Judith Chow, Desert Research Institute

"$PM_{2.5}$ Measurement Methods and Implementation"

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Judith C. Chow
John G. Watson
Desert Research Institute
Reno, NV

$PM_{2.5}$ Sampling and Analysis Workshop
DOE Federal Energy Technology Center
Pittsburgh, PA

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OBJECTIVES

- Review current status of $PM_{2.5}$ measurements.
- Discuss issues in $PM_{2.5}$ monitoring.
- Specify laboratory analysis methods.
- Address aerosol measurement research needs.

NEW PM STANDARDS

Particle Size	Level	Averaging Time	Requirements
$PM_{2.5}$	15 μg/m³	Annual	Arithmetic mean, 3-year averaging, spatial averaging.
$PM_{2.5}$	65 μg/m³	24-hour	98th percentile, 3-year averaging, at each monitor.
PM_{10}	50 μg/m³	Annual	Same as current – no spatial averaging.
PM_{10}	150 μg/m³	24-hour	99th percentile, averaged over 3 years.

PROPOSED $PM_{2.5}$ NETWORKS

- Population-oriented or community-representative (CORE) sites for compliance. (Initially 850 sites nationwide. Total of 1,500 sites phased in over 3 years.)
- Collocation with PAMS sites.
- Special purpose monitoring sites to evaluate source contributions and to evaluate zones of representation for long-term sites.
- Transport and background sites for regional source assessment.

SPATIAL SCALES OF $PM_{2.5}$ MONITORING

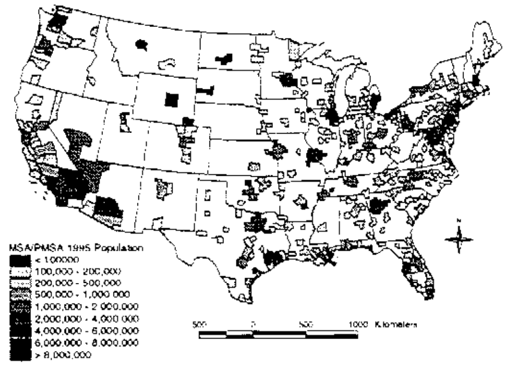
Category	Distance
Collocated Scale	1 – 10 m
Microscale	10 – 100 m
Middle Scale	100 – 1,000 m
Neighborhood Scale	1 – 10 km
Urban Scale	10 – 100 km
Regional Scale (background)	100 – 1,000 km
Continental Scale (background)	1,000 – 10,000 km
Global Scale (background)	> 10,000 km

Required Number of Core SLAMS According to MSA Population

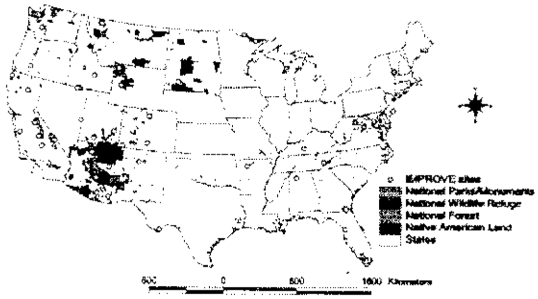
MSA Population	Minimum Required No. of Core Sites[1]
>1 M	3
>2 M	4
>4 M	6
>6 M	8
>8 M	10

[1] Core SLAMS at PAMS are in addition to these numbers.

Metropolitan Statistical Areas



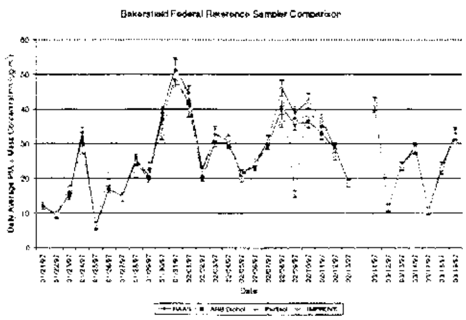
National Parks and Monuments, National Wildlife Refuges, National Forests, Indian Reservations, and IMPROVE Background Monitoring Sites



PROPOSED $PM_{2.5}$ MEASUREMENTS

- Federal Reference Method (FRM) has well-defined $PM_{2.5}$ size fraction for core site monitoring.
  - Inlets, transfer tubes, filter media, and filter holders specified by design standards. Flow and temperature controls specified by performance standards.
- Continuous instruments as Class III federal equivalent method (FEM) for non-core-site monitoring.
- IMPROVE samplers for transport and background monitoring.

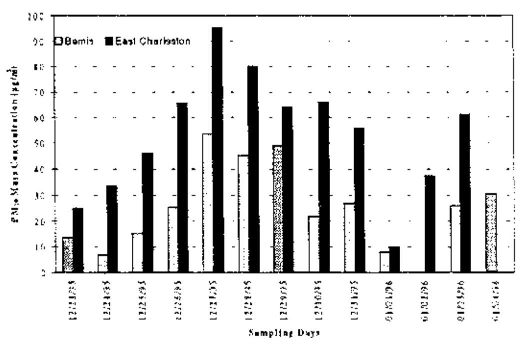
Temporal Variations of $PM_{2.5}$ Concentrations at the Bakersfield, CA, FRM site between 01/21/97 and 03/19/97



TEST SPECIFICATIONS FOR $PM_{2.5}$ EQUIVALENCE TO FRM

Concentration Range:	10 to 200 $\mu g/m^3$
No. of Test Sites:	One for "Class I" monitors, two for "Class II" monitors
No. of Samplers:	Three FRMs, three candidates
No. of Samples:	Ten 24-hour (3 > 40 $\mu g/m^3$, 3 < 40 $\mu g/m^3$)
Collocated Precision:	2 $\mu g/m^3$ or 5% (largest)
Regression Slope:	1 ± 0.05
Intercept:	0 ± 1 $\mu g/m^3$
Correlation:	≥ 0.97

SIXTH-DAY vs. DAILY



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NON-FRM FILTER-BASED ALTERNATIVES

- **Sequential Samplers**
  - Can take several filter measurements in a row without an operator.
- **Multi-Filter Samplers**
  - Can acquire samples on different filters for different analyses.
- **Denuder Samplers**
  - Measure precursor gases and particles.
- **Battery-Powered Samplers**
  - Can operate in many different locations without power or security.

AVAILABLE CONTINUOUS MONITORS

- **AISI Paper Tape Sampler (COH)**
  - Measures light absorption.
- **Aethalometer Continuous Filter Sampler**
  - Measures light absorption.
- **Nephelometer**
  - Measures light scattering.
- **Beta Attenuation**
  - Measures attenuation of beta particles (mass).
- **Tapered Element Oscillating Microbalance (TEOM)**
  - Measures mass.

RESEARCH CONTINUOUS PARTICLE MONITORS

- **Optical Particle Counter**
  - Measures size by light scattering.
- **Differential Mobility Analyzer**
  - Measures size by electrical mobility.
- **Piezoelectric Mass Monitor**
  - Measures mass by oscillating crystal.
- **Diffusion Battery / CCN Counter**
  - Measures condensation nuclei in different size ranges.
- **Time of Flight Mass Spectrometry**
  - Measures size and composition of individual particles.

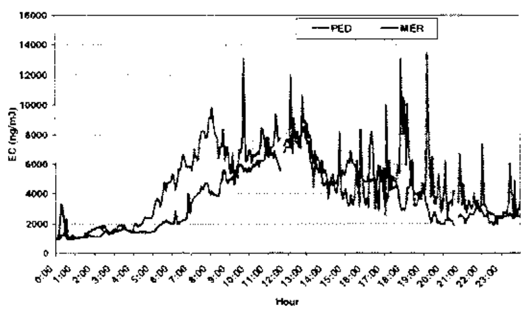
RESEARCH CONTINUOUS PARTICLE MONITORS (continued)

- **Nuclepore Filter Pressure Differential**
  - Infers mass increments from increases in pressure drop as intercepted particles reduce pore size.
- **Carbon by Combustion**
  - Particles on filter are heated and detected with a CO_2 monitor or FID.
- **Ammonium Sulfate Decomposition by Continuous Heating**
  - SO_2 denuded particle stream passes through heaters at different temperatures that decompose ammonium sulfate and sulfuric acid for detection by a high sensitivity sulfur monitor.

RESEARCH CONTINUOUS PARTICLE MONITORS (continued)

- **Flash Volatilization of Sulfate and Nitrate**
  - Detection by High Sensitivity Sulfur and NO_x Monitors.
- **Ammonia Oxidation**
  - Detection by High Sensitivity NO_x Monitors.
- **Photoacoustic Absorption**
  - Change in speed of sound as surrounding air is heated by light-absorbing carbon.
- **Streaker / DRUM / SMART**
  - Expose 1-hour segments of Nuclepore or Mylar filter strip with elemental analysis by PIXE. (Sulfur is the most useful element.)

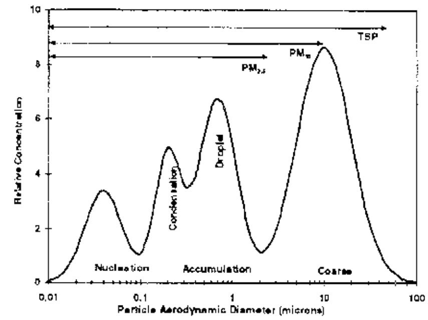
3/10/97 Aethalometer, Pedregal and Merced



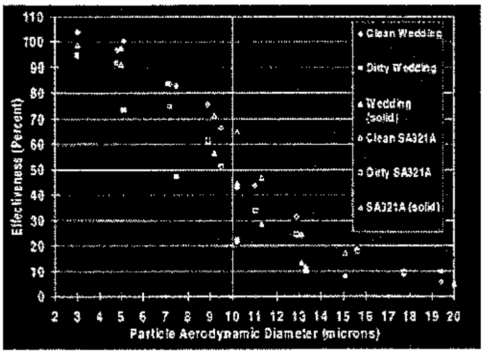
CONCERNS IN PARTICLE SAMPLING

- Changes in inlet cut-points.
- Evaporation of volatile species
- Vapor adsorption on filters.
- Liquid water content.
- Passive deposition during idle periods
- Contamination during filter handling.
- Changes in flow rate and filter load.

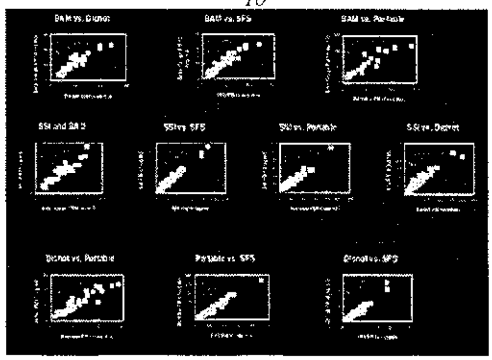
Idealized Size Distribution of Particles in Ambient Air



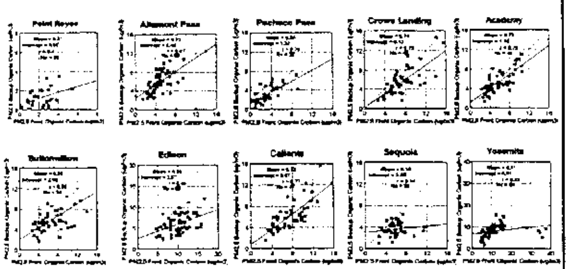
Inlet Wind Tunnel Test Results



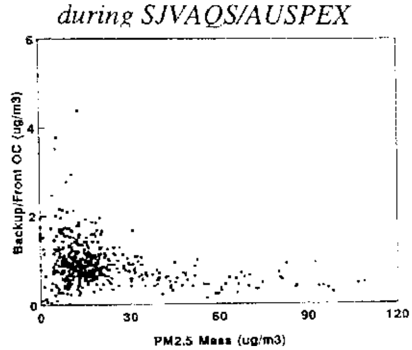
Collocated PM_{10} Measurements



Comparison between $PM_{2.5}$ Particulate Organic Carbon and Gaseous Organic Carbon at the Ten SJVAQS/AUSPEX Sites



Relationship between the Ratio of Backup to Front Filter Organic Carbon and $PM_{2.5}$ Mass during SJVAQS/AUSPEX



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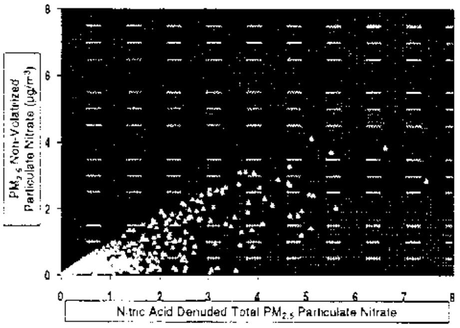
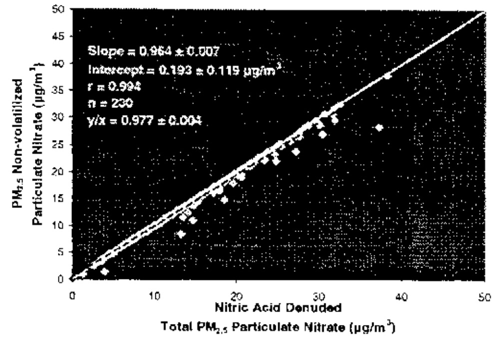
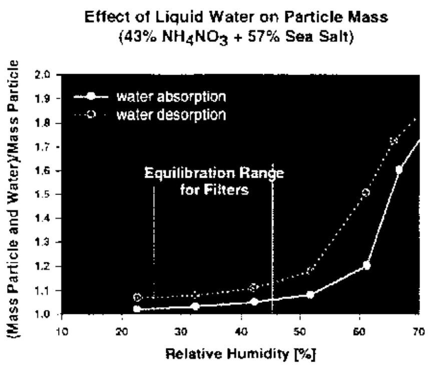
SUMMER $PM_{2.5}$ NITRATE VOLATILIZATION
(San Joaquin Valley, AUSPEX, 1990)



WINTER $PM_{2.5}$ NITRATE VOLATILIZATION
(San Joaquin Valley, IMS95, 1995)





Criteria for Selecting Filter Substrate

- Mechanical Stability
- Temperature Stability
- Particle Sampling Efficiency
- Flow Resistance and Loading Capacity
- Blank Concentrations
- Cost and Availability

Filter Interferences

- Artifact Formation
- Losses of Volatile Species
- Filter Integrity
- Particle Loss in Transport
- Relative Humidity

Commonly Used Sampling Substrates

- Membrane-Type Filters
  - Gelman Ringed Teflon-Membrane Filters
  - Gelman Backed Teflon-Membrane (Zefluor) Filters
  - Gelman Nylon-Membrane Filters
  - Millipore Silver-Membrane Filters
  - Millipore Cellulose Esters-Membrane Filters
  - Polyvinyl Chloride-Membrane Filters
  - Nuclepore Polycarbonate-Membrane Filters

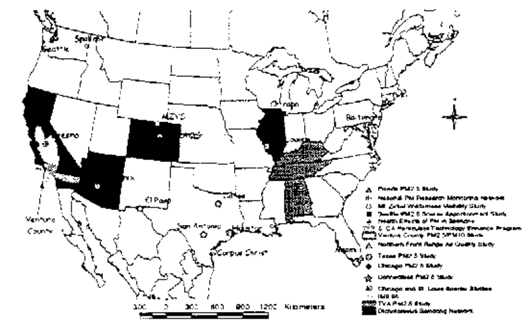
Commonly Used Sampling Substrates (cont.)

- Fiber-Type Filters
  - Pallflex Quartz-Fiber (QAT-UP) Filters
  - Whatman Mixed Quartz-Fiber Filters
  - Whatman 41 Cellulose-Fiber Filters
  - Whatman 31 ET Chromatography Paper
  - Pallflex Teflon-Coated Glass-Fiber Filters

CHEMICAL SPECIATION

- 50 $PM_{2.5}$ sites subject to chemical characterization of major components:
  - Elements (Na to U)
  - Ions ($SO_4^=$, NO_3^-, Cl^-, NH_4^+, Na^+, K^+)
  - Carbon (OC, EC).
- A subset of samples may be analyzed for:
  - Organic compounds
  - Single particle characterization
  - Air toxic species [e.g., Fe(II), Fe(III), Cr(III), Cr(VI), As(III), As(V)]

RECENT AND CURRENT $PM_{2.5}$ STUDIES



RECENT AND CURRENT $PM_{2.5}$ STUDIES

- Seattle, WA, $PM_{2.5}$ Source Apportionment Study (1996-97)
  - $PM_{2.5}$
- Health Effects of PM in Spokane, WA (1995-97)
  - $PM_{2.5}$ and health data
- SJVAQS/AUSPEX (1990)
  - $PM_{2.5}$, PM_{10}, NH_3, HNO_3, SO_2 (5- and 7-hour)
- California's San Joaquin Valley Integrated Monitoring Study (1995)
  - $PM_{2.5}$, PM_{10}, NH_3, HNO_3 (3-hour)
- Ventura County, CA, $PM_{2.5}/PM_{10}$ Study (1996-97)
  - $PM_{2.5}$, PM_{10} (ions only)

RECENT AND CURRENT $PM_{2.5}$ STUDIES (cont.)

- Southern California's Particulate Technology Enhancement Program (1995)
  - $PM_{2.5}$, PM_{10}, NH_3, HNO_3
- Southern California Ozone Study (SCOS) (1997)
  - $PM_{2.5}$, PM_{10}, NH_3, HNO_3, organics (4- to 7-hour)
  - Single particle (hourly)
- Mt. Zirkel Wilderness Area, CO, Visibility Study (1995)
  - $PM_{2.5}$, NH_3, HNO_3, SO_2 (6- and 12-hour)
- Northern Front Range, CO, Air Quality Study (1996-97)
  - $PM_{2.5}$, NH_3, HNO_3, SO_2, organics (6- and 12-hour)

RECENT AND CURRENT $PM_{2.5}$ STUDIES (cont.)

- Texas $PM_{2.5}$ Study (1997-98)
  - Houston, Dallas, San Antonio, Corpus Christi, El Paso
  - $PM_{2.5}$, volatilized NO_3^-
- Chicago, IL, $PM_{2.5}$ Study (1995-2001)
  - $PM_{2.5}$, PM_{10}
- Southeast Aerosol and Visibility Study (1995)
  - Great Smoky Mountains
  - $PM_{2.5}$, NH_3, HNO_3, hygroscopicity, organics (12-hour)
- TVA $PM_{2.5}$ Study (1997-99)
  - Kentucky, Tennessee, Alabama
  - $PM_{2.5}$
- Chicago, IL, and St. Louis, MO, metropolitan area special studies (1987-95)
  - $PM_{2.5}$, PM_{10}

RECENT AND CURRENT $PM_{2.5}$ STUDIES (cont.)

- Connecticut $PM_{2.5}$ Study (1997-98)
  - New Haven, Bridgeport, Westport
  - $PM_{2.5}$
- Florida $PM_{2.5}$ Study (1992. 1998-2001)
  - Miami, Everglades National Park
  - $PM_{2.5}$. Hg
- National PM Research Monitoring Network (1995-99)
  - Baltimore. MD; Phoenix. AZ; Fresno. CA
  - $PM_{2.5}$, PM_{10}, organics
- Urban IMPROVE sites
  - Seattle. WA; South Lake Tahoe, CA; Washington DC

RECENT AND CURRENT $PM_{2.5}$ STUDIES (cont.)

- Dichotomous Sampling Network (since 1990s)
  - California, Colorado, Arizona, Illinois
- Mexico City Aerosol Characterization Study (1997)
  - $PM_{2.5}$. PM_{10}, NH_3. HNO_3, organics

IMPLEMENTATION

- Provide specifications and training to establish regional and local laboratories for filter handling, weighing, and chemical speciation.
- Formulate standard operating procedures as part of EPA QA manual.
- Establish national PM chemical speciation data base.
- Standardize analysis methods for health-related chemical components.

PM RESEARCH NEEDS

- **Ambient Measurements**
  - Simultaneously monitor precursor gases, meteorology (e.g., RH, temperature, wind fields), and $PM_{2.5}$.
  - Resolve organic carbon sampling/analysis artifacts in different environments.
  - Determine important organic particle and precursor compounds.
  - Ascertain magnitude of nitrate volatilization.
  - Establish hydrogen ion sampling/analysis methods.
  - Encourage short sampling intervals (e.g., 3-hour) to address diurnal variations and modeling requirements.
  - Perform saturation monitoring to assess zone of representation, source zones of influence, and spatial variations.

PM RESEARCH NEEDS (cont.)

- **Source Measurements**
  - Improve NH_3 and VOC emissions estimation methods.
  - Measure, document, and consolidate inorganic, organic, and single-particle source profiles.
- **Meteorology**
  - Characterize transport and mixing aloft (radar profilers) in long-term network.
  - Determine dispersion under low wind speeds.

PM RESEARCH NEEDS (cont.)

- **Data Analysis/Modeling**
  - Define procedures for data validation/descriptive data analysis prior to air quality modeling.
  - Establish linkage between measurement and modeling to formulate integrated PM and O_3 control strategies.

PM RESEARCH NEEDS (cont.)

- **Control Method Effectiveness**
  - Evaluate I&M program alternatives, including remote sensing.
  - Perfect and evaluate I&M testing for primary particles.
  - Develop performance specifications for dust suppressants and sweepers.
  - Determine optimal agricultural and forest management practices for dust, burning, and ammonia emissions.