
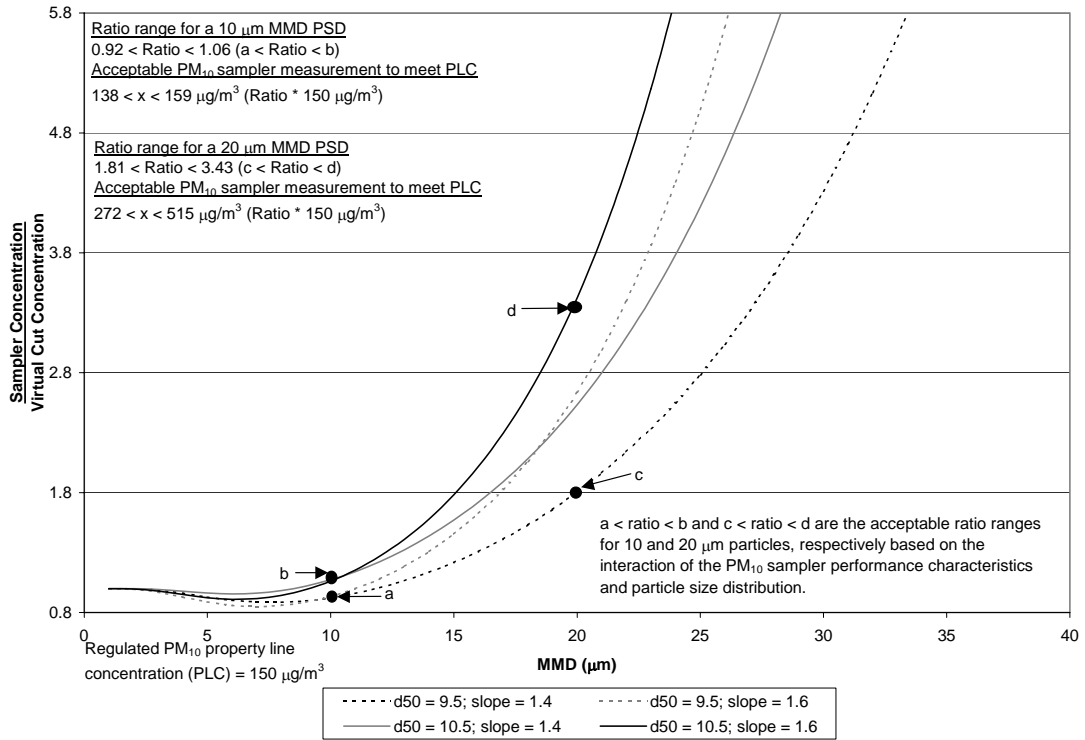
Figure 8. Ratios of the theoretical PM$_{10}$ sampler concentrations to PM$_{10}$ concentrations based on a PSD virtual cut (PSD – GSD = 1.5)
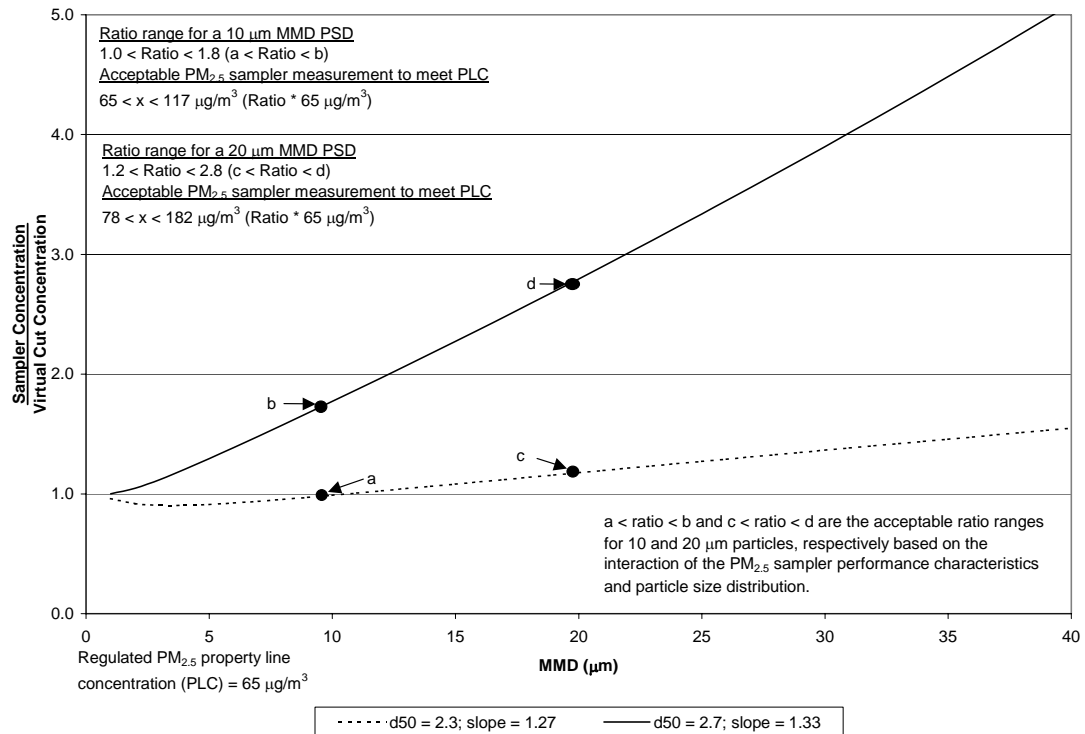

Figure 9. Ratios of the theoretical PM$_{2.5}$ sampler concentrations to PM$_{2.5}$ concentrations based on a PSD virtual cut (PSD – GSD = 2.0)

The data presented in Figure 10 is based on the same assumptions as Figure 9, except the data are based on a GSD of 1.5. When comparing Figures 9 and 10, it is clear that ratios and ratio ranges 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 a MMD of 10 μm AED and a GSD of 1.5 then the acceptable range of $PM_{2.5}$ concentrations would be 188 to 851 μg/acm. However, if a PSD were characterized by a MMD of 20 μm AED and a GSD of 1.5 then the acceptable range of $PM_{2.5}$ concentrations would be 962 to 11,901 μg/acm. Based on this information, not only should agricultural operations be concerned with the current method regulating $PM_{2.5}$ but other industries such as coal-fired power plants should be extremely concerned with the current method of regulating $PM_{2.5}$.

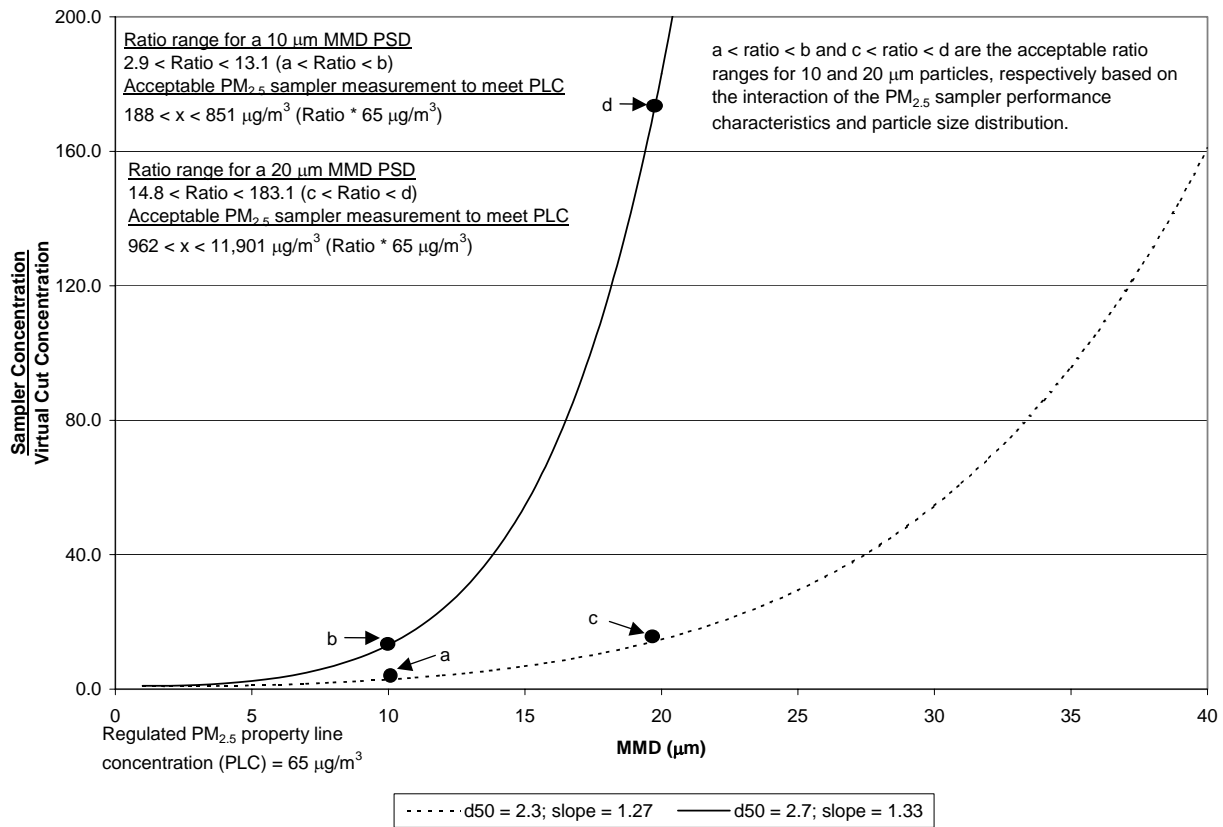**Figure 10.** Ratios of the theoretical $PM_{2.5}$ sampler concentrations to $PM_{2.5}$ concentrations based on a PSD virtual cut (PSD – GSD = 1.5)

Figure 11 is a generalized graph to illustrate how MMD and GSD affect the concentration ratios for a PM_{10} sampler with a d_{50} 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 (approach 1) as the GSD increases. A similar observation can be drawn from Figure 12, which illustrates how MMD and GSD affect the concentration ratios for a $PM_{2.5}$ sampler with a d_{50} of 2.5 μm and a slope of 1.3.
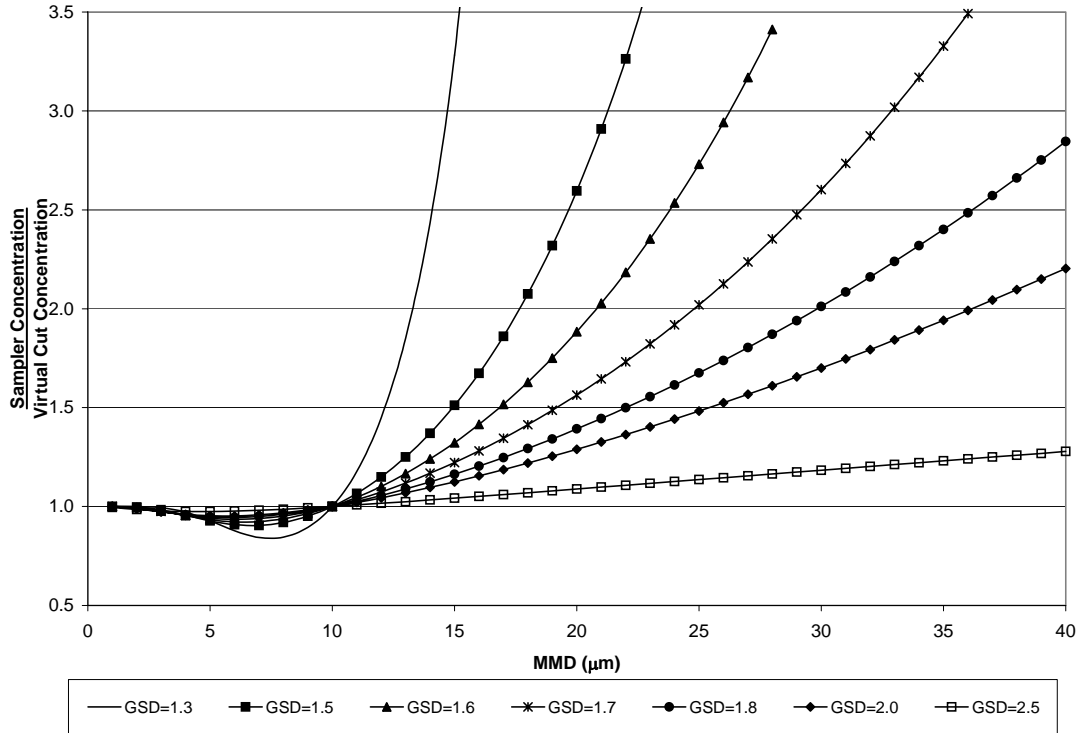
Figure 11. Ratios of the theoretical PM_{10} sampler concentrations to PM_{10} concentrations based on a PSD virtual cut (PM_{10} sampler characteristics; $d_{50} = 10$ μm and slope = 1.5)
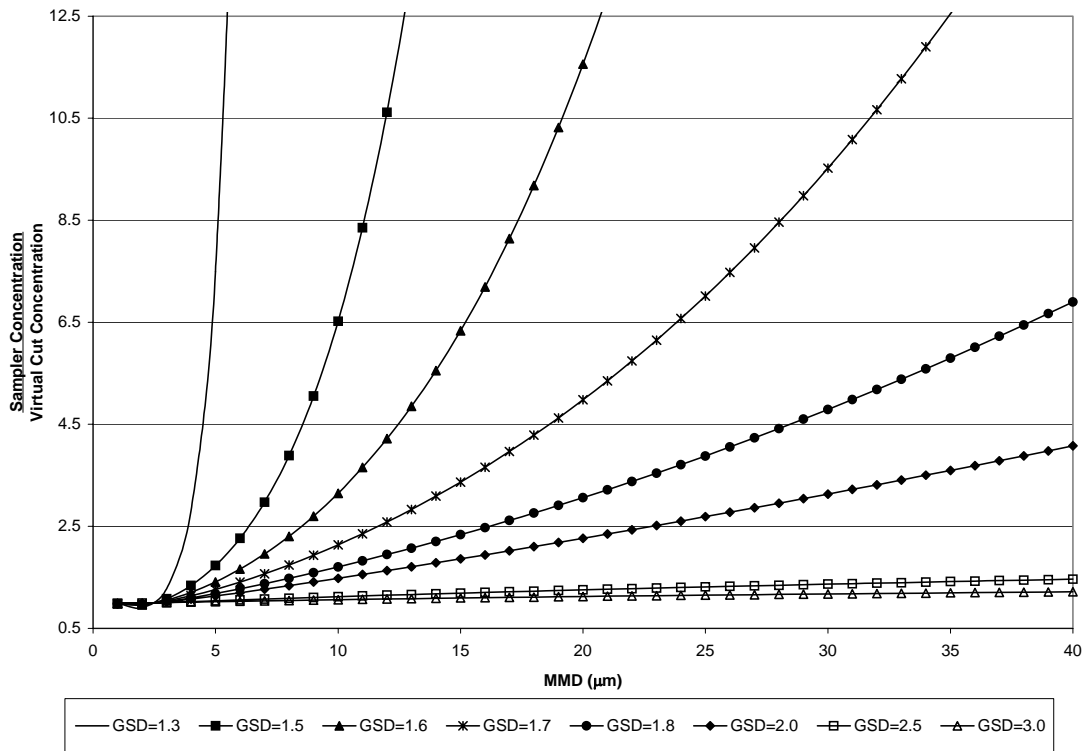

Figure 12. Ratios of the theoretical $PM_{2.5}$ sampler concentrations to $PM_{2.5}$ concentrations based on a PSD virtual cut ($PM_{2.5}$ sampler characteristics; $d_{50} = 2.5$ m and slope = 1.3)

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Figures 13 and 14 further expand on how the concentration ratios are impacted by GSD. The data presented in Figure 13 are based on MMDs of 10 and 20 μm, sampler performance characteristics of d_{50} = 9.5 with a slope of 1.4 and d_{50} = 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 MMD = 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. Similar conclusions can be drawn from Figure 14, which is similar to Figure 13 except the sampler performance characteristics are d_{50} = 2.3 μm with a slope of 1.27 and d50 = 2.7 μm with a slope of 1.33.
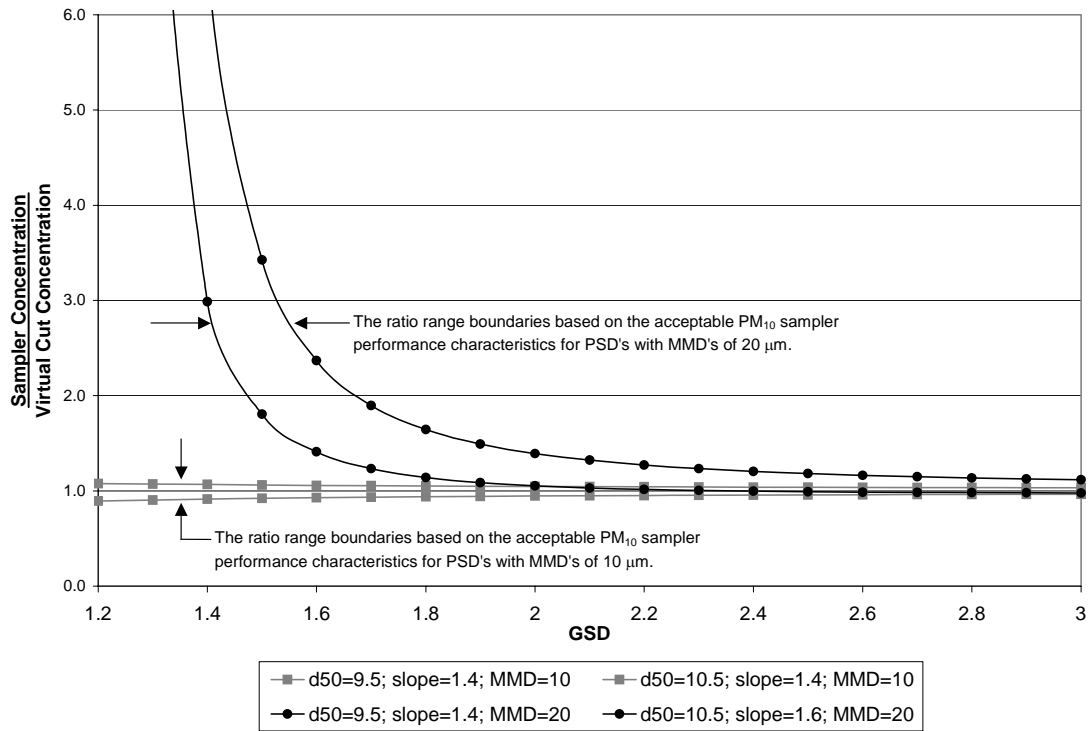

Figure 13. Ratios of the theoretical PM_{10} sampler concentrations to PM_{10} concentrations based on a PSD virtual cut.
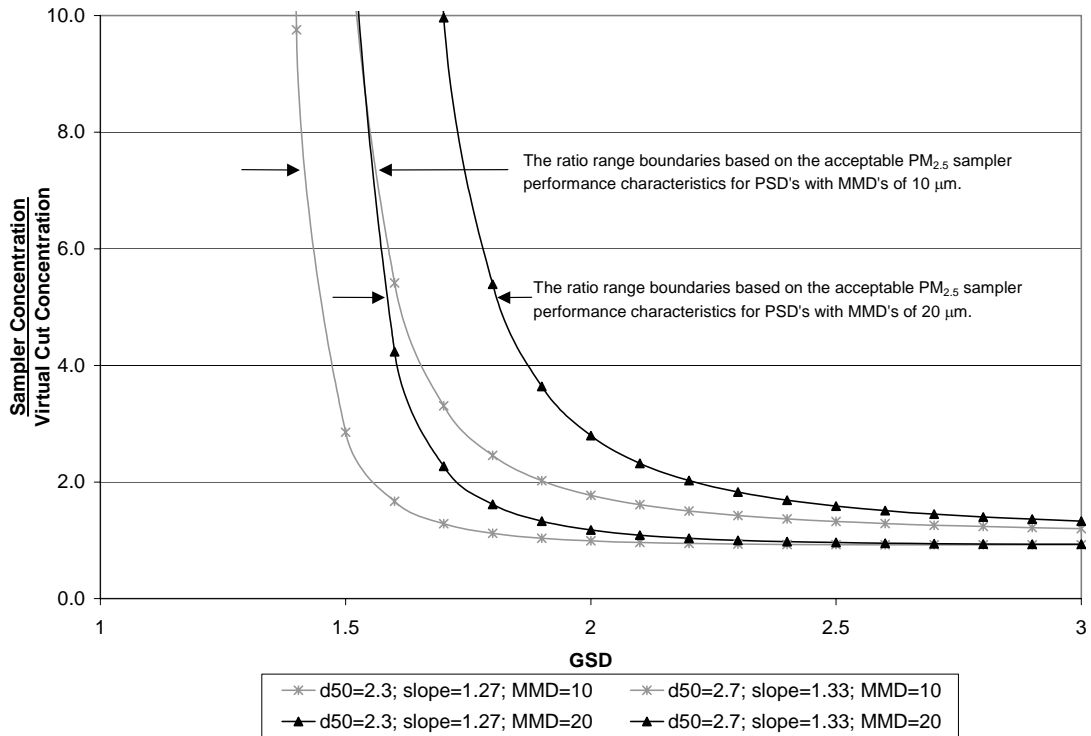
Figure 14. Ratios of the theoretical $PM_{2.5}$ sampler concentrations to $PM_{2.5}$ concentrations based on a PSD virtual cut.

Figures 15 thru 18 are used to illustrate how d_{50} and slope impact the concentration ratio. In these four graphs, the values for d_{50} range from 1 to 13 μm and the values for slope vary from 1.1 to 2.5. In Figure 15 the MMD and GSD are 10.0 μm AED and 2.0, respectively. Two general observations that can be drawn from Figures 15 thru 18 are: (1) the concentration ratio increases as d_{50} decreases for d_{50}'s less than the MMD, and (2) the concentration ratio increases as the slope increases for d_{50}'s less than the MMD. For example, in Figure 15 if the sampler d_{50} is 2.5 μm and the slope is 1.2, the actual concentration would be 93 μg/acm; however, if the slope were increased to 1.5, the actual concentration would be 171 μg/acm. In Figure 16, the GSD is decreased to 1.5. Based on this information, if the sampler d_{50} was 2.5 μm and the slope was 1.2, the corresponding actual concentration would be 189 μg/acm; however, if the slope were increased to 1.5 then the actual concentration would be 1,619 μg/acm. In Figures 17 and 18 the MMD's were increased to 20 μm AED. A GSD of 2.0 was used to generate Figure 17. Based on Figure 17, if the sampler's d_{50} were 2.5 μm and the slope was 1.2 then the actual concentration would be 91 μg/acm; however, if the slope were increased to 1.5 then the actual concentration would be 234 μg/acm. In Figure 18, the GSD is decreased to 1.5. Based on the data presented in this graph, if the sampler d_{50} were 2.5 μm and the slope was 1.2 the actual concentration would be 644 μg/acm; however, if the slope were increased to 1.5 then the actual concentration would be 64,032 μg/acm.
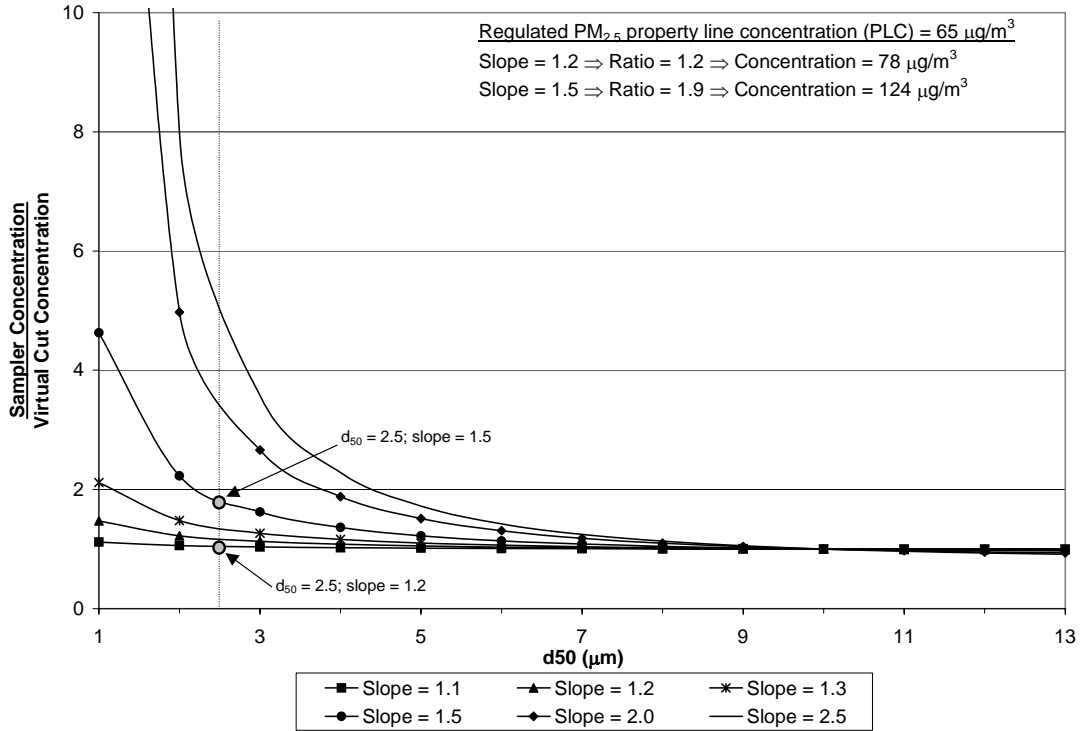
Figure 15. Ratios of the theoretical sampler concentrations to concentrations based on a PSD virtual cut (PSD – MMD = 10 μm; GSD = 2.0).
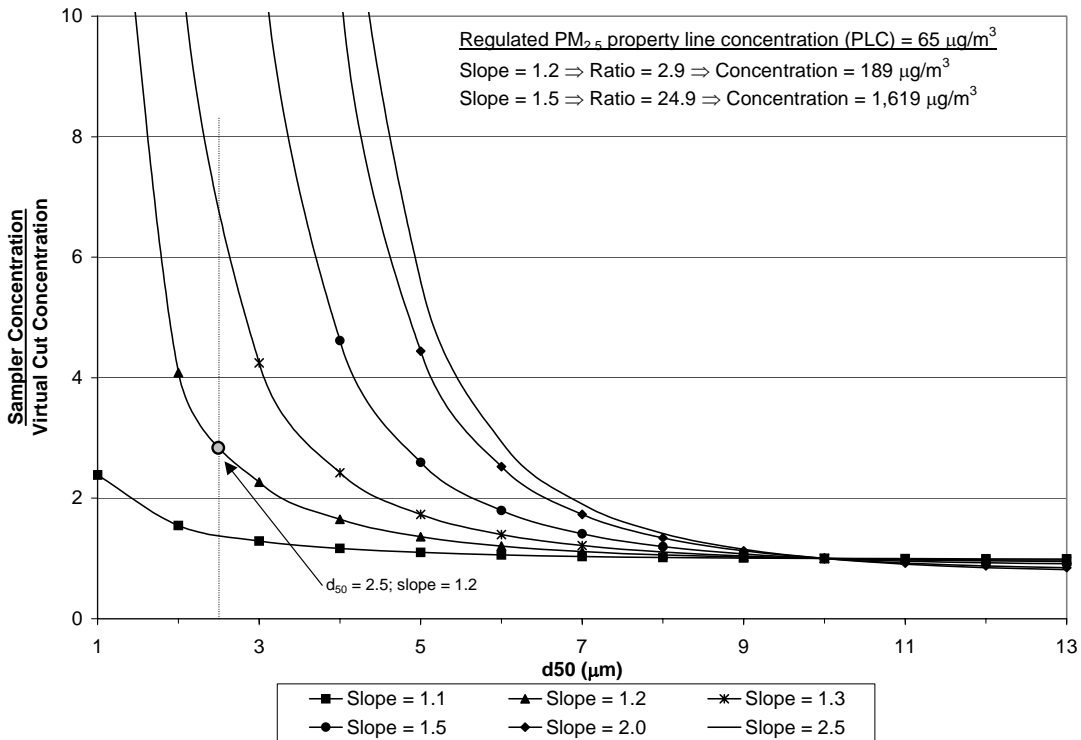

Figure 16. Ratios of the theoretical sampler concentrations to concentrations based on a PSD virtual cut (PSD – MMD = 10 μm; GSD = 1.5).
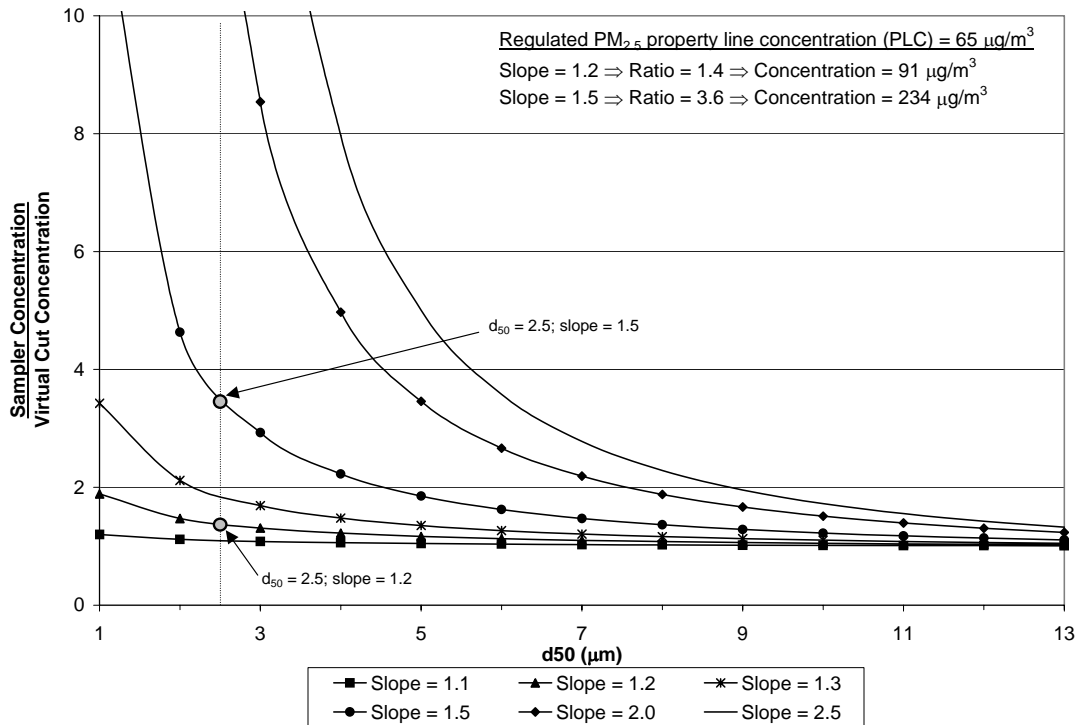
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Figure 17. Ratios of the theoretical sampler concentrations to concentrations based on a PSD virtual cut (PSD – MMD = 20 μm; GSD = 2.0).
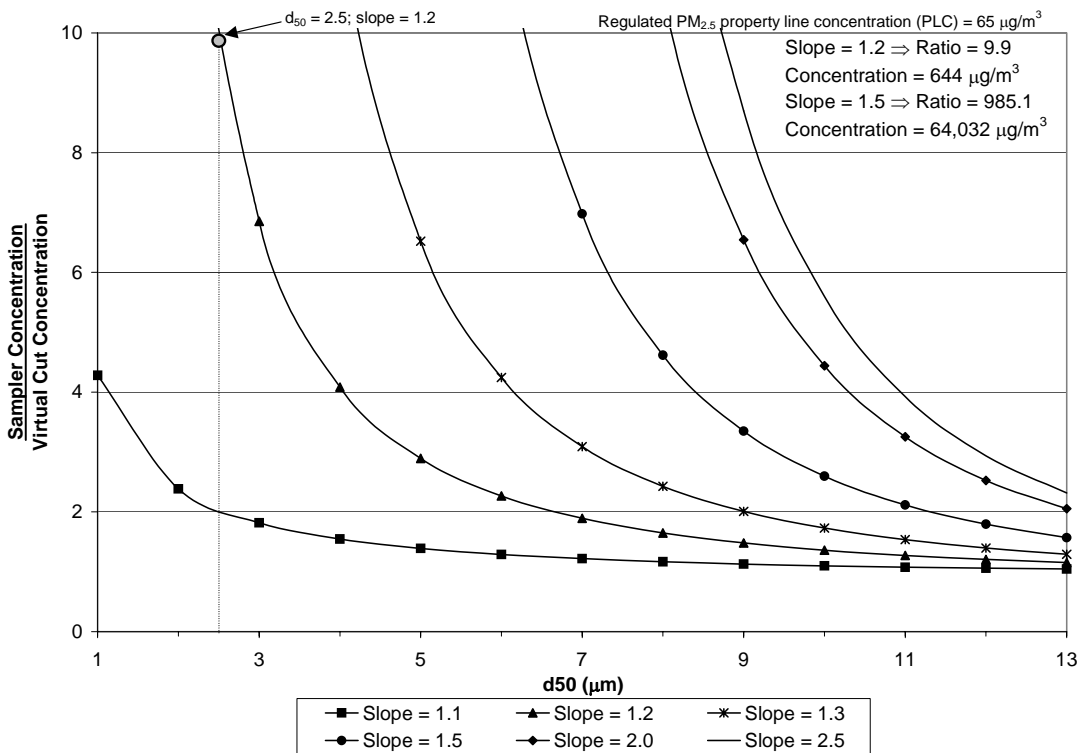

Figure 18. Ratios of the theoretical sampler concentrations to concentrations based on a PSD virtual cut (PSD – MMD = 20 μm; GSD = 1.5).

Summary and Conclusions

There are several biases associated with the current air pollution rules and regulations established by EPA, which should be minimized to assure an appropriate, fair, and equal regulation of air pollutants between and within all industries. Potentially, one the most significant biases 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 <u>NOT</u> virtual-cut 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 PSD virtual-cut 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.

What is the impact of this bias? The following example will demonstrate the impacts of this bias. Assume:

- PSD associated with a coal-fired power plant is described by a MMD = 10 μm and a GSD = 1.5;
- PSD associated with a agricultural operation is described by a MMD = 20 μm and a GSD = 1.5;
- PM is currently regulated in terms of PM_{10} and $PM_{2.5}$ sampler concentrations with maximum property line concentrations limits of 150 and 65 μg/acm, respectively;
- PM_{10} sampler performance characteristics are described by a $d_{50} = 10 \pm 0.5$ μm and a slope of 1.5 $\pm$ 0.1; and
- $PM_{2.5}$ sampler performance characteristics are described by a $d_{50} = 2.5 \pm 0.2$ μm and a slope of 1.3 $\pm$ 0.03;

Based on the current method of regulating PM, both the coal-fired power plant and the agricultural operation must not exceed the property line PM_{10} and $PM_{2.5}$ concentrations of 150 and 65 μg/acm, respectively (based on sampler measurements) in order to maintain compliance with the NAAQS. This current method of regulation does <u>NOT</u> account for the biases associated with the sampler performance characteristics or biases associated with the interaction of the industry specific PSD and sampler performance characteristics. In order to adequately account for these biases, the maximum allowable compliance levels must be established based on the sampler performance characteristics that produce the largest concentration levels and the maximum allowable compliance levels must be based on virtual cut concentrations. In other words:

- the PM_{10} sampler performance characteristics that should be used to estimate the maximum allowable compliance levels of PM_{10} are a d_{50} of 10.5 μm and a slope of 1.6;
- the $PM_{2.5}$ sampler performance characteristics that should be used to estimate the maximum allowable compliance levels of $PM_{2.5}$ are a d_{50} of 2.7 μm and a slope of 1.33; and
- the maximum allowable compliance levels should be based virtual-cut concentrations (150 μg/acm for PM_{10} and 65 μg/acm for $PM_{2.5}$), meaning that if PM_{10} and $PM_{2.5}$ concentrations are determined by the corresponding size specific samplers that the measured concentrations must be corrected to represent virtual-cut concentrations;

Adjusting the maximum allowable compliance levels for these biases the following results are obtained:

- For the coal-fired power plant, a PM_{10} sampler could measure concentrations as high as 159 μg/acm and still be in compliance with the NAAQS. This results in a 6% bias due to the sampler performance characteristics.
- For the coal-fired power plant, a $PM_{2.5}$ sampler could measure concentrations as high as 851 μg/acm and still be in compliance with the NAAQS. This results in a 1209% bias due to the sampler performance characteristics and interactions of the PSD and sampler performance characteristics.

- For the agricultural operation, a PM_{10} sampler could measure concentrations as high as 515 μg/acm and still be in compliance with the NAAQS. This results in a 243% bias due to the sampler performance characteristics and interactions of the PSD and sampler performance characteristics.
- For the agricultural operation, a $PM_{2.5}$ sampler could measure concentrations as high as 11,901 μg/acm and still be in compliance with the NAAQS. This results in an 18,209% bias due to the sampler performance characteristics and the interactions of the PSD and sampler performance characteristics.

Further, based on this analysis, the agricultural operation is currently being regulated at a level, which is 3.2 and 14.0 times more stringent for PM_{10} and $PM_{2.5}$, respectively than that for a coal-fired power plant (under the previously stated assumptions).

The following are generalized conclusions drawn from the analysis in this manuscript:
- if $MMD < d_{50}$ then $C_{measured} < C_{virtual}$;
- if $MMD = d_{50}$ then $C_{measured} = C_{virtual}$;
- if $MMD > d_{50}$ then $C_{measured} > C_{virtual}$;
- as GSD increases the concentration ration of $C_{measured}$ to $C_{virtual}$ decreases; and
- as sampler slope decreases the concentration ration of $C_{measured}$ to $C_{virtual}$ decreases.

Results of the analysis presented in this manuscript 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 EPA and enforced by SAPRA's.

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