

# Continuous Analysis of Fresno Aerosols by Size, Time, and Elemental Concentrations, March – December, 2001

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# Purpose of the Study

Fresno, California, has one of the highest childhood asthma rates in California.

Fresno also is in violation of state and federal air quality criteria –

ozone in summer,

PM<sub>10</sub> and PM<sub>2.5</sub> in winter.

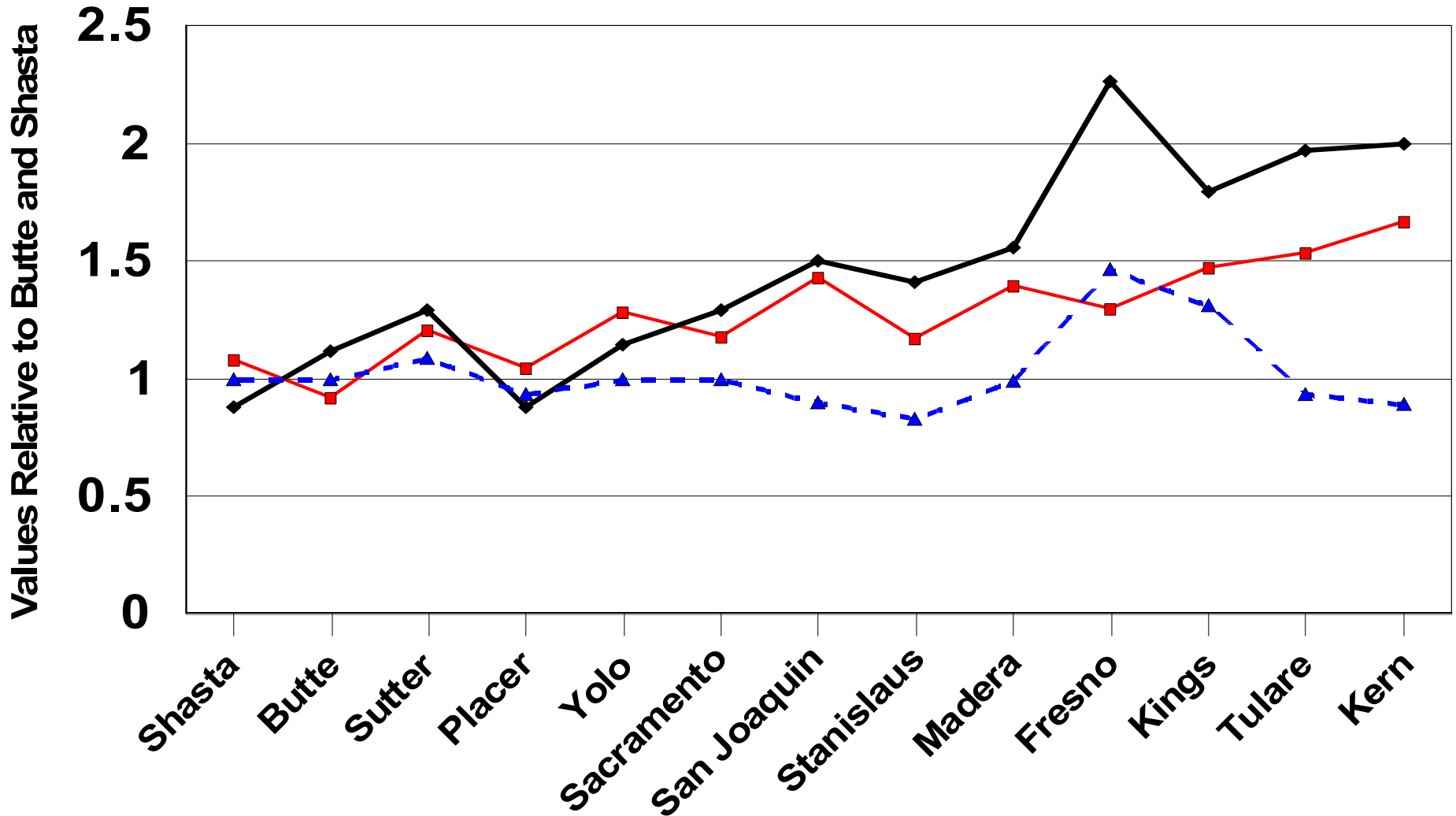
To what degree does Fresno pollution impact the asthma rate?



# Health and Aerosols in the Central Valley of California

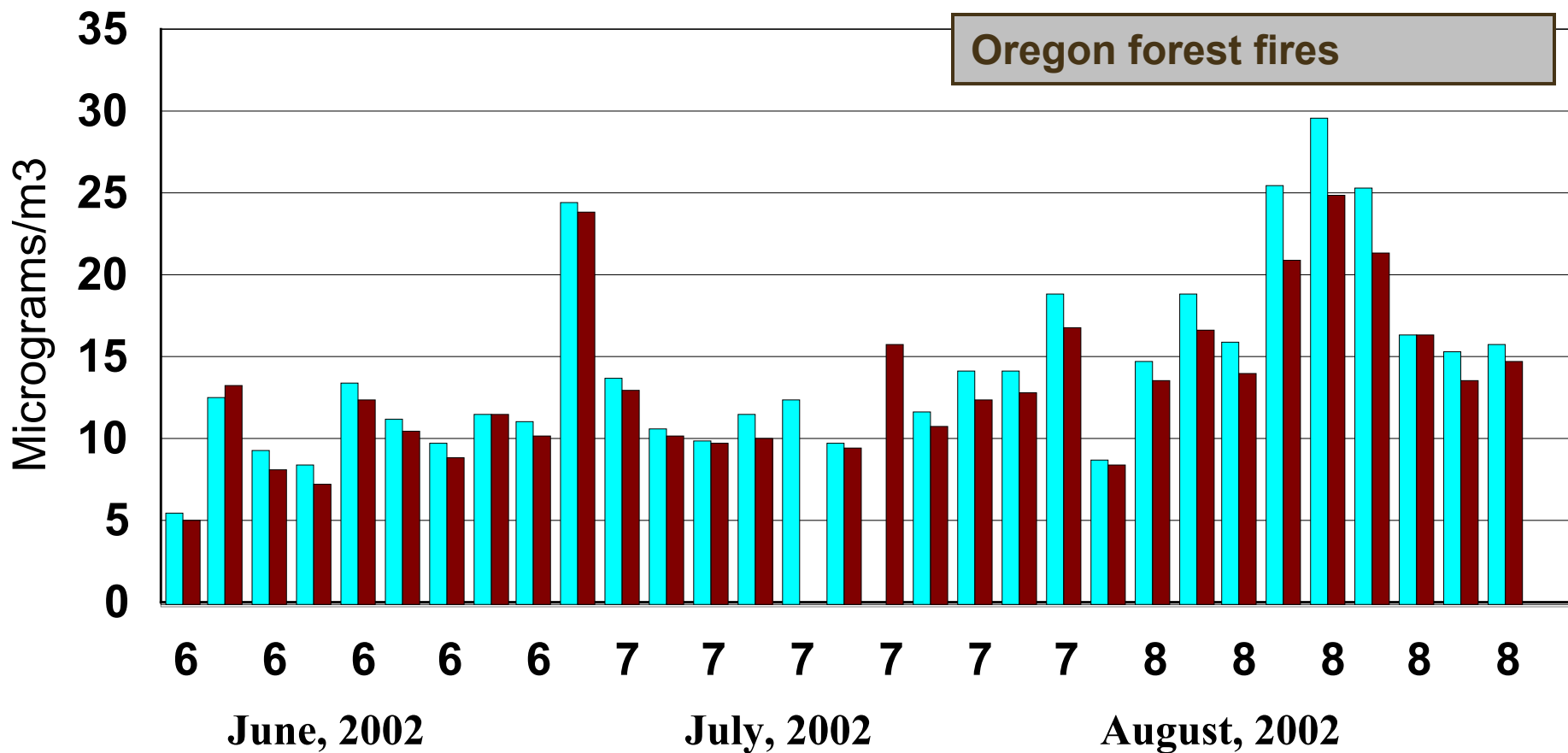
## Data Relative to Shasta and Butte counties

■ Ischemic Heart Mortality    ◆ Annual PM10    -▲- Childhood Asthma



# Fine aerosols at the Sequoia NP IMPROVE site

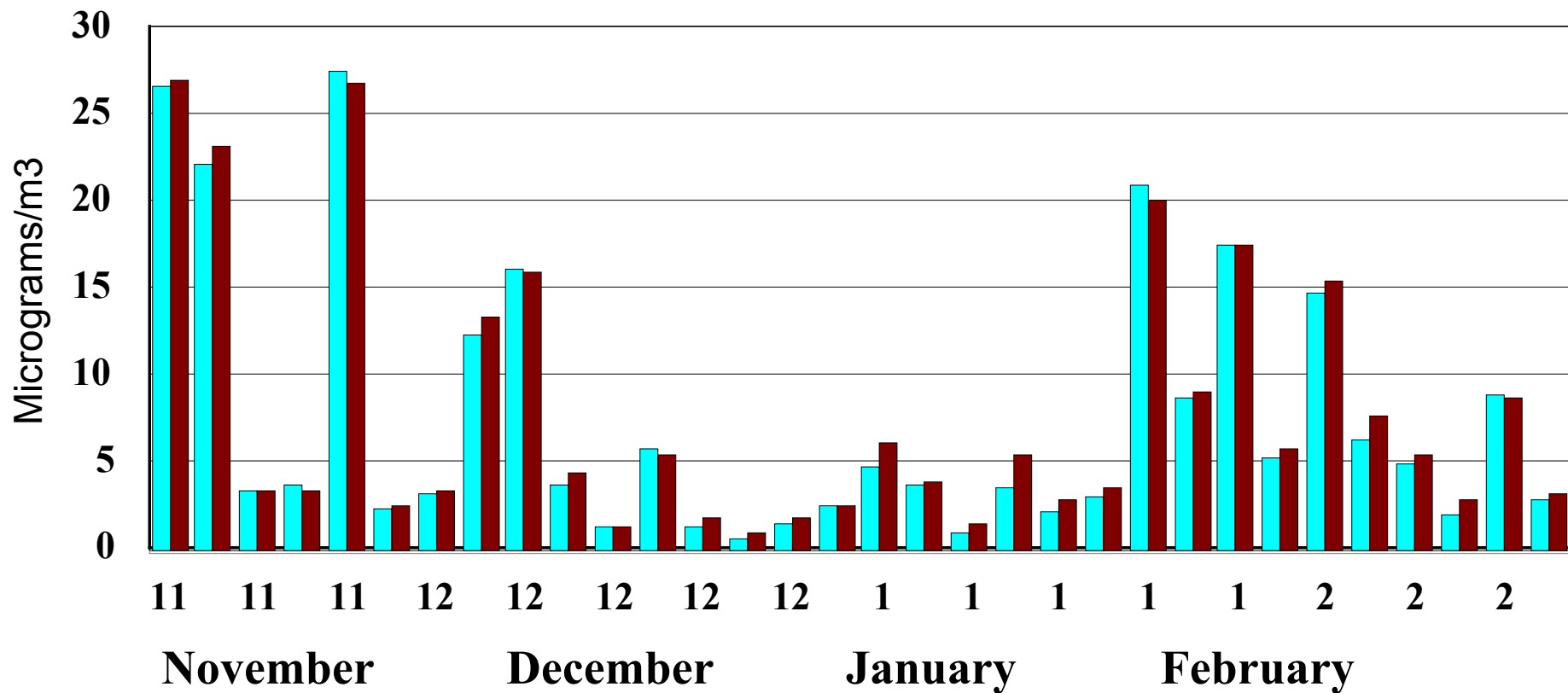
PM 2.5 mass      PM 2.5 mass (sum of species)



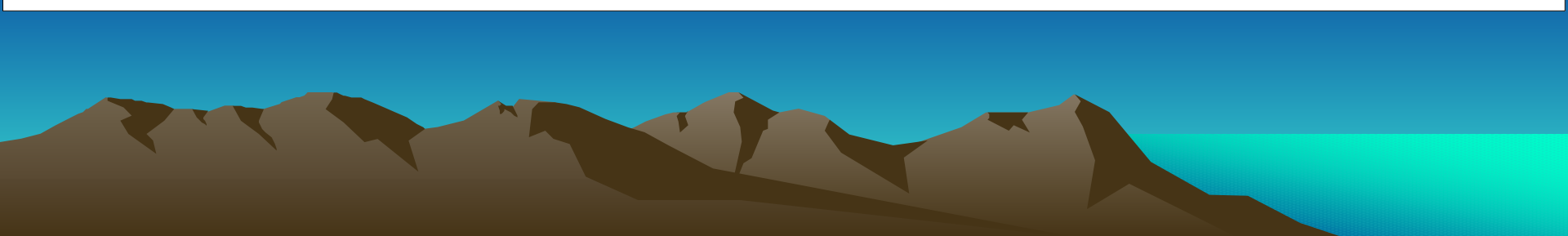
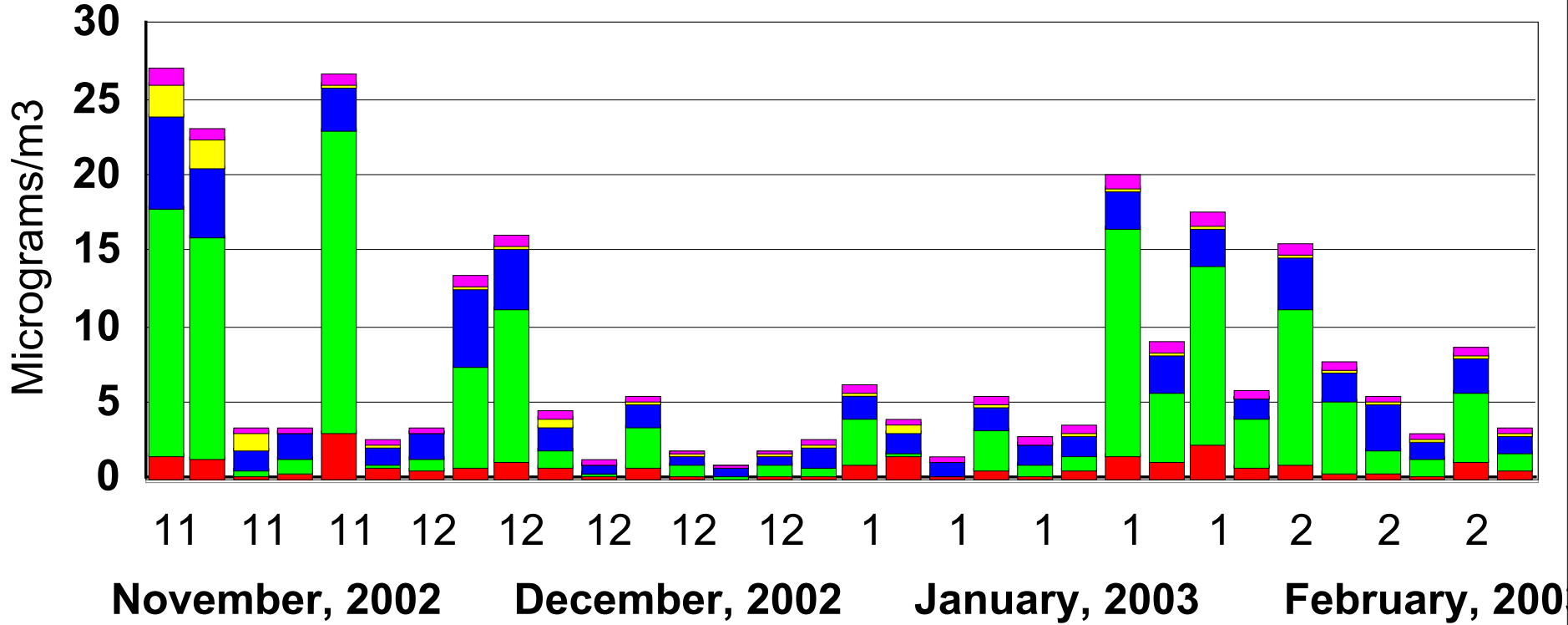


# Fine aerosols at the Sequoia NP IMPROVE site

PM 2.5 mass      PM 2.5 mass (sum of species)



# Fine aerosols at the Sequoia NP IMPROVE site



# Design of the Study

In response to the need to get a wide variety of aerosol metals as a function of size and time to support **short term medical data** for the **Fresno Asthmatic Children's Environment Study (FACES)**, the DELTA Group designed and implemented

- **continuous aerosol sampling** with
- 6 hr or 3 hr time resolution (set by the analysis protocols)
- in **8 size modes** from 10  $\mu\text{m}$  to 0.09  $\mu\text{m}$
- from March 10, 2001 to December 21, 2001,
- at the Fresno First Street Super-site in a residential neighborhood,
- examining over **1500 time periods, 12,000 samples,** and yielding over **1/3 million S-XRF elemental values.**



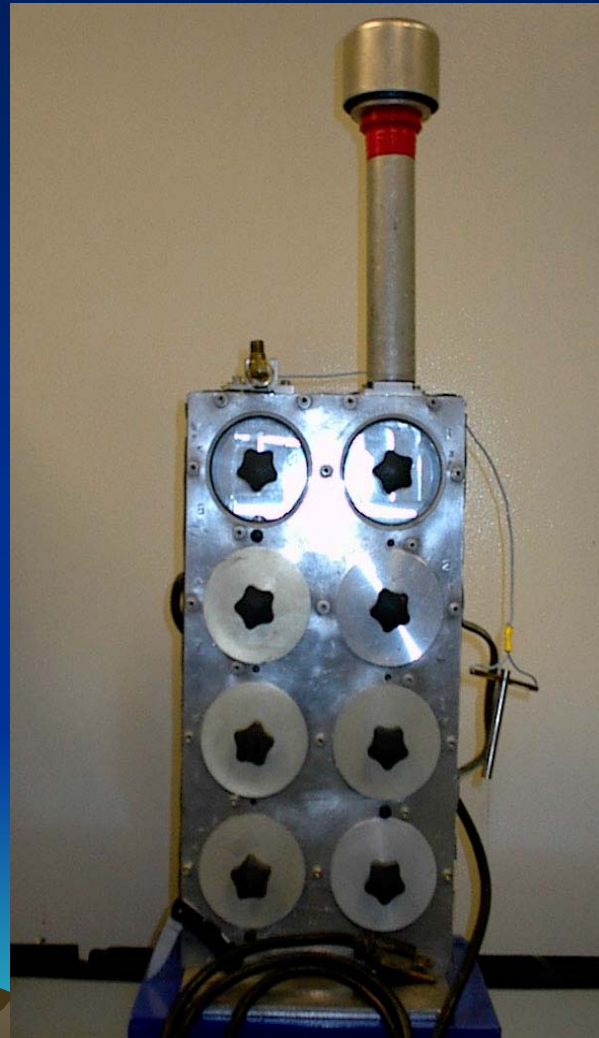


# Implementation

- **Sampling:** a PM10 modified DELTA Group slotted DRUM impactor, with size cuts at 10, 5, 2.5, 1.15, 0.75, 0.56, 0.34, 0.26, and 0.09  $\mu\text{m}$  aerodynamic diameter (Raabe-Marple values).
- **Analysis:** Synchrotron x-ray fluorescence (SXRF) at the DELTA Group x-ray microprobe of the Advanced Light Source, Lawrence Berkeley National Laboratory.
- **Quality Control:**
  - Routine re-analysis of previously analyzed samples,
  - Comparison with side by side Dichot samplers,
  - Re-analysis of ARB Dichot samples,
  - Comparisons with IMPROVE PIXE, XRF.

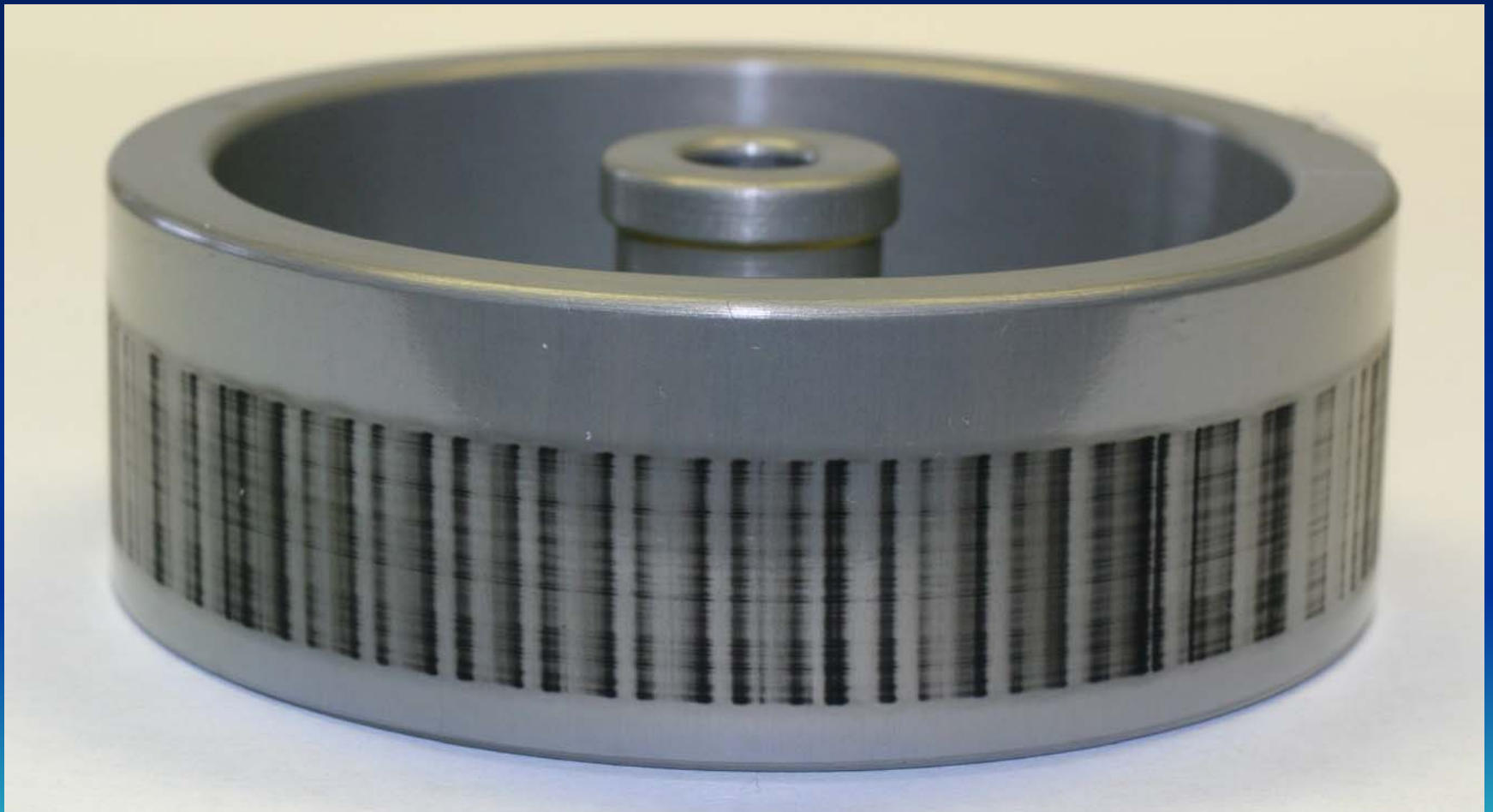


# DELTA Group slotted 8 DRUM Impactor

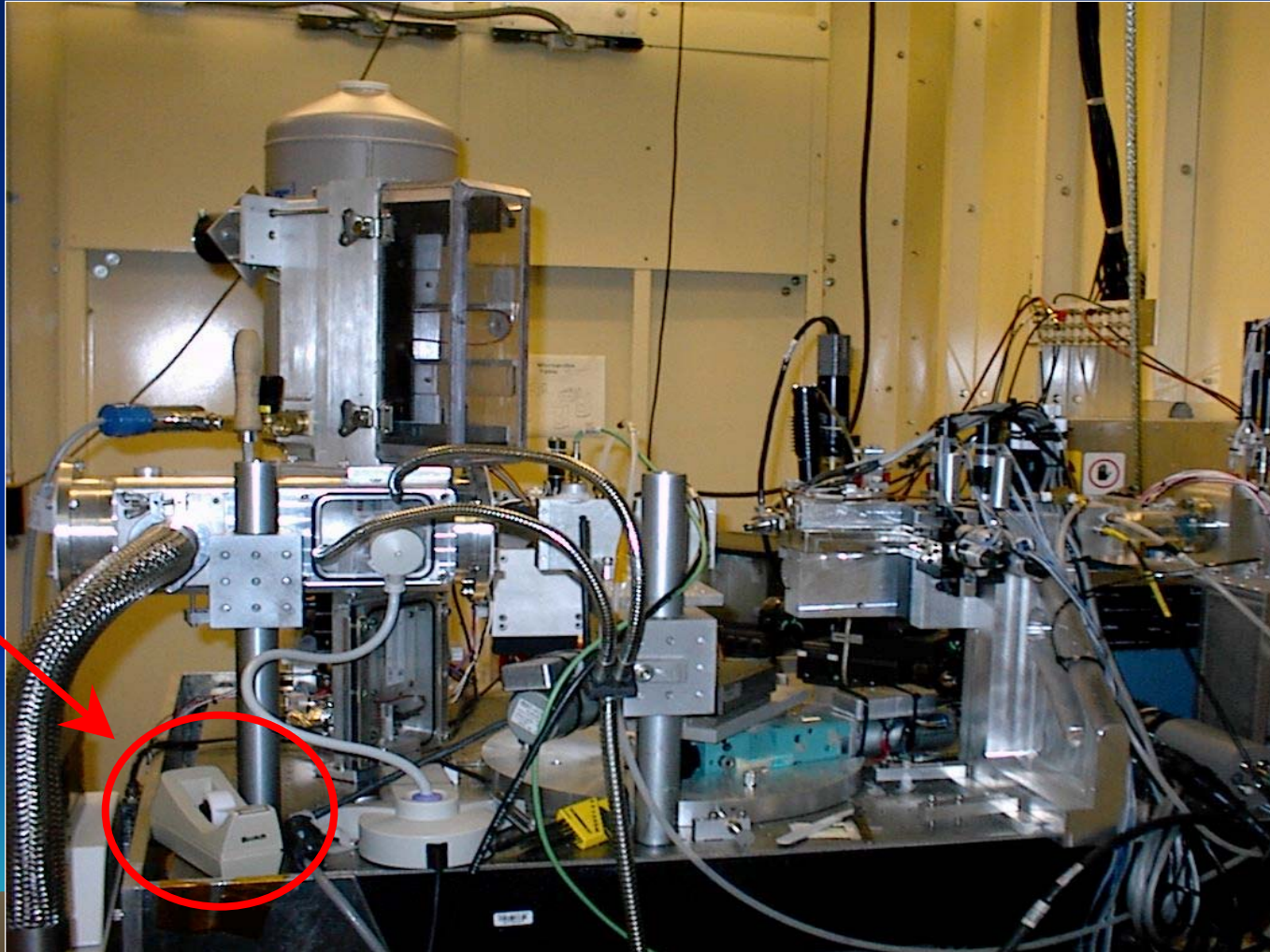


- 8 size ranges:
  - 10.0 to 5.0  $\mu\text{m}$  (std  $\text{PM}_{10}$  inlet)
  - 5.0 to 2.5  $\mu\text{m}$
  - 2.5 to 1.15  $\mu\text{m}$
  - 1.15 to 0.75  $\mu\text{m}$
  - 0.75 to 0.56  $\mu\text{m}$
  - 0.56 to 0.34  $\mu\text{m}$
  - 0.34 to 0.26  $\mu\text{m}$
  - 0.26 to 0.09  $\mu\text{m}$
- 16.7 l/min, critical orifice control,  $\frac{1}{4}$  hp pump
- 10.0 x 168 mm Mylar strips
- For 42 day run, 4 mm/day, **S-XRF beam 0.5 mm, = 3 hr.**
- Field portable
  - 10 kg, 43 cm  $\times$  22 cm  $\times$  13 cm

**Stage 8 of DRUM ,  $0.26 > D_p > 0.09 \mu\text{m}$   
diameter, showing strong diurnal pattern;  
the deposit shown covers 3 weeks.**



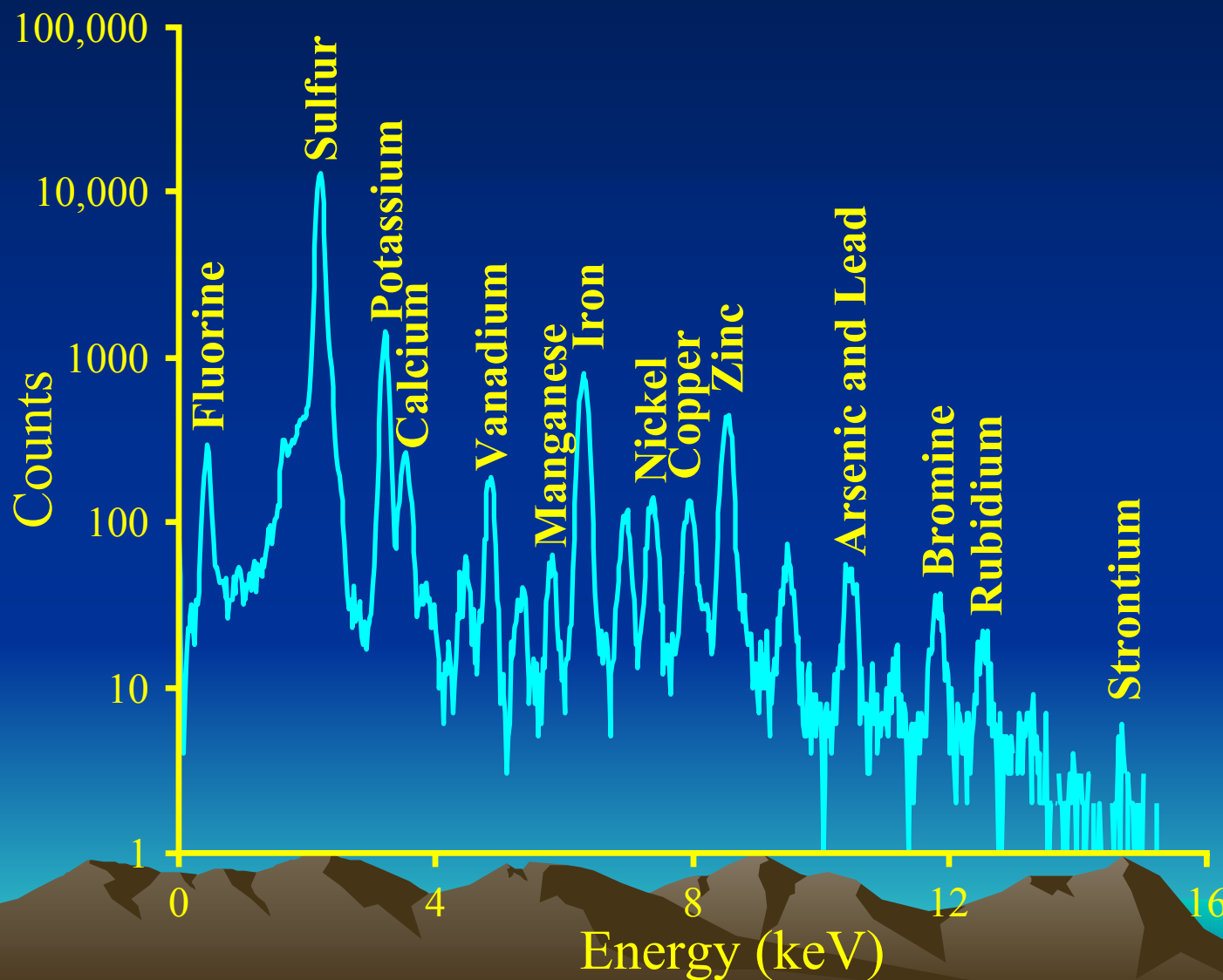
# DELTA Group Synchrotron-XRF Facility at the LBNL Advanced Light Source



For scale?  
(At least  
it's not  
duct tape.)

# Typical S-XRF Spectrum

Raw data, Teflon substrate with no blank subtraction



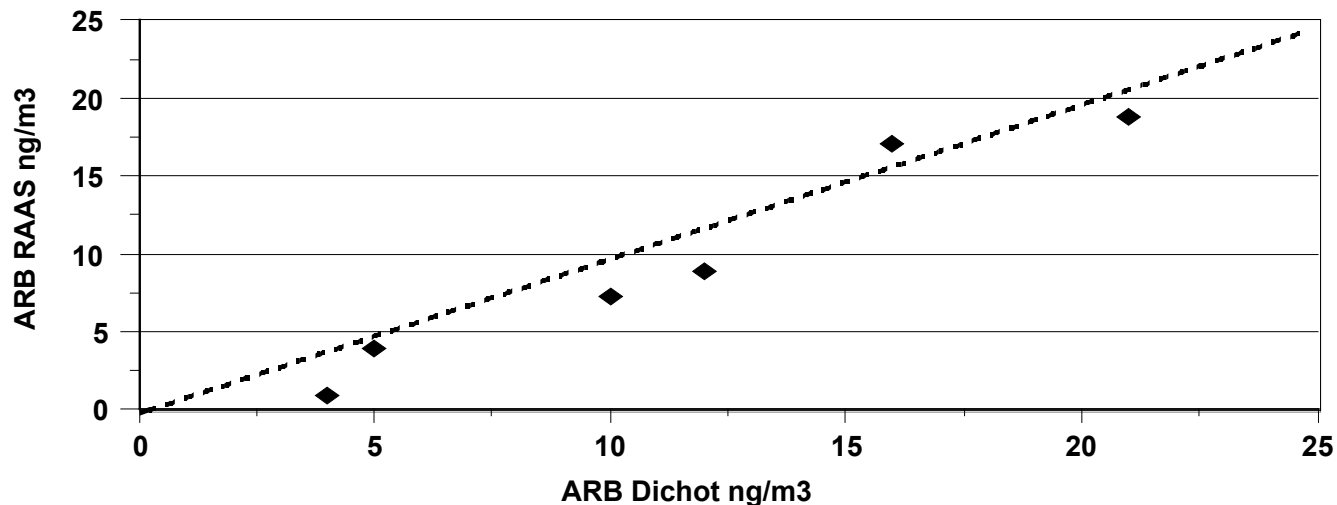
	RTI XRF	IMPROVE	S-XRF
Na	15	10	14
Si	8	23	3
S	4	20	3
V	1	6	0.1
Ni	0.9	0.9	0.2
As	1.7	0.5	0.1
Sr	2.3	1.3	0.3
Cd	7.6	NA	NA
Ba	84	NA	1.0
Pb	4	2	0.6

MDL values (ng/cm<sup>2</sup>)

# Fresno FACES Filter Intercomparison

ARB Dichot vs ARB RAAS

Zinc



All filters S-XRF  
vs ARB XRF

$1.02 \pm 0.11$

vs ARB RAAS

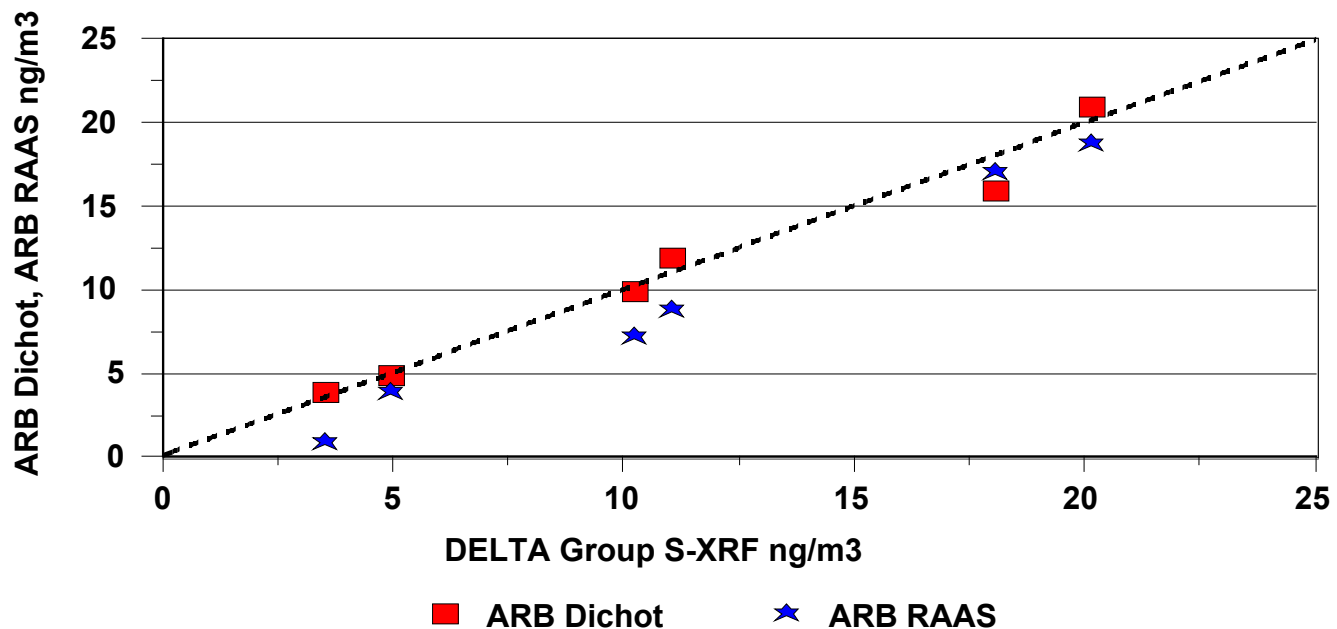
$1.29 \pm 0.58$

ARB XRF vs ARB  
RAAS

$1.29 \pm 0.63$

DELTA S-XRF vs ARB Dichot and ARB RAAS Filters

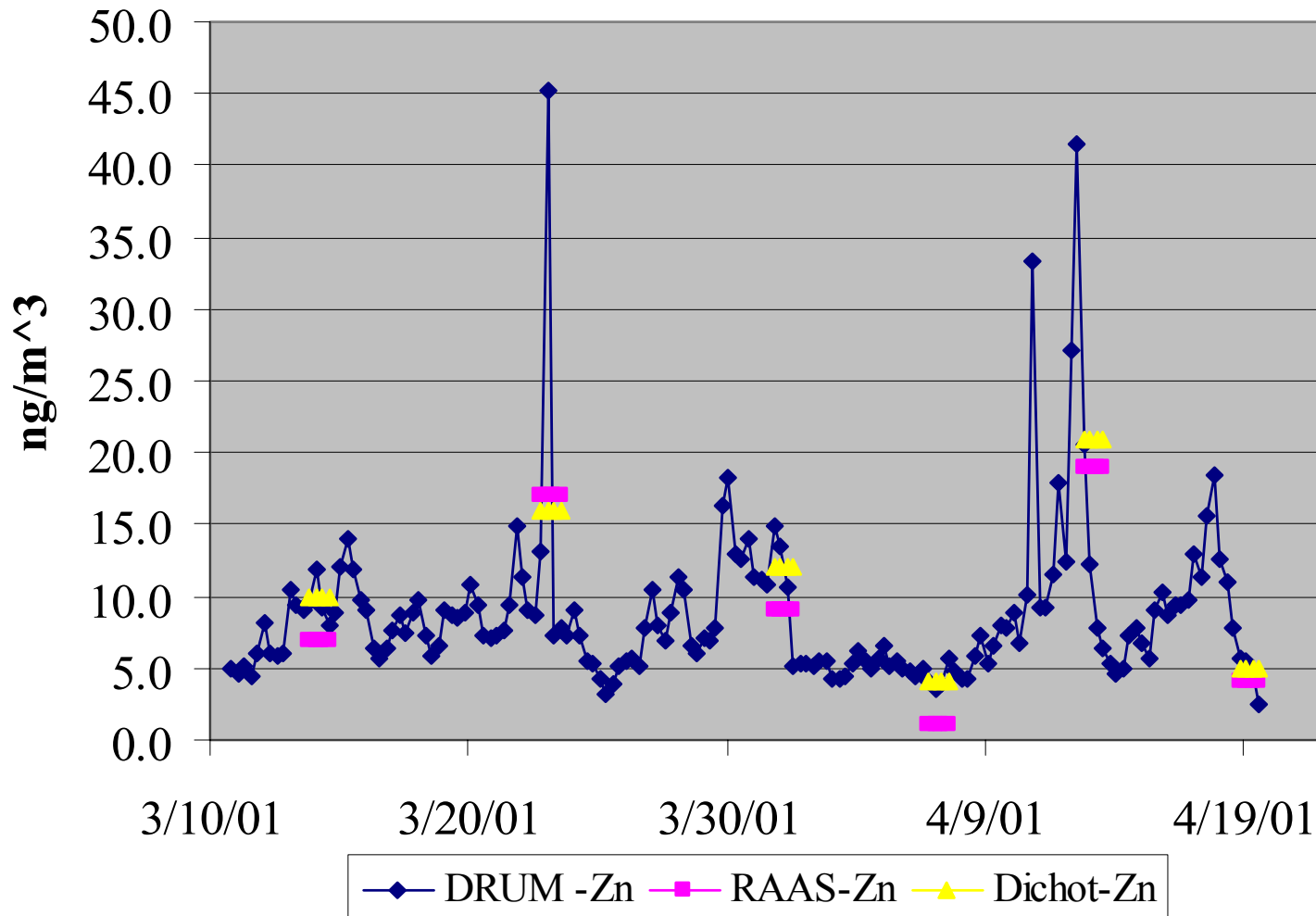
Zinc



# DRUM S-XRF vs ARB XRF and ARB RAAS

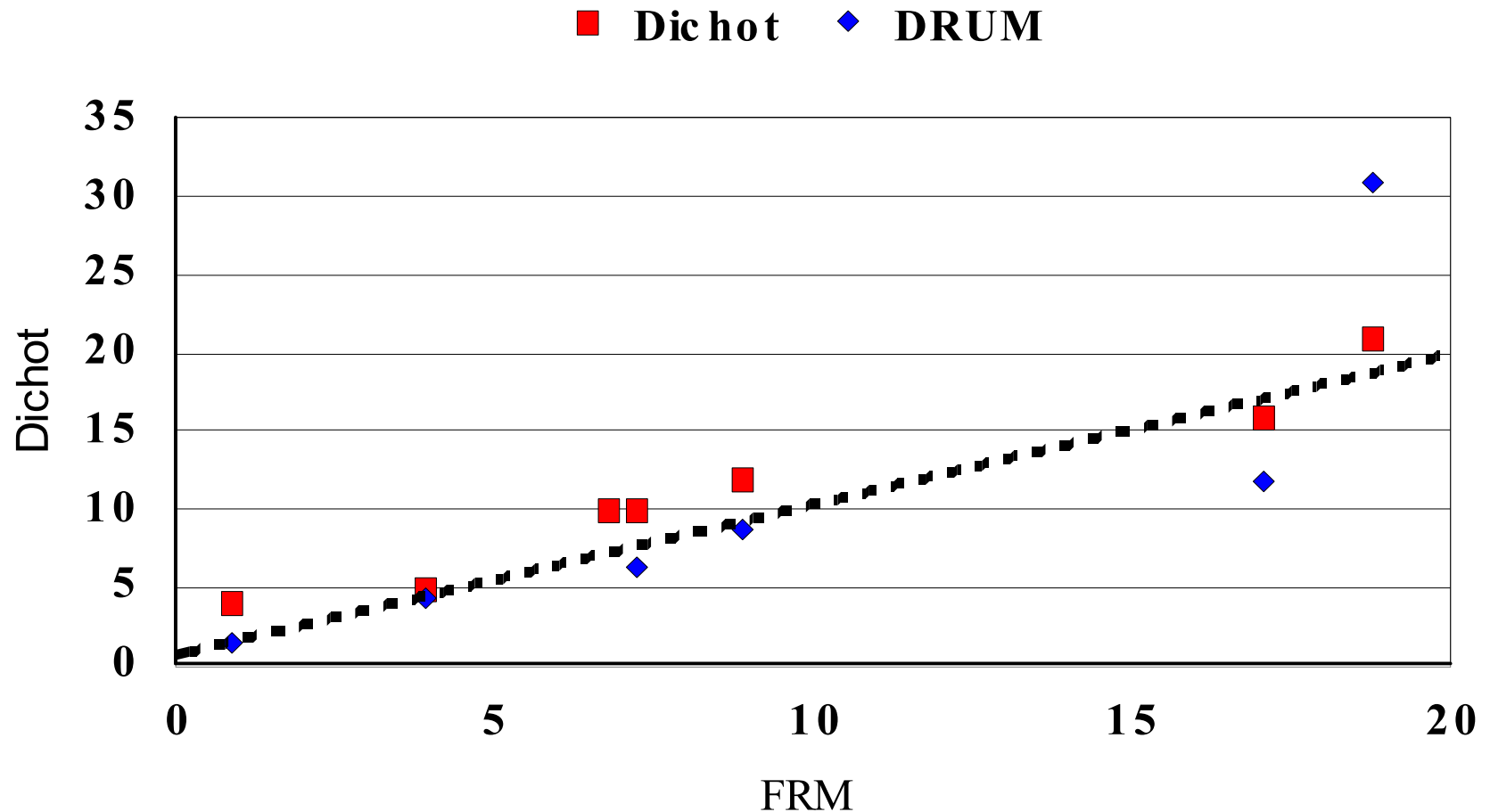
note: it takes 24 6 hr 6 size cuts S-XRF measurements to match a single 24 hr PM<sub>2.5</sub> filter

## PM-2.5 Zn Concentration vs. Date (6-hour data)



# DRUM, Dichot, and FRM agree well for fine particles

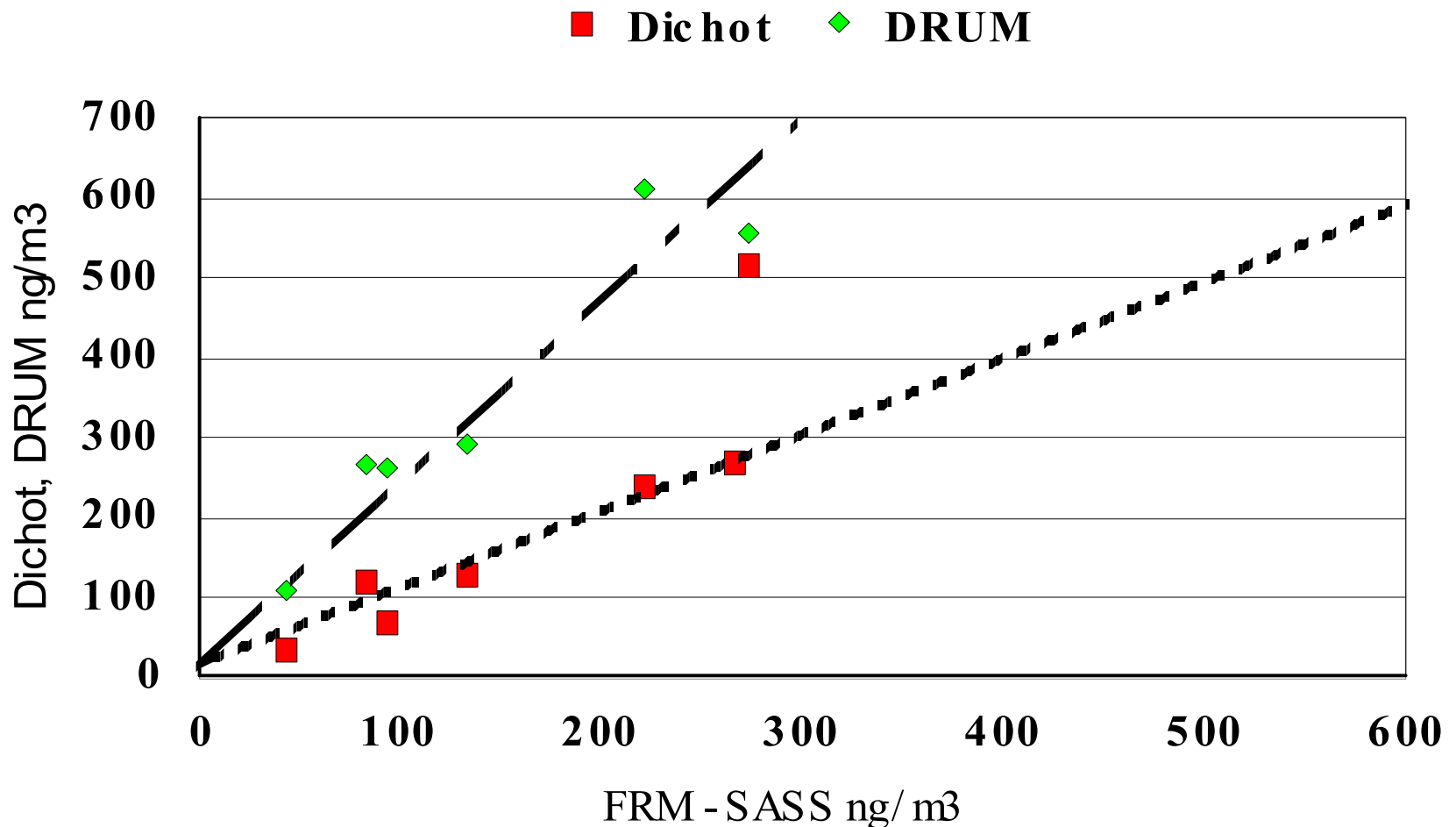
## Zinc; Dichot and DRUM vs FRM





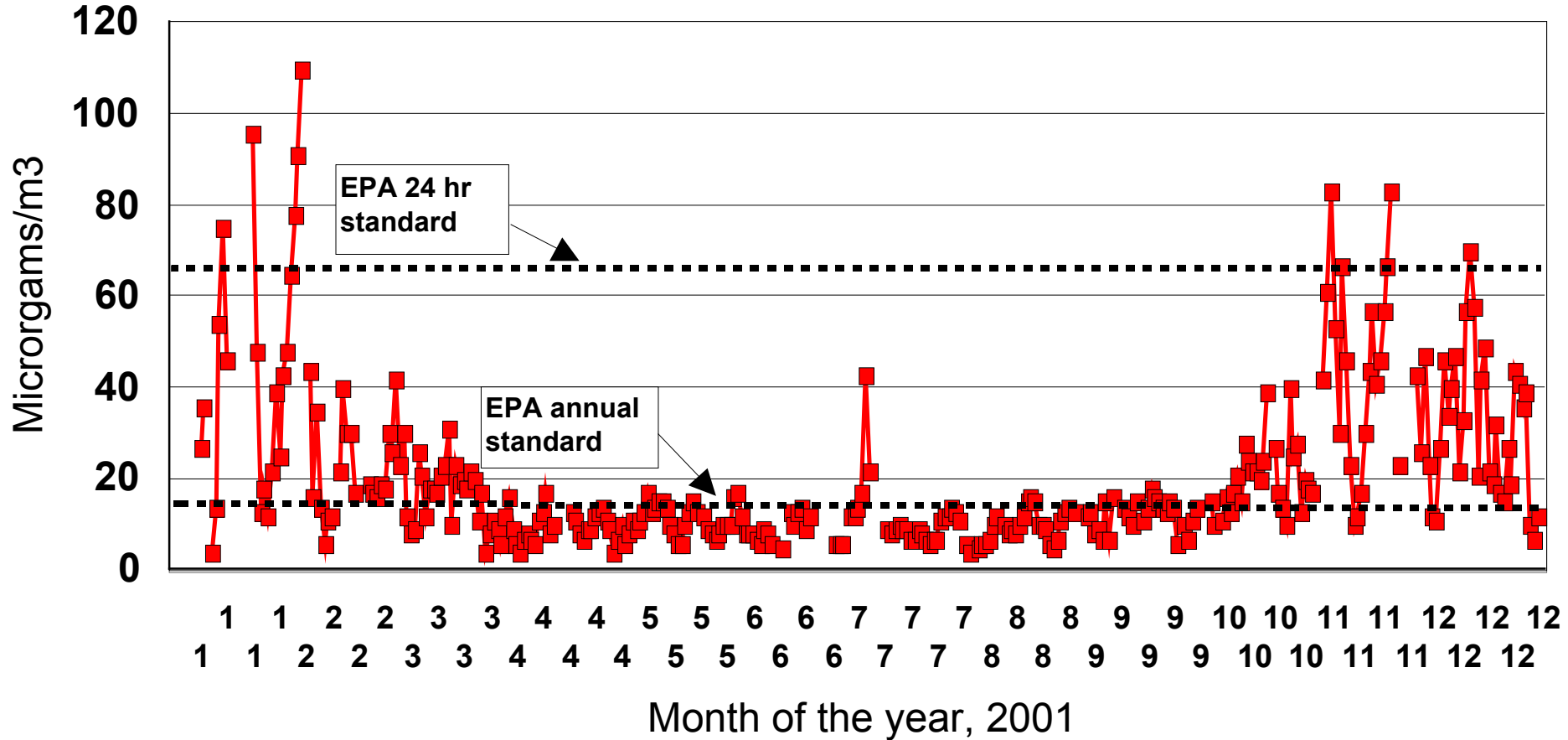
The DRUM sees more soil, almost all lying between 2.5 and 1.15  $\mu\text{m}$

## Silicon Dichot vs FRM



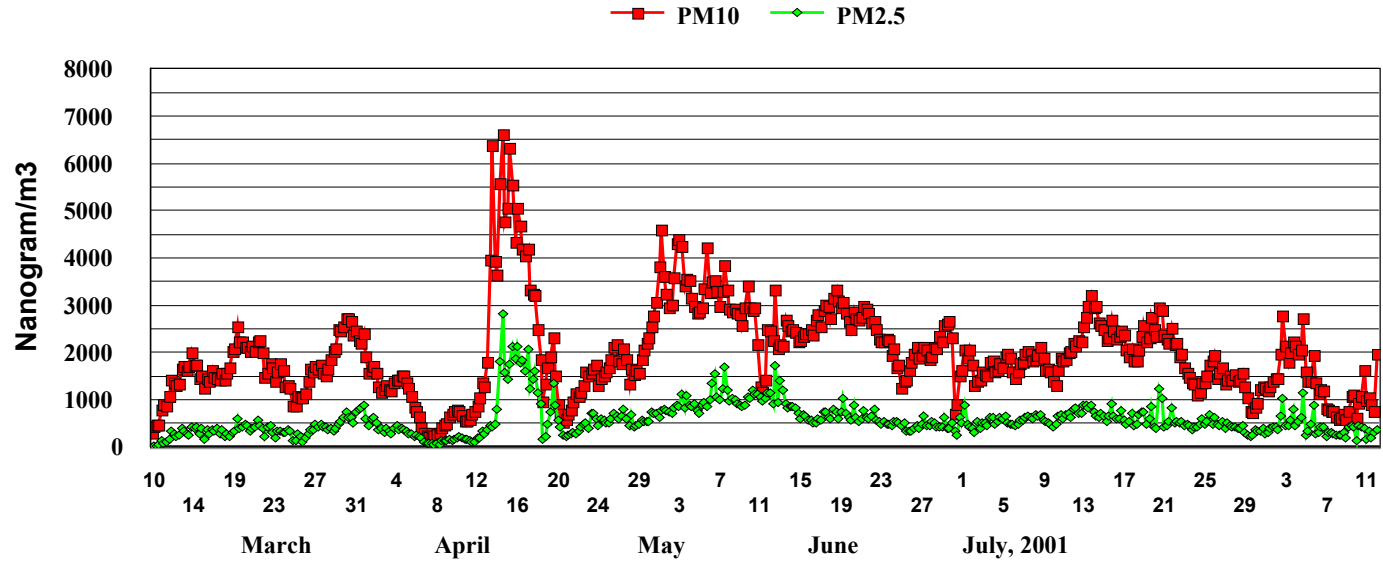
# Aerosols at the Fresno 1st Street Supersite

—■— PM2.5 Mass, 2001

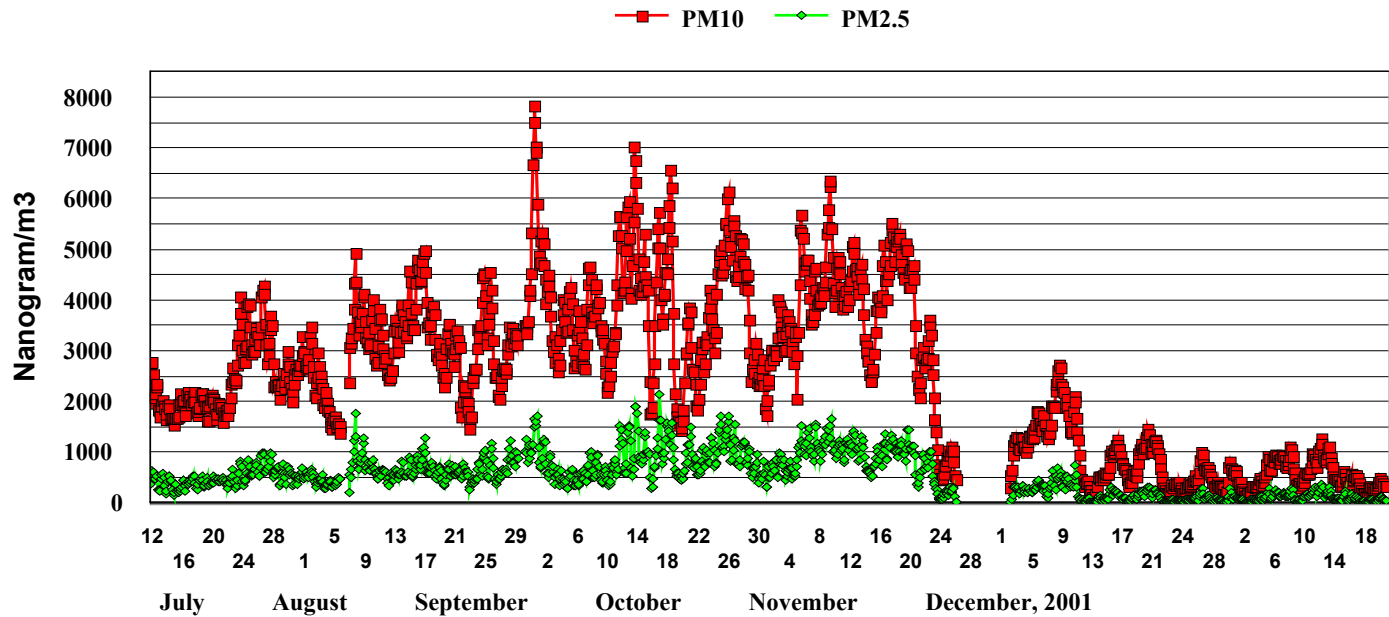


# Silicon Aerosols at Fresno during the FACES Study

## DRUM Impactor, S-XRF Analysis Data, 6 hr resolution



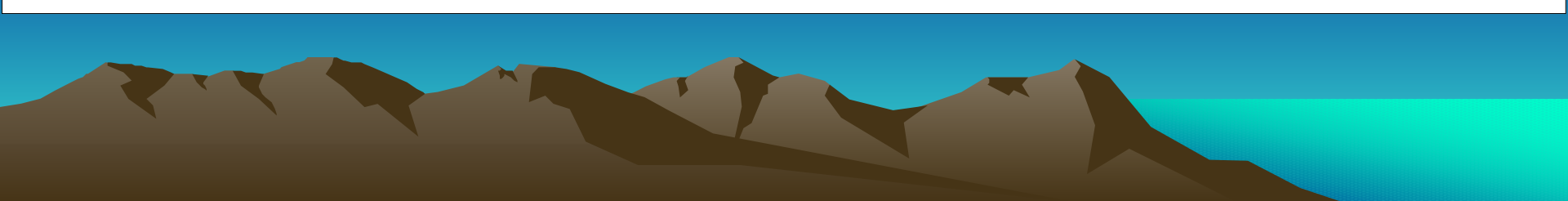
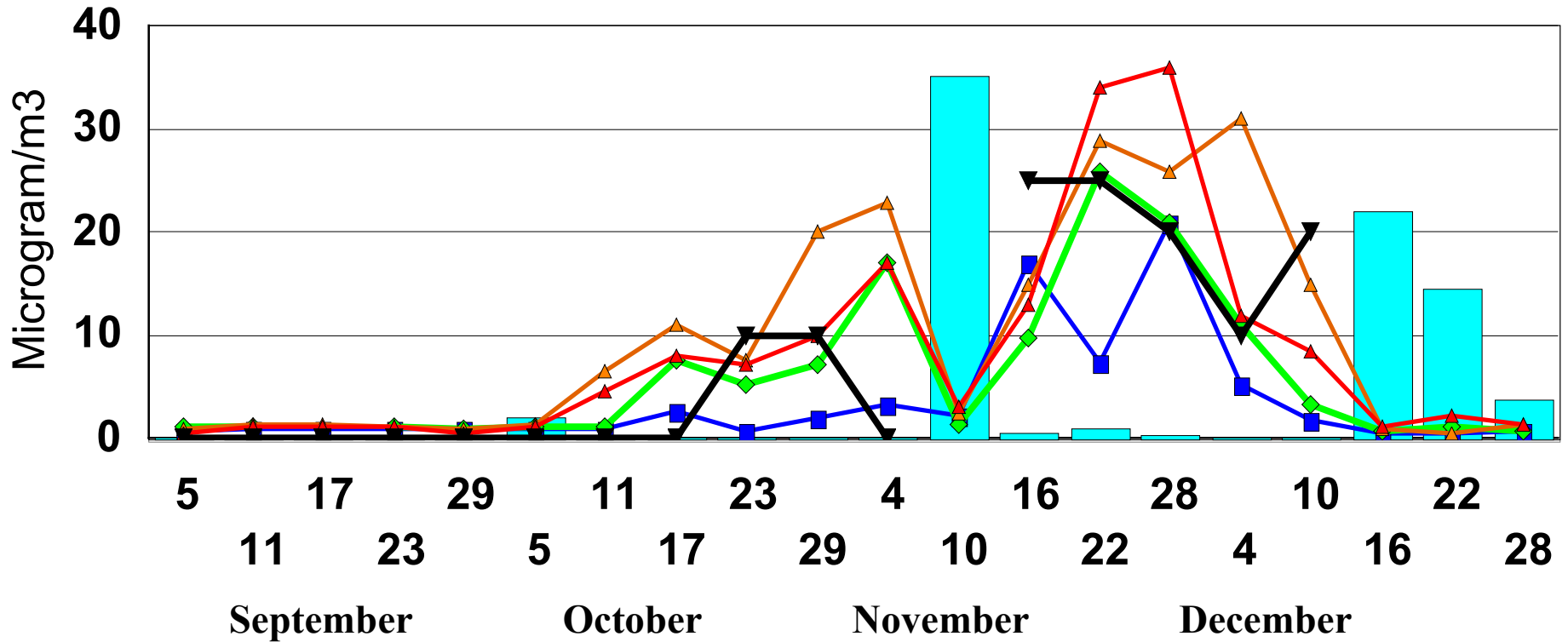
## DRUM Impactor, S-XRF Analysis Data, 3 hr resolution



# 24 hr Nitrate Aerosols

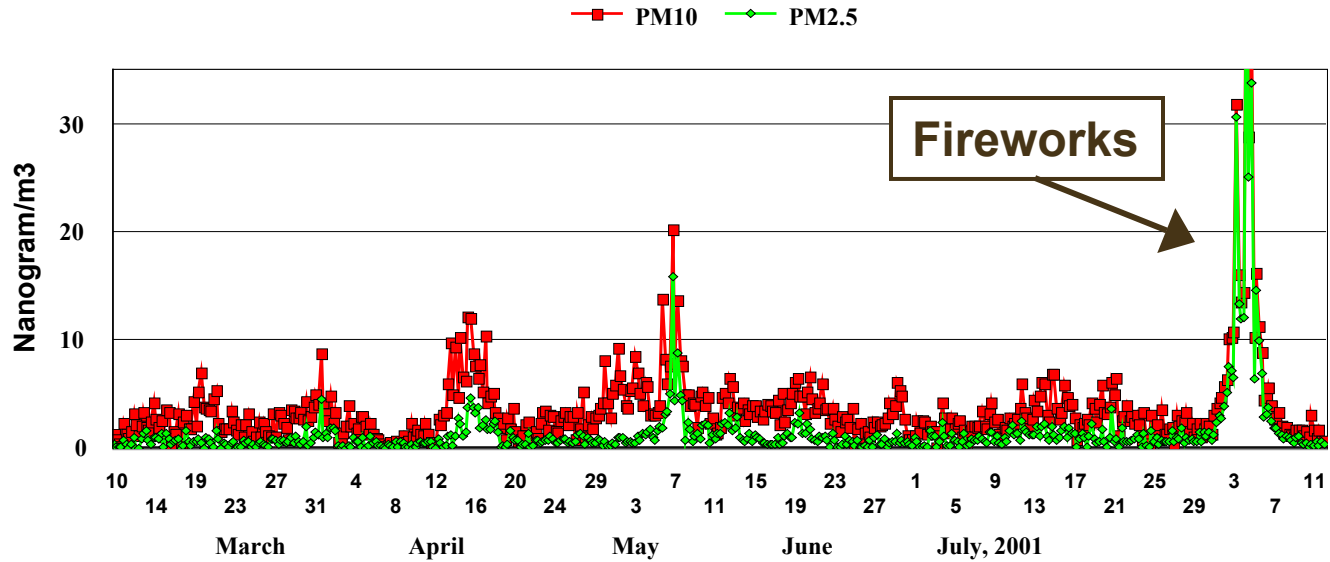
## Fall, 2002

- Sacramento
- ▲ Corcoran
- ▼ Fog days at Fresno x 5, no rain
- ◆ Fresno
- ▲ Bakersfield
- Rain prev 5 days, Fresno

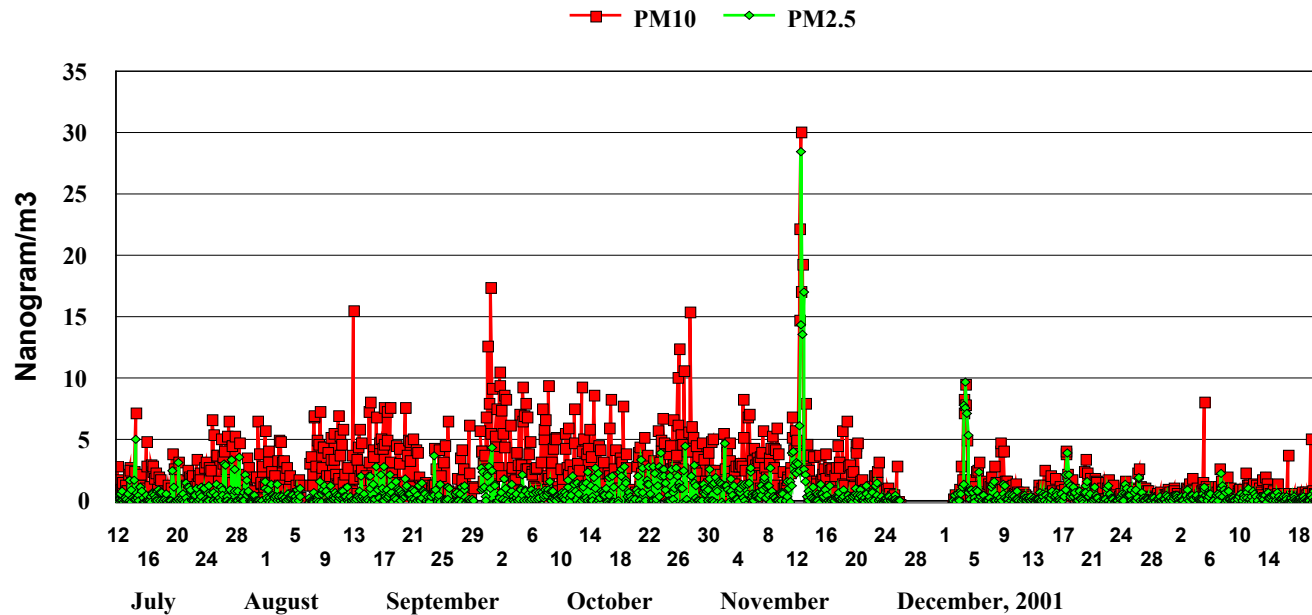


# Strontium Aerosols at Fresno during the FACES Study

## DRUM Impactor, S-XRF Analysis Data, 6 hr resolution

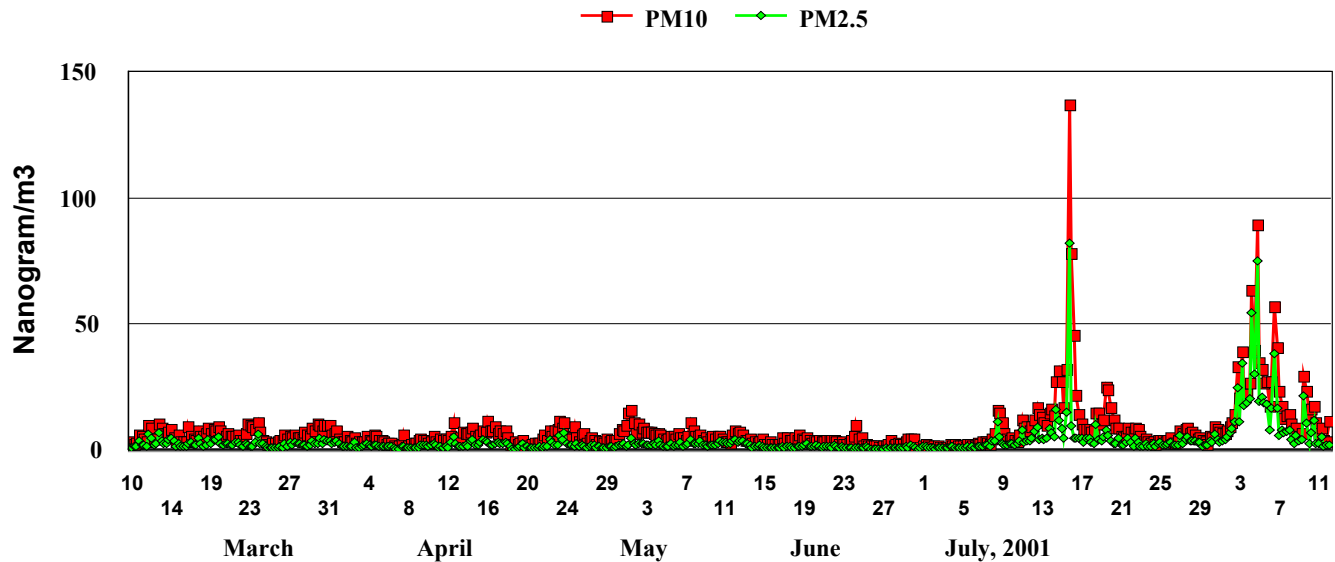


## DRUM Impactor, S-XRF Analysis Data, 3 hr resolution

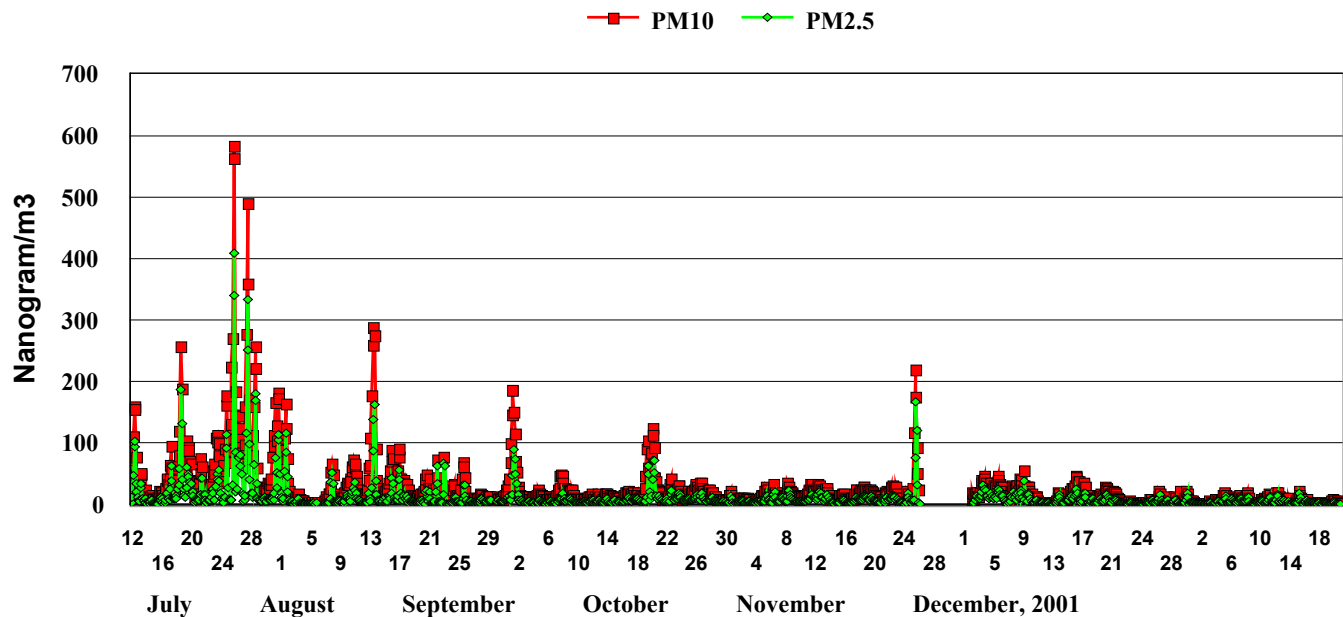


# Copper Aerosols at Fresno during the FACES Study

## DRUM Impactor, S-XRF Analysis Data, 6 hr resolution

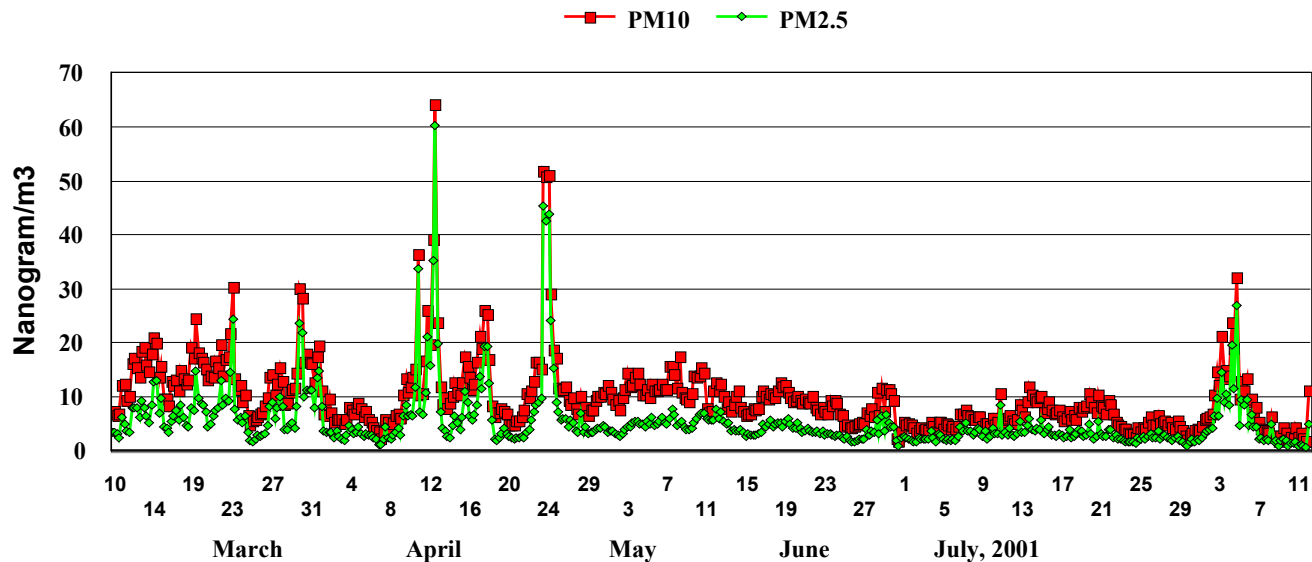


## DRUM Impactor, S-XRF Analysis Data, 3 hr resolution

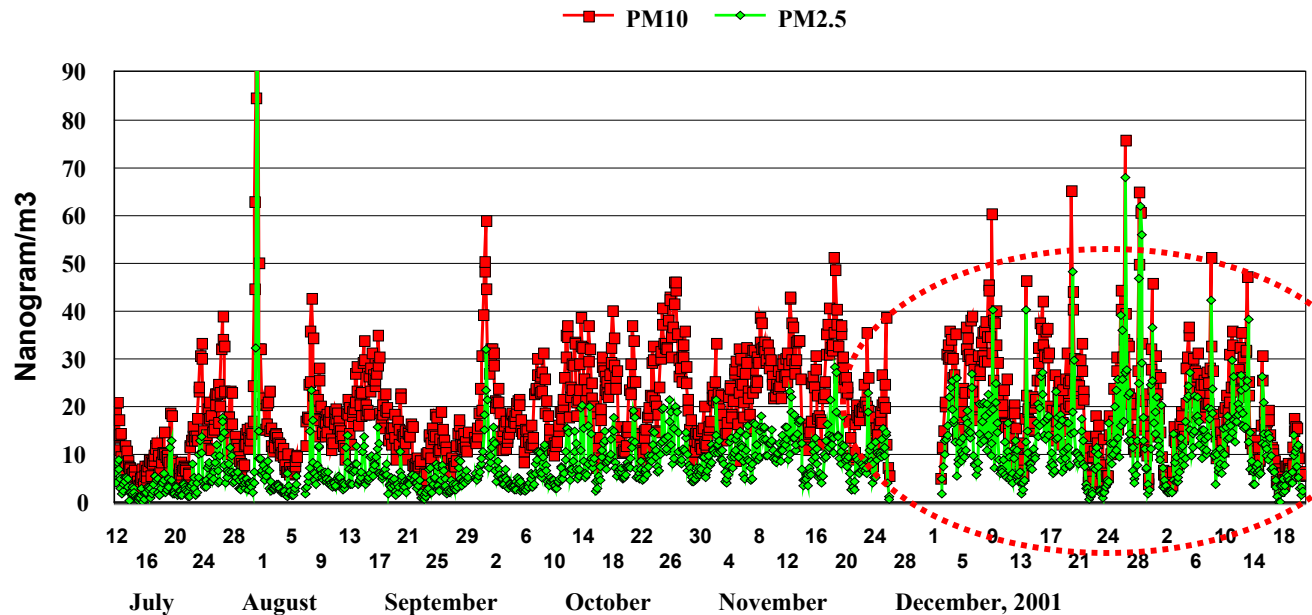


# Zinc Aerosols at Fresno during the FACES Study

## DRUM Impactor, S-XRF Analysis Data, 6 hr resolution



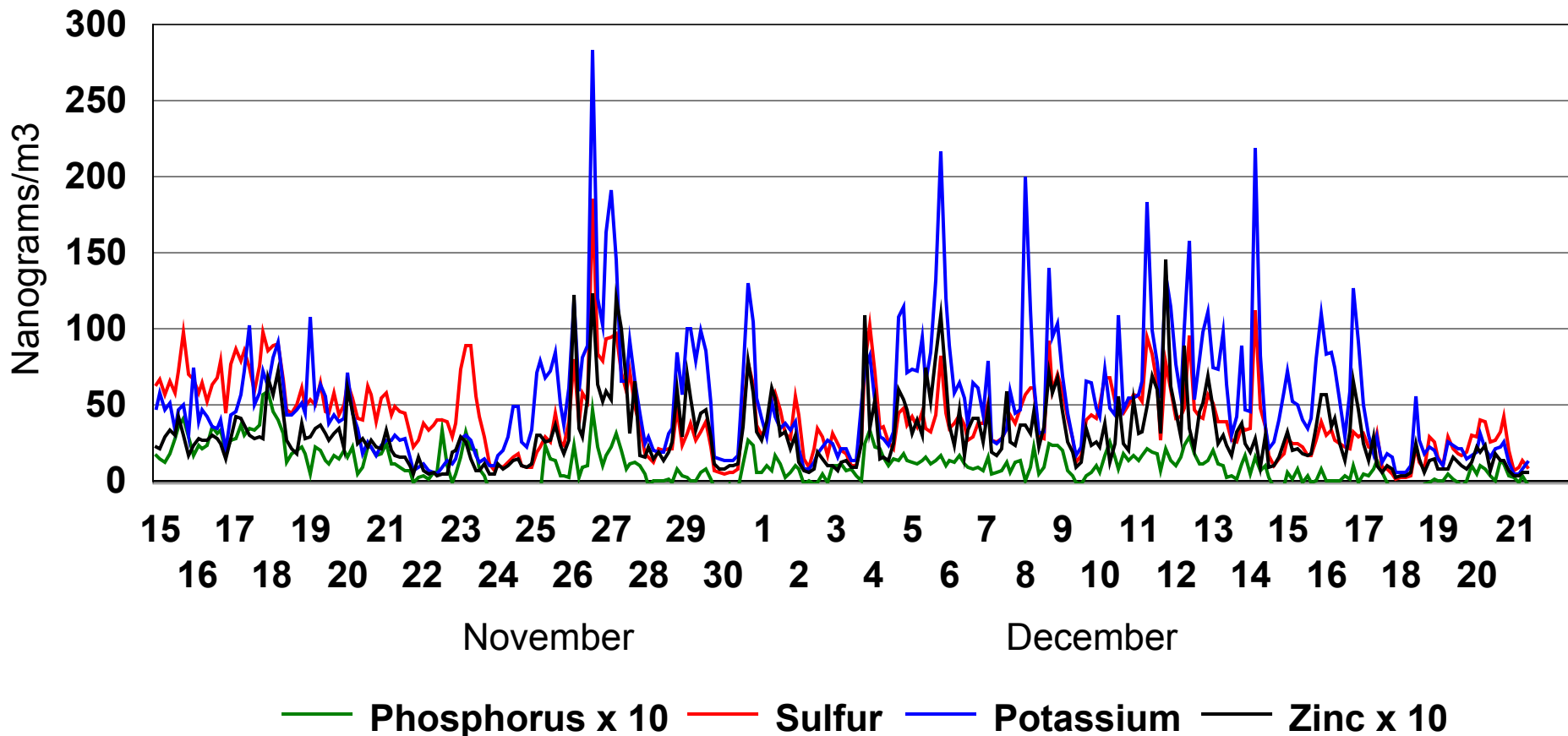
## DRUM Impactor, S-XRF Analysis Data, 3 hr resolution



# Very fine aerosols characteristic of diesels/smoking cars

## Aerosols at the Fresno First Street Super-site

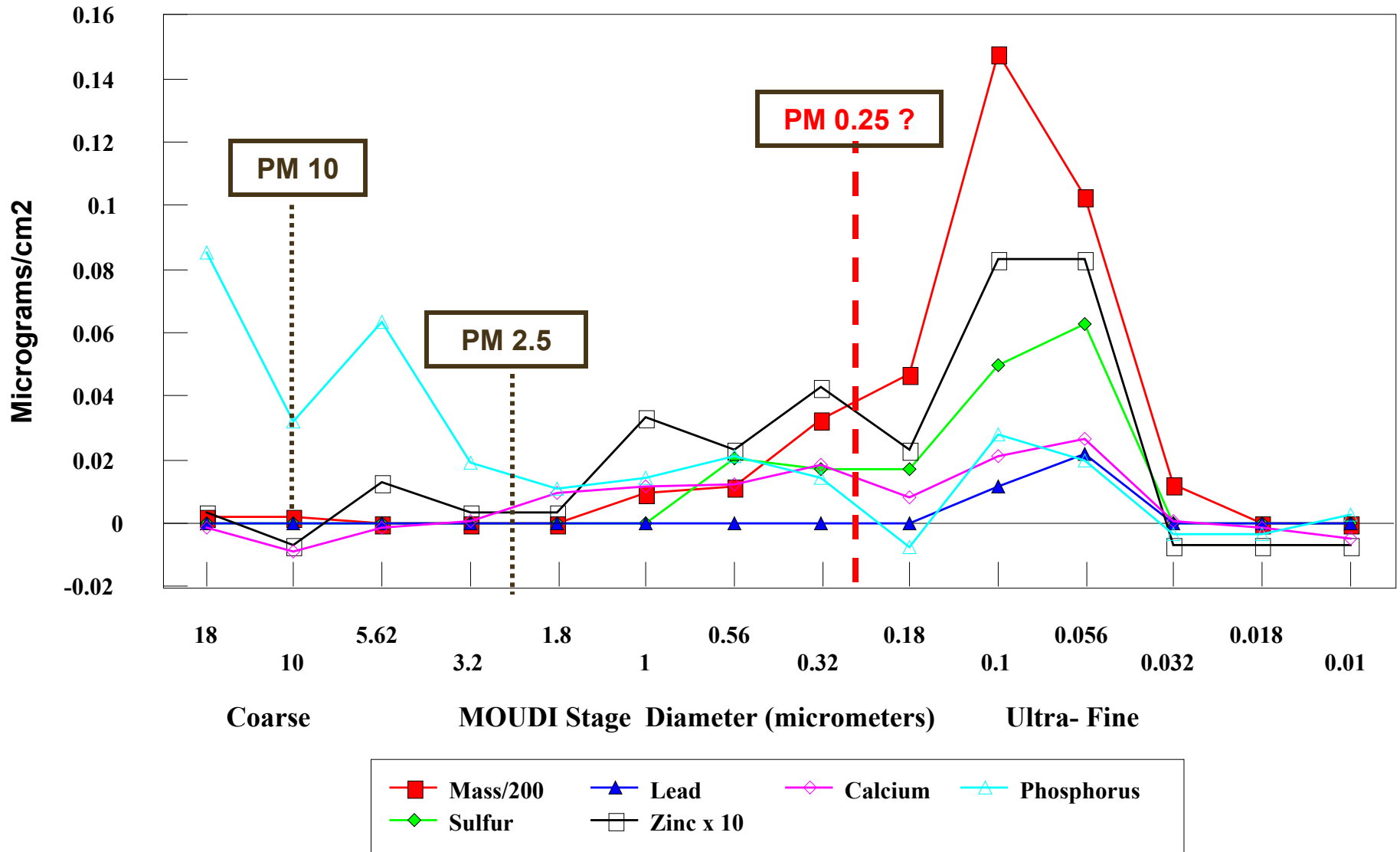
Very fine ( $0.26 > D_p > 0.09$  micron) elemental concentrations for FACES, CARB S-XRF analyses via DELTA Group, UC Davis





# Diesel Particles by MOUDI Impactor and S-XRF

Sample Run # 4, CA Fuel; no grease



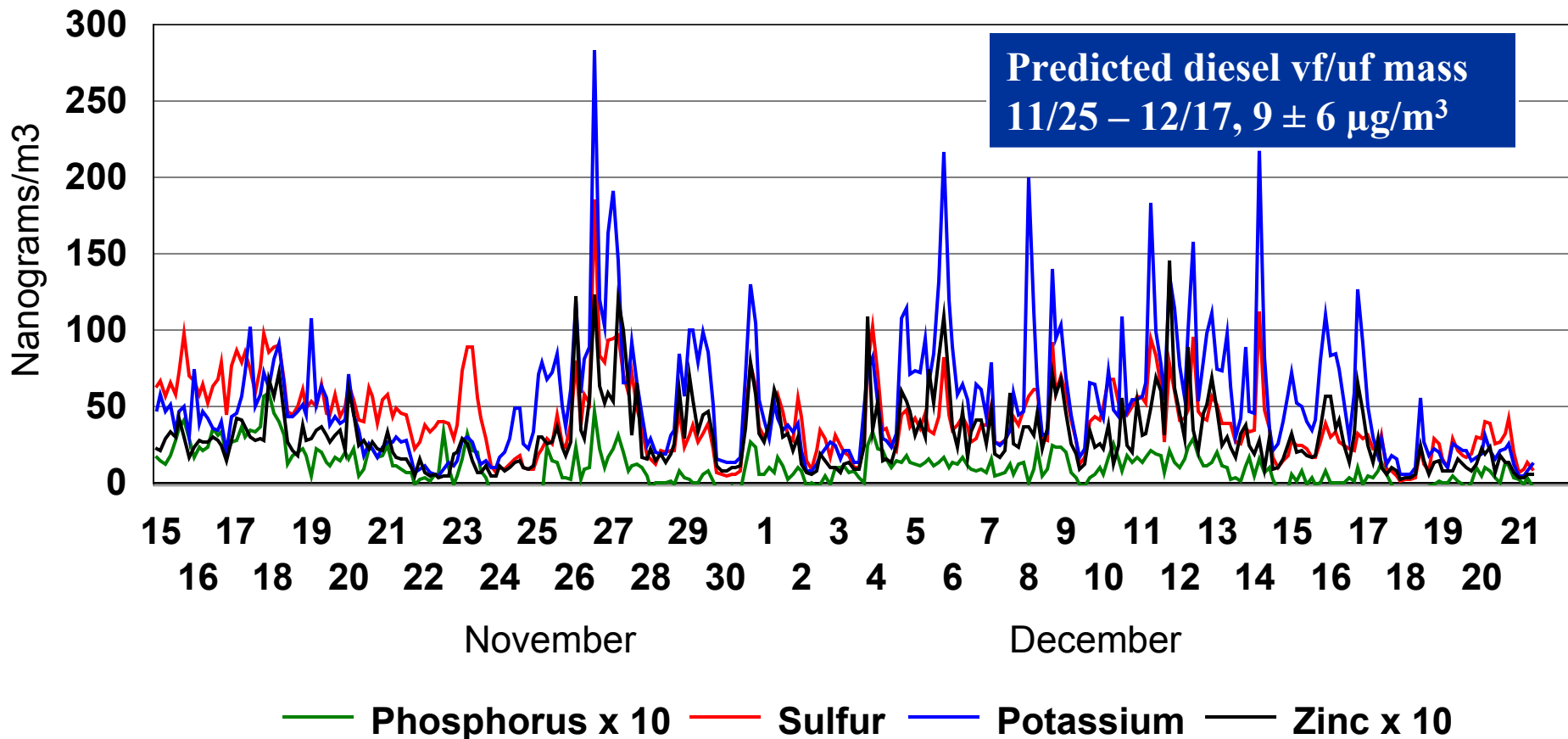
For micrograms/m<sup>3</sup>, times 8.7  
DELTA Group, S-XRF, UC Davis

**Very fine zinc to diesel mass = 1800 ± 1300**

# Very fine aerosols characteristic of diesels/smoking cars

## Aerosols at the Fresno First Street Super-site

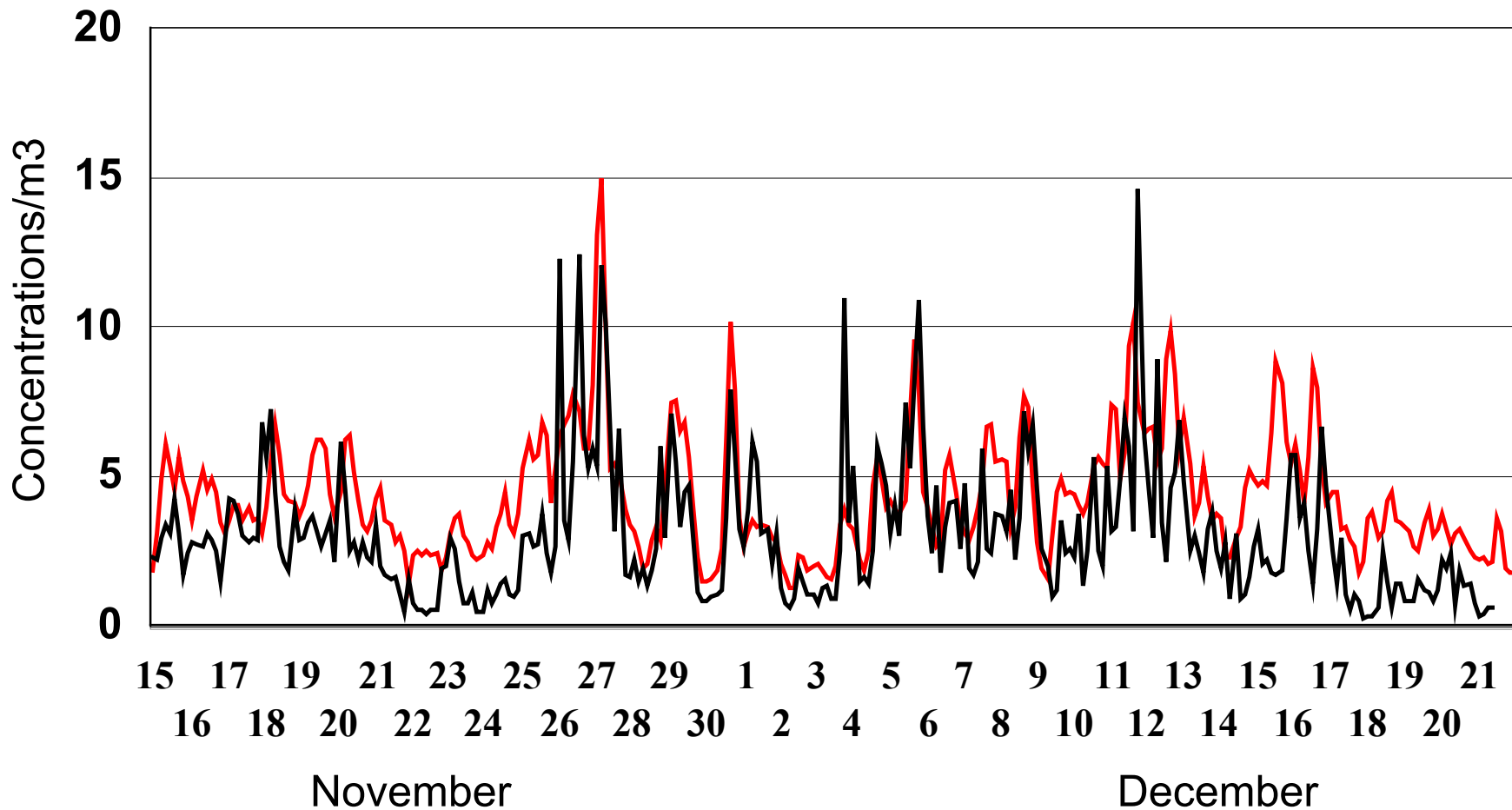
Very fine ( $0.26 > D_p > 0.09$  micron) elemental concentrations for FACES, CARB S-XRF analyses via DELTA Group, UC Davis



# Very fine ( $0.26 > D_p > 0.09$ ) Aerosols at Fresno, CA

— Mass by soft betas ( $\mu\text{g}/\text{m}^3$ )

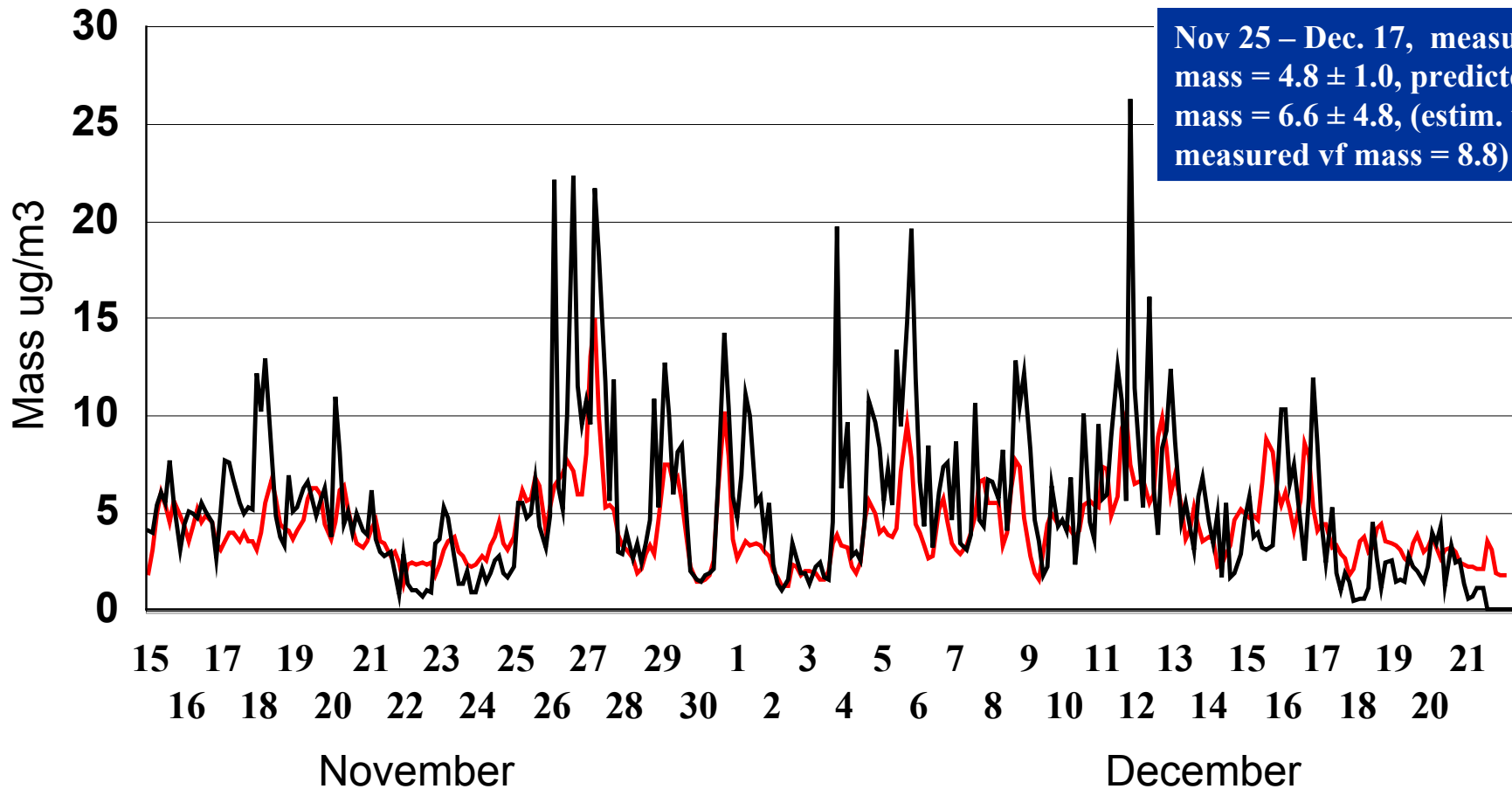
— Zinc by S-XRF ( $\text{ng}/\text{m}^3$ )



# Very fine ( $0.26 > D_p > 0.09$ ) Aerosols at Fresno, CA

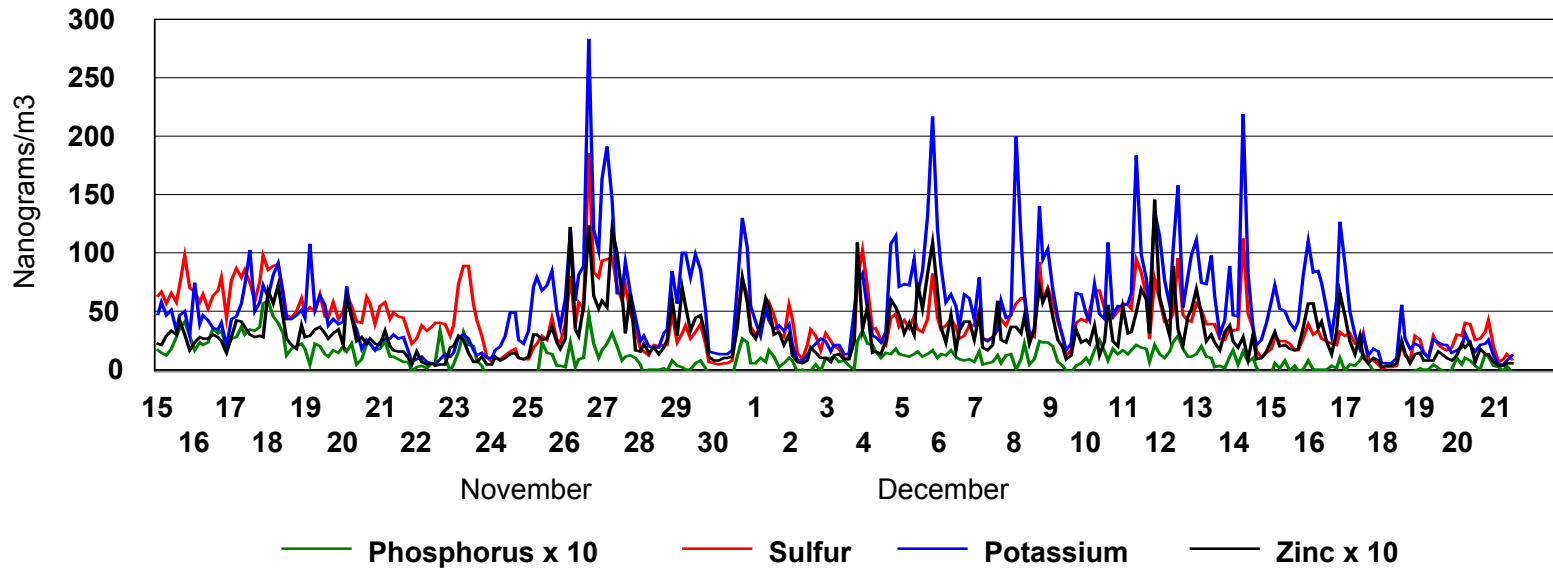
Supersite, First Street, > 1 km from nearest freeway

— Mass measured    — Mass predicted based on U. Minn. diesels, CA fuel



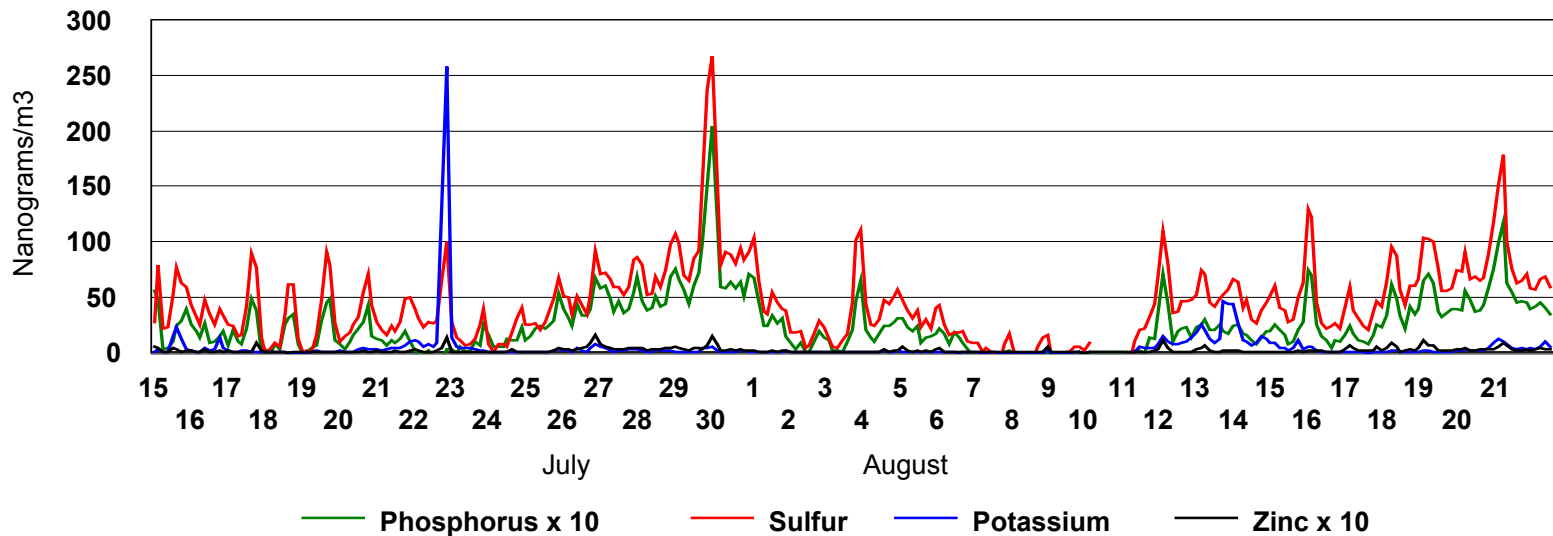
### Aerosols at the Fresno First Street Super-site

Very fine ( $0.26 > D_p > 0.09$  micron) elemental concentrations for FACES, CARB  
S-XRF analyses via DELTA Group, UC Davis



### Aerosols at the Fresno First Street Super-site

Very fine ( $0.26 > D_p > 0.09$  micron) elemental concentrations for FACES, CARB  
S-XRF analyses via DELTA Group, UC Davis

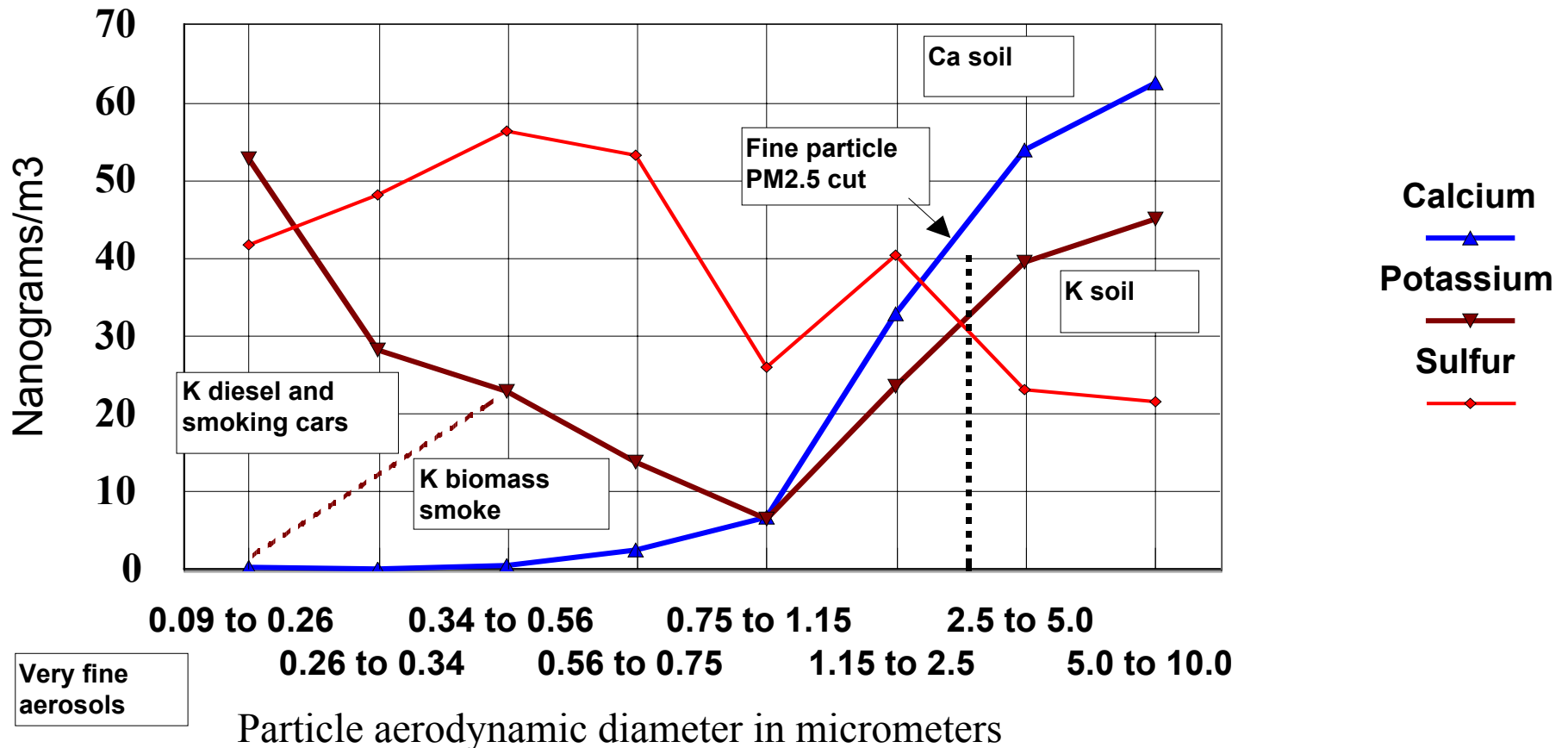


# Aerosol Information from Particle Size

## Aerosol size distributions at the Fresno Super-site

November 15 - December 22, 2001

Soil, biomass, and diesel/smoking car elements derived elements

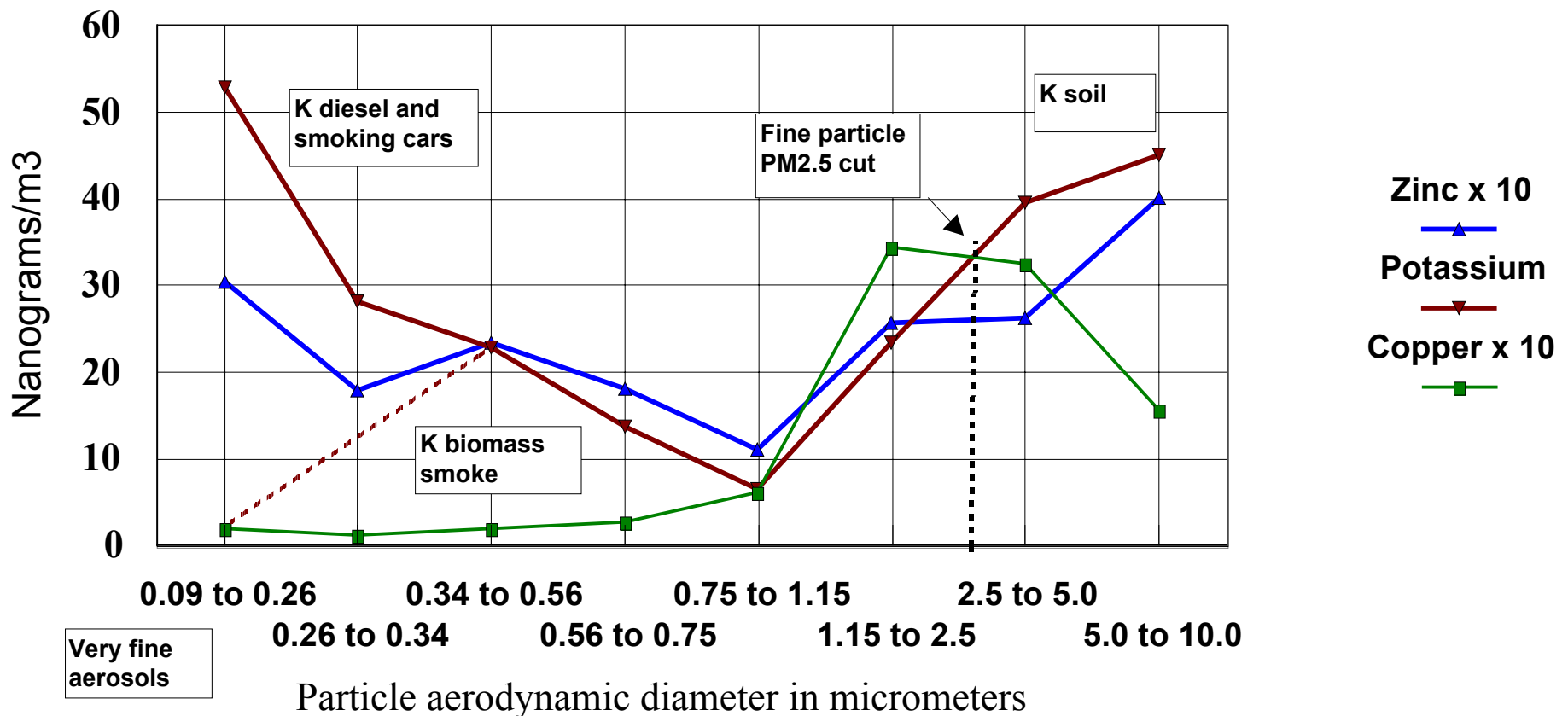


# Aerosol Information from Particle Size

## Aerosol size distributions at the Fresno Super-site

November 15 - December 22, 2001

Soil, biomass, and diesel/smoking car elements derived elements



# Conclusions

- We have provided 1500 distinct periods, mostly 3 hr (some 6 hr) duration for comparison with asthma data.
- In each of these periods, we can provide particle size (8 modes) and elemental composition (32 elements).
- We find that there are sharp (order of magnitude) excursions in transition metals of a few hours duration throughout the year.
- Winter time exhibits a high level of very fine particles associated with diesels and smoking cars.
- While there are inherent differences between continuous impactor sampling and filters, we have achieved excellent S-XRF quality assurance comparisons against ARB XRF, IMPROVE and university laboratories.





# Acknowledgements

- California Air Resources Board – Fresno FACES study
- National Renewable Energy Laboratory – DRI diesel tests
- Department of Energy - Lawrence Berkeley NL and the Advanced Light Source – S-XRF capabilities
- National Science Foundation – ACE-Asia DRUM samplers and development

