PARTICULATE MATTER SAMPLER ERRORS DUE TO THE INTERACTION OF PARTICLE SIZE AND SAMPLER PERFORMANCE CHARACTERISTICS: PM₁₀ AND PM_{2.5} AMBIENT AIR SAMPLERS

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

ABSTRACT

Agricultural operations across the United States are encountering difficulties complying with the current air pollution regulations for particulate matter (PM). The National Ambient Air Quality Standards (NAAQS) for PM in terms of PM₁₀ and PM_{2.5} are ambient air concentration limits set by EPA that should not be exceeded. Further, some 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 limits. The primary NAAQSs are health-based standards and therefore, an exceedance implies that it is likely that there will be adverse health effects for the public. Prior to and since the inclusion of the PM₁₀ standard and prior to and since the proposal of the PM_{2.5} standard, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulation, methods of determining PM₁₀ and PM_{2.5}, etc. A common trend among many of these publications is the use of samplers to collect information on PM₁₀ and PM_{2.5}. Often, the sampler data is assumed to be accurate measures of PM₁₀ and 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 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 PM₁₀ and PM_{2.5} ambient air samplers. Results from the PM₁₀ simulations indicated that a source emitting PM characterized by a mass median diameter (MMD) of 20 µm and a geometric standard deviation (GSD) of 1.5 could be forced to comply with a PM₁₀ standard that is 3.2 times more stringent than that required for a source emitting PM characterized by a MMD of 10 µm and a GSD of 1.5. Results from the PM_{2.5} simulations indicated that a source emitting PM characterized by a mass median diameter (MMD) of 20 µm and a geometric standard deviation (GSD) of 1.5 could be forced to comply with a PM_{2.5} standard that is 14 times more stringent than that required for a source emitting PM characterized by a MMD of 10 µm and a GSD of 1.5. Therefore, in order to achieve equal regulation among differing industries, PM₁₀ and PM_{2.5} measurements MUST be based on true concentration measurements.

KEYWORDS. Air, Air pollution, Environmental impact, Legislation, Mathematical models, Particle size distribution, PM, PM₁₀, PM_{2.5}, Pollution, Samplers, Sampling, Sampler performance, Sampler uncertainty.

INTRODUCTION

The NAAQS for PM in terms of PM_{10} and $PM_{2.5}$, are the concentration limits set by EPA that should not be exceeded (U. S. Environmental Protection Agency, 2000a). Further, some 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 limits. The regional or area consequences for multiple exceedances of the NAAQS are having an area designated as non-attainment with a corresponding reduction in the permit allowable emission rates for all sources of PM in the area. The source-specific consequence of an exceedance of the NAAQS at the property line is the SAPRA denying an operating permit. The current PM_{10} primary 24-hour NAAQS is 150 micrograms per actual cubic meter (µg/acm) (U. S. Environmental Protection Agency, 2000a). The proposed $PM_{2.5}$ primary 24-hour NAAQS is 65 micrograms per actual cubic meter (µg/acm) Agency, 2000a). The secondary NAAQS for PM_{10} and $PM_{2.5}$ are set at the same levels as the corresponding primary NAAQS.

In the initial manuscript in this series of manuscripts entitled "Particulate Matter Sampler Errors Due to the Interaction of Particle Size and Sampler Performance Characteristics: Background and Theory" the evolution of the PM₁₀ and PM_{2.5} regulations was briefly discussed. Prior to and since the inclusion of the PM₁₀ standard and prior to and since the proposal of the PM_{2.5} standard into EPA's regulation guidelines, numerous journal articles and technical references have been written to discuss the epidemiological effects, trends, regulation, methods of determining PM₁₀ and PM_{2.5}, etc. A common trend among many of these publications is the use of samplers to collect information on PM₁₀ and PM_{2.5}. The data collected from these samplers are commonly used in statistical correlations and statistical comparisons to draw conclusions about PM₁₀ and PM_{2.5} emission concentrations. All too often, the sampler data are assumed to be accurate measures of PM₁₀ and 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 PM₁₀ and PM_{2.5} ambient air samplers, and the effect of these interactions on the regulatory process.

GOVERNING EQUATIONS

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

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

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

$$P_{m}(d_{50}, slope) = 1 - \int_{0}^{\infty} \left[\frac{1}{d_{p} \ln(slope) \sqrt{2\pi}} exp \left[\frac{-(\ln d_{p} - \ln d_{50})^{2}}{2(\ln(slope))^{2}} \right] \right] dd_{p}$$
(2)

where d_{50} and *slope* represent the particle size where 50% of the particulate matter (PM) is capture by the pre-separator and 50% of the PM penetrates to the filter and the slope of the cumulative penetration curve, respectively. A more complete definition of slope is provided in the initial manuscript. In addition, the initial manuscript defined a true cumulative penetration curve or cut as a step function, which was defined as:

$$P_{t}(d_{p}, d_{50}) = \begin{cases} 1 & \text{if } d_{p} \le d_{50} \\ 0 & \text{if } d_{p} > d_{50} \end{cases}$$
(3)

In order to solve equation 2, additional information is needed to define the d_{50} and *slope* associated with the PM₁₀ and PM_{2.5} ambient air samplers.

Sampler Performance Characteristics of the PM₁₀ Ambient Air Sampler

EPA essentially defines the d_{50} and slope associated with the PM₁₀ ambient air sampler in 40CFR53 in the discussion of tests required for a candidate sampler to receive EPA approval. The d_{50} for the PM₁₀ sampler is explicitly stated in the EPA standards as $10.0 \pm 0.5 \,\mu$ m. 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 PM₁₀ samplers; however, it was found that no single cumulative lognormal curve adequately represented the EPA data sets in 40CFR53 (2000b). 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 PM₁₀ performance criteria. Therefore, it appears that the EPA defined penetration data was a composition of two or more penetration curves, which would account for the variability or range of PM₁₀ sampler slopes. This issue will be discussed in greater detail in the following paragraphs.

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 with 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. For the purposes of this manuscript, the PM_{10} sampler performance characteristics will be defined as having a d_{50} equal to 10 ± 0.5 µm and a slope equal to 1.5 ± 0.1 .

Figure 1 illustrates the boundary penetration efficiency curves for the PM₁₀ sampler, based the previously defined sampler performance characteristics by Hinds (1982). When comparing the boundary penetration efficiency curves in Figure 1, it is apparent that there is an acceptable range of penetration efficiencies for the PM₁₀ 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 one form of inherent errors associated with PM₁₀ samplers. Figure 2 illustrates the comparison of the penetration curve defined by Hinds (1982) and EPA's ideal PM₁₀ sampler penetration efficiency curve. The ideal penetration curve is encompassed by the penetration curves defined by Hinds (1982) for particle diameters ranging from 6.5 to 14.5 µm. In order to determine if a sampler meets EPA's criteria as a PM₁₀ sampler, the proposed sampler's penetration efficiency curve (determined in wind tunnel tests) along with interval mass concentrations (defined by EPA in 40 CFR 53, 2000b) are used to determine expected sampler concentrations. If these calculated concentrations are within $\pm 10\%$ of the concentrations based on EPA's ideal penetration curve and the cut-point falls within the range of $10.0 \pm 0.5 \,\mu\text{m}$, then the proposed sampler meets the acceptance criteria. The boundary penetration curves defined by Hinds (1982) met the criteria.

Sampler Performance Characteristics of the PM2.5 Ambient Air Sampler

Now that the PM10 sampler performance characteristics have been defined, the PM_{2.5} sampler characteristics 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 $2.5 \pm 0.2 \mu m$. 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 (2000b). It should be noted that this penetration data along with EPA defined interval mass concentrations, and mass penetration tolerances are used to determine if a proposed sampler meets 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 expected $PM_{2.5}$ sampler slopes. This issue will be discussed in greater detail in the following paragraphs.



Figure 1. PM₁₀ sampler penetration curves based on the defining performance characteristics



Figure 2. Comparison EPA's (2000b) ideal PM₁₀ sampler penetration data to the PM₁₀ sampler performance characteristics defined by Hinds (1982)

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 μ m than the slope associated with the particle sizes larger than 2.5 μ m. 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 \pm 0.03. For the purposes of this manuscript, the PM_{2.5} sampler performance characteristics will be defined as having a d₅₀ equal to 2.5 \pm 0.2 μ m and a slope equal to 1.3 \pm 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 penetration efficiencies for the $PM_{2.5}$ sampler. The acceptable range of penetration efficiencies for 2.5 μ m AED is 36 to 63%. These ranges are considered one form of inherent error associated with $PM_{2.5}$ samplers.



Figure 3. PM_{2.5} sampler penetration curves based on the defining performance characteristics

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 determine 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 $d_{50} = 2.5 \mu m$ and a slope = 1.33 or when the $d_{50} = 2.7 \mu m$ 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 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 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 μ m 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. 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 the initial manuscript in this series. On the other hand, according to the literature it was EPA's intent for the PM_{2.5} sampler to be a true measure of PM with a particle diameter less than or equal to 2.5 μ m AED. An assumption made in the PM₁₀ (PM_{2.5}) regulations is that it pertains to a measure of particles with an AED less than or equal to a <u>nominal</u> 10 (2.5) μ m. The term nominal implies that the measured PM does not account for all mass associated with particles less than or equal to 10 (2.5) μ m.



Figure 5. PM_{2.5}, PM₁₀, and TSP penetration curves

This issue of nominal values leads to a primary focus of this series of manuscripts, that is, industries that emit PM with a MMD less than or equal to 5.7 μ m (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 μ m. This unequal regulation is primarily due to the interaction of the sampler performance and PSD characteristics. The initial manuscript in this series discussed this error in general terms. This manuscript will focus on defining these errors for the PM₁₀ and PM_{2.5} ambient air samplers.

Estimating sampler and true cut concentrations

Sampler and true concentrations can be theoretically estimated using PSD and sampler performance characteristics. According to Hinds (1998) and using equations 1 and 2, sampler concentrations, $C_m(MMD,GSD,d_{50},slope)$, can be estimated by

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

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

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

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

$$E(x) = \frac{(Measured - True)}{True} = \left(\frac{Measured}{True}\right) - 1 \tag{6}$$

where *Measured* and *True* represent the estimated sampler and the true concentrations, respectively. Substituting equations 4 and 5 into equation 6 and canceling like terms, yields

$$E(MMD,GSD,d_{50},slope) + 1 = \begin{bmatrix} \int_{0}^{\infty} f(d_{p},MMD,GSD)P_{m}(d_{p},d_{50},slope)dd_{p} \\ \int_{0}^{d_{50}} f(d_{p},MMD,GSD)dd_{p} \end{bmatrix}$$
(7)

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.

Equation 7 will be solved for various PSD and sampler performance characteristics in order to estimate the errors associated with the interaction of these two characteristics.

RESULTS AND DISCUSSION

An initial evaluation was conducted using Mathcad 2000 to solve equation 7 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 μ m with a GSD of 1.5 and MMD's of 15 and 20 μ m with a GSD of 2.0. The sampler performance characteristics included the nine combinations of d₅₀ and slope for the PM₁₀ sampler and the nine combinations of d₅₀ and slope for the PM₁₀ sampler and 2 list the results of this evaluation for the PM₁₀ and PM_{2.5} samplers, respectively.

Table 1. Percent differences between theoretical PM_{10} true and sampler based 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/m ³) ^ς	Ratio ^γ	Conc. (μg/m ³) ^ς	Ratio ⁷	Conc. (μg/m³) ^ς	Ratio ⁷	Conc. (μg/m³) ^ς	Ratio ⁷		
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 μ m; slope = 1.4	142.1	94.7%	150.0	100.0%	160.8	107.2%	174.2	116.1%		
d_{50} = 10.0 μ m; slope = 1.5	139.1	92.7%	150.0	100.0%	164.9	109.9%	183.5	122.3%		
d_{50} = 10.0 μ m; slope = 1.6	136.2	90.8%	150.0	100.0%	168.8	112.5%	192.8	128.5%		
d_{50} = 10.5 μ m; slope = 1.4	144.5	96.3%	161.1	107.4%	172.8	115.2%	190.5	127.0%		
d_{50} = 10.5 μ m; slope = 1.5	141.5	94.3%	160.2	106.8%	176.4	117.6%	199.7	133.1%		
d_{50} = 10.5 μ m; slope = 1.6	138.6	92.4%	159.5	106.3%	180.0	120.0%	208.8	139.2%		

^{*ζ*} Values are based on the assumption that true concentrations are the correct estimates of the corresponding PM.

 $^{\gamma}$ Concentrations are based on the corresponding regulations and adjusted for the ratio. Property line concentrations for PM $_{10}$ are 150 μ g/m3

Table 2. Percent differences between theoretical $PM_{2.5}$ true and sampler based concentrations for various particle size and sampler performance characteristics

		Particle Size distribution (PSD) Characteristics									
		MMD = 5 μm		MMD = 10 μm		MMD = 15 μm		MMD = 20 μm			
PM 2.5 sampler characteristics		GSD = 1.5		GSD = 1.5		GSD = 2.0		GSD = 2.0			
Cutpoint (µm)	Slope	Conc. (μg/m ³) ^ζ	Ratio ^γ	Conc. (μg/m³) ^ζ	Ratio ^γ	Conc. (μg/m³) ^ζ	Ratio ^γ	Conc. (μg/m³) ^ζ	Ratio ^γ		
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%		

^C Values are based on the assumption that true concentrations are the correct estimates of the corresponding PM.

 $^{\gamma}$ Concentrations are based on the corresponding regulations and adjusted by the ratio. Property line concentrations for PM_{2.5} are 65 μ g/m³.

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

$$C_{Acceptable} = Ratio * C_{NAAOS}$$
(8)

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 PM₁₀ and PM_{2.5} are 150 and 65 µg/acm, respectively. The following conclusions can be drawn from Table 1: (1) the PM₁₀ sampler performance characteristics that define the range of acceptable concentrations are a d₅₀ of 9.5 µm with a slope of 1.4 and 1.6 and a d₅₀ of 10.5 µm with a slope of 1.4 and 1.6, (2) the ratios for PM₁₀ range from 89 to 139%, and (3) the ratio is equal to 100% only when the sampler d₅₀ is equal to the PSD's MMD. The following conclusions can be drawn from Table 2: (1) the PM_{2.5} sampler performance characteristics that define the range of acceptable concentrations are a d₅₀ of 2.3 µm with a slope of 1.27 and a d₅₀ of 2.7 µm with a slope of 1.33 for PSDs characterized by MMDs greater than 2.5 µm and (2) the ratios for PM_{2.5} range from 108 to 1,314%. This initial evaluation was expanded to incorporate a larger range of MMDs and GSDs for the PM₁₀ and PM_{2.5} ambient air samplers.

PM₁₀ Ambient Air Samplers

In order to define the differences in the simulated sampler measured and true PM_{10} concentrations, equations 4 and 5 were solved using Mathcad 2000 for a d₅₀ equal to 10.5 µm, slope of 1.6, GSD of 1.5, and MMDs ranging from 1 to 40 µm. Results of this simulation are illustrated in Figure 6. In Figure 6, 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 about 9% [i.e. (true percent less than 5.7 µm – sampled percent less than 5.7 µm)/(true percent less than 5.7 µm)] lower than the true concentration. Further when comparing the sampled to true concentrations for the range of agricultural type dusts, the sampled concentrations were 75 to 700% [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 7 and 8 over a range of parameters. These parameters included MMD values ranging from 1 to 40 μ m (in increments of 1 μ m), 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 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 μ m AED and when the ratio is greater than 1 the current method overestimates the concentration of PM less than or equal to 10 μ m AED. For example, if a PSD were characterized by a MMD of 10 μ m AED and a GSD of 2.0 then the acceptable range of PM₁₀ concentrations would be 142 to 158 μ g/acm (i.e. ratios of 0.95 and 1.05 obtained from Figure 7 and multiplied by 150 μ g/acm the current NAAQS for PM₁₀). However, if a PSD were characterized by a MMD of 20 μ m AED and a GSD of 2.0 then the acceptable range of PM₁₀ concentrations would be 158 to 209 μ g/acm (i.e. ratios of 1.05 and 1.39 obtained from Figure 7 and multiplied by 150 μ g/acm the current NAAQS for PM₁₀).



Figure 6. Comparison of true and sampled PM_{10} percentages for a range of PSD mass median diameters and a GSD of 1.5



Figure 7. Theoretical ratios of PM10 sampler to true PSD concentrations (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 μ m AED and a GSD of 1.5 then the acceptable range of PM₁₀ concentrations would be 138 to 159 μ g/acm (i.e. ratios of 0.92 and 1.07 obtained from Figure 8 and multiplied by 150 μ g/acm the current NAAQS for PM₁₀). However, if a PSD were characterized by a MMD of 20 μ m AED and a GSD of 1.5 then the acceptable range of PM₁₀ concentrations would be 272 to 515 μ g/acm (i.e. ratios of 1.81 and 3.43 obtained from Figure 8 and multiplied by 150 μ g/acm the current NAAQS for PM₁₀). Another conclusion that can be drawn from the data presented in Figures 7 and 8 is that the range of acceptable concentrations increases as the GSD increases.



Figure 8. Theoretical ratios of PM_{10} sampler to true PSD concentrations (PSD – GSD = 1.5)

Figure 9 is a generalized graph to illustrate how MMD's and GSD's 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 (ratio approaches 1.0) as the GSD increases. Figure 10 further expands on how the concentration ratios are impacted by GSD. The data presented in Figure 10 are based on MMDs of 10 and 20 µm, sampler performance characteristics of $d_{50} = 9.5$ µm with a slope of 1.4 and $d_{50} = 10.5$ µm with a slope of 1.6, and variable GSD's ranging from 1.2 to 3.0. The general conclusions that should be drawn from this graph include: (1) when the MMD is equal to the d_{50} the range of concentration ratios is centered around 1.0 for all GSD's, (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.



Figure 9. Theoretical ratios of PM_{10} sampler to true PSD concentrations (PM_{10} sampler characteristics; cut-point = 10 μ m and slope = 1.5)



Figure 10. Theoretical PM_{10} sampler to true concentration ratio boundaries based on varying GSDs for PSD's with MMDs of 10 and 20 μ m

PM2.5 Ambient Air Samplers

In order to define the differences in the simulated sampler measured and true $PM_{2.5}$ concentrations, equations 4 and 5 were solved using Mathcad 2000 for a d₅₀ 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 11. In Figure 11, 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 {25µm} – sampled percent less than 15 µm {25µm})/(true percent less than 15 µm {25µm})



Figure 11. Comparison of true and sampled PM_{2.5} percentages for a range of PSD mass median diameters and a GSD of 2.0

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 7 and 8 over a range of parameters. These parameters included MMD values ranging from 1 to 40 μ m (in increments of 1 μ m), 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 12, 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=d₅₀, (2) the average ratio is greater than 1 when MMD>d₅₀, 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 μ m AED and when the ratio is greater than 1 the current method overestimates the concentration of PM less than or equal to 2.5 μ m AED and when the ratio is greater than 1 the current method overestimates the concentration of PM less than or equal to 2.5 μ m AED and a GSD of 2.0 then the acceptable range of PM_{2.5} concentrations would be 60 to 87 μ g/acm (i.e. ratios of 0.92 and 1.34 obtained from Figure 12 and multiplied by 65 μ g/acm, the proposed NAAQS for PM_{2.5}). However, if a PSD were characterized by a MMD of 20 μ m AED and a GSD of 2.0 then the acceptable range of PM_{2.5} concentrations would be 77 to 182 μ g/acm (i.e. ratios of 1.18 and 2.80 obtained from Figure 12 and multiplied by 65 μ g/acm, the proposed NAAQS for PM_{2.5}).



Figure 12. Theoretical ratios of $PM_{2.5}$ sampler to true PSD concentrations (PSD – GSD = 2.0)

The data presented in Figure 13 are based on the same assumptions as Figure 12, except the data are based on a GSD of 1.5. When comparing Figures 12 and 13, 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 μ m AED and a GSD of 1.5 then the acceptable range of PM_{2.5} concentrations would be 81 to 193 μ g/acm (i.e. ratios of 1.24 and 2.96 obtained from Figure 13 and multiplied by 65 μ g/acm, the proposed NAAQS for PM_{2.5}). However, if a PSD were characterized by a MMD of 20 μ m AED and a GSD of 1.5 then the acceptable range of PM_{2.5} concentrations would be 963 to 11,929 μ g/acm (i.e. ratios of 14.81 and 183.5 obtained from Figure 13 and multiplied by 65 μ g/acm, the proposed NAAQS for PM_{2.5}). Another conclusion that can be drawn from the data presented in Figures 12 and 13 is that the range of acceptable concentrations increases as the GSD increases.

Figure 14 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 15 further expands on how the concentration ratios are impacted by

GSD. The data presented in Figure 15 are based on MMDs of 10 and 20 μ m, sampler performance characteristics of d₅₀ = 2.3 μ m with a slope of 1.27 and d₅₀ = 2.7 μ m 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.



Figure 13. Theoretical ratios of $PM_{2.5}$ sampler to true PSD concentrations (PSD – GSD = 1.5)



Figure 14. Theoretical ratios of $PM_{2.5}$ sampler to true PSD concentrations ($PM_{2.5}$ sampler characteristics; cutpoint = 2.5 µm and slope = 1.3)

SUMMARY AND CONCLUSION

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 <u>NOT</u> 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 less than the size of interest less than the size of interest less than the size of account for all the mass associated with particle diameters less 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. Assume:

- PSD associated with a coal-fired power plant is described by a MMD = 10 μ m and a GSD = 1.5;
- PSD associated with a agricultural operation is described by a MMD = 20 μ m and a GSD = 1.5;
- PM is currently regulated in terms of PM₁₀ sampler concentrations with a maximum property line concentrations limit of 150 μg/acm;
- PM₁₀ ambient air sampler performance characteristics are described by a $d_{50} = 10 \pm 0.5$ µm and a slope of 1.5 ± 0.1 .

Based on the current method of regulating PM_{10} , both the coal-fired power plant and the agricultural operation must not exceed the property line PM_{10} concentrations of 150 µg/acm

(based on sampler measurements), in order to maintain compliance with the regulations. The current method of regulation does \underline{NOT} 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 established based on true concentrations and the sampler performance characteristics that produce the largest concentration levels. In other words:

- the PM_{10} ambient air sampler performance characteristics that should be used are a d_{50} of 10.5 μ m and a slope of 1.6; and
- a true concentration (150 μ g/acm for PM₁₀) should be used, meaning that if PM₁₀ 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_{10} sampler could measure concentrations as high as 159 µg/acm and still comply with the regulations. This results in a 6% error due to the sampler performance characteristics.
- For the agricultural operation, a PM_{10} sampler could measure concentrations as high as 515 µg/acm and still comply with the regulations. This results in a 243% 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 3.2 times more stringent for PM_{10} than that for a coal-fired power plant (under the previously stated assumptions). If this example were applied to a $PM_{2.5}$ ambient air sampler, the agricultural operation would be regulated at a level that is 14 times more stringent than that for a coal-fired power plant.

The following are generalized conclusions drawn from the analysis in this manuscript:

- if MMD < d₅₀ then C_{measured} < C_{true};
- if MMD = d_{50} then $C_{\text{measured}} = C_{\text{true}}$;
- if MMD > d_{50} then $C_{\text{measured}} > C_{\text{true}}$;
- 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 and that <u>ALL</u> industries should be concerned with the current site-specific regulations implemented by EPA and enforced by SAPRA's.

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