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Update on Lead Federal Reference Method Research Activities

Presented as a Briefing for Lead NAAQS Review Panel of the Clean Air Scientific Advisory Committee

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Presentation Outline

- Updates on new FEM designations for Pb analysis
- Summary of 2008 FRM sampling techniques (TSP and PM_{10})
- Specifications and uncertainties associated with current Pb NAAQS sampling methods
- Discussion of research initiatives to address limitations of current Pb sampling methods
  - Design Features and development approach for a new Pb FRM sampler
  - Development of a new FRM for TSP filter analysis using ICP-MS

Recent Method Designations (2010-2012)

Metric	Applicant	Designation	Extraction	Analysis
TSP	Inter-Mountain Laboratories	EQL-0310-189	Hot plate w/ HNO_3	ICP-MS
TSP	EPA/OAQPS	EQL-0510-191	Heated ultrasonic w/ HCL/HNO_3	ICP-MS
TSP	EPA/Region 9	EQL-0710-192	Hot block w/ HNO_3	ICP-MS
TSP	EPA/OAQPS	EQL-0311-196	Heated w/ HCL/HNO_3	ICP-AES
TSP	ERG	pending	Heated w/ $HCL/HNO_3/H_2O_2$	ICP-MS
PM_{10}	ERG	pending	Heated w/ $HCL/HNO_3/H_2O_2/HF$	ICP-MS

Summary of Pb NAAQS: Sampling and Analytical Techniques

The two different sampling FRMs (Pb-TSP and Pb-PM_{10}) have correspondingly different analytical FRMs associated with them

Source-oriented sites tend to produce high concentrations of large Pb-bearing particles

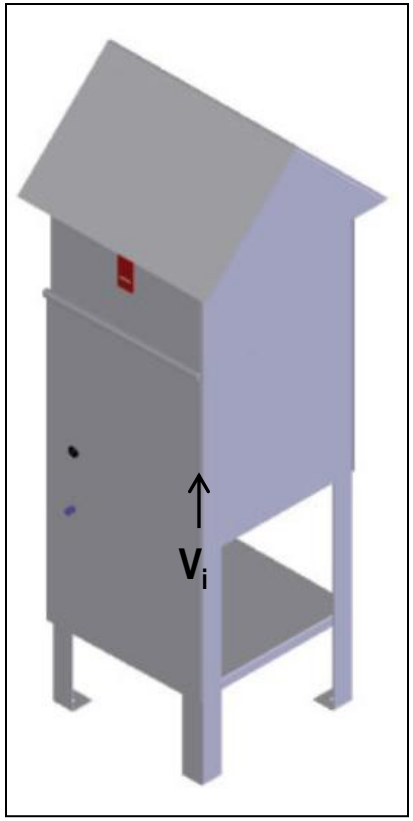
Hi-Vol TSP Sampling (~ 50 cfm)

- 40 CFR Part 50 Appendix B
- Sampling at source-oriented sites
- Analytical FRM involves extraction of Pb on 8" x 10" glass fiber filters using acid extraction followed by flame AA analysis (40 CFR Part 50 Appendix G)

PM_{10} Sampling (16.7 Lpm)

- 40 CFR Part 50 Appendix Q
- Sampling at non-source-oriented sites and at selected source-oriented sites where ultra-coarse emissions are expected to be minimal
- Analytical FRM involves XRF analysis of Pb on 46.2 mm diameter teflon filters

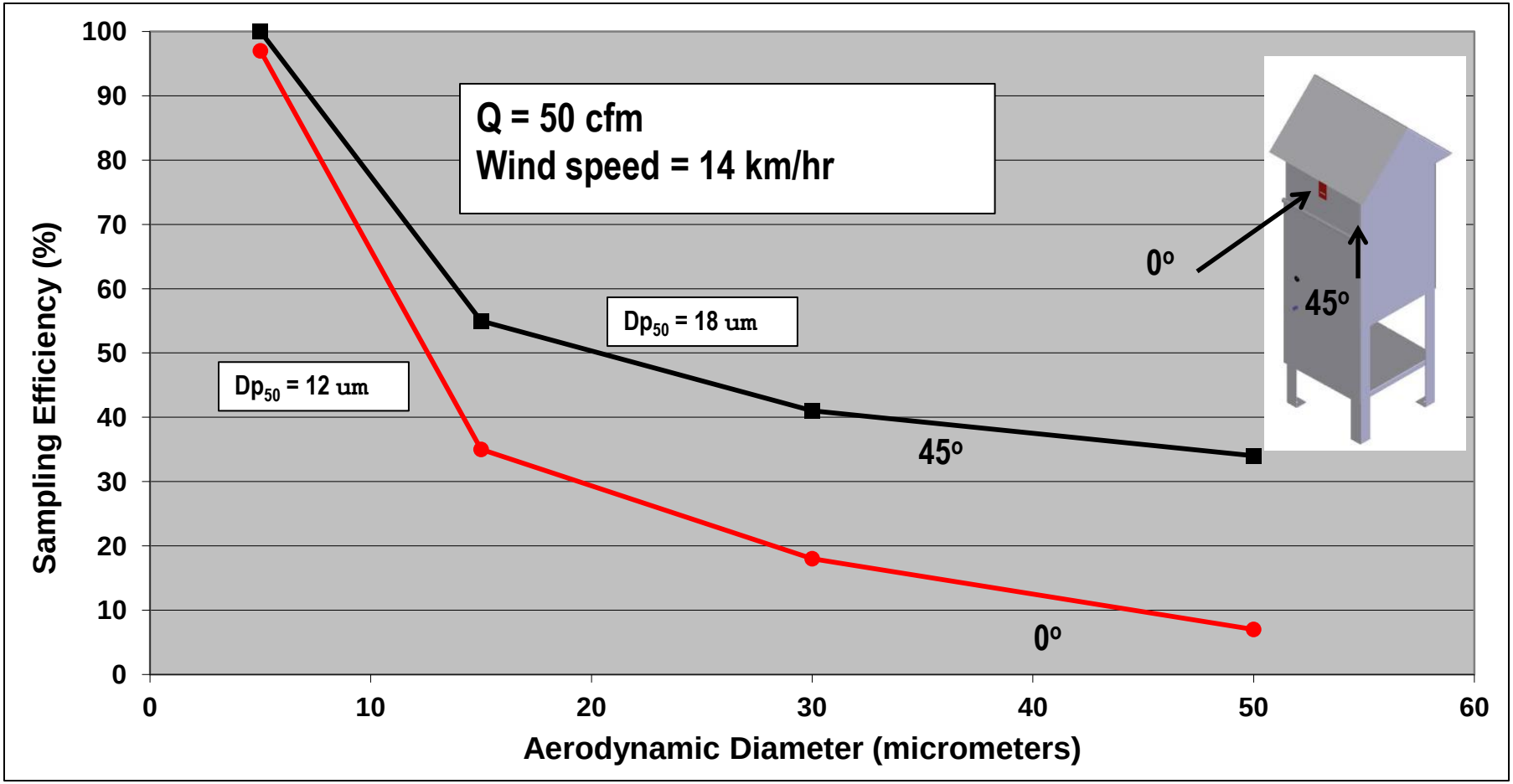
Design Specifications of the Hi-Vol TSP Sampler



- Roof shape: gabled, rectangular
- Sampling flow rate: 39 to 60 cfm
- Inlet velocity (V_i): 20 to 35 cm/sec
  (25 cm/sec recommended but not required)
- No inlet dimensions specified
- Filter: glass fiber, 8” x 10”
- Timer accuracy: ± 30 min

Issue: The size selective performance (i.e., aspiration efficiency versus aerodynamic particle size) of ambient samplers is a strong function of sampling flow rate and inlet dimensions

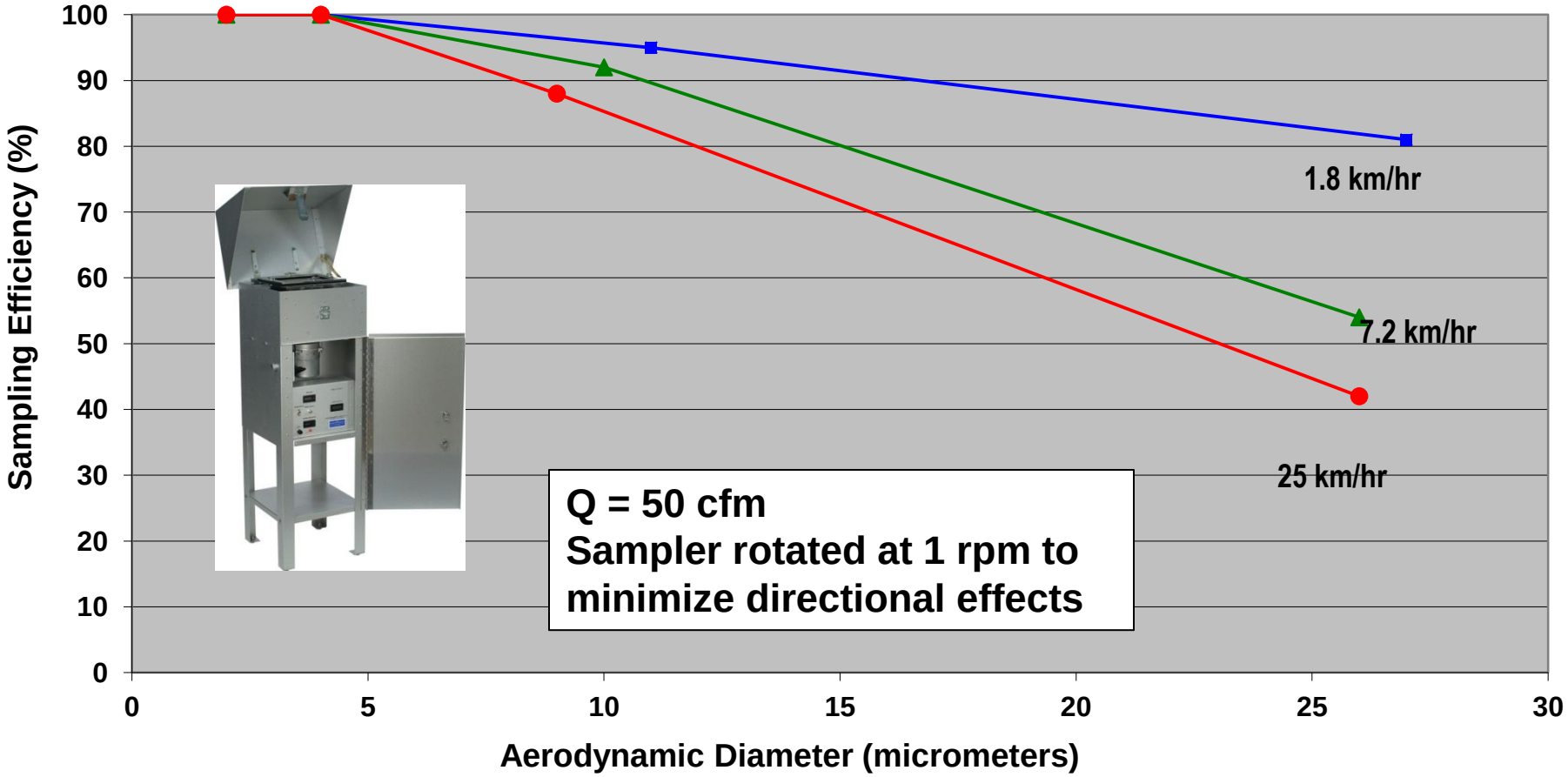
High-Vol TSP Sampling Efficiency vs Wind Direction



The angle at which airborne particles approach the Hi-Vol TSP sampler strongly affects the efficiency with which they are collected.

Source: Wedding et al. (1977)

High-Vol TSP Sampling Efficiency vs Wind Speed



The Hi-Vol TSP sampler displays notable decreases in particle collection efficiency at increasing ambient wind speeds.

Source: McFarland et al. (1979)

Limitations of the High-Vol TSP

- Wide range of allowed flow rates (39 to 60 cfm) – there have been no wind tunnel tests versus flow rate
- Wide range of allowed air inlet velocities (20 to 35 cm/sec) – there have been no wind tunnel tests versus inlet velocity
- No fixed inlet dimensions
- Limited wind tunnel evaluations have demonstrated there's strong dependence of particle collection characteristics versus ambient wind speed and direction
- Evidence of aerosol collection during non-sampling periods
- Design does not enable sequential, multiple-event sampling
- Large filter size is not readily amenable to gravimetric or XRF analysis

Features of the Pb-PM_{10} Sampler

- Inlet specifications (dimensions, tolerances, materials, and finishes) fully specified in *Federal Register* using 17 design drawings
- Sampler operates at a fixed 16.7 aLpm flow rate independent of ambient conditions
- Inlet's omnidirectional design avoids measurement bias due to wind direction
- Method's low flow rate and use of 46.2 mm diameter filters enables adaption to sequential, multi-event design and multiple analytical techniques
- Inlet design minimizes rain and insect intrusion
- Strong interlaboratory test results have been obtained during wind tunnel studies of size-selective performance

Performance of the Low-Vol Pb-PM_{10} Inlet

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

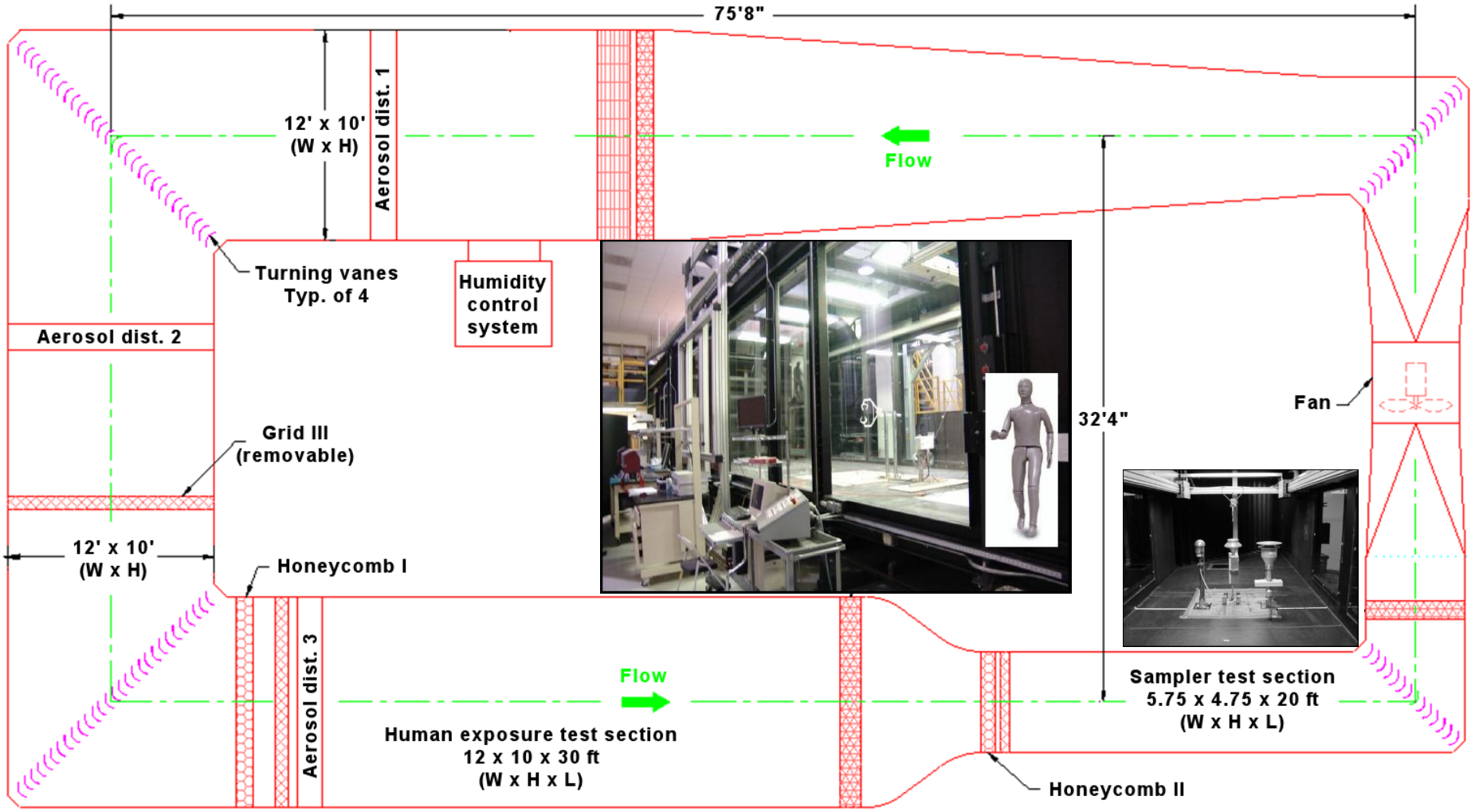
Design Features for a New Pb FRM Sampler

- New FRM designed to replace both the hi-vol and PM10 sampler with a single sampler and a single analytical method
- Fixed inlet dimensions, fixed flow rate, and omnidirectional inlet
- Acceptable variation in size selective performance as a function of ambient wind speeds (2 to 24 km/hr)
- Cutpoint in the 18 to 20 µm size range would quantify all Pb-bearing particles currently measured by the Pb-PM_{10} FRM while accounting for a portion of Pb-bearing particles above 10 µm

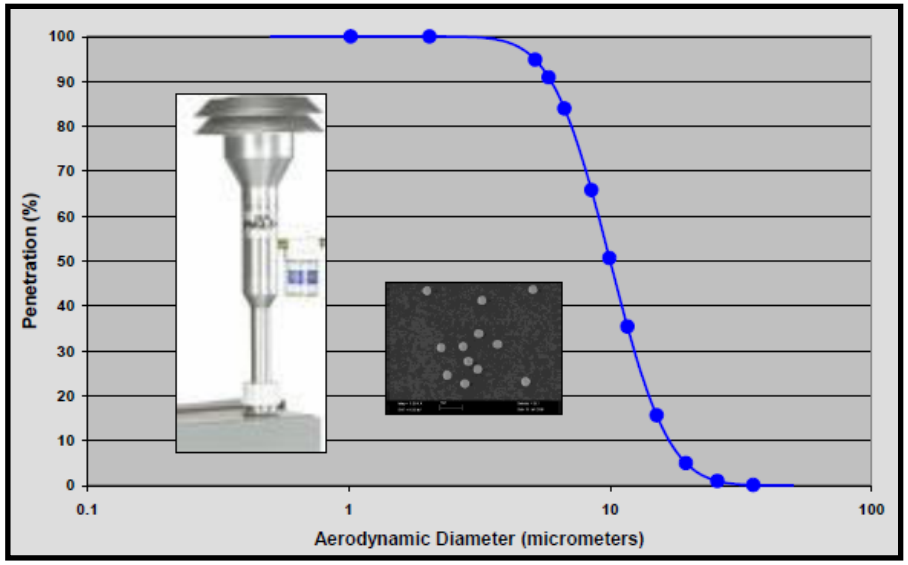
Developmental Approach

- Develop and validate techniques for generation, transport, and measurement of large aerodynamic particles
- Optimize EPA's ATF wind tunnel for conducting size-selective experiments (2, 8, 24 km/hr)
- Conduct size-selective evaluation of EPA's PM_{10} inlet to validate generation and measurement techniques
- Conduct survey of commercially available low-flow rate inlets and test viable candidates
- As needed, design and evaluate new prototype inlets
- Conduct limited field evaluation of final inlet design to determine inherent precision and to compare results with collocated Pb-TSP and Pb-PM_{10} samplers

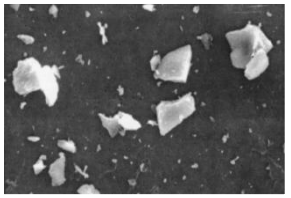
EPA's Aerosol Wind Tunnel

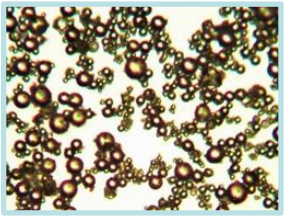


Aerosol Generation Initiatives



Schenck Dust Dispenser





Multisizer IV Coulter Counter

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

Size-selective calibrations using <u>monodisperse</u> aerosols typically provide quality test results but are time-consuming and expensive, especially during inlet development efforts where extensive design modifications and retesting may be required

Use of <u>polydisperse</u> calibration aerosols generated from bulk materials (e.g., Arizona Test Dust, glass beads) potentially enables more rapid determination of inlet size selective performance than can be achieved using monodisperse calibration aerosols

Aerosol Generation Initiatives (cont)

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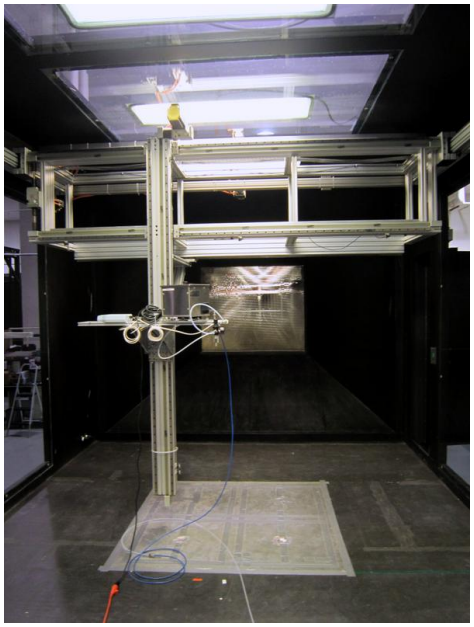
Apparatus used for dispensing, aerosolizing, and charge neutralizing calibration material into the aerosol wind tunnel



Upstream view of aerosol generation equipment mounted on movable traverse

Isokinetic nozzles (114 Lpm, 90 mm filter) designed for determination of reference concentrations

Survey of Low-Volume Inlets

Airmetrics Mini-Vol (original) 5 Lpm

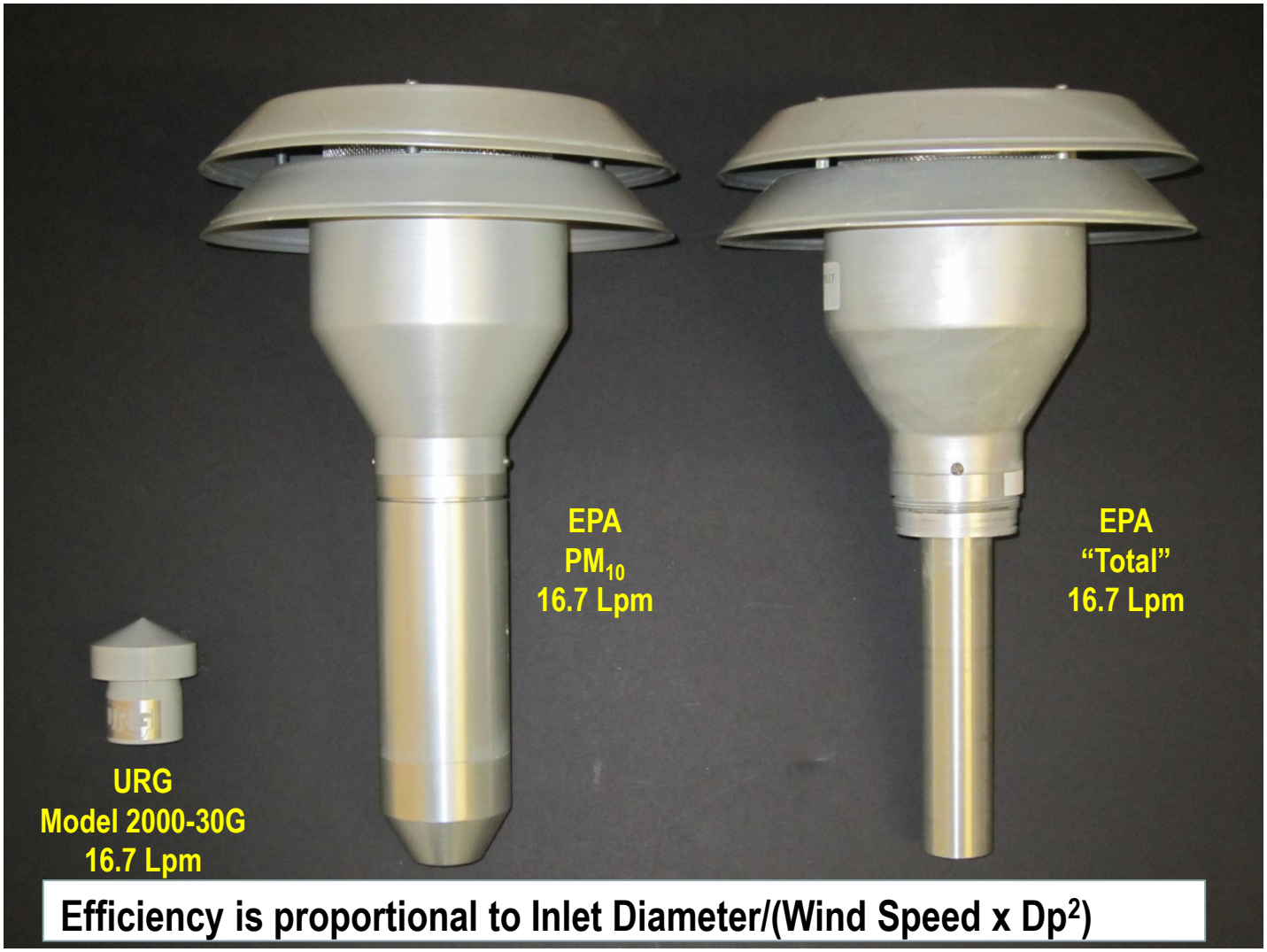
Airmetrics Mini-Vol (louvered) 5 Lpm

BGI Omni 5 Lpm

URG Model 200-30G 16.7 Lpm

Texas A&M LVTSP 16.7 Lpm

Comparative Sizes of 16.7 Lpm Inlets



Proposed New Analytical FRM for Pb in TSP

- Designed to meet lower detection limit requirements of new Pb NAAQS
- Method based on two recently designated FEMs
  - EQL-0510-191
  - EQL-0710-192
- Extraction options: Heated ultrasonic with HCl/HNO_3 or hot block with HNO_3
- Analysis Method: ICP-MS
- Applicable to glass fiber, quartz, and teflon filters
- Interlaboratory results from RTI, ERG, ORIA, and ORD are favorable for precision and comparability

Lead Research Initiatives and Next Steps

- Develop generation and measurement techniques for wind tunnel calibration aerosols (ongoing)
- Optimization of EPA's aerosol wind tunnel for upcoming size selective tests (ongoing)
- Develop, wind tunnel evaluate, and finalize design of a new candidate inlet for the Pb FRM
- Conduct any necessary field evaluation of the proposed Pb FRM

Summary

- **EPA is currently performing research on both sampling and analytical federal reference and equivalent methods for the measurement of lead in ambient air.**
- **Further research is needed both in laboratory (i.e., wind tunnel) and field settings to develop and assess these methods for lead including the identification of potential sampling interferences an/or challenges and to evaluate their use in routine monitoring.**
- **The results of this research may serve an informative role in the NAAQS review process for lead including the sampling and analytical methods used for its regulatory determination.**

Acknowledgments/Disclaimer

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Disclaimer

Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.