PM$_{2.5}$ SAMPLER ERRORS DUE TO THE INTERACTION OF PARTICLE SIZE AND SAMPLER PERFORMANCE CHARACTERISTICS

Michael D. Buser
Cotton Production and Processing Research Unit, USDA/ARS
Lubbock, TX
Calvin B. Parnell, Jr., Ronald E. Lacey, and Bryan W. Shaw
Agricultural Engineering Department, Texas A&M University
College Station, TX

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$_{2.5}$, are ambient air concentration limits set by EPA that should not be exceeded. Further, State Air Pollution Regulatory Agencies (SAPRA's) utilize the NAAQS to regulate criteria pollutants emitted by industries by applying the NAAQS as property line concentration limit. The primary NAAQS are health-based standards and therefore, an exceedance implies that it is likely that there will be adverse health effects for the public. Since the proposal of the PM$_{2.5}$ regulation, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulation, methods of determining PM$_{2.5}$, etc. A common trend among many of these publications is the use of samplers to collect information on PM$_{2.5}$. All too often, the sampler data are assumed to be an accurate measure of PM$_{2.5}$. The fact is that 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 errors associated with the particle size distribution (PSD) characteristics of the material in the air that is being sampled, sampler performance characteristics, the interaction between these two characteristics, and the effect of this interaction on the regulatory process. Theoretical simulations were conducted to determine the range of errors associated with this interaction for the PM$_{2.5}$ sampler. Results from these simulations indicated that a source emitting PM characterized by a mass median diameter (MMD) of 20 µm and a geometric standard deviation (GSD) of 1.5 could be forced to comply with a 14 times more stringent regulation than a source emitting PM characterized by a MMD of 10 µm and a GSD of 1.5. Therefore, in order to achieve equal regulation among differing industries, PM$_{2.5}$ measurements **MUST** be based on true concentration measurements.

Introduction

The Federal Clean Air Act (FCAA) of 1960 and subsequent amendments established national goals for air quality and incorporated the use of standards for the control of pollutants in the environment. The 1970 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) (U.S. Environmental Protection Agency, 1996). 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, manmade 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 (Federal Register, 1971). The NAAQS for particulate matter (PM) was established and total suspended particulate (TSP) was defined as a criteria pollutant. 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 TSP with a new criteria pollutant 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 incorporated an additional criteria pollutant for the ambient air standards that would account for particles with an AED less than or equal to a nominal 2.5 µm (PM$_{2.5}$) (Federal Register, 1987. (Cooper and Alley, 1994)

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 fraction of PM. Note that virtually no respirable PM (PM that can penetrate into the alveolar

region of the human lung) is greater than 10 μm, whereas 50% of the 3.5 μm particles are considered respirable and can reach the alveolar region, as shown in Figure 1. (U.S. Environmental Protection Agency, 1996)

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 cut-point values ranging from 3.5 to 5.0 μm for "healthy adults" (ISO, 1993). 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 (U. S. Environmental Protection Agency, 1996). 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 cut-point of 2.4 μm, which is claimed to relate to the deposition of particles in the lungs of children and adults with certain lung diseases.

The NAAQS for PM in terms of $PM_{2.5}$, are the concentration limits set by EPA that should not be exceeded (U. S. Environmental Protection Agency, 2000a). 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 proposed $PM_{2.5}$ primary 24-hour NAAQS is 65 micrograms per actual cubic meter (μg/acm) (U. S. Environmental Protection Agency, 2000a). The secondary NAAQS for $PM_{2.5}$ is set at the same level as the primary NAAQS.

Prior to and since $PM_{2.5}$ was included into EPA's regulation guidelines, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulation, methods of determining $PM_{2.5}$, etc. A common trend among many of these publications is the use of samplers to collect information on $PM_{2.5}$. The data collected from the samplers are commonly used in statistical correlations and statistical comparisons to draw conclusions about $PM_{2.5}$ emission concentrations. All too often, the sampler data are assumed to be an accurate measure of $PM_{2.5}$. The fact is that 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 particle size distribution (PSD) characteristics of the material in the air that is being sampled, sampler performance characteristics, the interaction between these two characteristics for $PM_{2.5}$ samplers, and the effect of this interaction on the regulatory process.

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". The significance of using a lognormal distribution is that the PSD can be described in terms of the mass median diameter (MMD) and the geometric standard deviation (GSD). The mathematical definition and manipulation of the lognormal distribution as described in equations 1 through 6 can be found in Hinds (1998) and Seinfeld and Pandis (1997). The lognormal mass density function is expressed as

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

For monodisperse particles the GSD is equal to 1.0 and for polydisperse particles the GSD is greater than 1.0. The fraction of the total particles df having particle diameters between d_p and $d_p + dd_p$ is

$$df = f(d_p, MMD, GSD)dd_p$$ (2)

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

$$\int_0^\infty f(d_p, MMD, GSD)dd_p = 1.0$$ (3)

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 as

$$f_{ab}(a,b,MMD,GSD) = \int_a^b f(d_p,MMD,GSD)dd_p \qquad (4)$$

The size distribution can also be presented as a cumulative distribution function, *F(a,MMD,GSD)*, defined by

$$F(a,MMD,GSD) = \int_0^a f(d_p,MMD,GSD)dd_p \qquad (5)$$

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*.

$$f_{ab}(a,b,MMD,GSD) = F(b,MMD,GSD) - F(a,MMD,GSD) \qquad (6)$$

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

$$C_{ab}(a,b,MMD,GSD) = C_T[F(b,MMD,GSD) - F(a,MMD,GSD)] \qquad (7)$$

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

Sampler Performance Characteristics

A sampler's performance is generally described by either a cumulative collection or penetration efficiency curve. The "sharpness of cut" of the sampler pre-separator or the "sharpness of 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, true, and sampler cut. An ideal cut corresponds to the penetration data provided in 40CFR53 (U. S. Environmental Protection Agency, 2000b). A true cut can be described as a step function; 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. A common perception is that PM$_{2.5}$ sampler concentrations are true concentrations and that the concentrations directly relate to PM with particle sizes less than 2.5 µm or true PM$_{2.5}$; however, these sampler concentrations are actually based on a sampler cut.

A sampler's pre-separator collection efficiency curve is most commonly represented by a lognormal distribution, characterized by a d$_{50}$ (also referred to as cut-point) and slope of the collection efficiency curve (Hinds, 1998). 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$_{50}$), 50% and 15.9% (d$_{50}$/d$_{15.9}$), or the square root of 84.1% and 15.9% ($\sqrt{d_{84.1}/d_{15.9}}$) (Hinds, 1998). 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 (U.S. Environmental Protection Agency, 2000b):

$$\varepsilon_m = \frac{C_{Pre-Separator}}{C_{ambient}} \qquad (8)$$

In equation 8, *C$_{Pre-Separator}$* is the concentration of particles captured by the pre-separator and *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 (U.S. Environmental Protection Agency, 2000b). Equations 9 through 13 mathematically define and relate theoretical sampler collection and penetration curves under various slope considerations. Similar equations were defined by Hinds (1998) and Seinfeld and Pandis (1997). The log-normal density distribution function for collection efficiency is defined as

$$\varepsilon_m(d_p, d_{50}, slope) = \left[\frac{1}{d_p \ln(slope)\sqrt{2\pi}} \exp\left[\frac{-(\ln d_p - \ln d_{50})^2}{2(\ln(slope))^2} \right] \right] \tag{9}$$

For a true cut 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

$$\psi_m(a, d_{50}, slope) = \int_0^a \varepsilon_m(d_p, d_{50}, slope) dd_p \tag{10}$$

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

$$P_m(a, d_{50}, slope) = 1 - \psi_m(a, d_{50}, slope) \tag{11}$$

Substituting equations 9 and 10 into equation 11 yields

$$P_m(a, d_{50}, slope) = 1 - \int_0^a \left[\frac{1}{d_p \ln(slope)\sqrt{2\pi}} \exp\left[\frac{-(\ln d_p - \ln d_{50})^2}{2(\ln(slope))^2} \right] \right] dd_p \tag{12}$$

where $P_m(a, d_{50}, slope)$ is the sampler penetration efficiency for particles having diameters less than a. Since a true cut is defined by a step function, equation 12 can be simplified so that the true cut penetration efficiency can be defined as

$$P_t(d_p, d_{50}, slope) = \begin{cases} 1 & if\ d_p \le d_{50} \\ 0 & if\ d_p > d_{50} \end{cases} \tag{13}$$

Now that the penetration function has been defined, the sampler performance characteristics for the $PM_{2.5}$ sampler need to be defined in terms of d_{50} and slope. EPA essentially defined these parameters in 40CFR53 in the discussion of tests required for a candidate sampler to receive EPA approval. The d_{50} for the $PM_{2.5}$ sampler is explicitly stated in the EPA standards as 2.5 ± 0.2 µm. No slope values for the sampler are listed in EPA's 40CFR53 (2000b) or any other current EPA standard; however, penetration data is presented in 40CFR53. Ideally, the penetration data could be fit to a cumulative lognormal distribution to determine the characteristic d_{50} and slope for the sampler; however, it was found that no single cumulative lognormal curve adequately represented the EPA data sets in 40CFR53. 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 EPA's $PM_{2.5}$ performance criteria. Therefore it appears that the EPA defined penetration data was a composition of two penetration curves that would account for the variability or range of $PM_{2.5}$ sampler slopes. This issue will be discussed in greater detail in the following paragraphs.

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 true concentration of $PM_{2.5}$, which would mean that, ideally, the slope would be equal to 1.0. However, from an engineering standpoint, it is not possible to design a sampler with a true cut. Work by Peters and Vanderpool (1996) suggested that a slope of 1.18 could be achieved with the WINS Impactor, an EPA approved 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 3 illustrates the boundary penetration efficiency curves for the $PM_{2.5}$ sampler, based on the previously defined sampler performance characteristics by Buch (1999). When comparing the boundary penetration efficiency curves in Figure 3, it is apparent that there is an acceptable range of penetration efficiencies for the $PM_{2.5}$ sampler. The acceptable range of penetra-

tion efficiencies for a particle size of 2.5 µm AED is 36 to 63%. These ranges are considered to be one form of inherent error associated with $PM_{2.5}$ samplers. Figure 4 illustrates the comparison of the penetration efficiency curves defined by Buch (1999) and EPA's ideal $PM_{2.5}$ sampler penetration efficiency curve. The ideal penetration curve is encompassed by the penetration curves defined by Buch (1999) for particle diameters less than approximately 2.7 µm and outside of this range for particle diameters greater than 2.7 µm. In order to determine if a sampler meets EPA's criteria as a $PM_{2.5}$ sampler, the proposed samplers penetration efficiency curve (determined in wind tunnel tests) along with coarse, typical coarse, and fine coarse aerosol size distributions (defined by EPA in 40 CFR 53) are used to determined estimated sampler concentrations. If these calculated concentrations are within ± 5% of the concentration based on EPA's ideal penetration curve and the cut-point falls within the range of 2.5 ± 0.2 µm then the proposed sampler meets the acceptance criteria. The boundary penetration curves defined by Buch (1999) passed the tests using the typical coarse and fine coarse aerosol size distributions; however, these curves did not meet the acceptance criteria for the coarse aerosol size distribution when the penetration curve was define as a d_{50} = 2.5 µm and a slope = 1.33 or when the d_{50} = 2.7 µm and the slope = 1.27, 1.30, or 1.33. It should be noted that Buch's (1999) work utilized fly ash filtered through a baffle type pre-separator as the dust entrained in the air when evaluating the $PM_{2.5}$ sampler performance characteristics; i.e. used poly-disperse particles as compared to the mono-disperse particles used in EPA's evaluation method. Figure 5 graphically illustrates the differences between a $PM_{2.5}$ sampler-cut, PM_{10} sampler-cut, TSP sampler-cut, $PM_{2.5}$ true-cut, and a PM_{10} true-cut in relationship to a PSD characterized by a MMD of 20 µm and a GSD of 2.0.

Methods and Procedures

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 measure of PM with a particle diameter less than or equal to 2.5 µm AED. An assumption made in the $PM_{2.5}$ regulation is that it pertains to a measure of particles with an AED less than or equal to a <u>nominal</u> 2.5 µm. The term nominal implies that the measured PM does not account for all mass associated with particles less than or equal to 2.5 µm and does include some of the mass associated with particles larger than 2.5 µm.

This issue of nominal values leads to a primary focus of this manuscript, that is, industries that emit PM with an MMD less than 5.7 µm (MMD associated with EPA's definition of an urban dust) are not regulated at the same level as agricultural operations, which typically emit PM with an MMD much greater than 5.7 µm. This unequal regulation is primarily due to the interaction of the sampler performance and PSD characteristics. In order to graphically illustrate this issue, EPA's defined PM_{10} sampler performance characteristics are used in Figures 6, 7, and 8. Similar figures could be constructed for the $PM_{2.5}$ sampler; however, due to the relatively small cut-point associated with the $PM_{2.5}$ sampler in comparison to the MMD of typical agricultural type dusts these illustrations would not be as visually clear. A common assumption made in the regulatory community to circumvent this problem is that mass of particles less than 10 µm and captured by the pre-separator (mass 1) is <u>equal</u> to the mass of particles greater than 10 µm and captured on the filter (mass 2), as shown in Figure 6 for a PM_{10} sampler. This assumption is valid when the density function of the PSD of the dust in air being sampled is represented by a uniform distribution. This assumption is also valid when the density function of the PSD is represented by a lognormal distribution with a MMD of 10 µm, as illustrated in Figure 7 (note: mass 1 is equal to mass 2). However as shown in Figure 8, this assumption introduces a major source of error (mass 1 is not equal to mass 2) when the PSD density function is represented by a lognormal distribution characterized by a MMD not equal to 10 µm; as is the case in virtually all situations involving PM in the air being sampled. For example, if the PM_{10} property line sampler concentration measurements from two industries are exactly the same and if 50% of industry A's PM (characterized by a MMD of 10 µm and a GSD of 1.5) is less than 10 µm and 16% of industry B's PM (characterized by a MMD of 20 mm and a GSD of 2.0) is less than 10 µm; then based on Figure 1 50% industry A's PM can potentially reach the alveolar region of the lungs as compared to 16% of industry B's PM. Therefore, under the current method of regulation PM_{10}, both industries A and B appear to be emitting the same levels of PM_{10} when in fact industry B is emitting 68% [(50-16)/50] less PM_{10} than industry A. 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} measurements **<u>MUST</u>** be based on true measurements. A similar parallel to the previous scenario can be drawn for the $PM_{2.5}$ sampler, except the impact would be much greater. A more in-depth discussion of this issue in regards to the $PM_{2.5}$ samplers will be addressed herein.

Estimating Sampler and True Cut Concentrations

Sampler and true concentrations can be theoretically estimated using PSD and sampler performance characteristics. According to Hinds (1998) sampler concentrations, $C_m(MMD,GSD,d_{50},slope)$, can be estimated by

$$C_m\left(MMD,GSD,d_{50},slope\right)=C_a\int_0^\infty f(d_p,MMD,GSD)P_m(d_p,d_{50},slope)dd_p \tag{14}$$

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

$$C_t\left(MMD,GSD,d_{50}\right)=C_a\int_0^{d_{50}} f(d_p,MMD,GSD)dd_p \tag{15}$$

Relative Differences Between Sampler and True Cut Concentrations

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

$$E(x)=\frac{(Measured-True)}{True}=\left(\frac{Measured}{True}\right)-1 \tag{16}$$

where *Measured* and *True* represent the estimated sampler and the true concentrations, respectively. Substituting equations 14 and 15 into equation 16 and canceling like terms, yields

$$E(MMD,GSD,d_{50},slope)+1=\left[\frac{\int_0^\infty f(d_p,MMD,GSD)P_m(d_p,d_{50},slope)dd_p}{\int_0^{d_{50}} f(d_p,MMD,GSD)dd_p}\right] \tag{17}$$

Throughout the remaining sections of this manuscript, *E(MMD, GSD, d_{50}, slope)+1* will be referred to as the ratio of the sampler to true concentration.

Results and Discussion

Mathcad 2000 was used to evaluate equation 17 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 the $PM_{2.5}$ sampler 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 true concentration. In other words the NAAQS are based on sampler concentrations; however the NAAQS should be based on true concentrations so that all industries are equally regulated. The mathematical definition for this assumption is

$$C_{Acceptable}=Ratio*C_{NAAQS} \tag{18}$$

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 true concentrations. The NAAQS for $PM_{2.5}$ is 65 µg/acm. The following conclusions can be drawn from Table 1: (1) 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 µm with a slope of 1.33 for PSDs characterized by MMDs greater than 2.5 µm, (2) the ratios for $PM_{2.5}$ range from 108 to 1,314%, and (3) the ratio is equal to 100% only when the sampler d_{50} is equal to the PSD's MMD.

In order to define the differences in the simulated sampler measured and true $PM_{2.5}$ concentrations, equations 14 and 15 were solved using Mathcad 2000 for a d_{50} equal to 2.7 µm, slope of 1.33, GSD of 2.0, and MMDs ranging from 1 to 40 µm. Results of this simulation are illustrated in Figure 9. In Figure 9, three MMDs are highlighted. The first corresponds to a MMD of 5.7 µm, MMD associated with urban dust as defined by EPA, and the other two correspond to the MMDs encompassing

the range of MMDs expected from agricultural type dusts, MMDs of 15 and 25 µm. When comparing the sampled to true concentrations for the urban dust, the sampled concentration is approximately 33% [i.e. (true percent less than 5.7 µm – sampled percent less than 5.7 µm)/(true percent less than 5.7 µm)] higher than the true concentration. Further when comparing the sampled to true concentrations for the range of agricultural type dusts, the sampled concentrations were 120 to 2,400% [i.e. (true percent less than 15 µm {25 µm} – sampled percent less than 15 µm {25 µm})/(true percent less than 15 µm {25 µm})] higher than the true concentrations.

To further describe how the interaction of the PSD and sampler characteristics affect the acceptable PM concentrations, a series of calculations were performed in Mathcad 2000 to generate a data file containing the solutions to equations 17 and 18 over a range of parameters. These parameters included MMD values ranging from 1 to 40 µm (in increments of 1 µm), and GSD values ranging from 1.3 to 2.5 (in increments of 0.1). To illustrate the results of this simulation, several graphs were created to demonstrate how each of the parameters affects the concentration ratio.

In Figure 10, 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 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 equal to 1 when MMD=d_{50}, (2) the average ratio is greater than 1 when MMD>d_{50}, and (3) the ratio range increases as the MMD increases. In general terms, when the ratio is equal to 1 the current method of regulating $PM_{2.5}$ results in an exact concentration measurement of PM less than or equal to 2.5 µm AED and when the ratio is greater than 1 the current method overestimates the concentration of PM less than or equal to 2.5 µm AED. For example, if a PSD were characterized by a MMD of 5.7 µm AED and a GSD of 2.0 then the acceptable range of $PM_{2.5}$ concentrations would be 60 to 87 µg/acm (i.e. ratios of 0.92 and 1.34 obtained from Figure 10 and multiplied by 65 µg/acm, the proposed NAAQS for $PM_{2.5}$). However, if a PSD were characterized by a MMD of 20 µm AED and a GSD of 2.0 then the acceptable range of $PM_{2.5}$ concentrations would be 77 to 182 µg/acm (i.e. ratios of 1.18 and 2.80 obtained from Figure 10 and multiplied by 65 µg/acm, the proposed NAAQS for $PM_{2.5}$).

The data presented in Figure 11 are based on the same assumptions as Figure 10, except the data are based on a GSD of 1.5. When comparing Figures 10 and 11, 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 5.7 µm AED and a GSD of 1.5 then the acceptable range of $PM_{2.5}$ concentrations would be 81 to 193 µg/acm (i.e. ratios of 1.24 and 2.96 obtained from Figure 11 and multiplied by 65 µg/acm, the proposed NAAQS for $PM_{2.5}$). 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 963 to 11,929 µg/acm (i.e. ratios of 14.81 and 183.5 obtained from Figure 11 and multiplied by 65 µg/acm, the proposed NAAQS for $PM_{2.5}$). Another conclusion that can be drawn from the data presented in Figures 10 and 11 is that the range of acceptable concentrations increases as the GSD increases.

Figure 12 is a generalized graph to illustrate how MMD's and GSD's affect the concentration ratios for a $PM_{2.5}$ sampler with a d_{50} of 2.5 µm and a slope of 1.3. 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 13 further expands 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} = 2.3 µm with a slope of 1.27 and d_{50} = 2.7 µm with a slope of 1.33, and variable GSD's ranging from 1.2 to 3.0. The general conclusions that should be drawn from this graph include: (1) as the GSD increases the concentration ratio decreases and approaches 1.0, and (2) as the GSD decreases the concentration ratio increases and approaches infinity.

Summary and Conclusions

There are several errors associated with the current air pollution rules and regulations established by EPA, which should be minimized to assure equal regulation of air pollutants between and within all industries. Potentially, one of the most significant errors is due to the interaction of the industry specific PSD and sampler performance characteristics. Currently, the regulation of PM is based on sampler measurements and __NOT__ true concentrations. The significance here is that sampler concentrations do not account for all the mass associated with the particle diameters less than the size of interest and further, sampler concentrations include a portion of the mass associated with particle diameters greater than the size of interest. The alternative to this method bases the regulations on a true concentration, which would account for all the mass associated with the particle diameters less than the size of interest and would not include mass associated with particle diameters greater than the size of interest.

What is the impact of this error? The following example demonstrates the impact of this error. 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 $PM_{2.5}$ sampler concentrations with a maximum property line concentration limit of 65 μg/acm;
- $PM_{2.5}$ sampler performance characteristics are described by a d_{50} = 2.5 ±•0.2 μm and a slope of 1.3 ±• 0.3.

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

- the $PM_{2.5}$ sampler performance characteristics that should be used are a d_{50} of 2.7 μm and a slope of 1.33; and
- a true concentration (65 μg/acm for $PM_{2.5}$) should be used, meaning that if the $PM_{2.5}$ concentrations are determined by the corresponding size specific samplers that the measured concentrations must be corrected to represent true concentrations;

After adjusting the concentrations for these errors, the following results are obtained:

- For the coal-fired power plant, a $PM_{2.5}$ sampler could measure concentrations as high as 854 μg/acm and still be in compliance with the regulations. This results in a 1,214% error 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 11,929 μg/acm and still be in compliance with the regulations. This results in a 18,252% error due to the sampler performance characteristics and 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 14 times more stringent for $PM_{2.5}$ 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 $C_{measured} < C_{true}$;
- if MMD = d_{50} then $C_{measured} = C_{true}$;
- if MMD > d_{50} then $C_{measured} > C_{true}$;
- as GSD increases the concentration ratio of $C_{measured}$ to C_{true} decreases; and
- as sampler slope decreases the concentration ratio of $C_{measured}$ to C_{true} decreases.

Results of the analysis presented in this manuscript show that not all industries are being equally regulated in terms of $PM_{2.5}$ and that <u>**ALL**</u> industries should be concerned with the current site-specific regulations implemented by EPA and enforced by SAPRA's.

Disclaimer

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

References

ACGIH. 1997. 1997 threshold limit values and biological exposure indices. Cincinnati, OH. American Conference of Governmental Industrial Hygienists.

Buch, U. M. 1999. Performance analysis of the cascade impactor, the federal reference method $PM_{2.5}$ sampler and the IMPROVE sampler. Thesis. Department of Agricultural Engineering, Texas A&M University, College Station, TX.

Cooper, C. D. and F. C. Alley. 1994. *Air Pollution Control, A Design Approach.* Prospect Heights, IL. Waveland Press, Inc.

Federal Register. 1971. National primary and secondary ambient air quality standard. F.R. (April 30), 36:8186-8201.

Federal Register. 1987. Revisions to the ambient air quality standards for particulate matter. F.R. (July 1), 52:24, 634-42, 669.

Hinds, W. C. 1982. *Aerosol Technology – Properties, Behavior, and Measurement of Airborne Particles*, 1st ed. New York, NY. John Wiley & Sons, Inc.

Hinds, W. C. 1998. *Aerosol Technology – Properties, Behavior, and Measurement of Airborne Particles*, 2nd ed. New York, NY. John Wiley & Sons, Inc.

International Standards Organization (ISO). 1993. Air quality – particle size fraction definitions for health-related sampling (revision of ISO/TR 7708:1983). Geneva, Switzerland: International Organization for Standardization; approved international standard no. ISO/DIS 7708.

Miller, F.J., D. E. Gardner, J. A. Graham, R. E. Lee, Jr., W. E. Wilson, and J. D. Buchmann. 1979. Size Considerations for Establishing a Standard for Inhalable Particles, J. Air Pollution Control Assoc. 29:610-615.

Peters, T. M. and R. W. Vanderpool. 1996. Modification and evaluation of the WINS Impactor. Final Report. EPA Contract Number 68-D5-0040. Research Triangle Park, N.C. National Exposure Research Laboratory, U.S. Environmental Protection Agency.

U. S. Environmental Protection Agency. 1996. Air quality criteria for particulate matter. Research Triangle Park, NC: Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office; EPA report no. EPA-600/P-95/001aF. Available from: NTIS, Springfield, VA; PB96-168232.

U. S. Environmental Protection Agency. 2000a. 40CFR Part 50 National Ambient Air Quality Standards for Particulate Matter; Final Rule. Federal Register Vol. 65, No. 247.

U. S. Environmental Protection Agency. 2000b. 40CFR Part 53 National Ambient Air Quality Standards for Particulate Matter; Final Rule. Federal Register Vol. 65, No. 249.

Table 1. Percent differences between theoretical sampler true 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$_{2.5}$ sampler characteristics		Conc. (µg/m^3)[ξ]	Ratio[γ]	Conc. (µg/m^3)[ξ]	Ratio[γ]	Conc. (µg/m^3)[ξ]	Ratio[γ]	Conc. (µg/m^3)[ξ]	Ratio[γ]
Cutpoint (µm)	Slope								
2.3	1.27	**73.65**	113.3%	**185.45**	285.3%	**70.40**	108.3%	**76.57**	117.8%
2.3	1.30	80.28	123.5%	242.19	372.6%	76.12	117.1%	84.76	130.4%
2.3	1.33	87.23	134.2%	313.30	482.0%	82.49	126.9%	94.06	144.7%
2.5	1.27	104.78	161.2%	345.35	531.3%	97.05	149.3%	109.92	169.1%
2.5	1.30	112.52	173.1%	423.87	652.1%	104.26	160.4%	120.90	186.0%
2.5	1.33	120.58	185.5%	534.17	821.8%	112.26	172.7%	133.19	204.9%
2.7	1.27	141.77	218.1%	559.07	860.1%	129.16	198.7%	151.97	233.8%
2.7	1.30	150.28	231.2%	693.49	1066.9%	138.06	212.4%	166.01	255.4%
2.7	1.33	**159.12**	244.8%	**854.10**	1314.0%	**147.81**	227.4%	**181.74**	279.6%

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

[γ] *Concentrations are based on the corresponding regulations and adjusted by the ratio. Property line concentrations for PM$_{2.5}$ are 65 µg/m^3.*
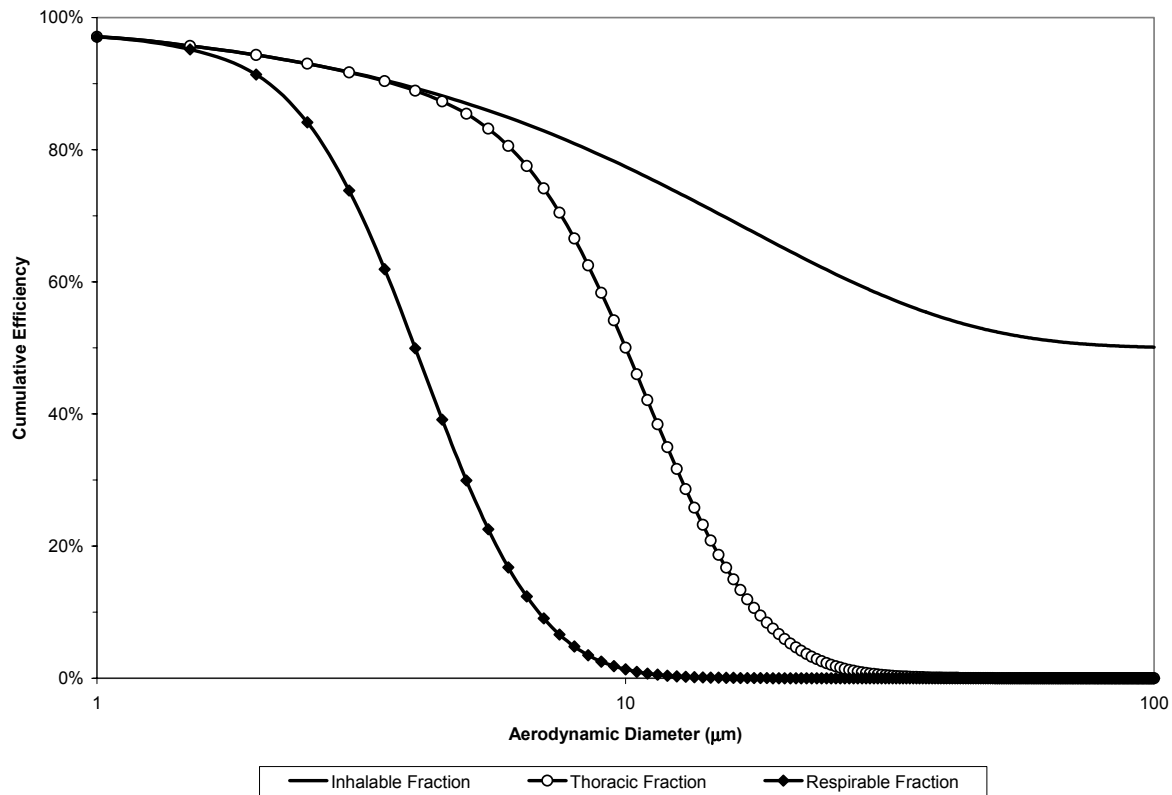
Figure 1. American Conference of Governmental Industrial Hygienists sampling criteria for inhalable, thoracic, and respirable fractions of PM (ACGIH, 1997).
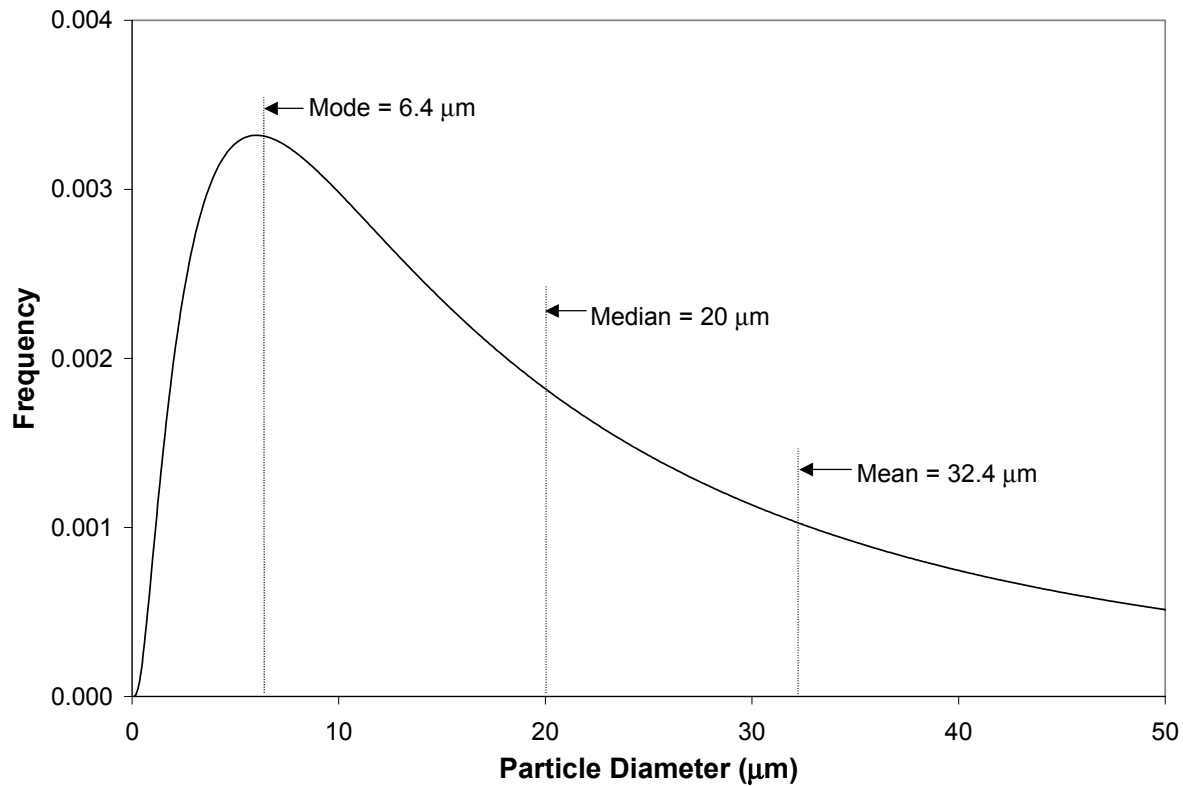

Figure 2. Lognormal particle size distribution defined by a MMD of 20 µm and a GSD of 3.0.
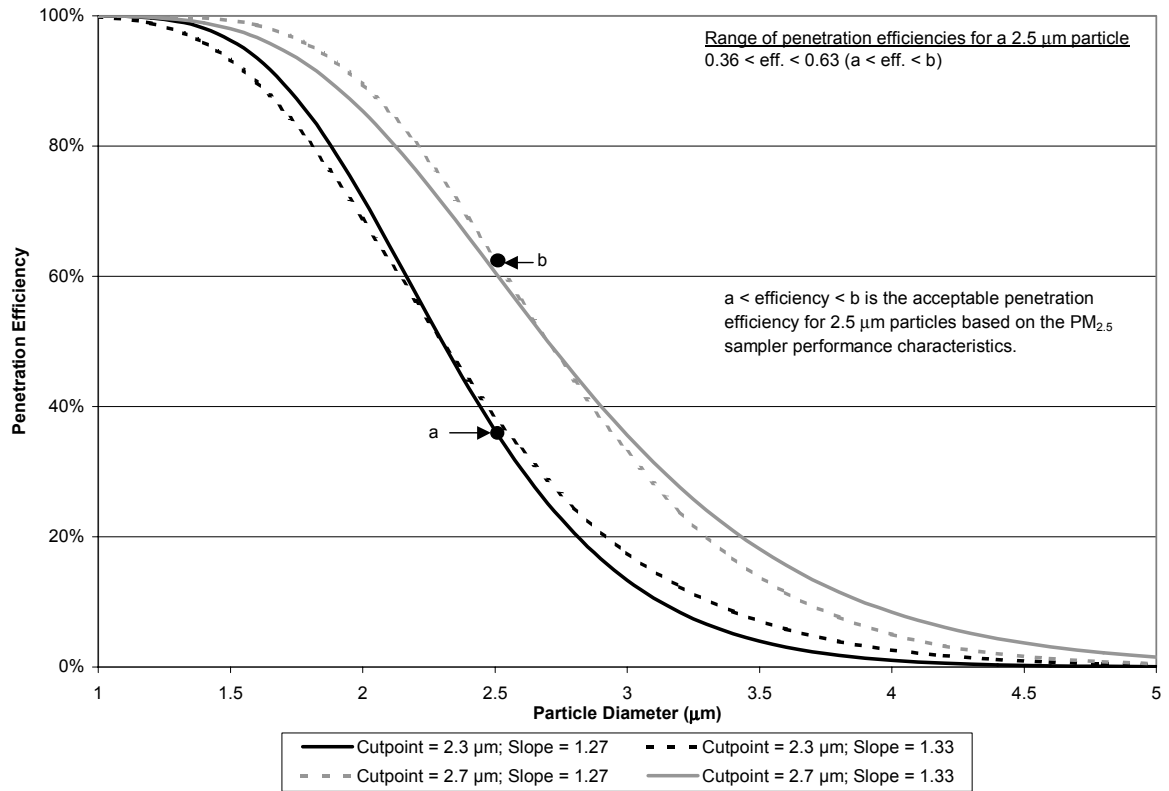
Figure 3. PM$_{2.5}$ sampler penetration curves based on the defining performance characteristics.
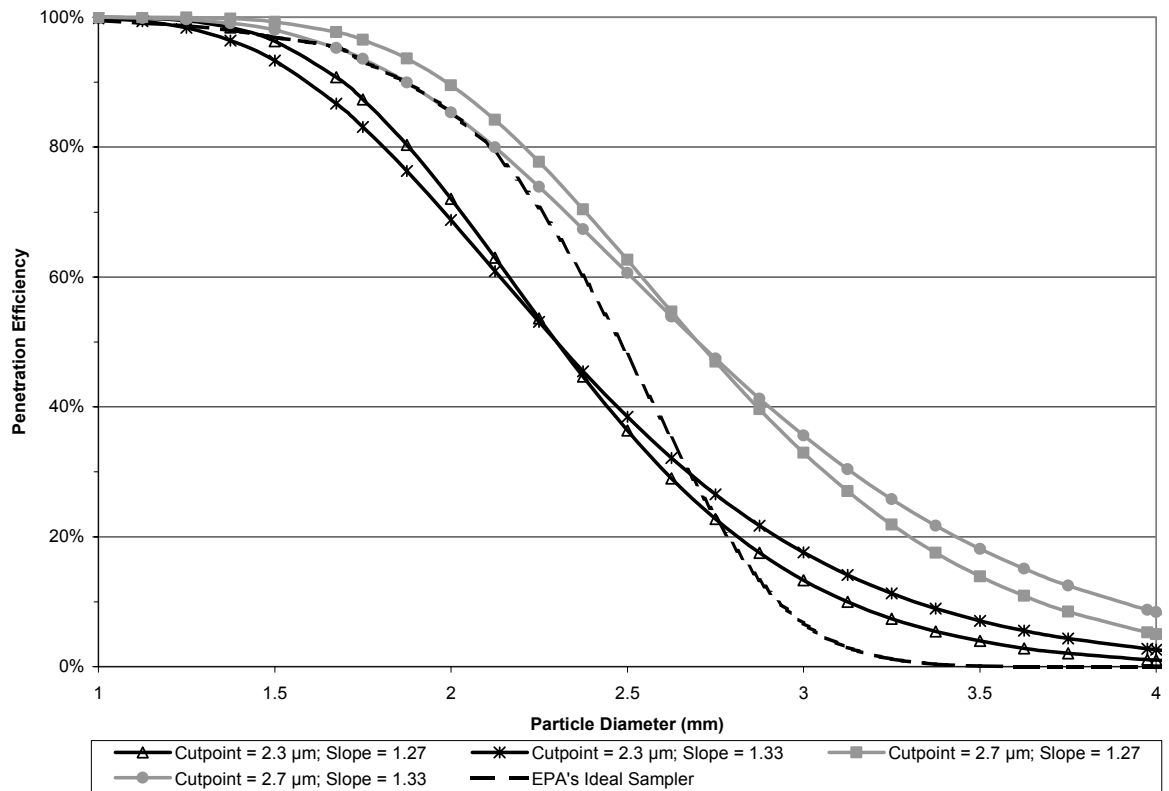

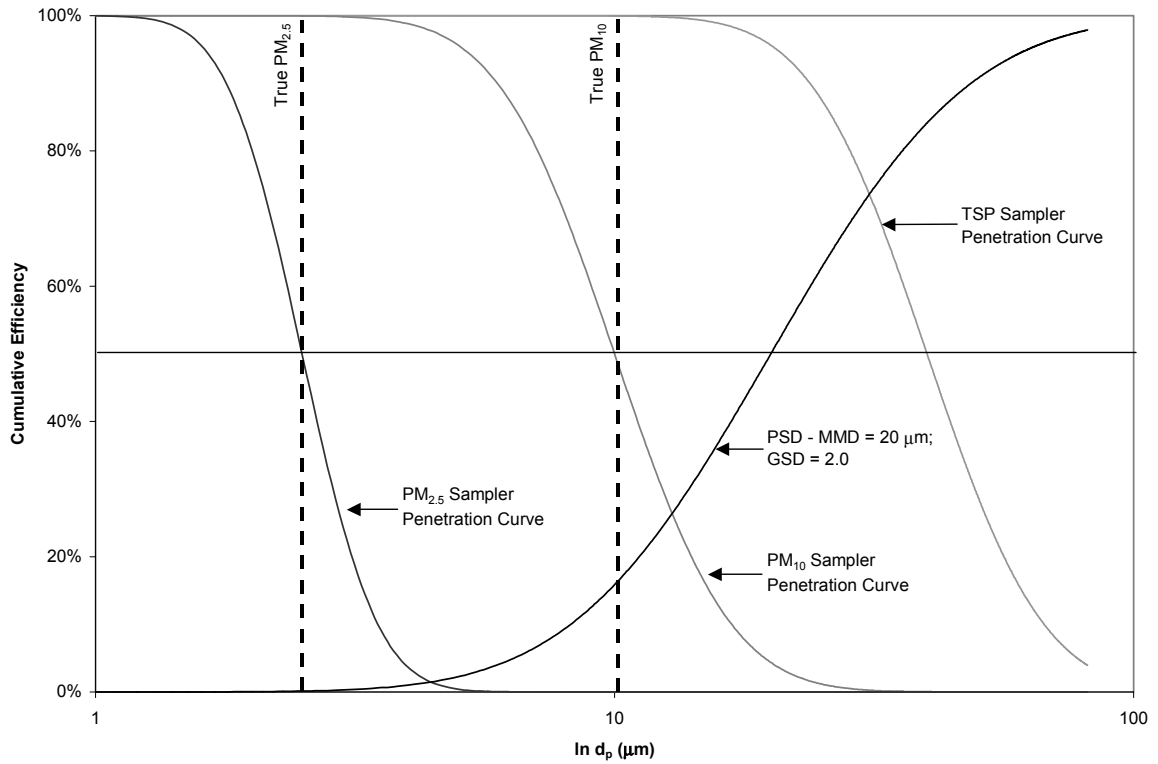Figure 4. Comparison EPA's (2000b) ideal PM$_{2.5}$ sampler penetration data to the PM$_{2.5}$ sampler performance characteristics defined by Buch (1999).

Figure 5. $PM_{2.5}$, PM_{10}, and TSP penetration curves.
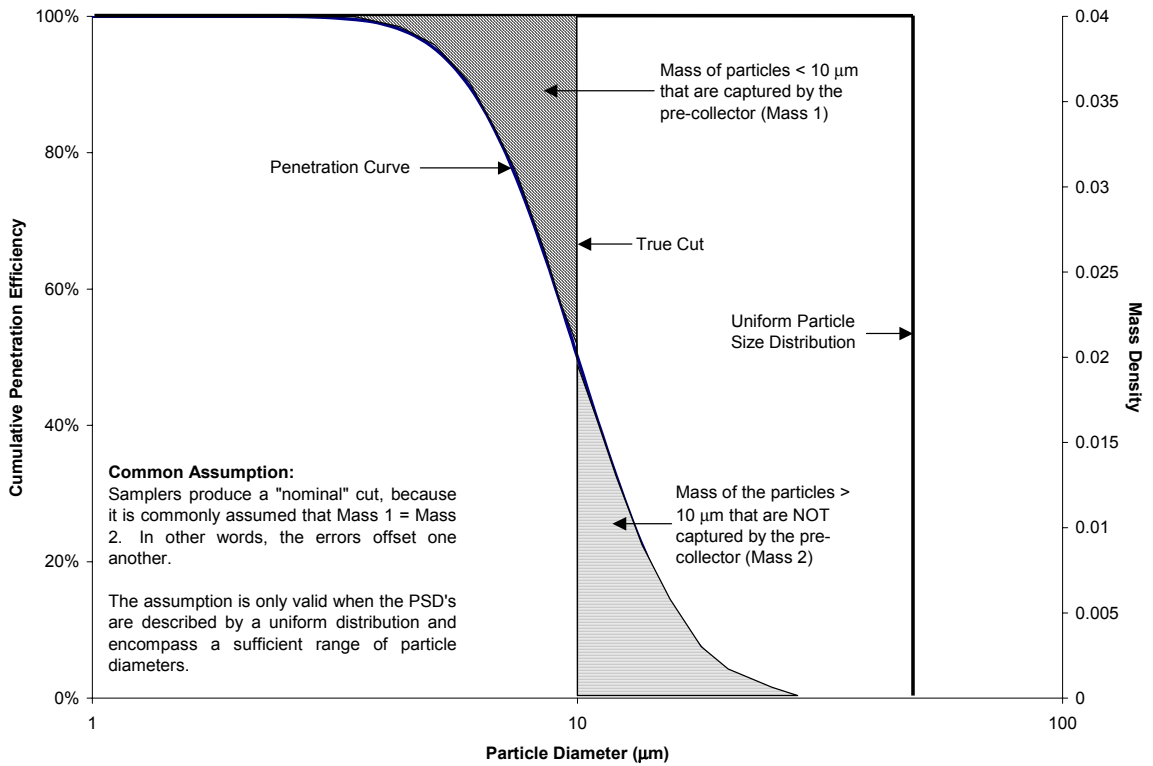
Figure 6. PM_{10} Sampler nominal cut for a uniform PSD.
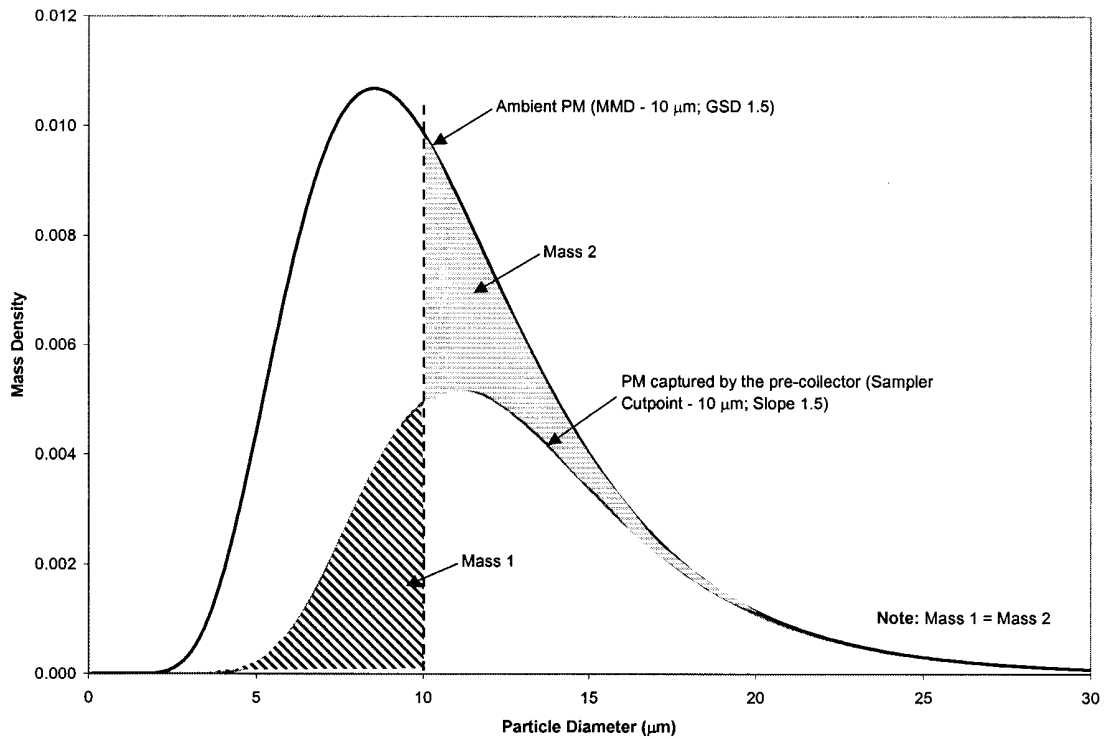
Figure 7. PM$_{10}$ Sampler nominal cut for a lognormal PSD with a MMD = 10 μm and GSD = 1.5.
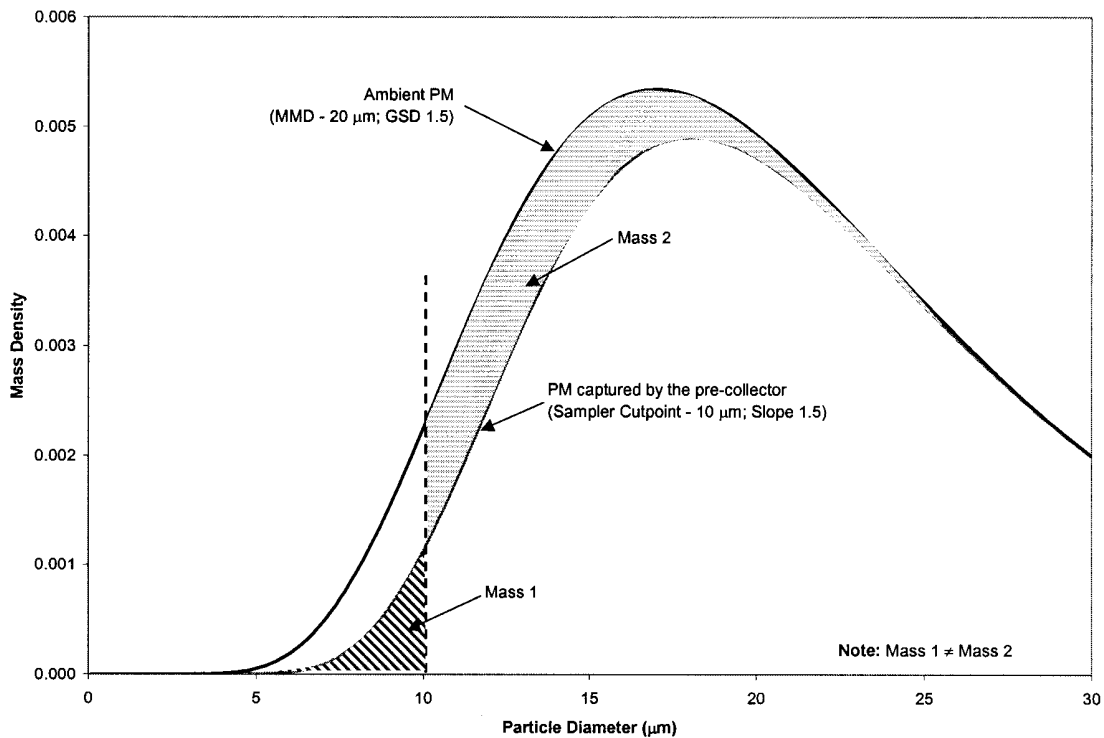
Figure 8. PM$_{10}$ Sampler nominal cut for a lognormal PSD with a MMD = 20 μm and GSD = 1.5.
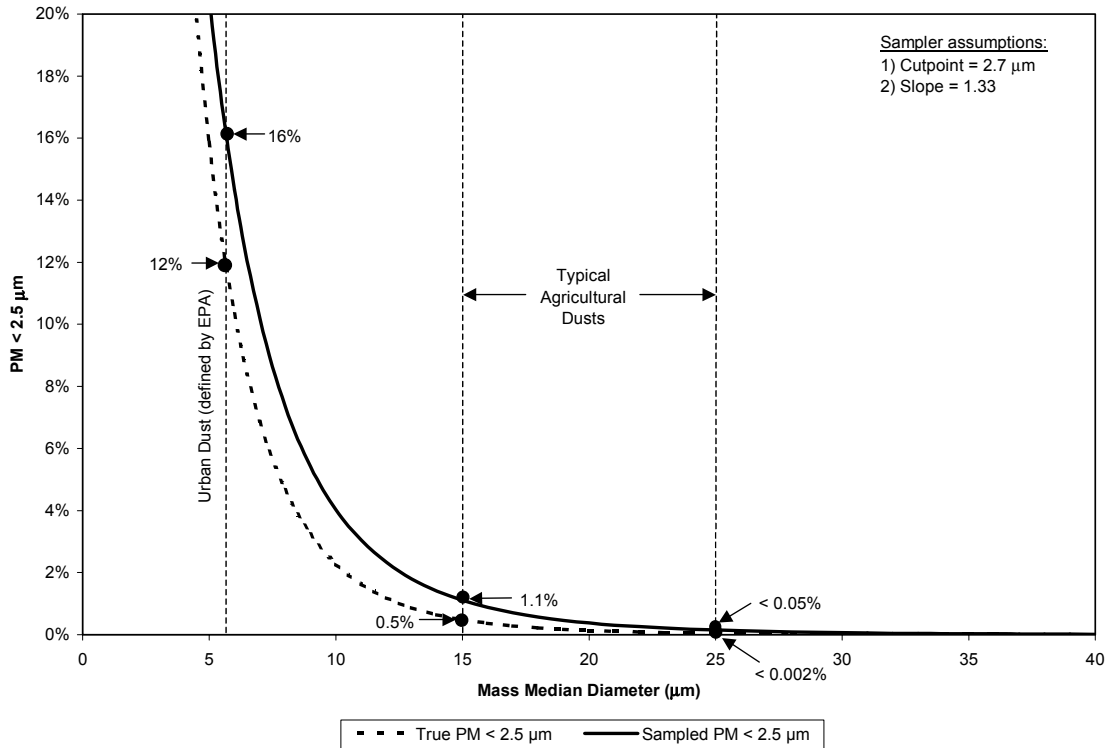
Figure 9. Comparison of true and sampled PM$_{2.5}$ percentages for a range of PSD mass median diameters and a GSD of 2.0.
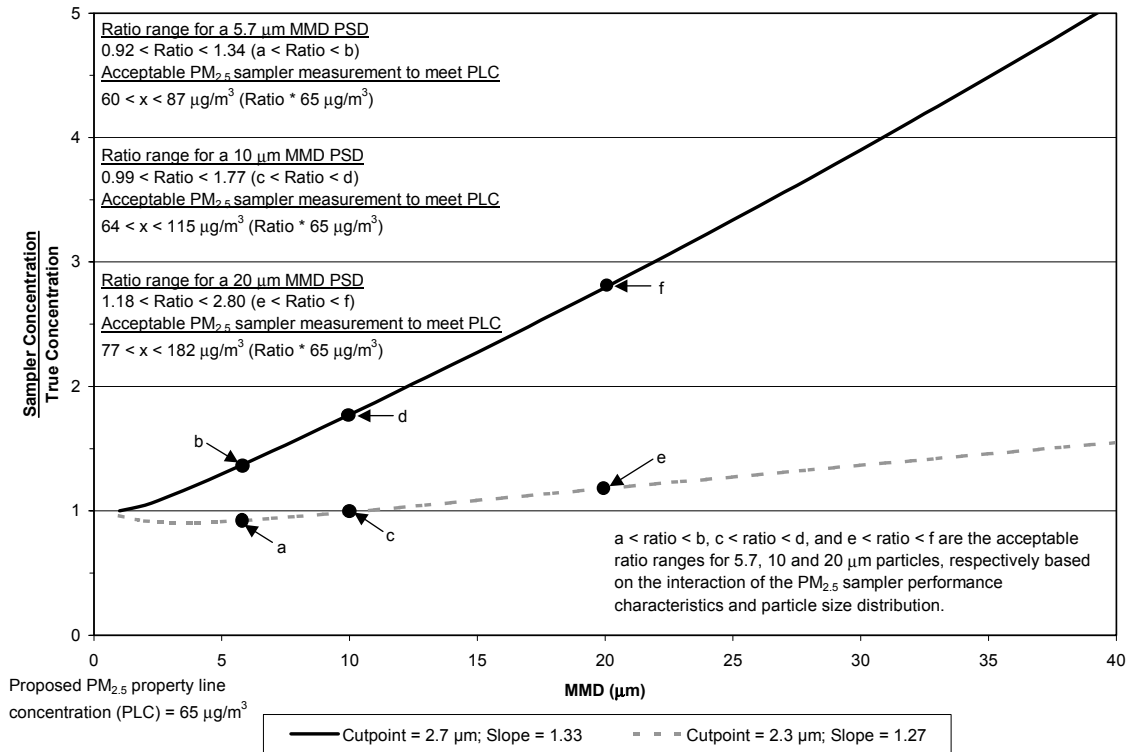

Figure 10. Theoretical ratios of PM$_{2.5}$ sampler to true PSD concentrations (PSD – GSD = 2.0).
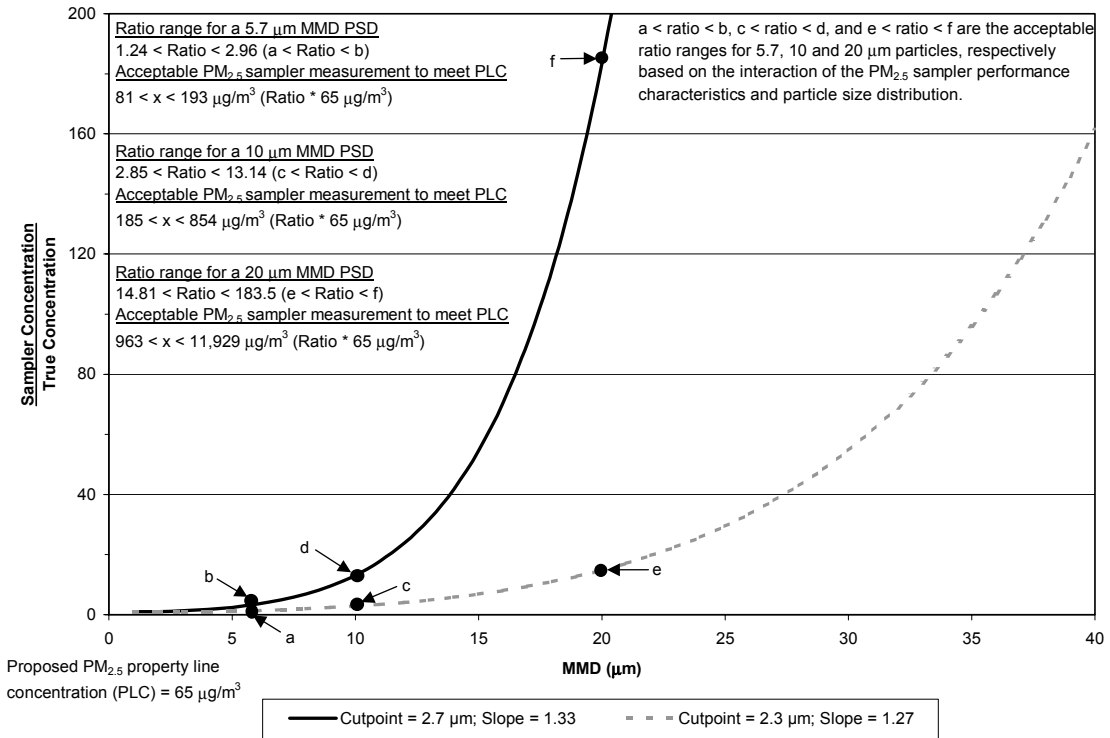
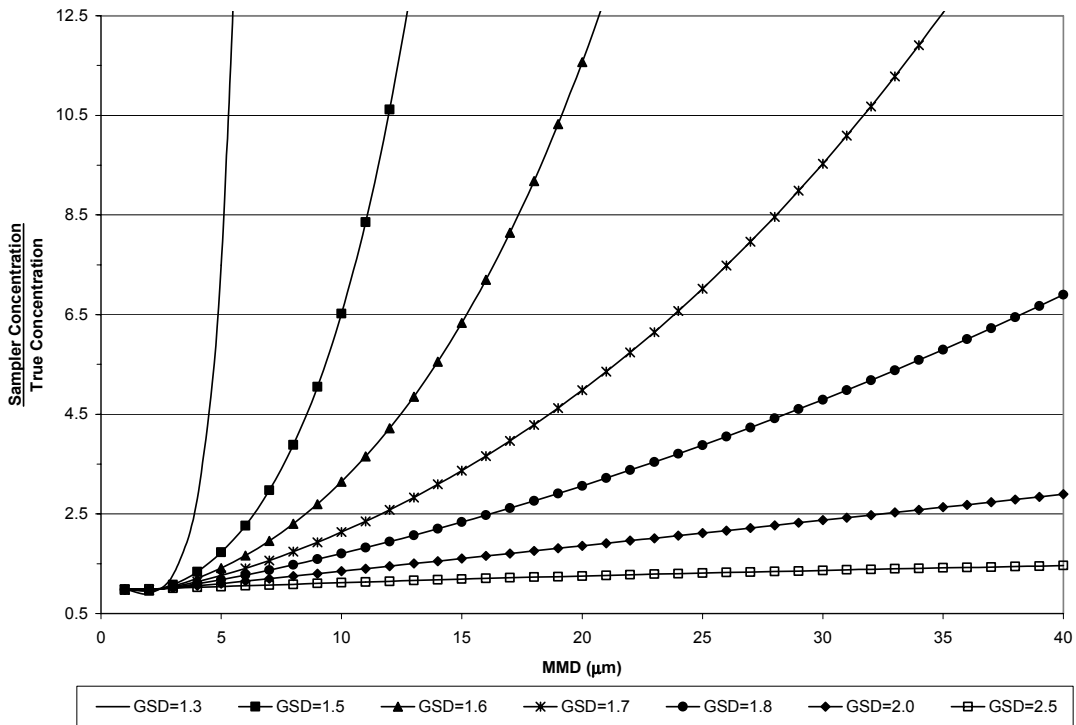Figure 11. Theoretical ratios of PM$_{2.5}$ sampler to true PSD concentrations (PSD – GSD = 1.5).

Figure 12. Theoretical ratios of PM$_{2.5}$ sampler to true PSD concentrations (PM$_{2.5}$ sampler characteristics; cutpoint = 2.5 μm and slope = 1.3).
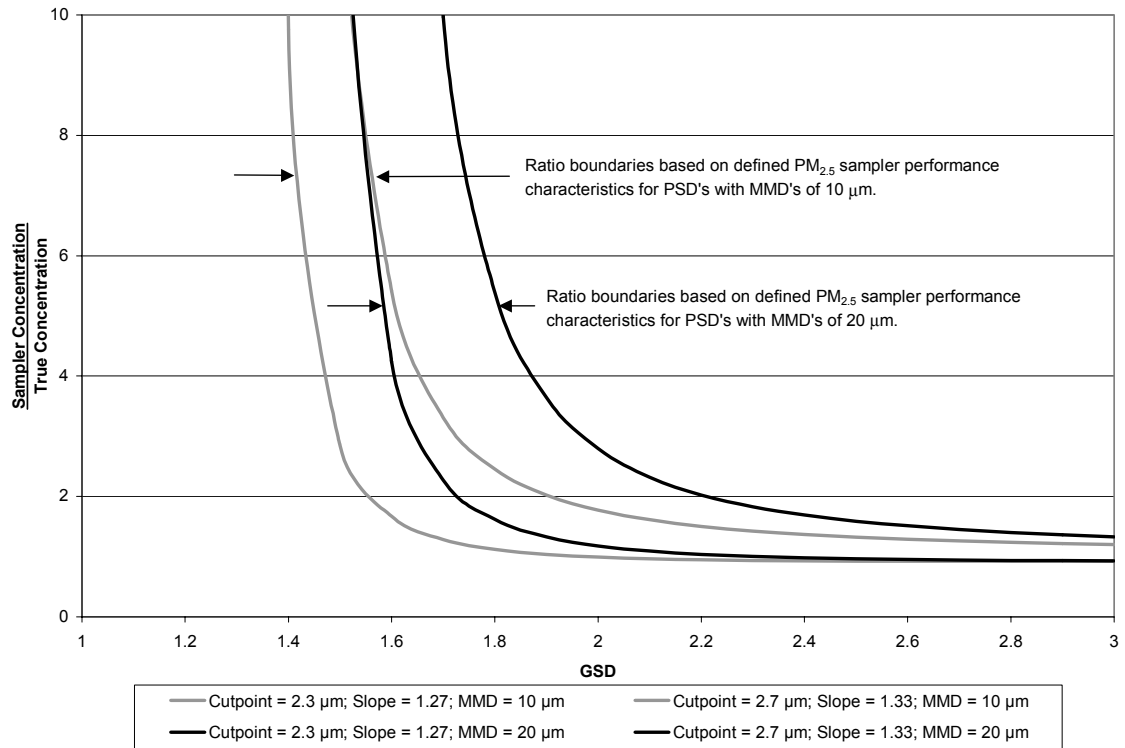
Figure 13. Theoretical PM$_{2.5}$ sampler to true concentration ratio boundaries based on varying GSDs for PSD's with MMDs of 10 and 20 µm.