Ambient Air Sampling for Particulate Matter

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Presentation Outline

- Background and statement of issues
- Characteristics of ambient aerosols (sources, size ranges, definitions of MMD, GSD, aerodynamic diameter)
- Size-selective measurement techniques (inertial impactors and cyclones, definitions of cutpoint and slope)
- Development of health-based PM standards – physiological basis for PM sampling conventions
- EPA's method development for PM_{10} and $PM_{2.5}$
- Review of TAMU's methodology for estimating "True" PM concentrations, and for estimating "oversampling" of EPA reference methods

Background

- To protect public health, the EPA has developed national ambient air quality standards (NAAQS) for airborne particulate matter (PM). Compliance with the PM NAAQS must be measured using EPA-approved samplers which were developed to accurately measure PM concentrations independent of wind speed and direction. FRM development was thoroughly peer-reviewed and independent evaluations of FRMs have validated their size-selective performance.

- The agricultural industry typically generates airborne PM with much larger mass median diameters (MMDs) than urban dusts, and has expressed the belief that certain agricultural operations are being over-regulated by EPA due to an over-estimation of PM emissions from these operations.

- In particular, the industry has stated that "…*all EPA-approved federal reference method (FRM) samplers do not accurately measure PM concentrations in the presence of the large PM that is typical of PM emitted by agricultural operations. The term for this phenomenon is "over-sampling"."*

- These "over-sampling" statements are directed towards source sampling methods (i.e., in-stack) as well as ambient sampling methods.

Background (cont)

- Representatives of the agricultural industry have conducted their own laboratory and field evaluations of EPA's $PM_{2.5}$ and PM_{10} FRM and have stated that these FRMs over-sample by a factor of 1.5 to 10 (i.e., 150% to 1000% over-sampling). Similar statements have been made regarding sampling of $PM_{2.5}$ aerosols.

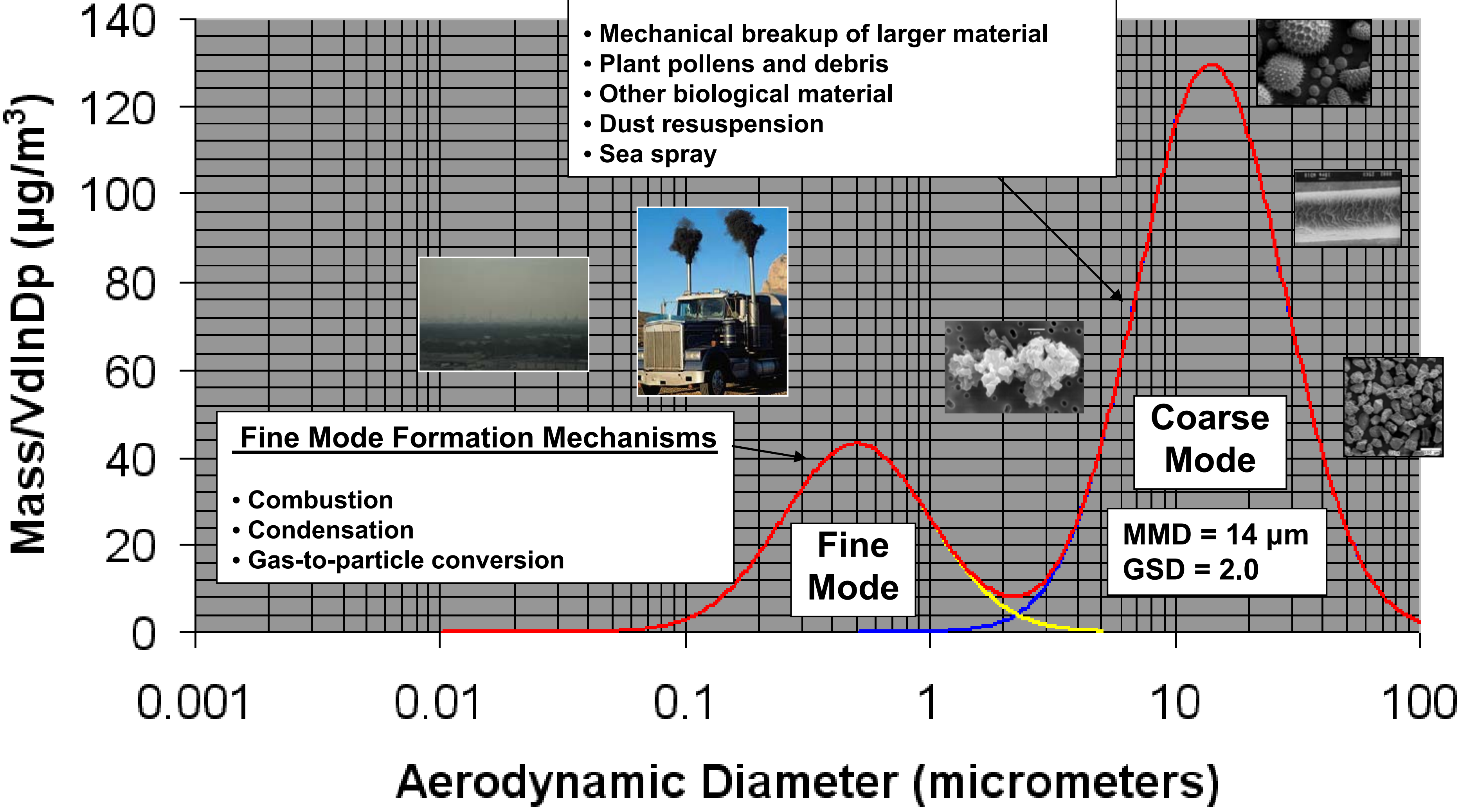
- The agricultural industry postulates that the mechanism for this over-sampling is the change in the sampler's size selective performance (i.e., cutpoint and slope) in the presence of large agricultural dusts.

- EPA has thoroughly examined these statements and does not agree with the fundamental basis for these statements, the methodology upon which the statements were based, nor the conclusions drawn from this research.

- During previous discussions, EPA and agricultural research staff have acknowledged that these are complex technical issues. EPA research staff appreciates the critical importance of accurately regulating the agricultural industry, and also for ensuring that public health is protected with an adequate margin of safety.

Characteristics of Ambient Particulate Matter

Ambient aerosols are bimodal in size and the relative modal concentrations can vary with site, season, and local activity. Modes are typically lognormal in shape.



Coarse Mode Formation Mechanisms

- Mechanical breakup of larger material
- Plant pollens and debris
- Other biological material
- Dust resuspension
- Sea spray

Fine Mode Formation Mechanisms

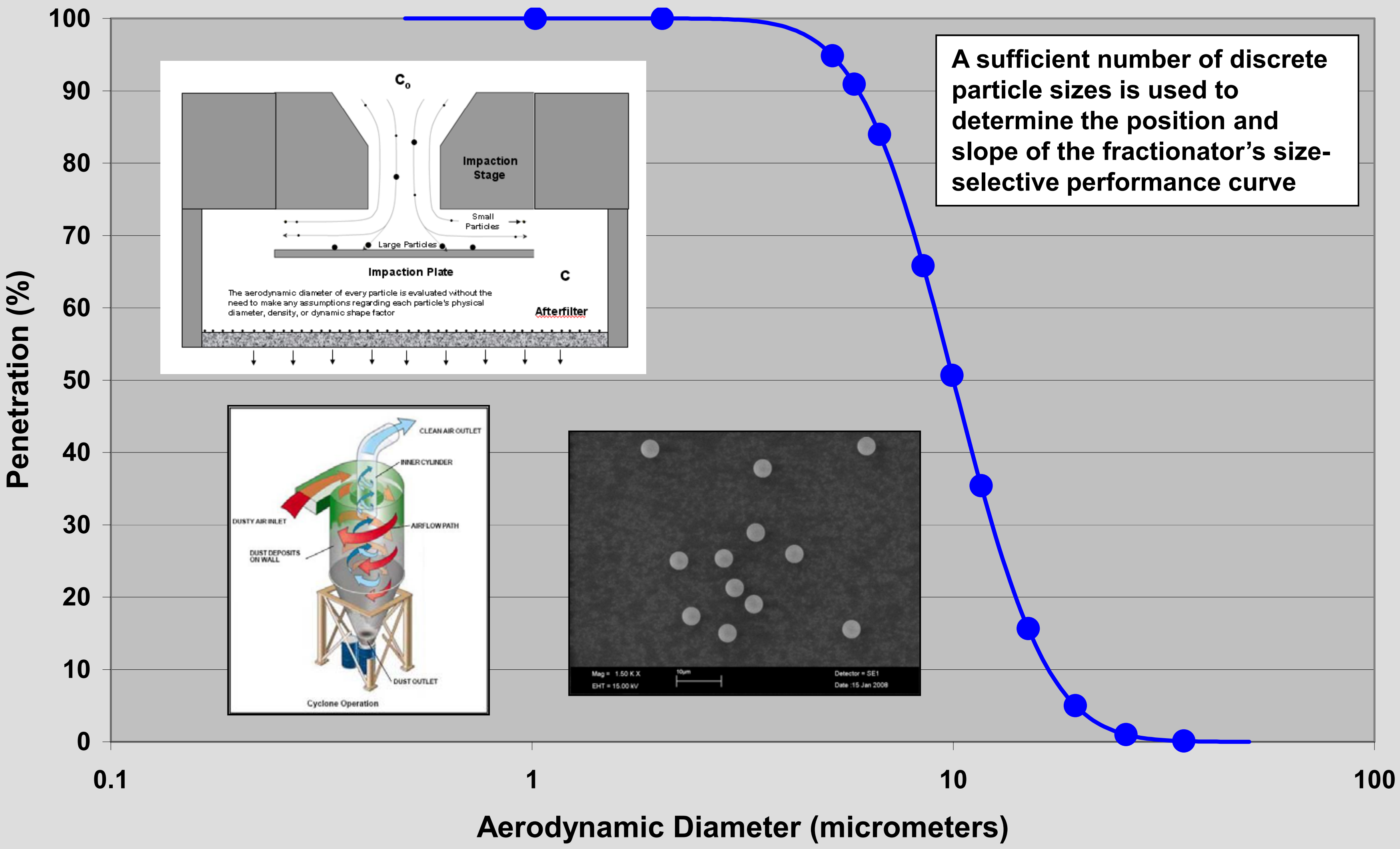
- Combustion
- Condensation
- Gas-to-particle conversion

Fine Mode

Coarse Mode

MMD = 14 µm
GSD = 2.0

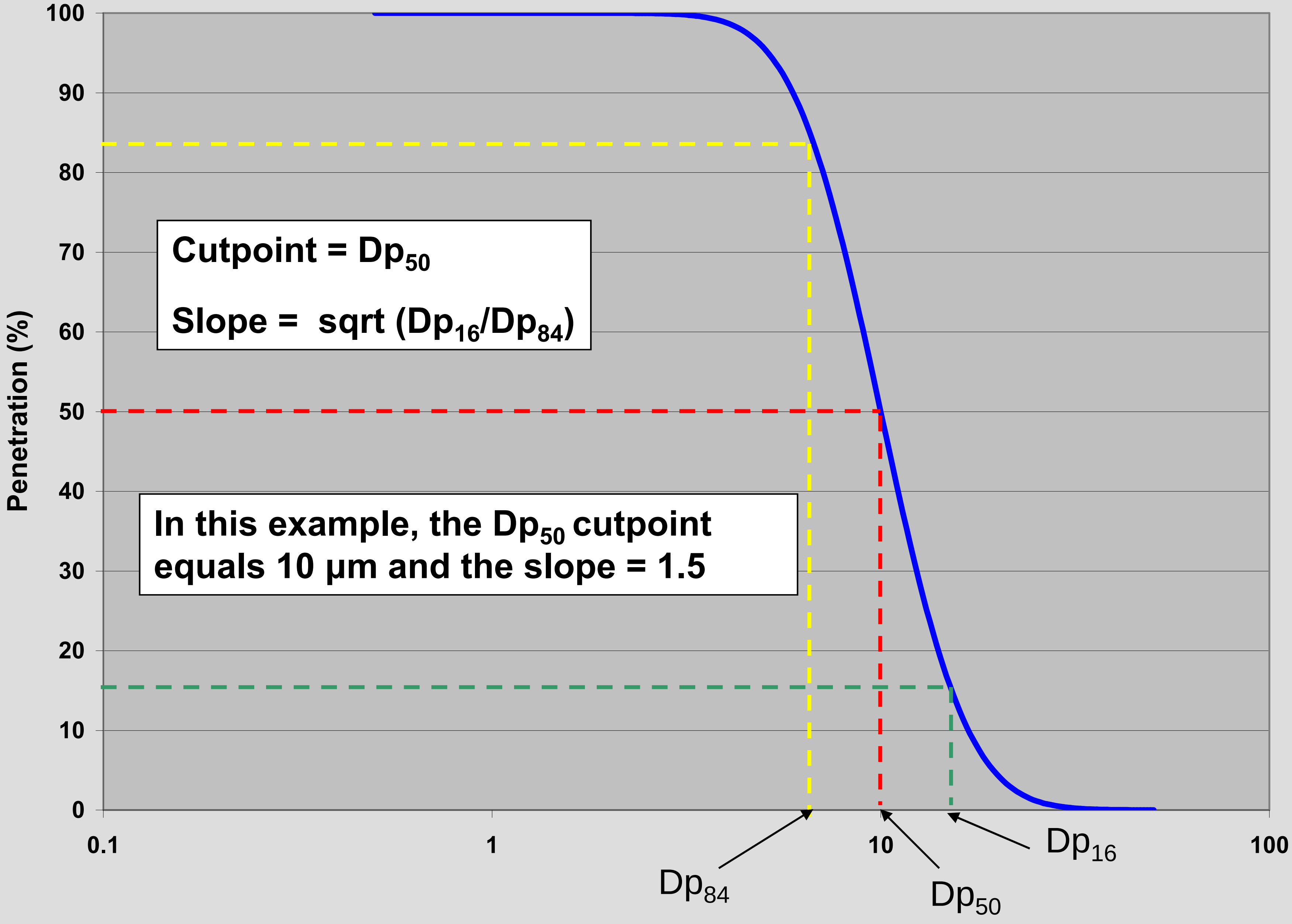
Laboratory Evaluation of Inertial Fractionators using Monodisperse, Primary Calibration Aerosols



A sufficient number of discrete particle sizes is used to determine the position and slope of the fractionator's size-selective performance curve

The aerodynamic diameter of every particle is evaluated without the need to make any assumptions regarding each particle's physical diameter, density, or dynamic shape factor

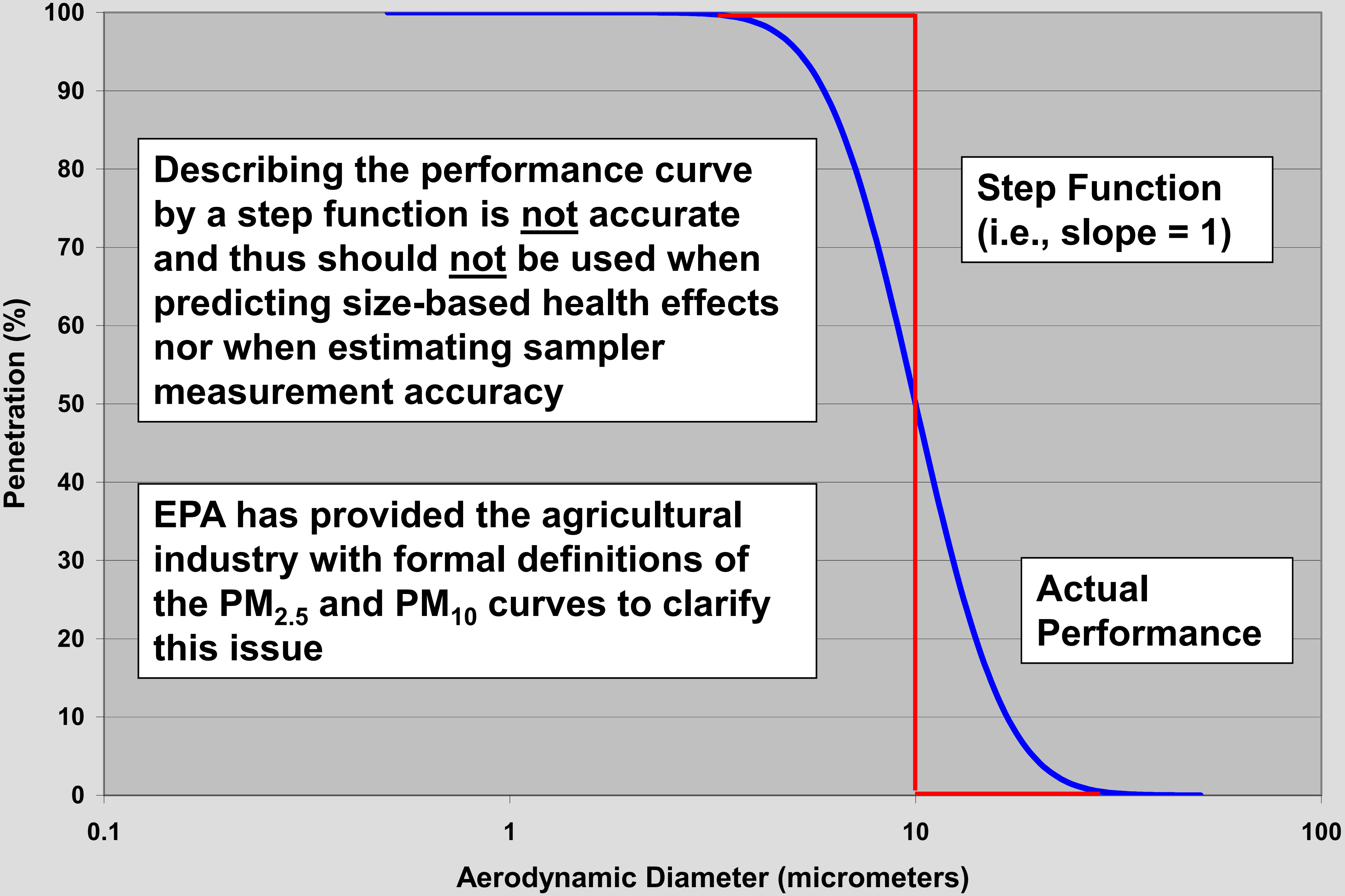
Definitions of Fractionator Cutpoint and Slope



Cutpoint = Dp$_{50}$

Slope = sqrt (Dp$_{16}$/Dp$_{84}$)

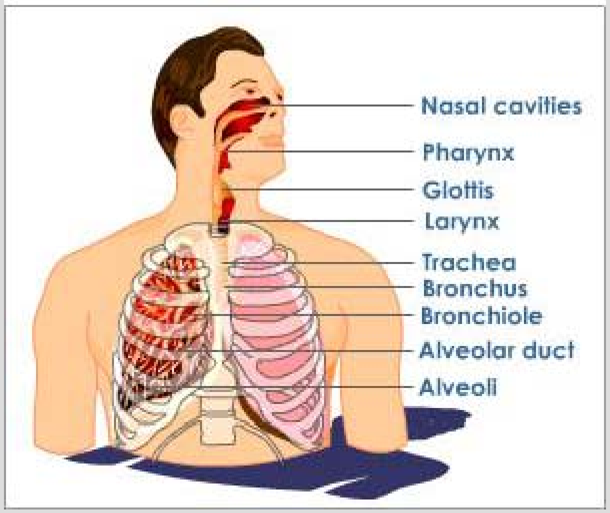
In this example, the Dp$_{50}$ cutpoint equals 10 µm and the slope = 1.5



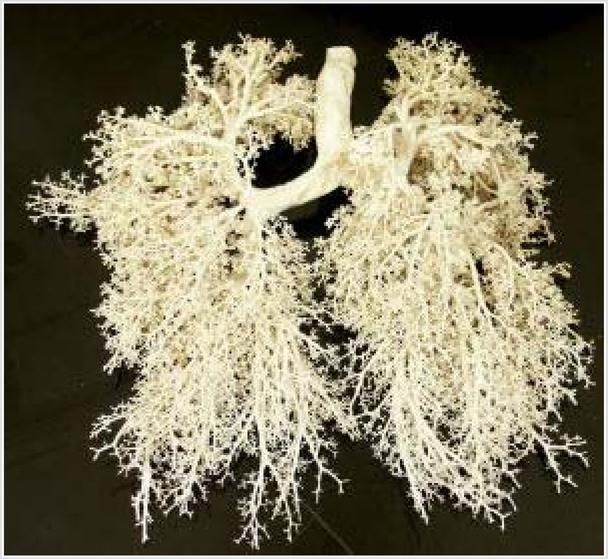
Describing the performance curve by a step function is not accurate and thus should not be used when predicting size-based health effects nor when estimating sampler measurement accuracy

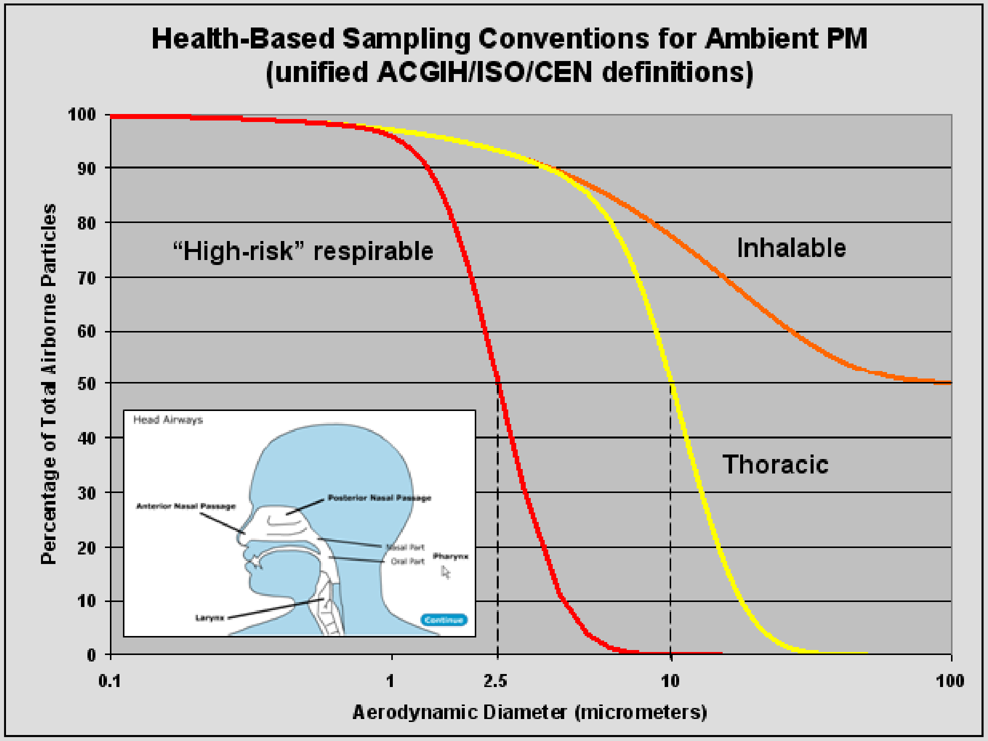
EPA has provided the agricultural industry with formal definitions of the $PM_{2.5}$ and PM_{10} curves to clarify this issue

Physiological Basis for Health-Based PM NAAQS

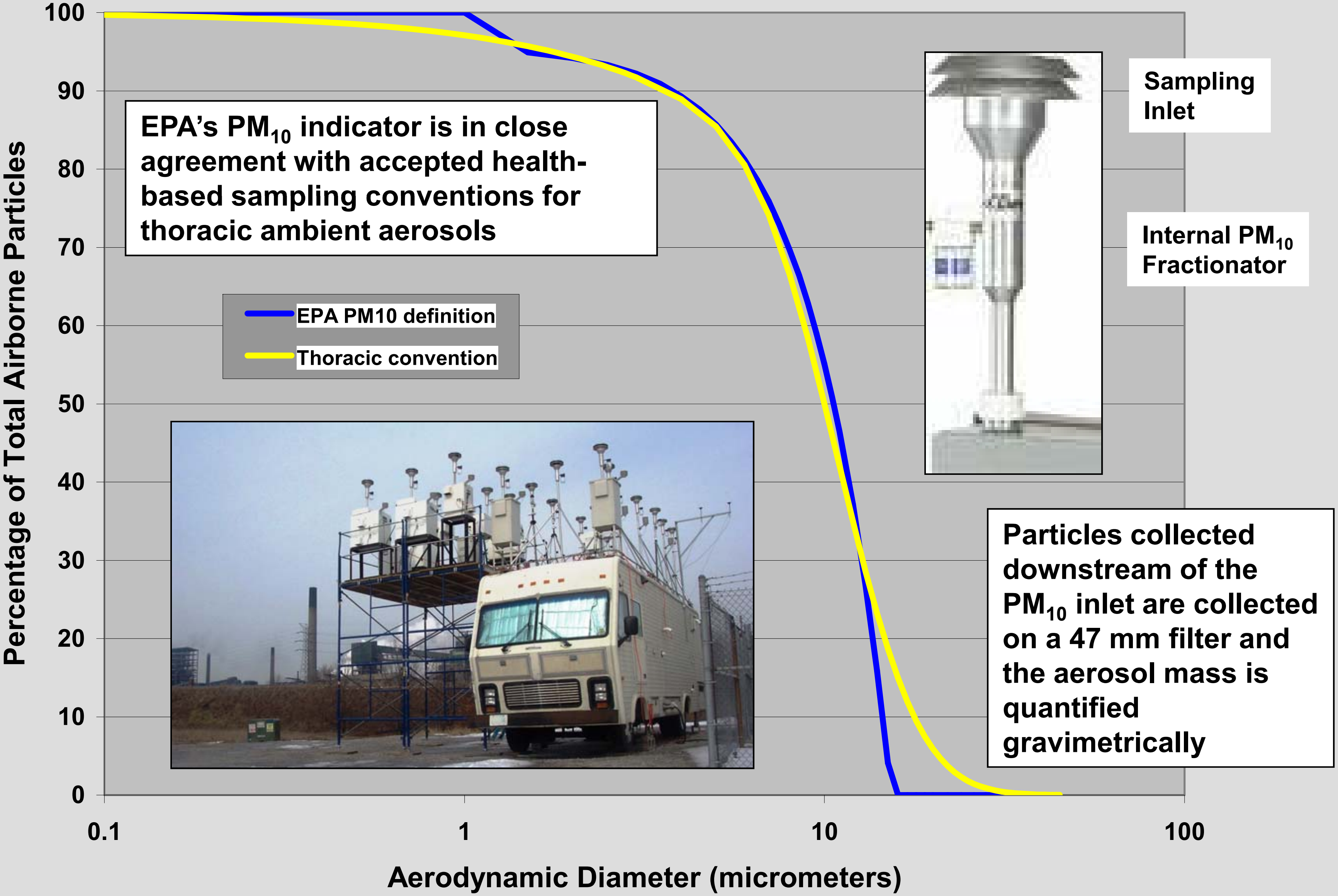


Since the 1970's, results from epidemiological studies, toxicological research, and deposition research have demonstrated that adverse health effects from exposure to airborne particles are primarily associated with those particles capable of entering the thoracic region of the human respiratory system (i.e., below the larynx)




Health-Based Sampling Conventions for Ambient PM (unified ACGIH/ISO/CEN definitions)

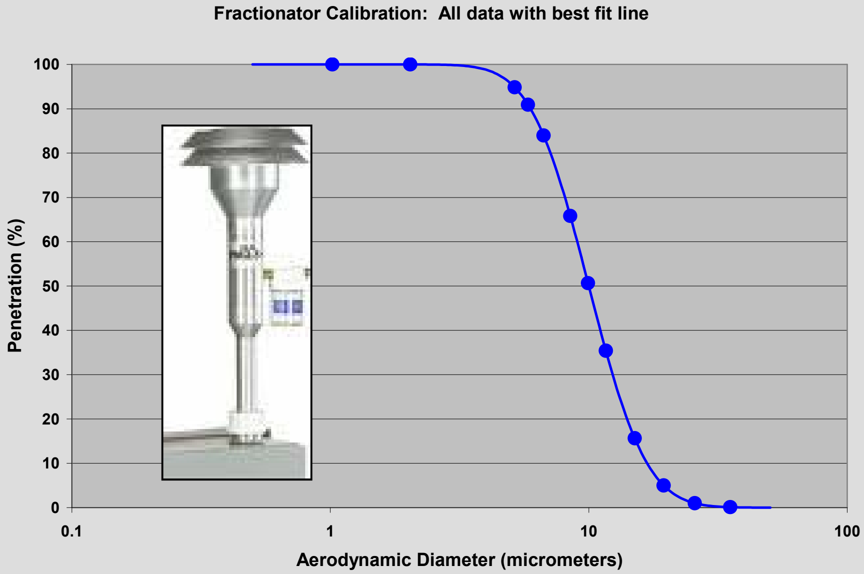
PM_{10} Method Development



EPA's PM_{10} indicator is in close agreement with accepted health-based sampling conventions for thoracic ambient aerosols

Particles collected downstream of the PM_{10} inlet are collected on a 47 mm filter and the aerosol mass is quantified gravimetrically

Wind Tunnel Evaluation of Size Selective Performance

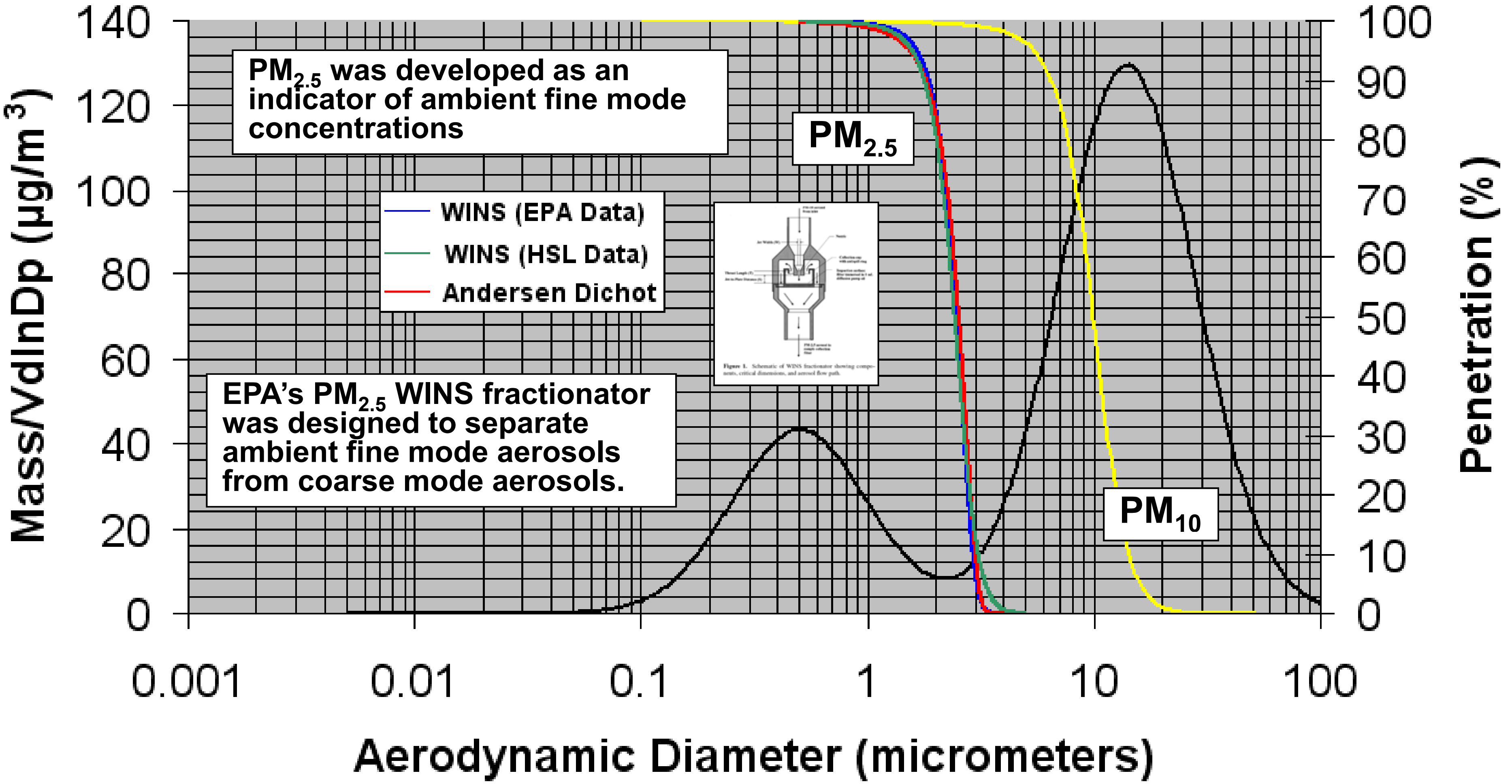


The size-selective performance of PM_{10} samplers must be demonstrated in an aerosol wind tunnel at wind speeds of 2, 8, and 24 km/hr, using monodisperse aerosols from 3 to 25 µm diameter.

Performance of the Low-Volume PM_{10} Dichotomous Inlet

Reference #	Test Aerosol	Inlet Model	Cutpoint (µm)		
			2 km/hr	8 km/hr	24 km/hr
McFarland and Ortiz (1984)	monodispersed aerosol	SA 246B	9.9	10.2	10.0
VanOsdell and Chen (1989)	monodispersed aerosol	SA 246B	9.8	10.0	9.9
VanOsdell (1991)	monodispersed aerosol	R&P 10 µm inlet	9.8	-	9.6
Tolocka et al. (2001)	monodispersed aerosol	Louvered dichot inlet	9.9	10.3	9.7

PM$_{2.5}$ Method Development



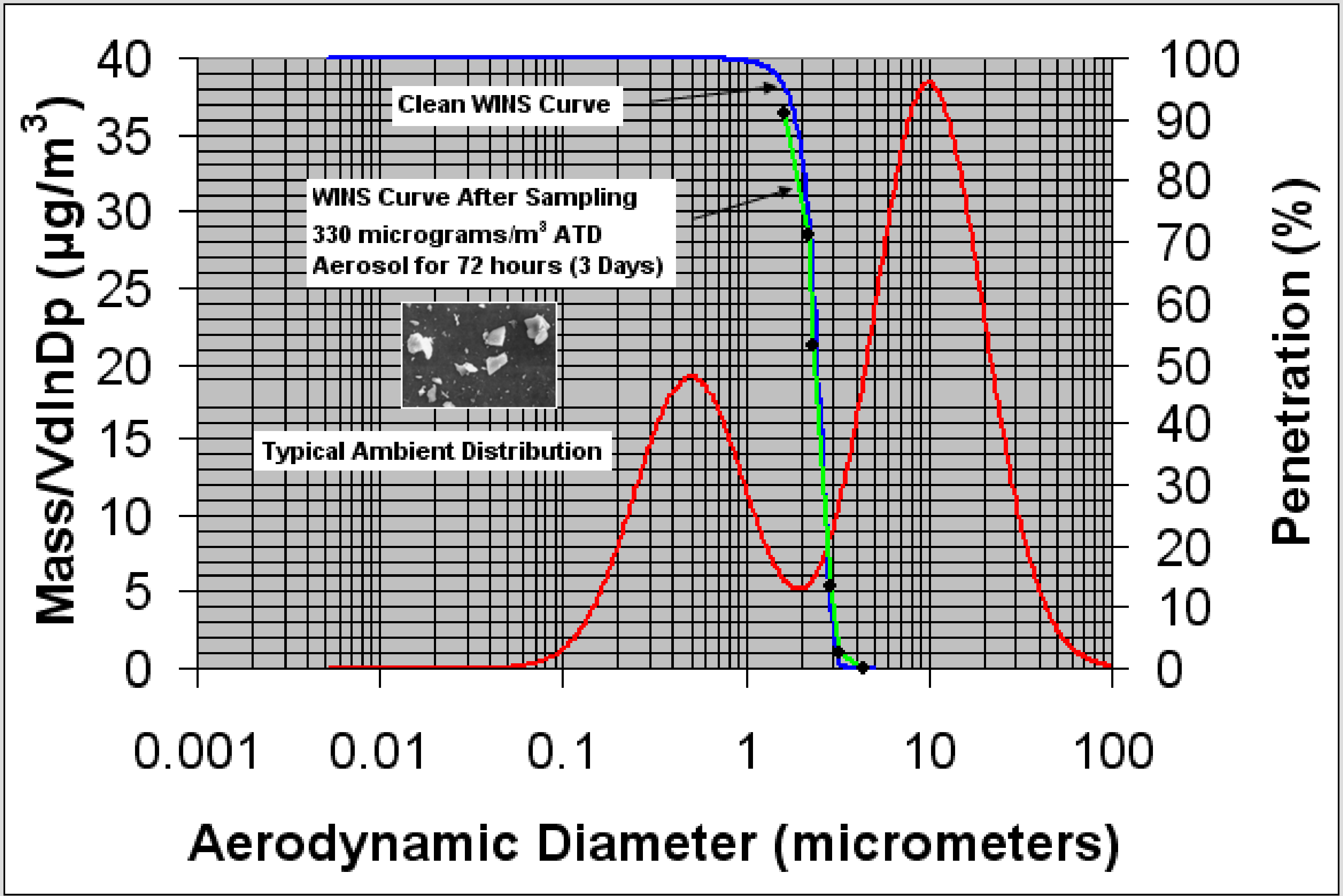
PM$_{2.5}$ was developed as an indicator of ambient fine mode concentrations

EPA's PM$_{2.5}$ WINS fractionator was designed to separate ambient fine mode aerosols from coarse mode aerosols.

During size-selective calibration of the WINS, very favorable inter-laboratory agreement was observed between EPA and England's Health and Safety Laboratory, for both cutpoint and slope.

The size-selective performance of the PM$_{2.5}$ WINS compares closely with the performance of the Andersen dichot's virtual impactor. The dichot had been used extensively during epidemiological studies and served as the basis for the position and shape of EPA's promulgated PM$_{2.5}$ performance curve.

Effect of WINS Loading on Size-Selective Performance



Sampling of high concentrations of Arizona Test Dust (ATD) results in a <u>decrease</u> in WINS cutpoint and thus does <u>not</u> result in positively biased $PM_{2.5}$ mass concentrations

BGI's Very Sharp Cut Cyclone: An Alternative Fractionator for EPA's $PM_{2.5}$ FRM

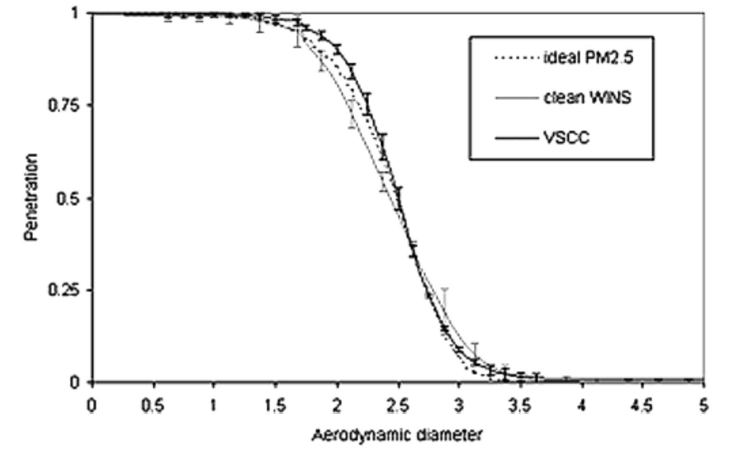


Figure 2. Comparison of WINS and VSCC showing curves fitted to data.

After loading the VSCC with ATD equivalent to 90 days sampling at a concentration of 150 $\mu g/m^3$, no change in the VSCC's cutpoint or slope was noted

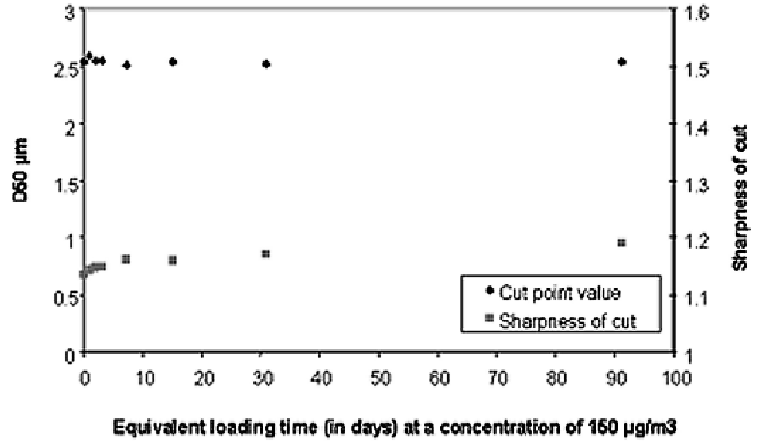


Figure 3. Effect of dust loading on VSCC D50 and sharpness of cut.

Definition of "Oversampling"

"True" PM_{10} is the mass fraction of the mass less than 10 µm AED obtained from a particle size distribution of PM captured with a TSP sampler, times the measured TSP concentration.

1) **Gravimetrically determine the mass concentrations of TSP and PM_{10} using collocated low-vol TSP (LVTSP) samplers and PM_{10} FRM samplers**

2) **Determine the particle size distribution (PSD) of collected PM on the LVTSP filter using Coulter counter analysis**

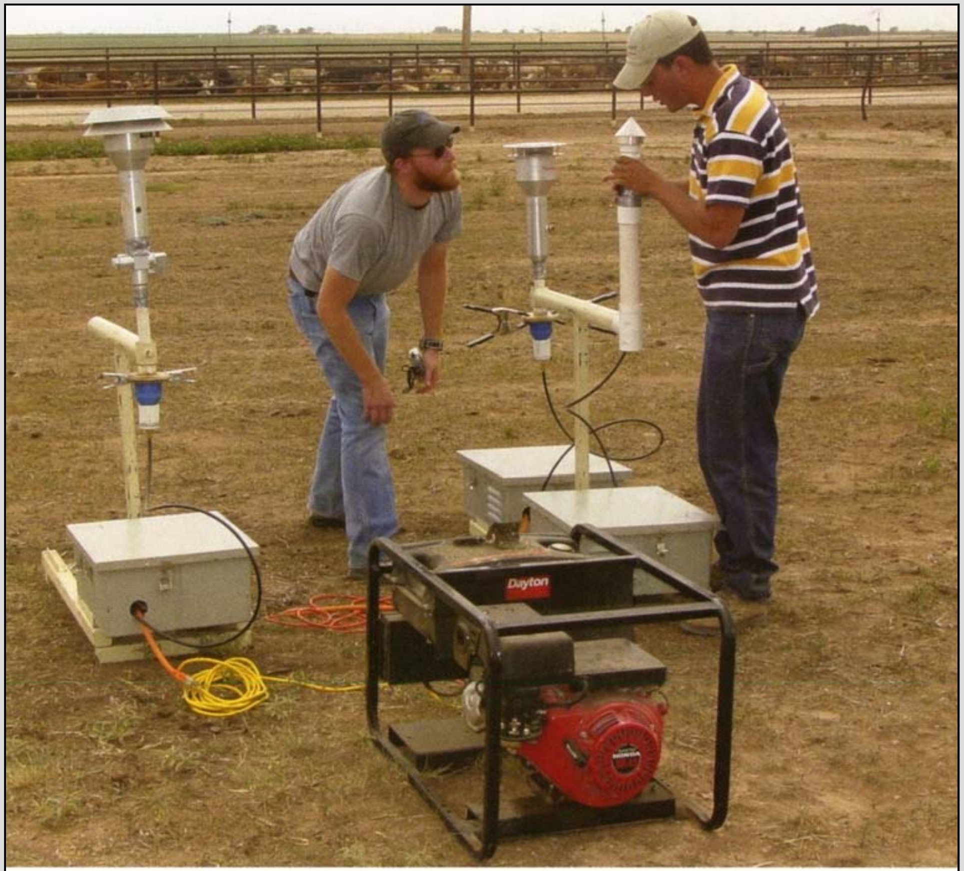
3) **Calculate the mass fraction of the collected LVTSP less than 10 µm AED from the measured PSD**

4) **Calculate the "true" PM_{10} concentration by multiplying the mass fraction times the LVTSP mass concentration**

5) **Calculate oversampling as:**

$$\text{Oversampling} = \left[\frac{\text{FRM } PM_{10}}{\text{"True" } PM_{10}} - 1 \right] * 100\%$$

Step 1: Gravimetrically determine mass concentrations of TSP and PM_{10} using collocated LVTSP samplers and PM_{10} FRM samplers



Above and top right: Sampling crew sets up co-lated FRM and PM_{10} samplers.

16 September/October 2010 RESOURCE

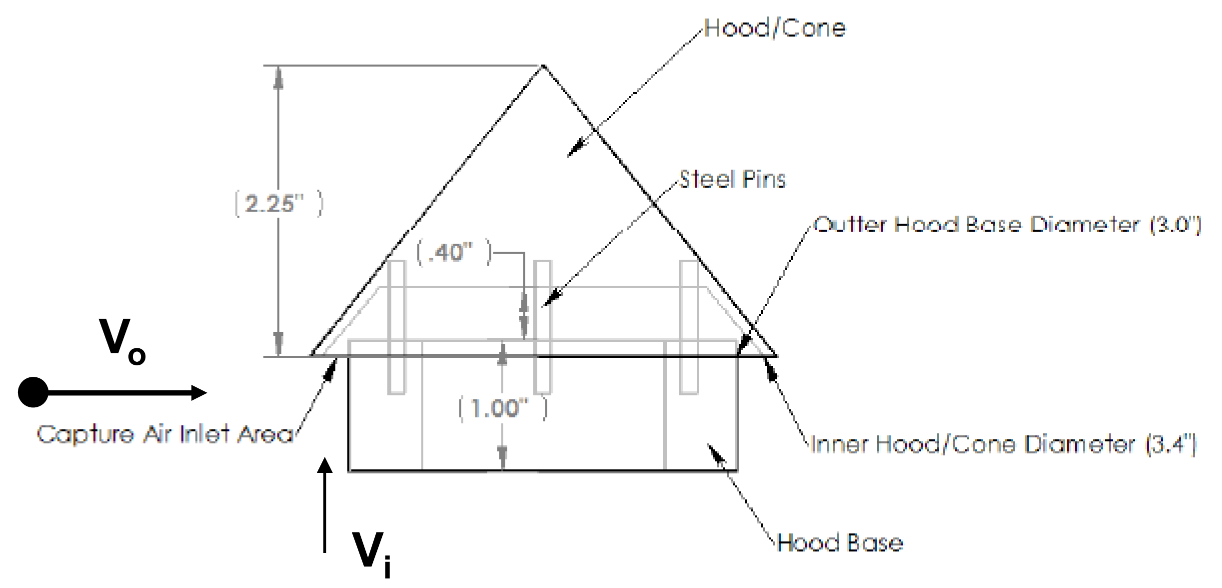
Problem:

TAMU's low-volume TSP (LVTSP) is fundamentally incapable of measuring total mass concentration in the ambient air. This will result in negatively biased mass concentrations, negatively biased "True PM_{10}", and thus will over-estimate the calculated FRM "over-sampling".

Design of the TAMU Low-Vol TSP (LVTSP) Sampler
Flow rate = 16.7 Lpm

Wind speeds (Vo)

2 km/hr = 55 cm/sec
8 km/hr = 222 cm/sec
24 km/hr = 667 cm/sec

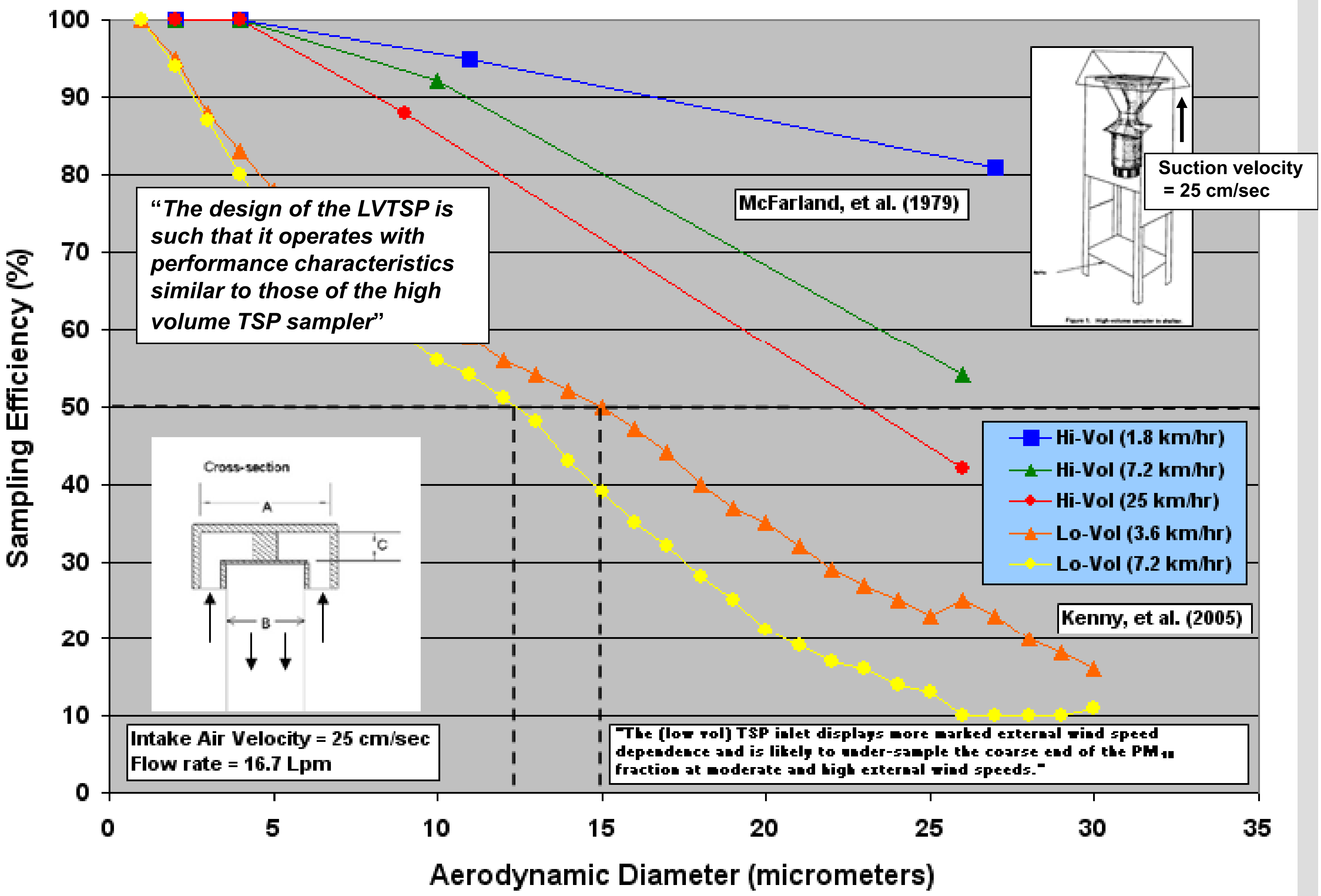


Design intake air velocity (Vi) = 21.5 cm/sec (i.e., designed to approximately match the settling velocity of 100 µm particles

Aspiration Efficiency α **1/St** α $D_i/(\rho_p D_p^2 V_o)$

Result: Small inlets with low sampling flow rates have poor aspiration efficiency particularly with respect to large particles in conjunction with high wind speeds.

Comparison of Hi-Vol TSP versus Lo-Vol TSP Sampling Efficiency



"The design of the LVTSP is such that it operates with performance characteristics similar to those of the high volume TSP sampler"

McFarland, et al. (1979)

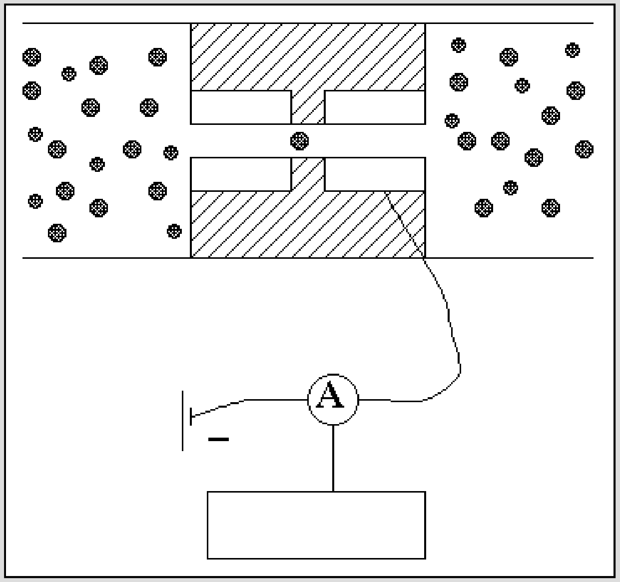
Suction velocity = 25 cm/sec

Kenny, et al. (2005)

Intake Air Velocity = 25 cm/sec
Flow rate = 16.7 Lpm

"The (low vol) TSP inlet displays more marked external wind speed dependence and is likely to under-sample the coarse end of the PM_{10} fraction at moderate and high external wind speeds."

Step 2: Determine the particle size distribution (PSD) of collected PM on the LVTSP filter using Coulter counter analysis



The Coulter method measures the <u>volume</u> of individual particles suspended in a lithium chloride/methanol electrolyte.

<u>Problem 1</u>:

The Coulter method assumes that all particles (independent of particle size) are removed from a filter with 100% efficiency without any change in the original aerosol's size distribution or mass concentration

Step 2 (cont): Determine the particle size distribution (PSD) of collected PM on the LVTSP filter using Coulter counter analysis

$$D_a = D_p\ (\rho_p / Κ\ \rho_a)^{0.5}$$

Problem 2:

Conversion of each particle's measured volume to mass requires knowledge of each particle's density (ρ_p) . Because the composition of ambient aerosols varies widely as a function of particle size, measuring and applying an "average density" to all measured particles is not accurate.

Problem 3:

Conversion of physical size to aerodynamic size requires knowledge of each particle's dynamic shape factor (Κ). Because dynamic shape factors vary substantially as a function of particle size, apply an "average shape factor" to all measured particles is not accurate.

Step 2 (cont): Determine the particle size distribution (PSD) of collected PM on the TSP filter using Coulter counter analysis

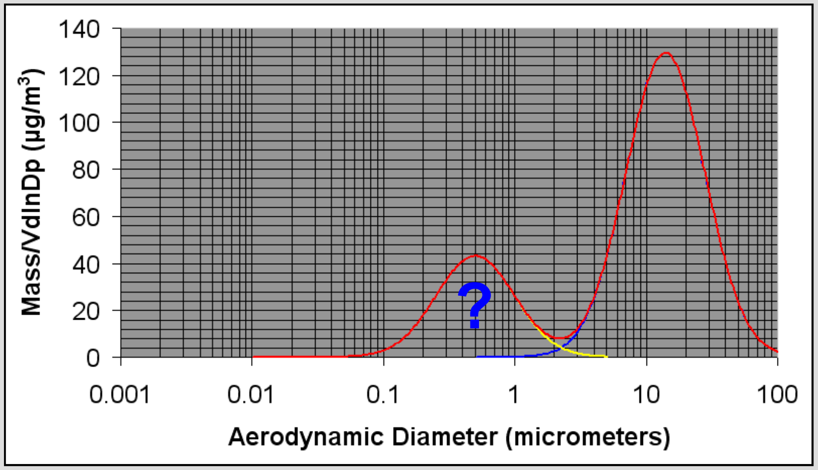
Problem 4: Size Limitations of the Coulter Counter

The Coulter counter is fundamentally incapable of detecting and measuring atmospheric fine mode particles, resulting in inaccurate size distribution determination. This will result in negatively biased mass concentrations and negatively biased "True PM_{10}"

"*Coulter counter apertures can be used to measure particles within a size range of 2% to 60% of its nominal diameter. For a 100 µm aperture, this translates to particle physical diameters between 2 µm and 60 µm.*"
Source: www.beckmancoulter.com

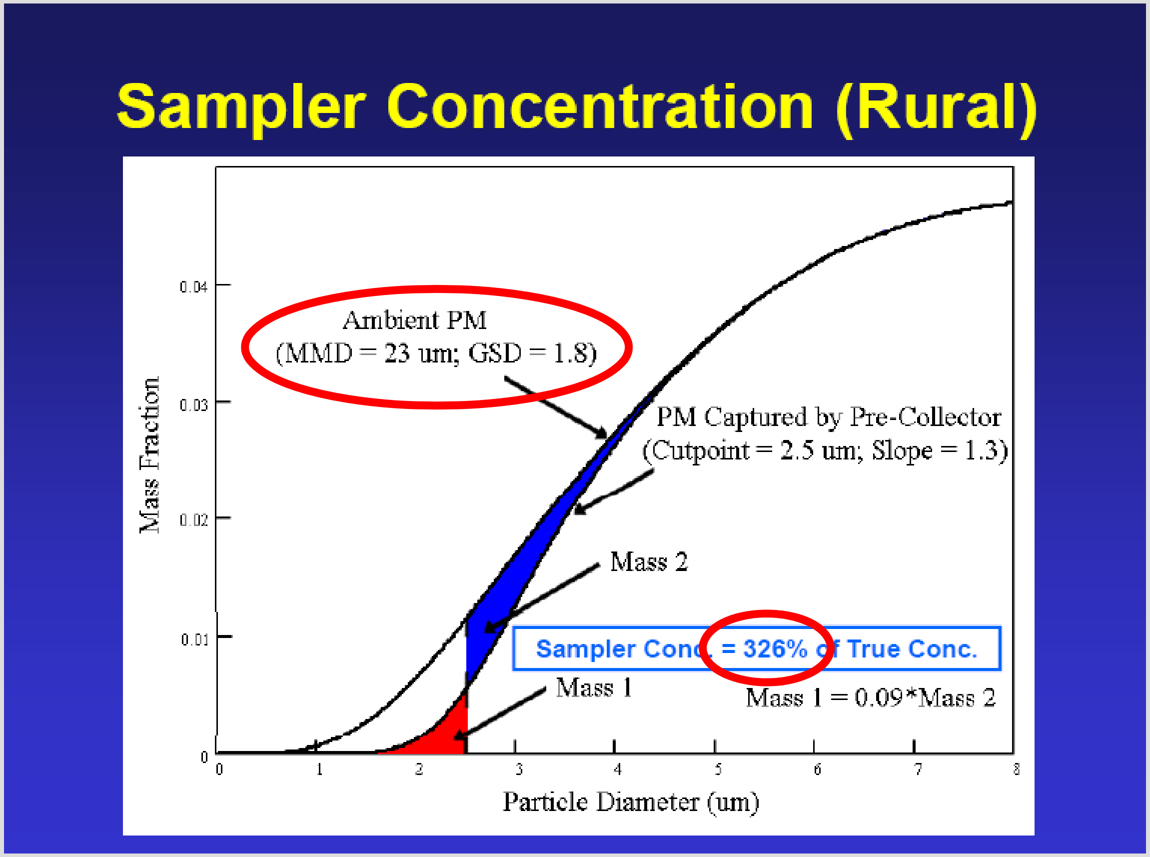
"TSP samplers quantified by a Coulter counter multisizer provide no information below an equivalent spherical diameter of 2 µm and therefore underestimate respirable PM."
Source: Park, et al. (TAMU) Atm. Env. 43 (2009) 280-289.

Use of the Coulter counter for ambient size distribution measurements thus misses the entire fine mode and can substantially underestimate total ambient mass concentrations.



Step 3: Calculate the mass fraction of the collected TSP less than 10 µm AED from the measured PSD

Problem: TAMU's modeling of $PM_{2.5}$ and PM_{10} FRM performance as step-functions results in negatively biased mass concentrations, negatively biased "True PM", and thus over-estimates the calculated FRM "over-sampling".

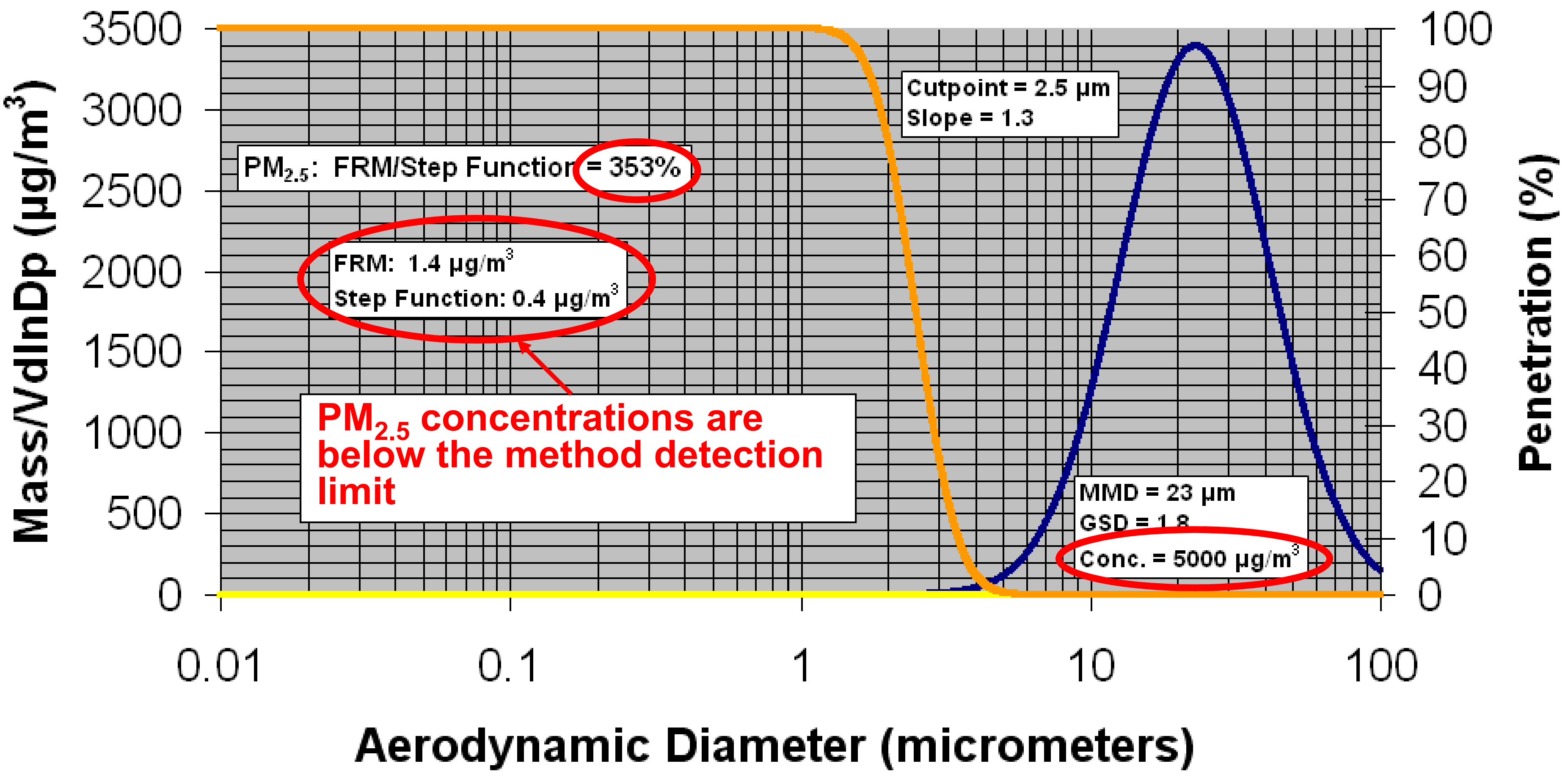


Sampler Concentration (Rural)

Sampler Conc. = 326% of True Conc.

Mass 1 = 0.09*Mass 2

Example presented by Dr. Faulkner to EPA (Jan. 2010)



Cutpoint = 2.5 µm
Slope = 1.3

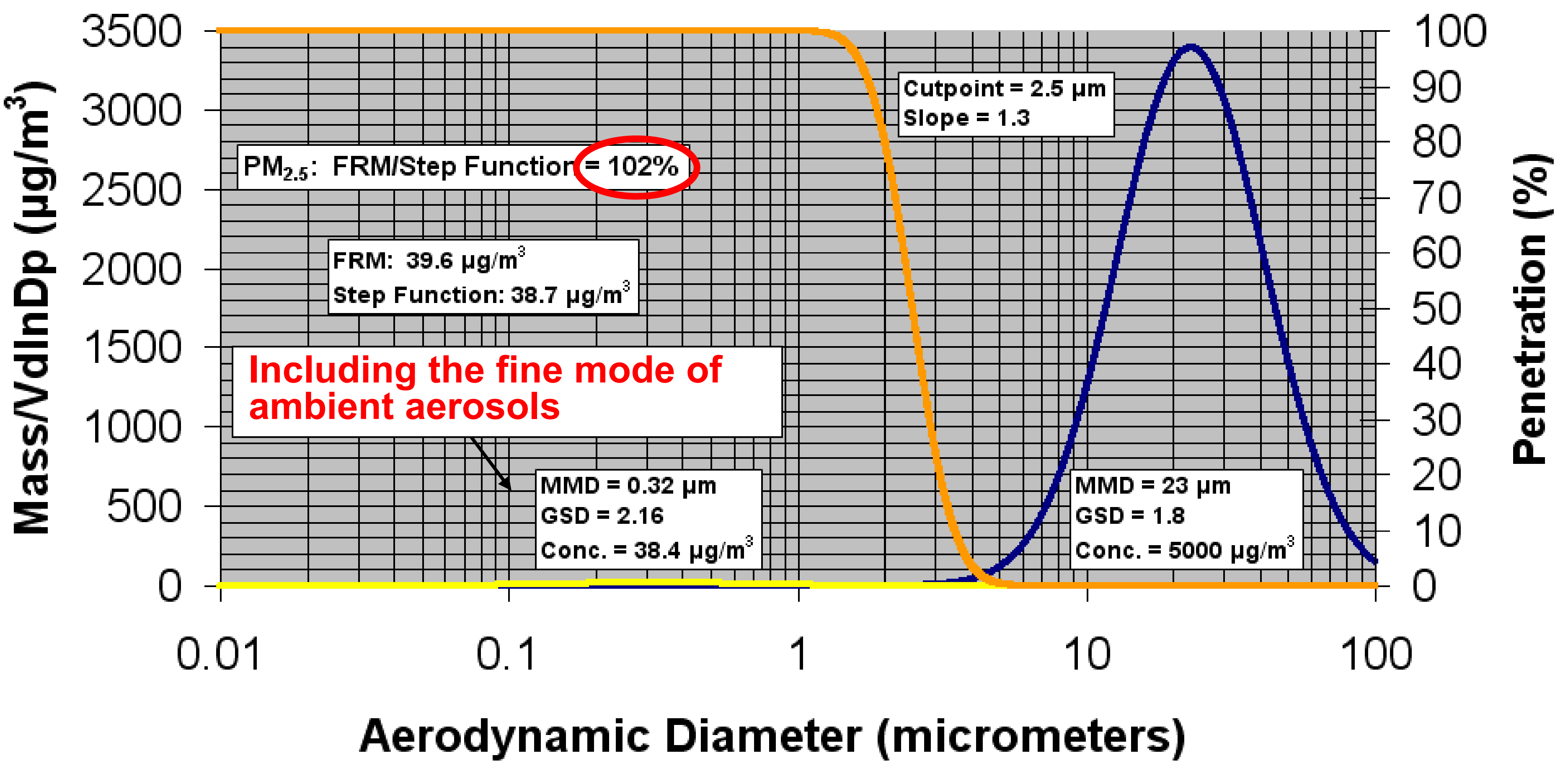
PM$_{2.5}$: FRM/Step Function = 353%

FRM: 1.4 µg/m^3
Step Function: 0.4 µg/m^3

PM$_{2.5}$ concentrations are below the method detection limit

MMD = 23 µm
GSD = 1.8
Conc. = 5000 µg/m^3

Even at extremely high coarse mode concentrations (5000 µg/m^3), predicted PM$_{2.5}$ concentrations are well below the method detection limit. The use of percentages thus tends to over-emphasize what are actually minor differences in mass concentrations.



Proper inclusion of an ambient atmosphere's fine mode virtually eliminates estimated differences between actual $PM_{2.5}$ concentrations versus those predicted using step functions. In this example, the fine mode concentration is less than 1% of the coarse mode concentration.

Example Publication


ESTIMATING FRM PM_{10} SAMPLER PERFORMANCE CHARACTERISTICS USING PARTICLE SIZE ANALYSIS AND COLLOCATED TSP AND PM_{10} SAMPLERS: COTTON GINS

***Estimating FRM PM_{10} Sampler Performance Characteristics Using Particle Size Analysis and Collocated TSP and PM_{10} Samplers: Cotton Gins*, Buser, et al., 2008. Transactions of the ASABE, Vol. 51(2): 695-702.**

Abstract

"Recent work at a south Texas cotton gin showed that … the cutpoint and slope of the FRM PM_{10} sampler shifted substantially and ranged from 13.8 to 34.5 µm and from 1.7 to 5.6, respectively, when exposed to large PM as is characteristic of agricultural sources."

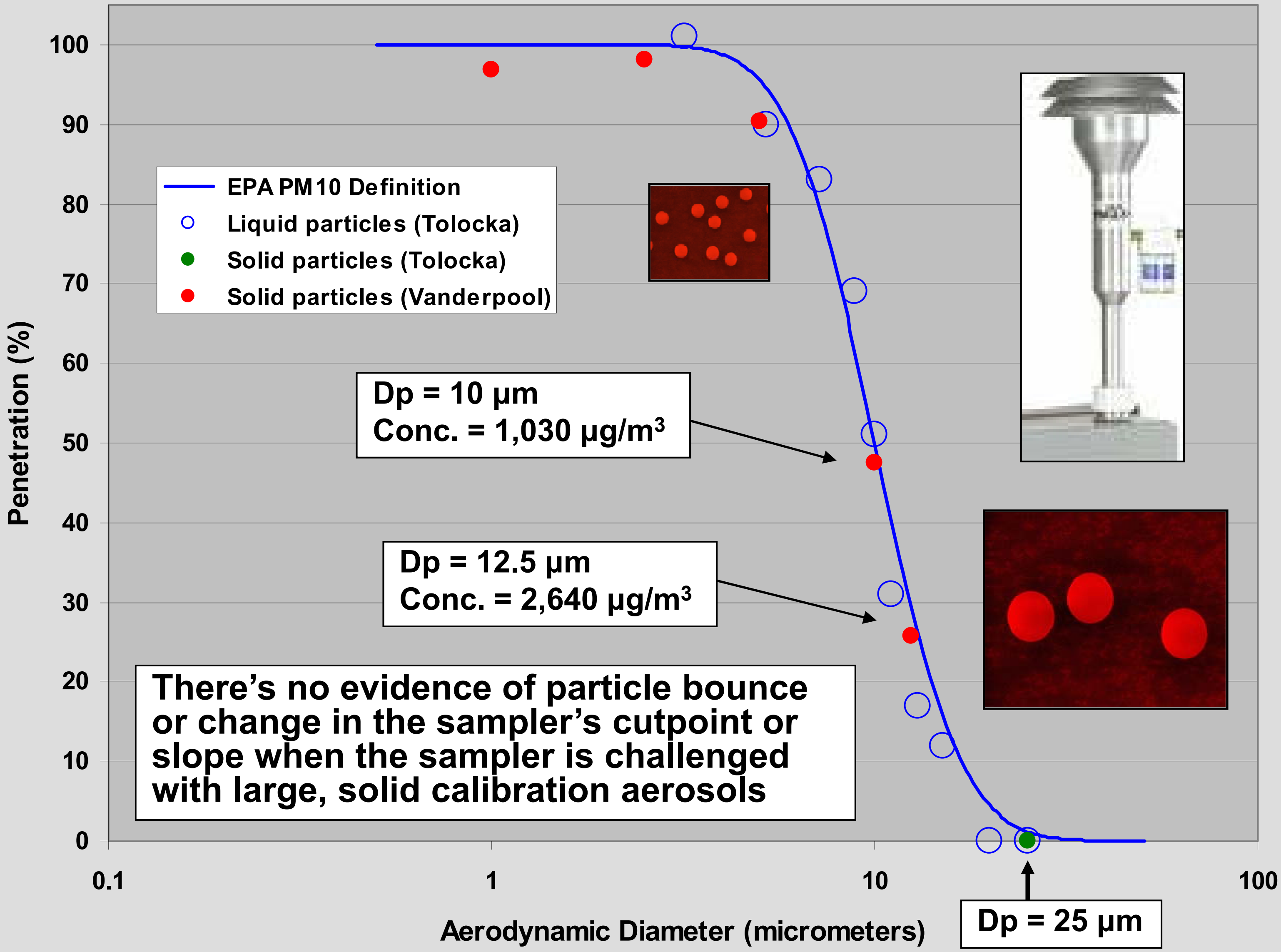
"These shifts in the cutpoint and slope of the FRM PM_{10} sampler resulted in overestimation of true PM_{10} concentrations by 145% to 287%."

MMD (µm)	GSD	Dust Conc. (µg/m³)	"True" PM_{10} (µg/m³)	FRM PM_{10} (µg/m³)	Estimated "Oversampling"	Estimated PM_{10} Cutpoint (µm)
13.6	2.3	1,385	494	1,099	122%	32.6

"*The assumption is that <u>particle bounce</u> in effect increases the cutpoint of the inlet*" (Parnell and McGee, 2010)

Size-Selective Performance of EPA's Louvered PM_{10} Inlet as a Function of Solid and Liquid Monodisperse Calibration Aerosols

Source: Tolocka et al. (2001), Vanderpool (2008)



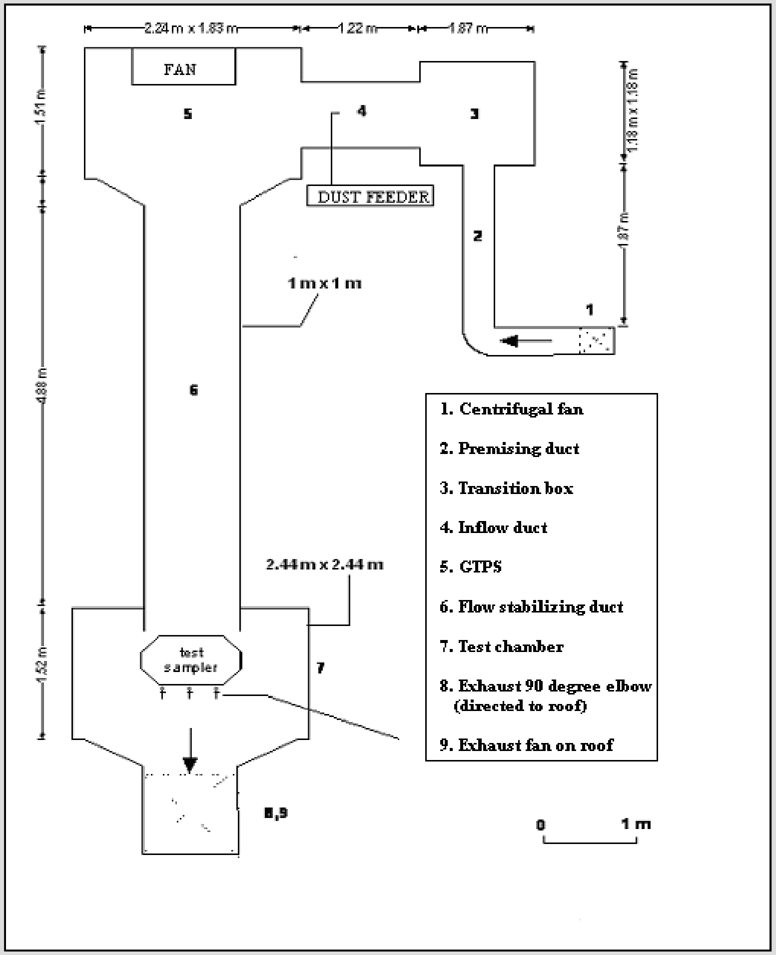
Dp = 10 µm
Conc. = 1,030 µg/m³

Dp = 12.5 µm
Conc. = 2,640 µg/m³

There's no evidence of particle bounce or change in the sampler's cutpoint or slope when the sampler is challenged with large, solid calibration aerosols

Dp = 25 µm

Texas A&M's Aerosol Wind Tunnel

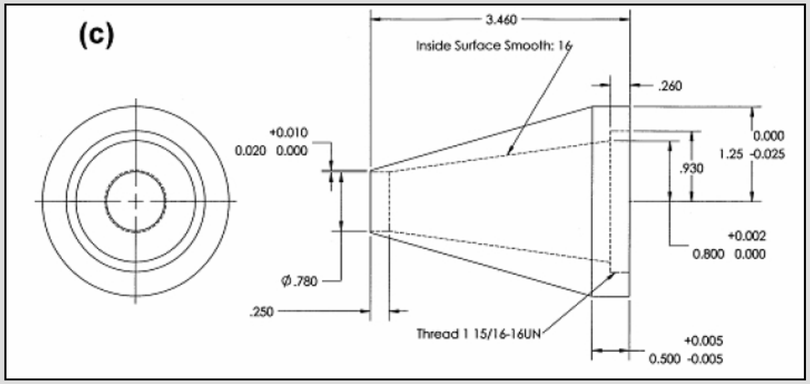


Schematic of TAMU's 1 m x 1m wind tunnel

Wind tunnel test section showing arrangement of isokinetic nozzle and PM_{10} test samplers

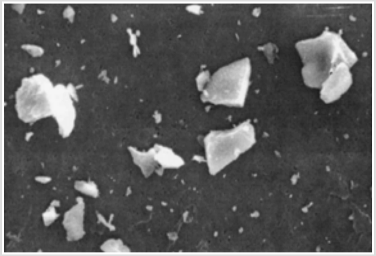
Wind speeds = 2, 8, 24 km/hr

Tests showed that the tunnel met EPA's requirements for spatially uniform aerosol concentrations and air velocities in the test section



Schematic of 2 km/hr isokinetic nozzle used for representative aerosol collection independent of aerodynamic particle size

Test Aerosol: Polydisperse Arizona Test Dust (ADT)

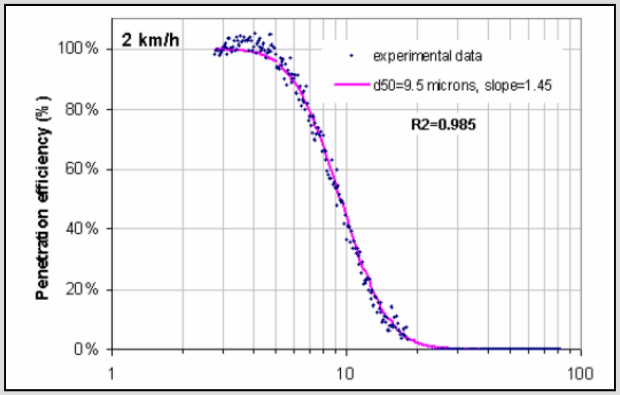


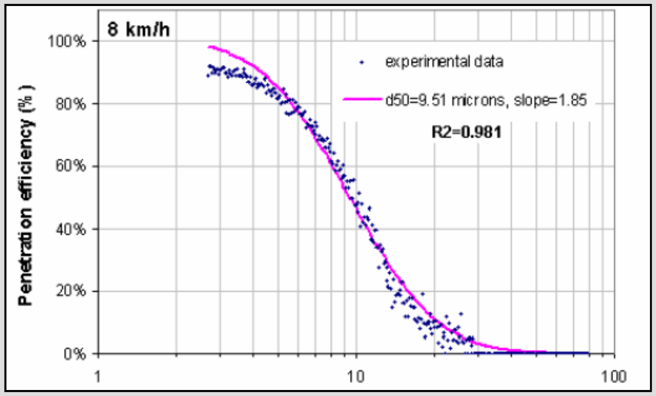
- ATD is commercially available from Powder Technology Inc. in a range of sizes characteristic of agricultural dust emissions. The source material is collected in bulk from windblown topsoils in the Salt River Valley in Arizona.
- ATD is formulated under controlled conditions from naturally occurring materials to possess consistent particles sizes and chemical composition (NIST standards)
- ADT is large, dry, readily dispersed, and insoluble and non-reactive in the Coulter counter's electrolyte. ADT is thus a suitable test aerosol for Coulter counter analysis.
- Known properties (density and shape factor) allows computation of aerodynamic diameter from Coulter diameter
- ATD's primary components (68-76% SiO_2 and 10-15% Al_2O_3) are hard minerals and very suitable for conducting PM sampler bounce tests
- Sampler evaluation involves comparing the freestream particle size distribution (from the isokinetic sampler) to the size distribution of particles on the PM_{10} FRM's after-filter

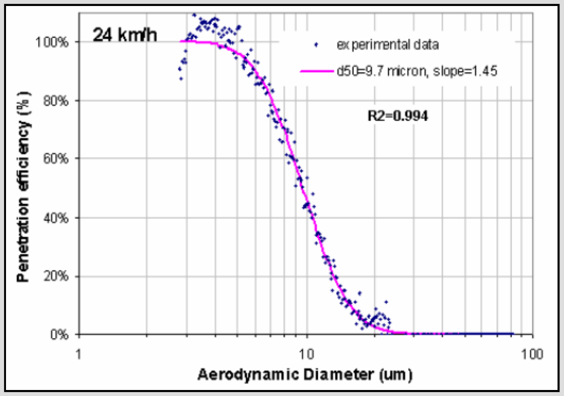
$$D_a = D_p (\rho_p / Κ \rho_a)^{0.5}$$

Density = 2.65 g/cm^3
Shape factor = 1.4-1.5

Texas A&M's Wind Tunnel Evaluation of EPA's Louvered PM$_{10}$ FRM Inlet
(Source: Chen and Shaw, 2007)







Performance of Low-Volume PM$_{10}$ Dichotomous Inlets

Reference #	Test Aerosol	Inlet Model	Cutpoint (µm)		
			2 km/hr	8 km/hr	24 km/hr
This study (TAMU)	polydisperse ATD	BGI PQ100/200	9.5	9.5	9.7
McFarland and Ortiz	monodispersed aerosol	SA 246B	9.9	10.2	10.0
VanOsdell and Chen	monodispersed aerosol	SA 246B	9.8	10.0	9.9
VanOsdell	monodispersed aerosol	R&P 10 µm inlet	9.8	-	9.6
Tolocka et al.	monodispersed aerosol	Louvered dichot	9.9	10.3	9.7

"The results of dust wind tunnel testing clearly indicated that the cutpoint of BGI PQ100/200 louvered dichotomous PM$_{10}$ inlet was within USEPA's requirement and the wind speed does not affect the cutpoint of the inlet."

Comparison of Measured to Predicted PM_{10} FRM Cutpoint when Exposed to Large PM

Source: Chen and Shaw, 2007

Wind speed (km/hr)	Test Aerosol MMD (µm)	Test Aerosol GSD	ATD Dust Conc. (µg/m³)	Ratio of Dust Conc. to 24-hr PM_{10} NAAQS (Note: NAAQS = 150 µg/m³)	Measured Cutpoint (µm)
2	9.5	2.1	16,500	110	9.5
8	10.1	2.3	25,000	167	9.5
24	12.6	1.9	13,000	87	9.7

Source: Buser, et al. "*Estimating FRM PM_{10} Sampling Performance Characteristics Using Particle Size Analysis and Collocated TSP and PM_{10} Samplers: Cotton Gins*"

Sample No.	MMD (µm)	GSD	Dust Conc. (µg/m³)	"True" PM_{10} (µg/m³)	FRM PM_{10} (µg/m³)	Estimated "Oversampling"	Estimated PM_{10} Cutpoint (µm)
1	12.8	2.0	1,770	642	1,152	79%	23.1
2	13.4	2.1	852	294	687	134%	29.6
8	13.6	2.3	1,385	494	1,099	122%	32.6
11	10.4	1.8	603	284	557	96%	34.5
12	13.0	1.8	2,254	743	1,708	130%	22.9

Conclusion: Sampling of high concentrations of large aerosols characteristic of agricultural emissions clearly does not change the FRM sampler's size selective performance. Thus, no "oversampling" of agricultural emissions occurs.

Summary and Conclusions

1. **EPA's FRM samplers for particulate matter were developed using strict design and performance criteria, have been thoroughly peer-reviewed, and their performance has been validated by independent researchers.**

2. **For the following reasons, the "True" method of estimating ambient concentrations is inherently negatively biased and should not be used for evaluating the accuracy of EPA's PM reference methods**

   - **Due to its design, the TAMU's low-vol TSP (LVTSP) undermeasures total mass concentrations, and its performance decreases with increasing particle size and increasing wind speed**
   - **The Coulter counter is incapable of accurately quantifying particles below approximately 2 µm and misses the entire fine mode of ambient aerosols, thus underestimating total mass concentration**
   - **Modeling $PM_{2.5}$ and/or PM_{10} performance curves using step-functions does not accurately reflect EPA's definition of these metrics, and results in an underprediction of actual mass concentration**

$$\text{Oversampling} = \left[\frac{\text{FRM } PM_{10}}{\text{"True" } PM_{10}} - 1 \right] * 100\%$$

Summary and Conclusions (cont)

3. **The proposed mechanism of oversampling by particle bounce is not supported by actual laboratory or field tests for either $PM_{2.5}$ or PM_{10} FRM samplers.**

4. **Texas A&M's own wind tunnel tests of EPA's PM_{10} FRM sampler conclusively prove that sampling of large, solid characteristic of the agricultural industry does <u>not</u> change the sampler's performance (i.e., cutpoint and slope), and thus does <u>not</u> result in oversampling of agricultural aerosols. These tests clearly demonstrate that the "True PM_{10}" method of assessing FRM performance is inherently inaccurate and should not be used.**

5. **EPA staff looks forward to continued discussions with agricultural industry representatives, and is committed to help resolve technical issues to help demonstrate that agricultural emissions are accurately measured and that agricultural operations are fairly regulated.**