Seminar: Sampling, Real-time Monitoring and Conditioning of Air Samples for Determination of Particle Mass

R&P Technology Roadmap
PM Measurement Issues
FDMS® System

2 April 2004
Copenhagen, Denmark

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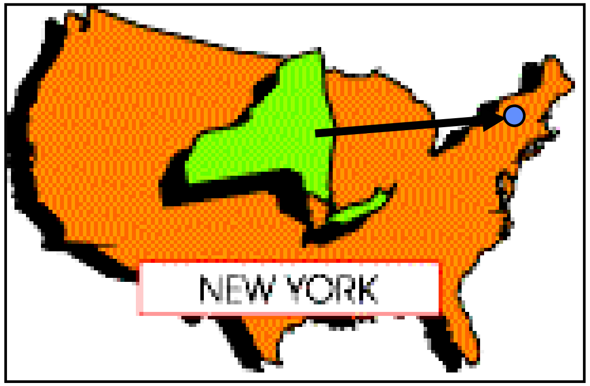
New Facility

Just East of Albany, New York (East Greenbush)



Moved 15 March 2004

Building designed for our needs brings together three facilities under one roof.

Expansion for present and future growth.
R&P will occupy 50,000 of 75,000 sq ft.

Company Information

- Incorporated in 1981 by Harvey Patashnick and Georg Rupprecht
- Research and manufacturing in East Greenbush, NY
- Approx 50% of products exported
- Approx 100 employees:
  - research scientists
  - mechanical and electrical engineers
  - designers and software programmers
  - assembly and quality assurance

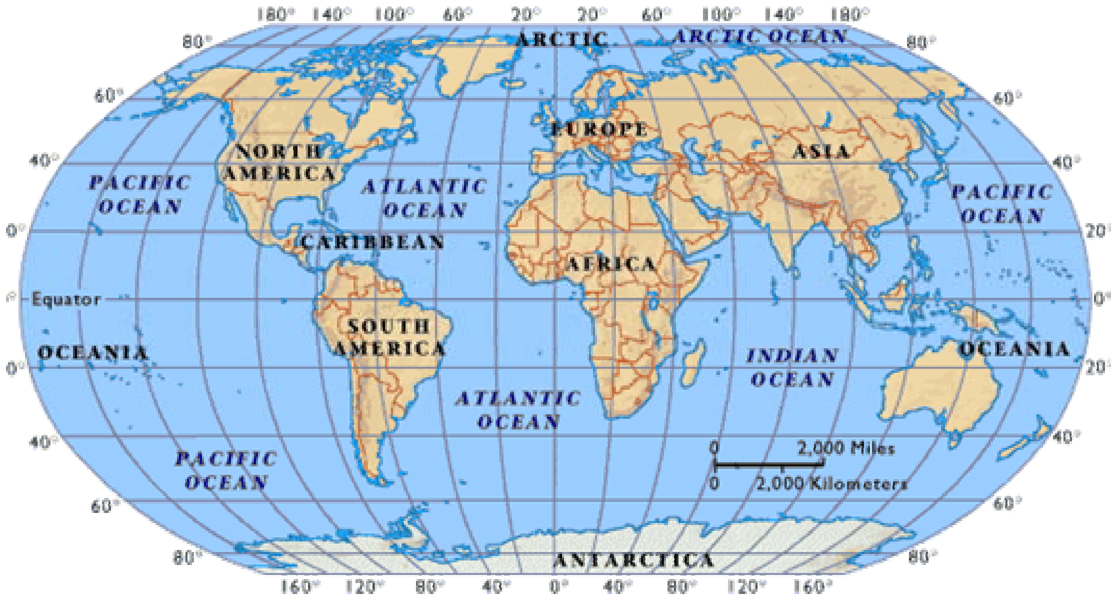
Company Information

- Strong research & development capabilities
- Worldwide marketing and distribution of PM samplers and monitors conforming to USEPA and International standards
- Latest ISO 9001:2000 certification level
- New applications in Homeland Security (Airborne Sample Analysis Platform – ASAP) and coal dust monitoring (Personal Dust Monitor – PDM)




Company Information

"Rupprecht & Patashnick is an international company located in the United States."



Company Milestones

- Contract with NASA for development of space-based mass measurement system
- Introduction of TEOM monitor for ambient air quality measurements in late 1980’s
- Partisol manual samplers used in USEPA national sampling network for PM-2.5
- Introduction of advanced PM speciation sampling and monitoring systems

Product Overview–Markets

Ambient air monitoring and sampling products

Mobile source particulate measurement for cleaner engines

Reaction kinetics research tool

Stationary source monitoring for process and emissions results

Ambient Air Monitoring Products

Stationary (Stack) and Mobile (Diesel) Source PM Monitoring Products

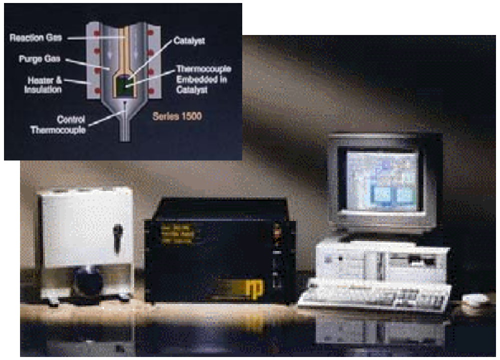
R&P Commercial Products Using The TEOM Mass Sensor

TEOM® Series 1400a
Ambient PM Monitor

TEOM® Series 1105
Diesel Particulate Monitor

TEOM® Series 4200
Combustion Efficiency Monitor

TEOM® Series 7000
Source PM Monitor



TEOM® Series 1500
Reaction Kinetics Analyzer

More to come…

Particulate Matter Measurement Issues

Filter Dynamics Measurement System (Series 8500 FDMS System)

PM Regulatory Standards Are Driven By Human Health Effects

Particulate Air Pollution as a Predictor of Mortality in a Prospective Study of U.S. Adults

C. ARDEN POPE, III, MICHAEL J. THUN, MOHAN M. NAMBOODIRI, DOUGLAS W. DOCKERY, JOHN S. EVANS, FRANK E. SPEIZER, and CLARK W. HEATH, JR.

Environmental Epidemiology Program and Interdisciplinary Program in Health, Department of Environmental Health, Harvard School of Public Health, Boston, Massachusetts; Department of Epidemiology and Statistics, American Cancer Society, Atlanta, Georgia, and The Channing Laboratory, Brigham and Women's Hospital, Harvard Medical School, Boston, Massachusetts

Time-series, cross-sectional, and prospective cohort studies have observed associations between mortal-
ity and particulate air pollution but have been limited by ecologic design or small number of subjects or
study areas. The present study evaluates effects of particulate air pollution on mortality using data from
a large cohort drawn from many study areas. We linked ambient air pollution data from 151 U.S. metropoli-
tan areas in 1980 with individual risk factor on 552,138 adults who resided in these areas when enrolled
in a prospective study in 1982. Deaths were ascertained through December, 1989. Exposure to sulfate and
fine particulate air pollution, which is primarily from fossil fuel combustion, was estimated from national
data bases. The relationships of air pollution to all-cause, lung cancer, and cardio-
examined using multivariate analysis which controlled for smoki...
though small compared with cigarette smoking...
tion was observed. Adjusted...
the ...

Death rates rise with air pollution

By Anita Manning
USA TODAY

More people die on bad air days, say toxicologists meeting this week in Baltimore.

Researchers who looked at the daily death rate in cities compared with the daily level of particles in the air from soot, road dust, industrial exhaust and other causes found "a consistent relationship between particles in the air and death," says Joseph L. Mauderly, director of the Inhalation Toxicology Research Institute in Albuquerque. He leads a symposium on the topic at the Society of Toxicology mee...

The findings are consis... he says, "in cities in the ... and foreign countries, ... though they're in differen... mates and have different ... of particles" in the air.

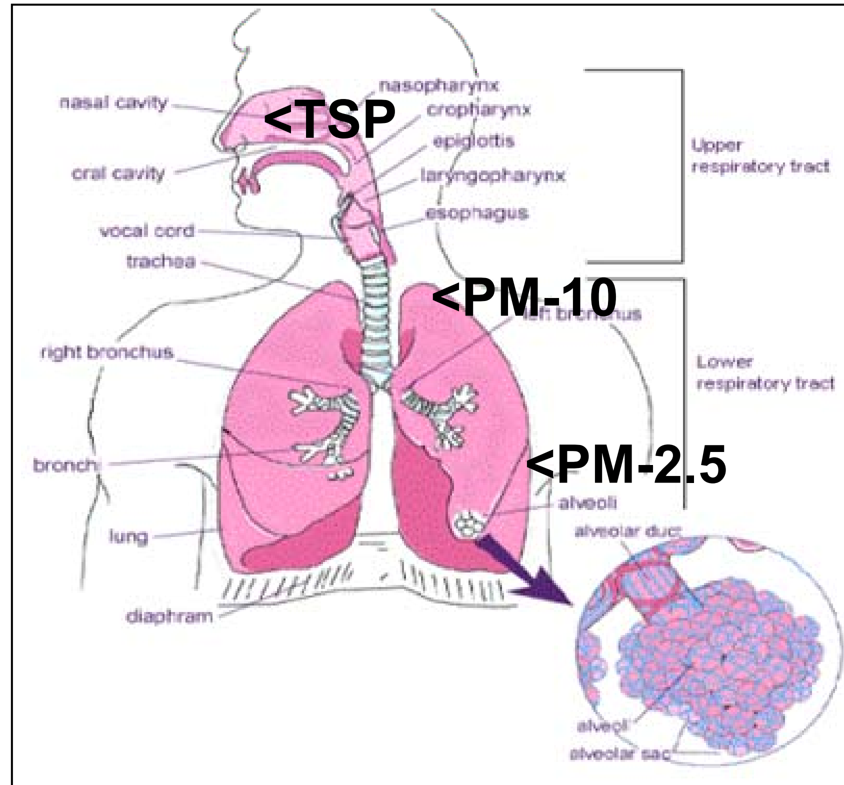
What's baffling, Maud... says, is that "particles ... known to cause death in ... mals or people but only at horrendous levels. No one should see mortality at the reasonably low levels you see in U.S. cities."

The relationship, "is more likely one of hastening the death of people who are somehow primed by disease to die," Mauderly says. "No one is suggesting it is causing healthy people to die." He adds that the findings are "statistically significant, but not huge."

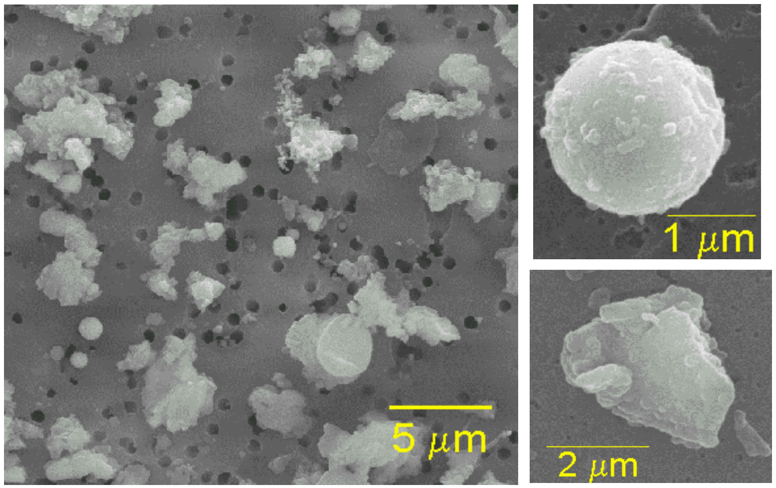
The data suggest mortality increases even when air pollution rates are within permitted standards, he says. Air pollution rates in cities have been

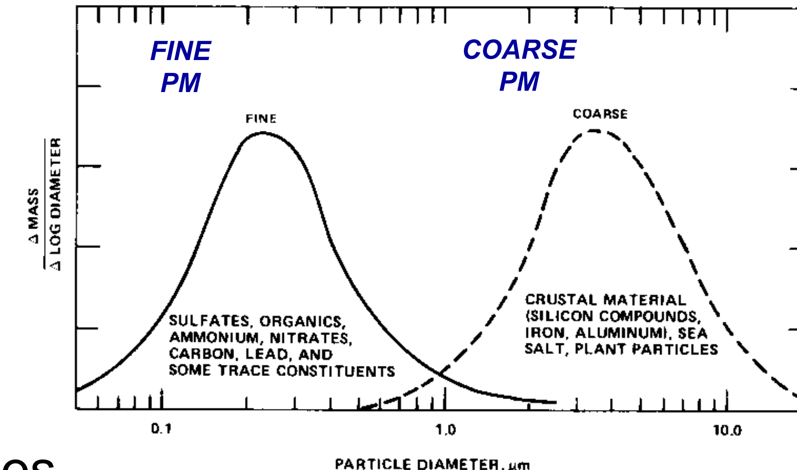
Particulates set to displace NO_2 as major air pollution hazard

Government policies on air pollution are likely to change following the conclusions of recent reports that NO_2 could be less damaging to health than is currently believed, but that particulate matter under 10µm (PM_{10}) is more damaging.



Particulate Matter (PM) - Composition and Size





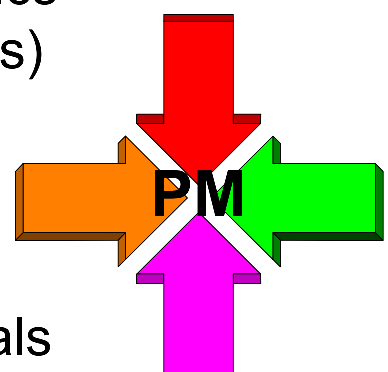
Nitrates

Organics (PAH's)

Smoke

Dirt

Salts (Na, Cl)



Soot

Soil

Sulfates

Heavy Metals (Fe, Pb, Cd)

Dust

Aerosols

Carbon (C)

Particulate Matter (PM)
Mass Concentration

The weighed stuff

$$PM_x = \frac{M}{V}$$

Where:

PM = Particulate Matter mass concentration [μg/m³] of particles less than ***x*** microns in diameter

M = ***Mass*** of sampled particles

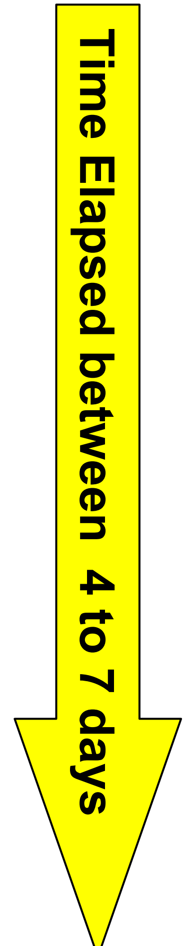
V = Volume of air sampled

Europe

Gravimetric PM Samplers

Sampling and Measurement Scheme

1. Condition (at least 24 hours)
2. Weigh
3. Transport
4. Wait (up to ? days)
5. Sample (usually 24 hours)
6. Wait (up to 7 days)
7. Transport
8. Condition (at least 24 hours)
9. Weigh



Sampling Semivolatile Species

(USEPA Statement)

"Several atmospheric species, such as ammonium nitrate and certain organic compounds, are semivolatile and are found in both gas and particle phases. The gas-particle distribution of semivolatile compounds depends on compound vapor pressure, total particle surface area, particle composition, and atmospheric temperature."

"The dynamic changes in gas-particle partitioning, caused by changes in temperature or total concentration, both in the atmosphere and after collection, cause sampling problems…"

Europe

Source: USEPA Air Quality Criteria for Particulate Matter, Volume I, Section 3.1.6 (1996)

Sampling Semivolatile Species
(CAFE – Clean Air for Europe)

"Measurement of PM mass concentrations brings along considerable uncertainties mainly because of the risk of alterations of the sample during sampling itself, the handling of samples and during the measurement process. This highly depends on the environmental conditions and composition of the particles. Loss of semi-volatile particles is one of the major problems."

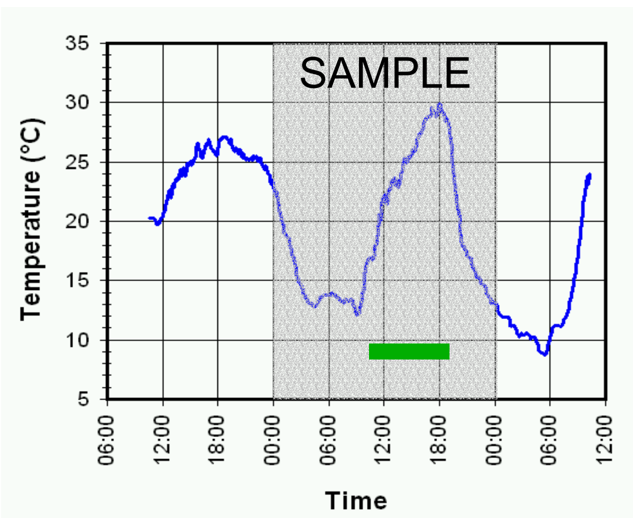
Source: Second Position Paper on Particulate Matter, 20 August 2003

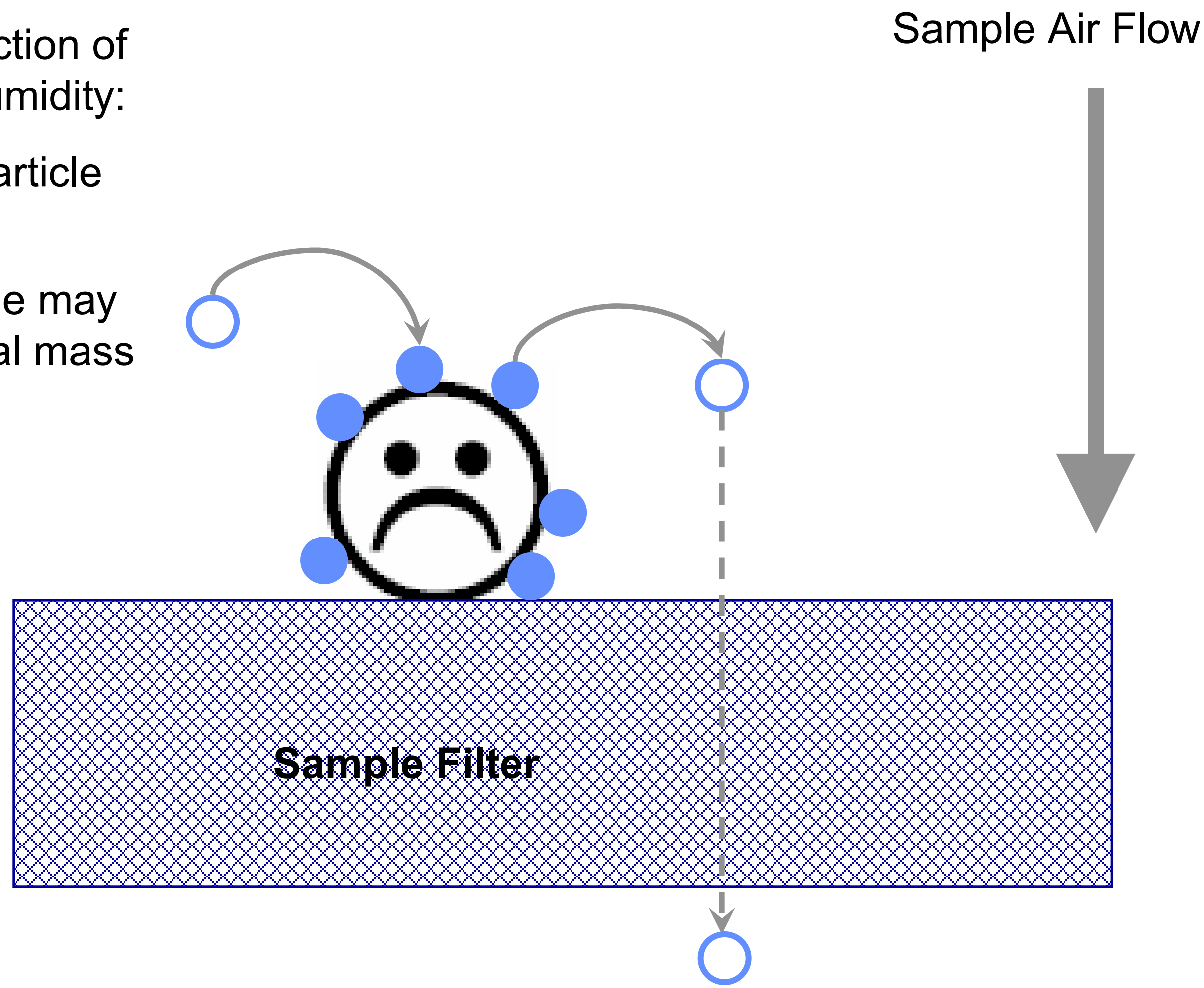
Sampling Artifacts

Gas-particle equilibrium is a function of temperature, vapor pressure, humidity:

- relative humidity increase → particle may take on water mass

- temperature increase → particle may lose semivolatile organic material mass





= particle phase molecule (e.g., H_2O, SVOC, NH_4NO_3)

= gas phase molecule (e.g., H_2O, SVOC, ammonia)

What are the Goals for PM Quantification?

(Continuous PM Monitoring in Air Quality Networks)

- Match the integrated reference (FRM) technique
- Minimize cross-interference by humidity, thermodynamic conditions, gas composition
- Use measurement methods that are traceable to a primary mass standard
- Provide high precision short-term data for public reporting (air quality index, mapping, forecasting), health effects studies, and for control strategy development

Why are these goals difficult to achieve?

- PM is the only criteria air pollutant not defined by its molecular composition
- Particle-bound water can make up a large fraction of PM mass
- Certain PM constituents can volatilize at ambient temperatures
- The time-integrated “reference method” is not a scientific standard – only a method (indicator)

Mass Measurement Approaches

- Indirect (1st generation)
  - Examples: beta attenuation, light scatter
  - Sensor responds to changes of particle properties other than mass
  - Requires empirical transfer function to estimate the PM mass concentration
- Direct (2nd generation)
  - Examples: quartz crystal microbalance, TEOM technology
  - Sensor responds only to changes in the mass of collected particles using the *laws of physics*
  - Similar to laboratory microbalance principle

Elimination of Mass Calibration Uncertainty

In order to measure PM mass directly, particles need to be collected (typically on a filter) and weighed. Elimination of *mass calibration uncertainty* is possible only when using sensors based upon first-principle physical laws (direct mass measurement).

THE REVIEW OF SCIENTIFIC INSTRUMENTS, Vol. 40, No. 8, 1008–1011, August 1969

Oscillating Fiber Microbalance

HARVEY PATASHNICK AND CURTIS L. HEMENWAY
State University of New York at Albany, and Dudley Observatory, Albany, New York 12205

(Received 21 October 1968; and in final form, 17 March 1969)

An instrument is described which enables direct mass determinations in the range 10^{-5}–10^{-11} g and can be modified to provide greater mass sensitivity if desired. The principle involved is that of an electrostatically driven oscillating thin fiber, clamped at one end and free at the other, which changes its resonant frequency when mass is added to the free end. The over-all electromechanical design eliminates many of the disadvantages of more conventional microbalances and surpasses them in sensitivity and accuracy.

THEORY

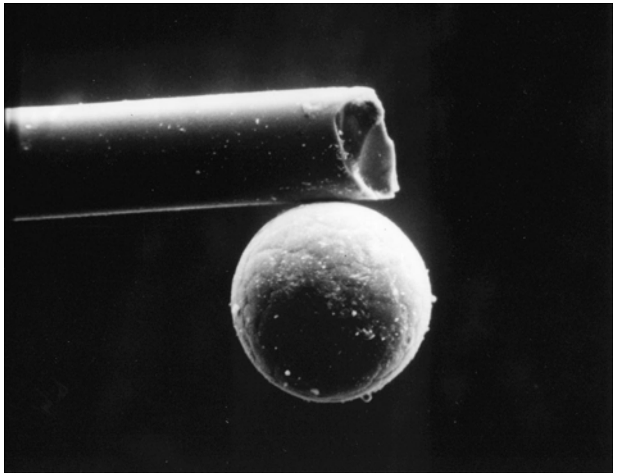
The equation of motion for a thin rod in transverse oscillation may be written (see Prescott[1])

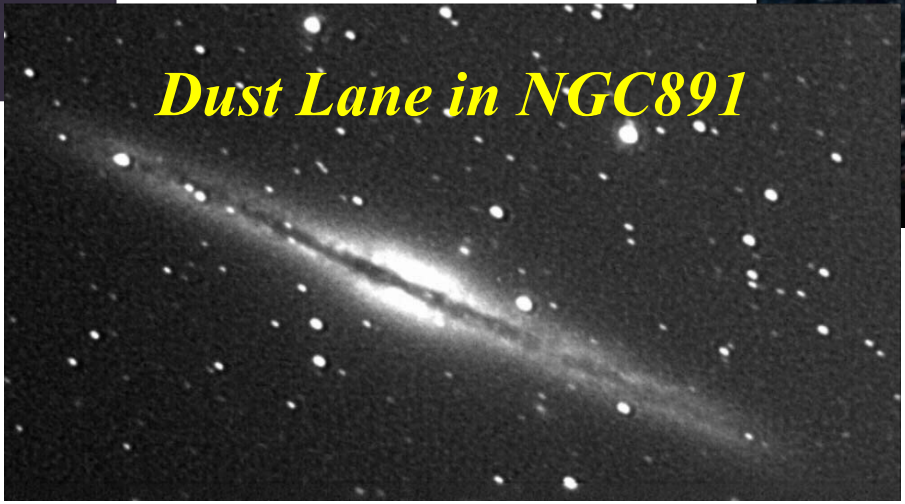
$$Ek^2\frac{\partial^4 y}{\partial x^4}=-\frac{w}{g}\frac{\partial^2 y}{\partial t^2}, \tag{1}$$

where E is Young's modulus, $4k$ the fiber diameter, w the weight per unit volume of the fiber, and g the gravitational constant.

Oscillating Element Microbalance

(Fundamentals and Evolution)





TEOM Mass Transducer

- Tapered element oscillates at its natural frequency (simple harmonic oscillator)
- Particulate matter collects on filter continuously
- Frequency decreases with accumulation of mass
- *Direct* relationship between mass and frequency change:

$$\Delta M(g) = K_o\left(\frac{1}{f_1^2} - \frac{1}{f_o^2}\right)$$

- The approach is similar to that of a laboratory microbalance. The mass detected by the sensor results from the measurement of a fundamental physical parameter (e.g., frequency, strain, displacement).

Tapered Element

TEOM® Series 1400a Continuous Particulate Monitor

- Direct, continuous technique for filter-based *true* mass measurement
- No radioactive components
- Superior time and mass resolution *and* precision (*hourly* precision: ±1.5 μg/m³)
- An accepted standard for particulate monitoring worldwide (regulatory, research, remediation, special studies)
- USEPA Equivalent Method EQPM-1090-079 for PM-10, CAC Monitor for PM-2.5
- Over 5,000 instruments deployed worldwide

Dual Differential TEOM® System

Aerosol Science and Technology 34: 42-45 (2001)

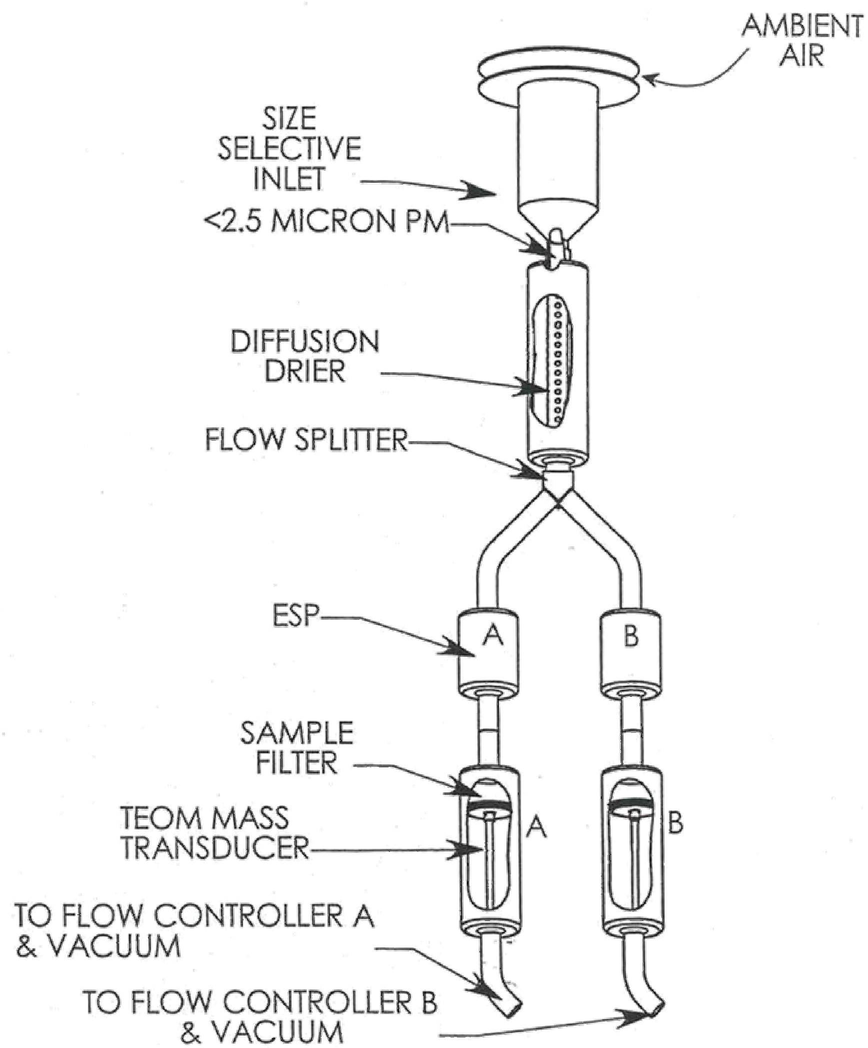
Published by Taylor and Francis
0278-6826/01/$12.00 + .OO

Development of a Reference Standard for Particulate Matter Mass in Ambient Air

Harvey Patashnick, Georg Rupprecht, Jeffrey L. Ambs, and Michael B. Meyer
Rupprecht & Patashnick Co., Inc., Albany, New York

TEOM Mass Sensor Governing Equation:

$$\Delta M = K_o \left(\frac{1}{f_{t1}^2} - \frac{1}{f_{t0}^2} \right)$$



Self-Referencing Differential TEOM Monitor

For time interval $\Delta t_{(n)}$, ESP off,
Particle-laden air stream:

$$M_{Base} = M_{pnv} + M_{pv} - \propto M_{pv} \pm M_{filt\ artifacts} \pm M_{inst\ effects}$$

For time interval $\Delta t_{(n+1)}$, ESP on,
Particle-free air stream:

$$M_{Reference} = - \propto M_{pv} \pm M_{filt\ artifacts} \pm M_{inst\ effects}$$

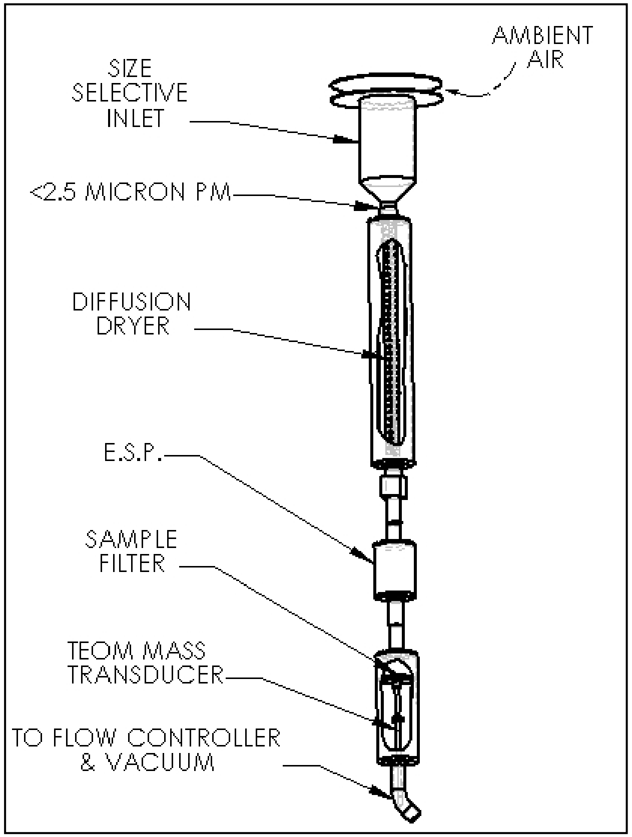
Therefore:

$$M_{Base} - M_{Reference} = M_{pnv} + M_{pv}$$

Ideally, switching time interval $\Delta t \rightarrow 0$

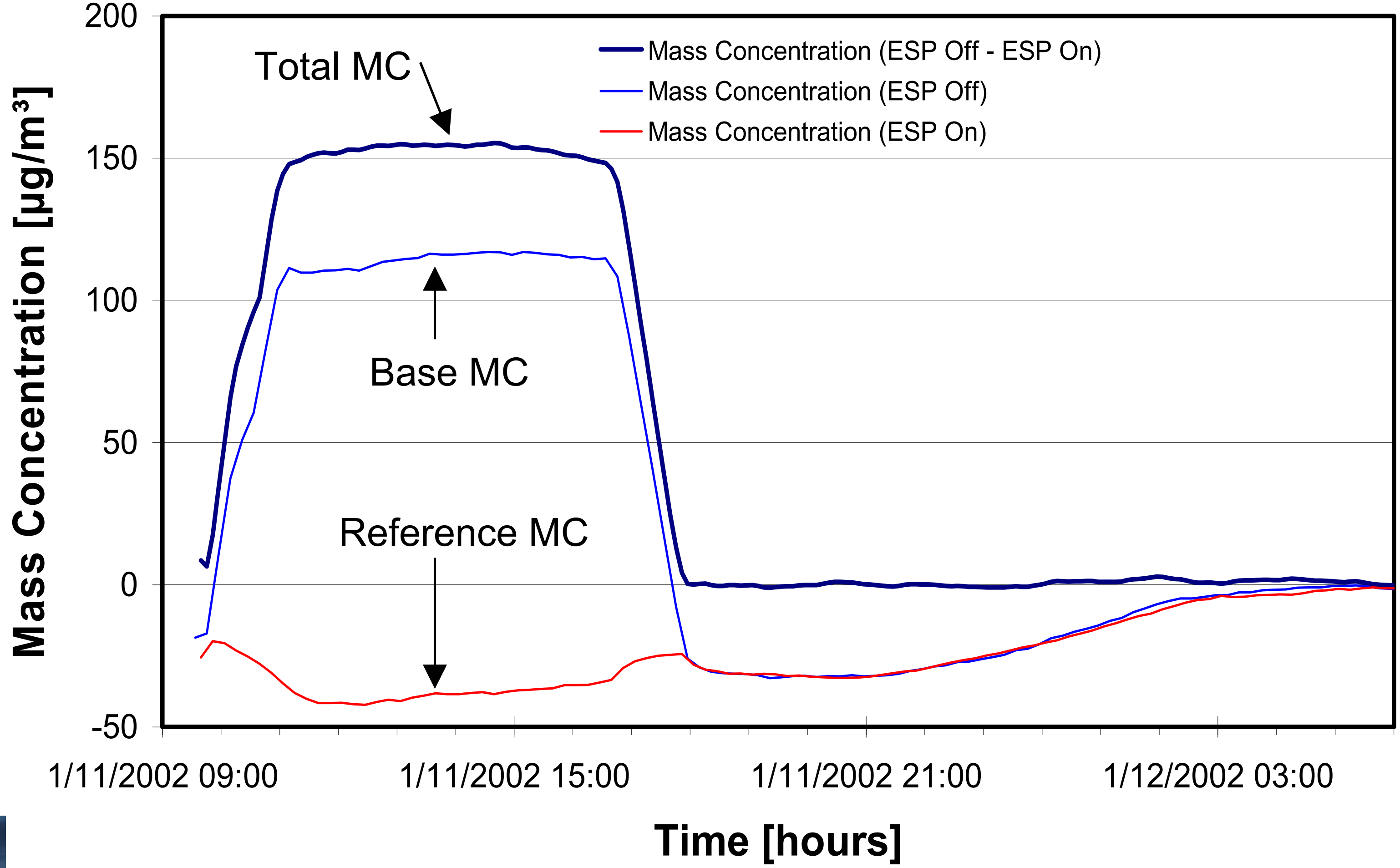
(Practically: faster than physicochemical processes – equilibration time constant for particles/gases)

(ESP and purge filter versions)



Differential TEOM System Response

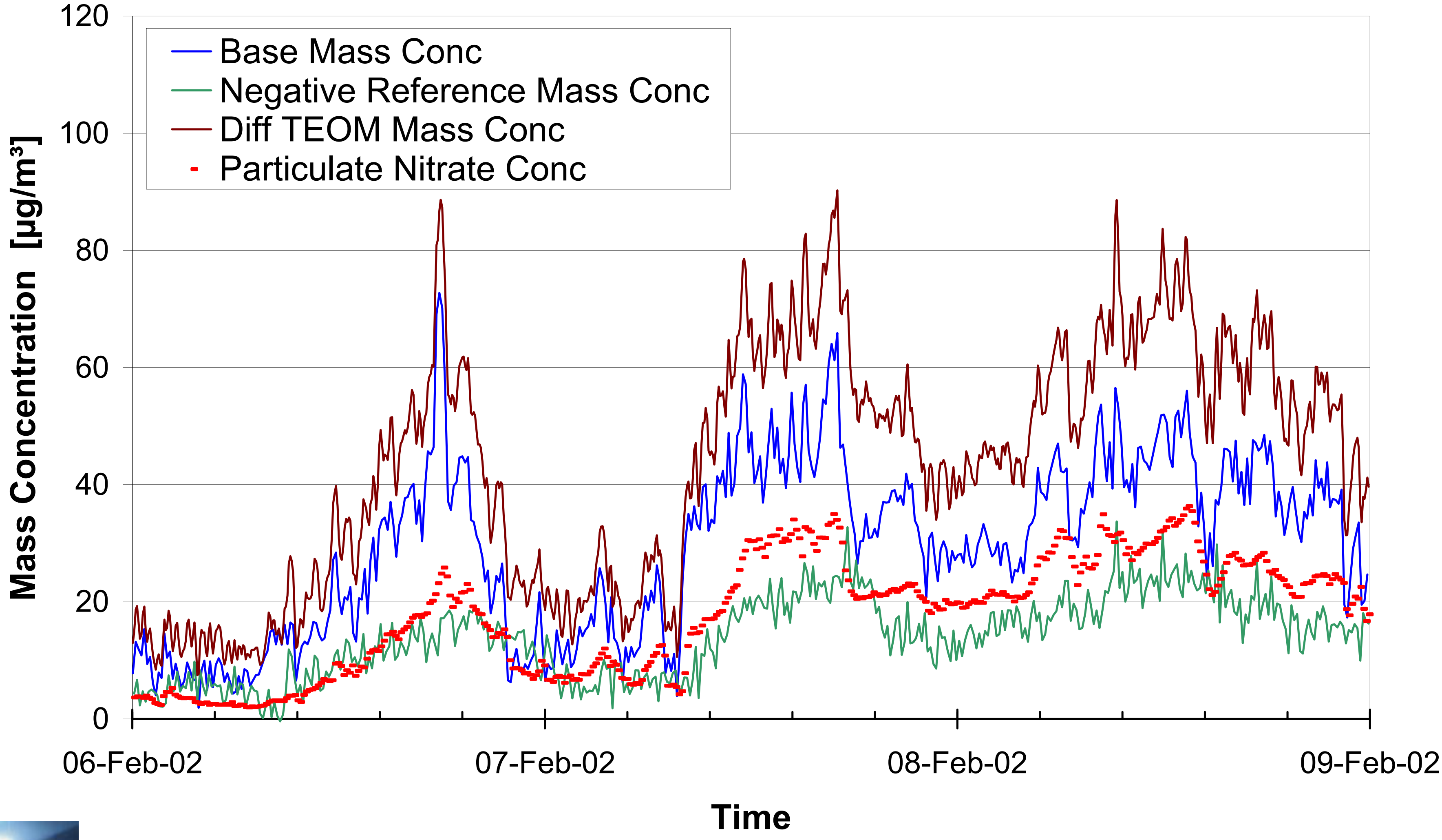
to Ammonium Nitrate Generated In An Aerosol Test Chamber



Source: Atmospheric Sciences Research Center, Albany, NY

Data on Vaporization Dynamics

Claremont, CA, 6-8 Feb 2002



Source: Aerosol Dynamics, Inc.

Filter Dynamics Measurement System

Series 8500 FDMS™ System

(Targeted Configuration of TEOM Series 1400a Monitor)

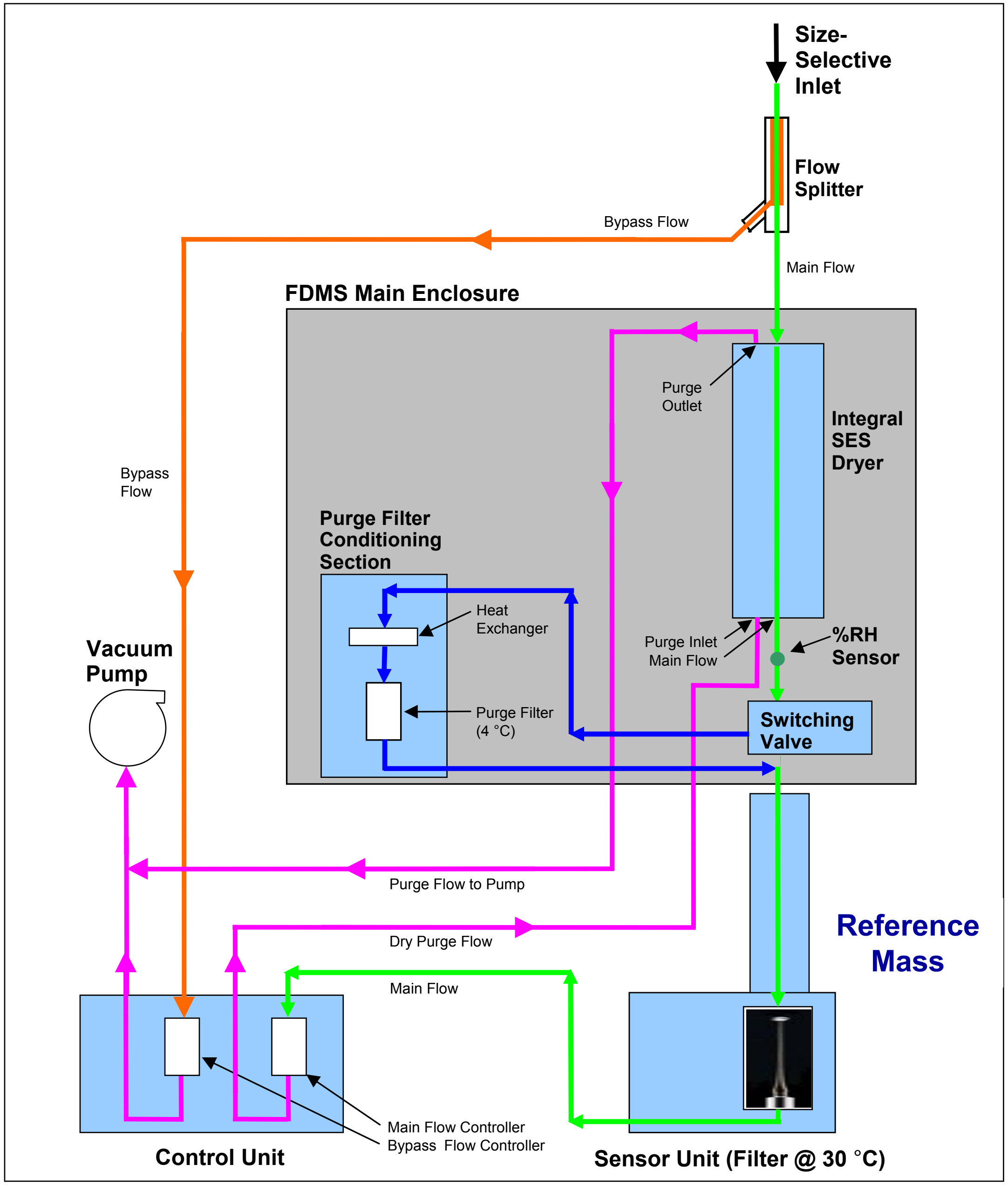
- Derivative of *Differential TEOM Monitor* (USEPA Research Contract)
- Quantifies combined *volatile and nonvolatile* components of PM mass concentration
- Incorporates *TEOM mass sensor technology* and specially-configured Nafion® dryer
- Provides determination of volatile mass using *self-referencing* gas conditioning scheme
- Concept: Total chemical speciation mass concentration monitor

FDMS Schematic

The switching valve alternates the flow through the sensor unit between the sample and purge flows every 6 minutes.

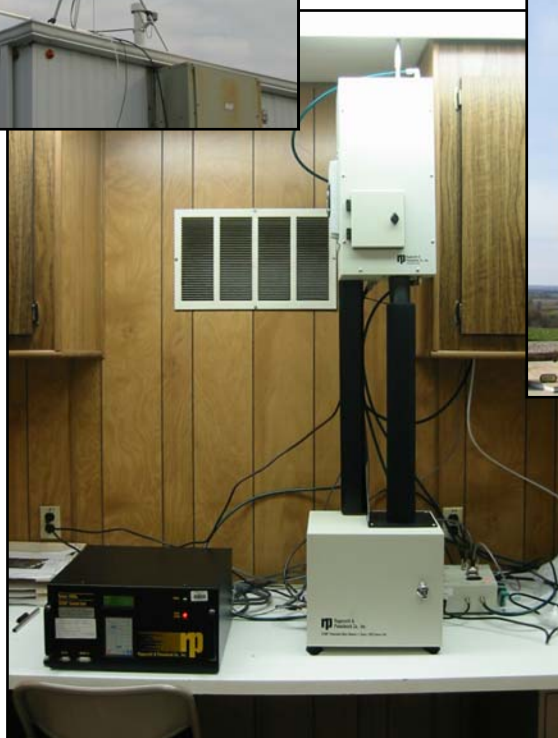
The purge filter is maintained at 4 °C to provide a time-integrated sample that can be used for subsequent laboratory analysis.

The FDMS System can be obtained as a complete system, or as kit used with existing TEOM Series 1400a (Revision B) monitors.



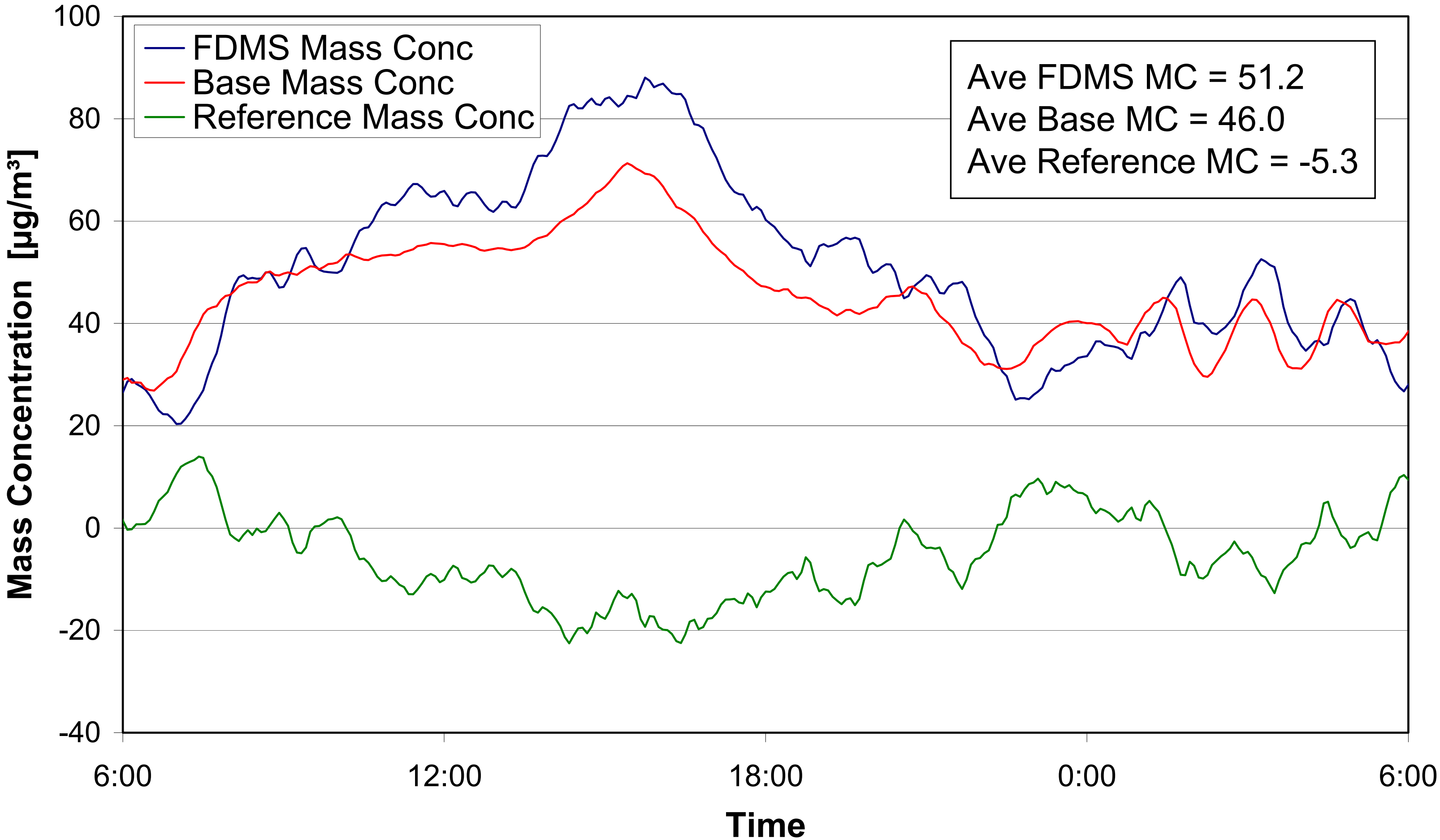
Series 8500 FDMS System

Field Installations



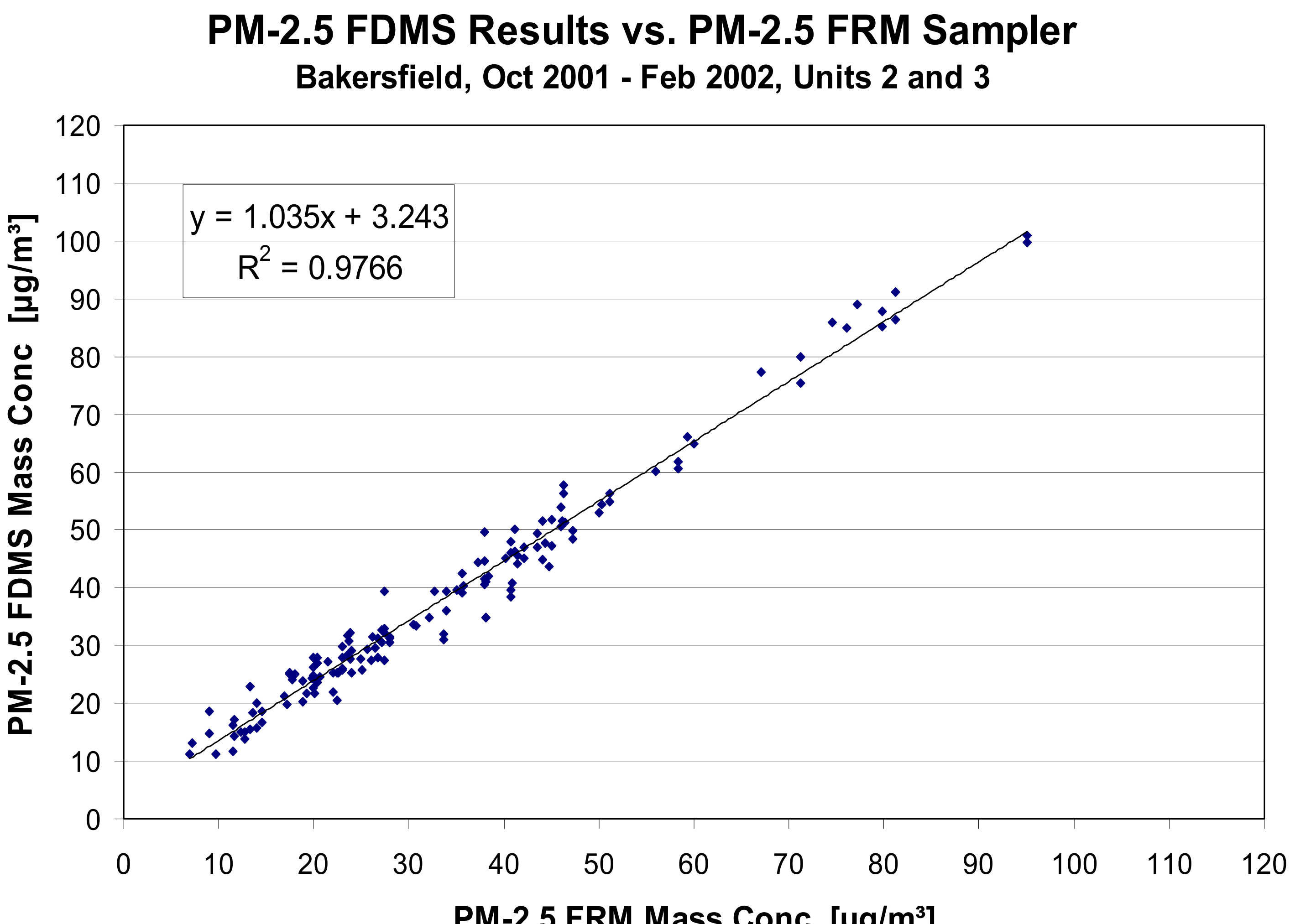
FDMS Field Data

Claremont, CA, Test Site, 2-3 Nov 2001



Source: Los Angeles Supersite and Los Angles USEPA PM Center

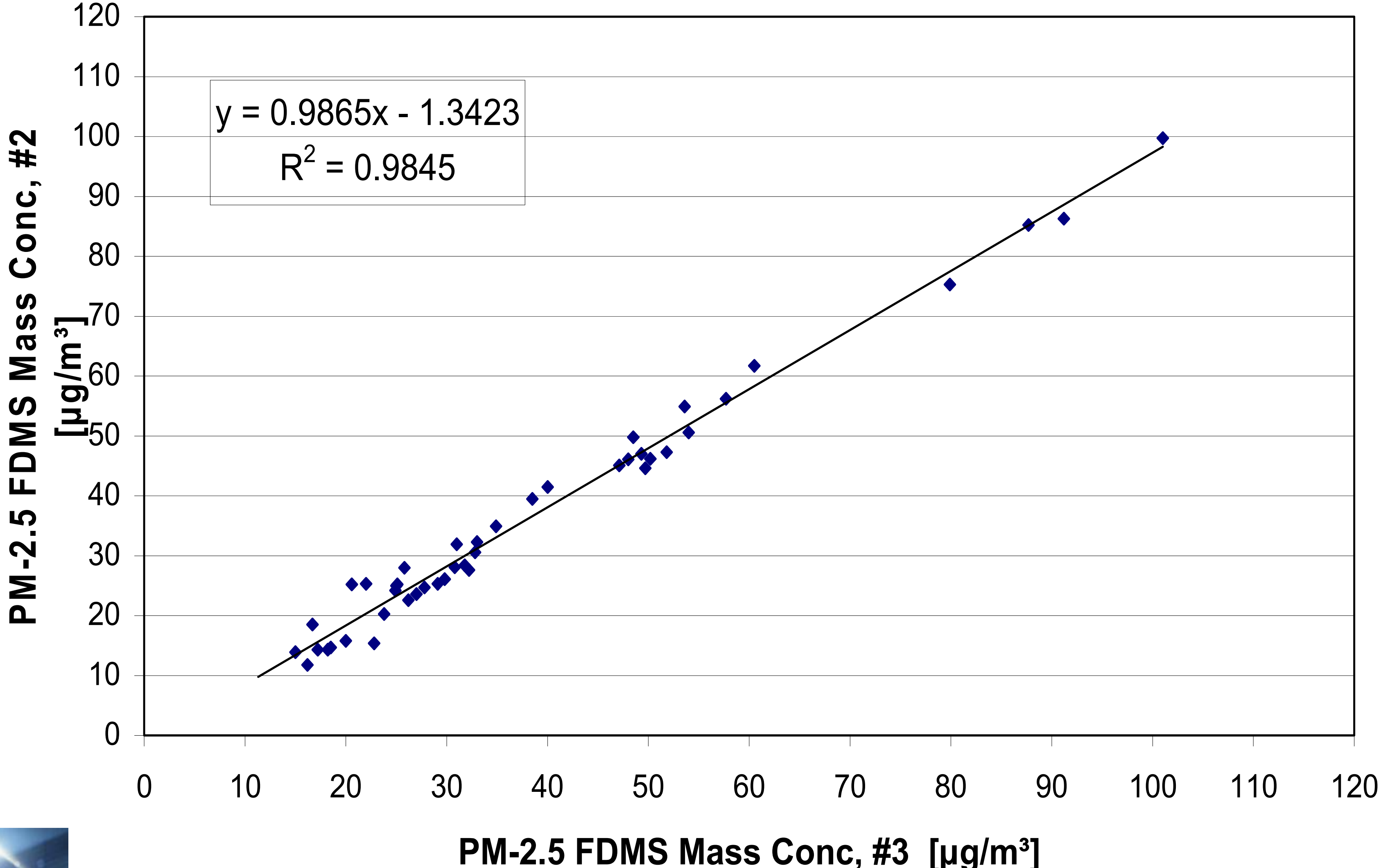
California ARB PM-2.5 Instrumentation Evaluation Study



Source: California Air Resources Board

FDMS Daily Precision Results

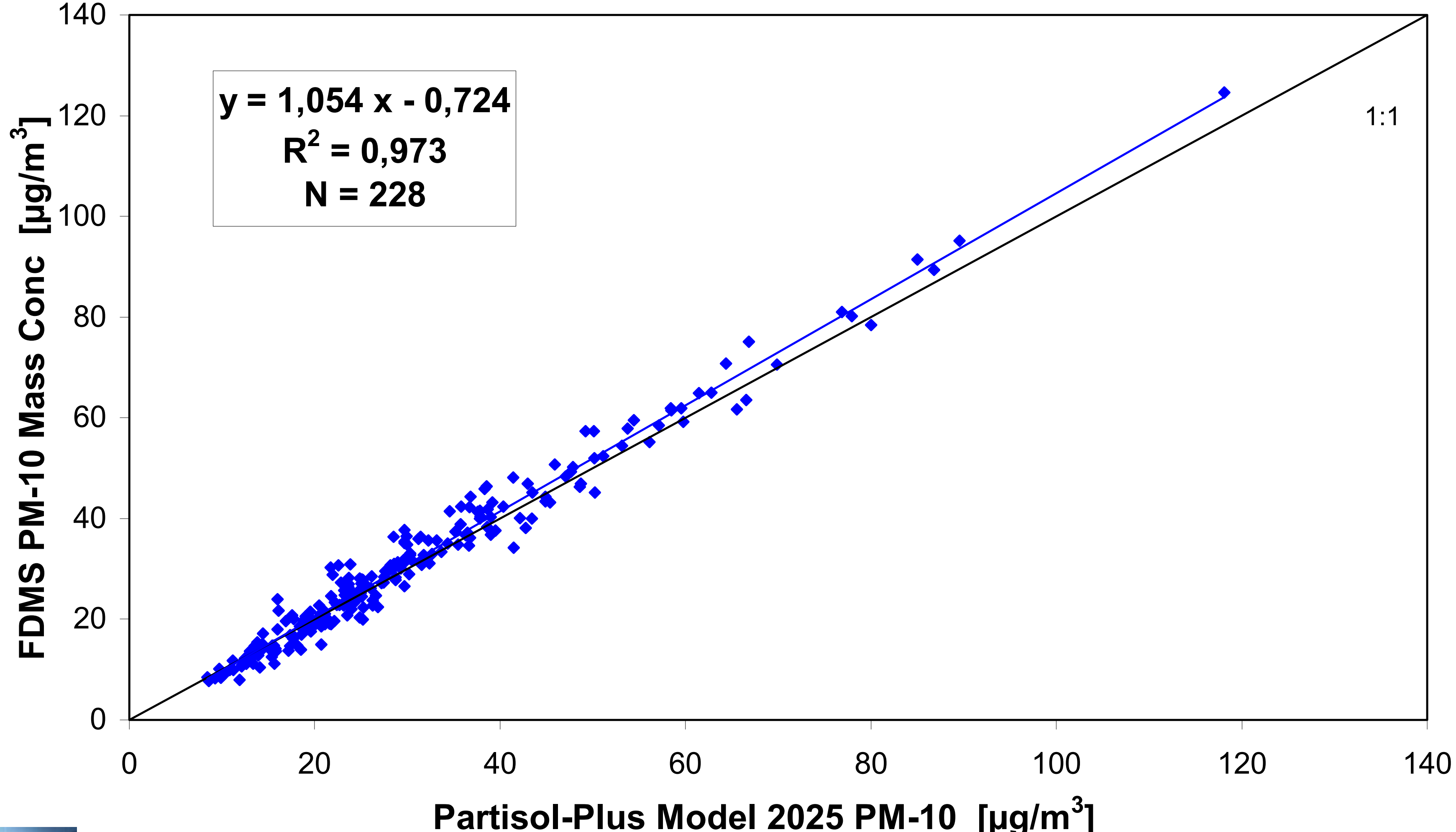
PM-2.5 Series 8500 FDMS System, Units 2 and 3



Source: California Air Resources Board

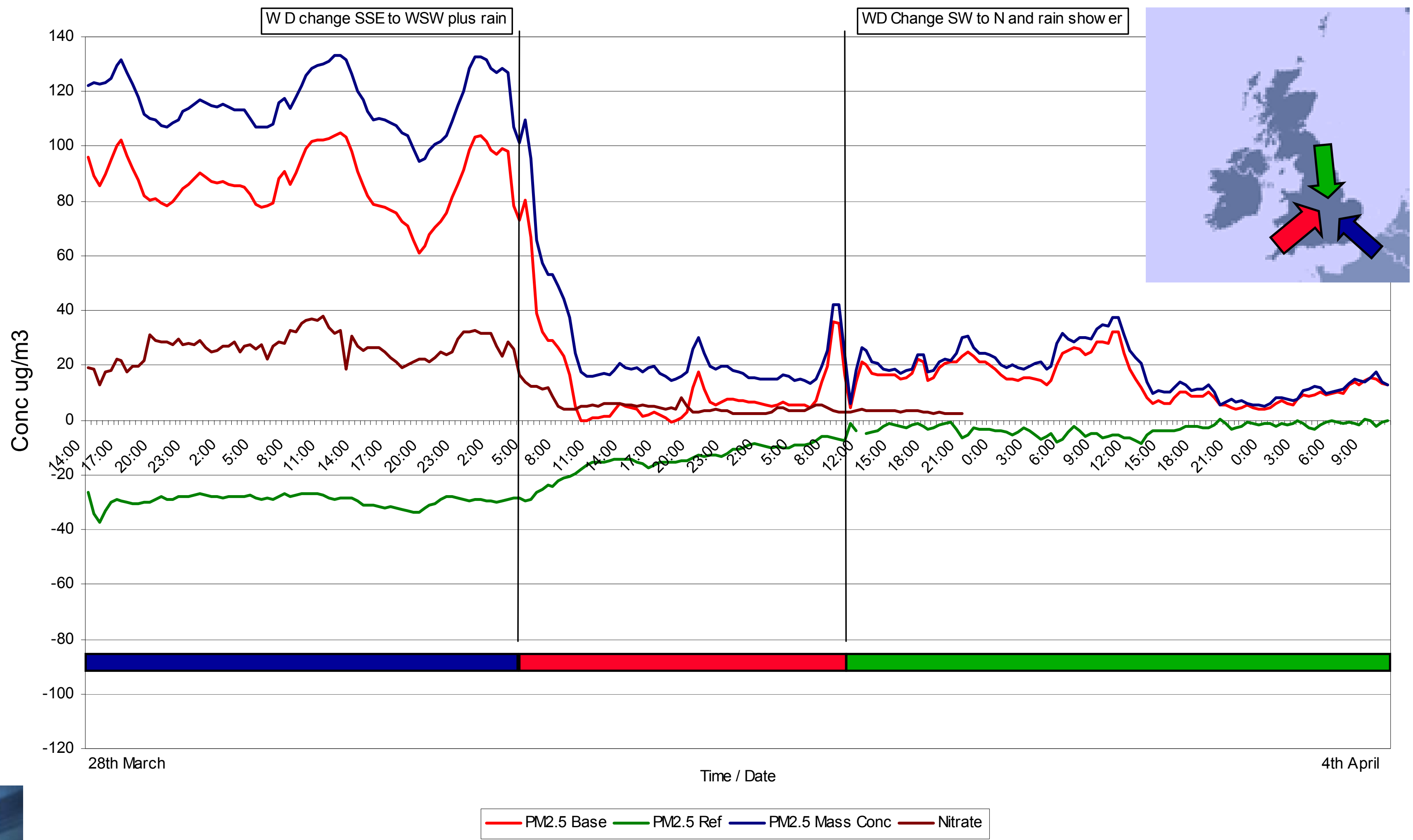
FDMS Results from France

Oct 2002-Summer 2003, Paris



Source: INERIS

UK FDMS Time Series Data



Source: National Physical Laboratory, Teddington, UK, Mar-Apr 2003

Thank you for your attention!