Overview of Characterization Methods for Submicron Particulate Matter (PM)

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General Characteristics of Submicron Particles

- Inertial properties are low—diffusion and phoretic effects predominate
- Isokinetic sampling is generally not critical
- Particles are of anthropogenic origin—little submicron PM is generated by natural processes such as wind-blown dust
- Combustion (internal and external) sources are most important—condensation and nucleation are primary particle forming mechanisms

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Characteristics (continued)

- Particle size distribution tends to be both lognormal and bimodal (nuclei and accumulation modes)
- Characterization of submicron PM is far more difficult than for supermicron PM requiring sophisticated methods and equipment
- Particle number concentration could be more important than mass concentration in health effects studies

On-Line Mass Measurement Techniques

- Tapered-element oscillating microbalance (TEOM)
- Quartz-crystal microbalance (QCM)
- Beta-attenuation mass monitors
- Mass transfer of volatiles—on/off collected sample is important in PM mass measurements

On-Line Techniques for Number Concentration

- Aerosol photometers
- Condensation nuclei counters (CNCs)
- *In-situ* single-particle optical counters and ensemble analysis techniques
- Extractive instruments generally limited to low particle concentrations—usually requires diluted sample stream

Techniques for Particle Size Distribution Measurement

- Electrical, quartz-crystal, and manual low-pressure cascade impactors (~ 30 nm to 10 μm aerodynamic diameter)
- Laser velocimeters (> 0.5 μm aerodynamic diameter)
- Scanning mobility particle sizer (differential mobility analyzer + CNC; 2 to ~ 500 nm electrical mobility diameter)

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Particle Size Distribution (continued)

- Serial- and parallel-flow diffusion batteries (with and without CNCs)
- Single-particle optical counters
- Data reduction and interpretation for most particle sizing instruments require considerable expertise especially when comparing data from different instruments

Manual Sample Collection/Analysis Techniques

- Filter sampling (e.g., prefired quartz filters for elemental/organic carbon)
- Electrostatic and thermal precipitators
- Scanning electron microscopy (with and without X-ray analysis for elemental composition)
- Electron microscopy can provide physical verification of other measurement techniques within certain limitations

On-Line Chemical Characterization Methods

- Photoelectric ionization sensors for polycyclic aromatic hydrocarbons
- Optical attenuation instruments for “black” and “blue” carbon
- Automated thermal/CO_2 analyzers for elemental/organic carbon
- On-line analyzers can provide near real-time results but must be validated against manual method for each source

Chemical Characterization of Collected Samples

- Elemental/organic carbon by NIOSH Method 5040
- Elemental composition by X-ray diffraction or X-ray fluorescence
- Water-soluble ions (e.g., SO_3^-) by ion chromatography
- Organic speciation by gas chromatography/mass spectroscopy
- Sample analyses are generally expensive and time consuming

Calibration Issues

- Most analyzers for submicron PM are essentially “black boxes” requiring substantial operator experience
- Calibration standards for nanoparticles are limited at best
- Dynamic instrument calibration is both expensive and difficult to implement
- Conversions between various particle conventions (e.g., aerodynamic diameter to electrical mobility diameter) require numerous assumptions and associated potential errors

Sources Recently Tested by APPCD

- Heavy-duty diesel engines
- Residential wood stoves and fireplaces
- Biomass burning
- Wood- and wood-waste-fired boilers

Contact Information

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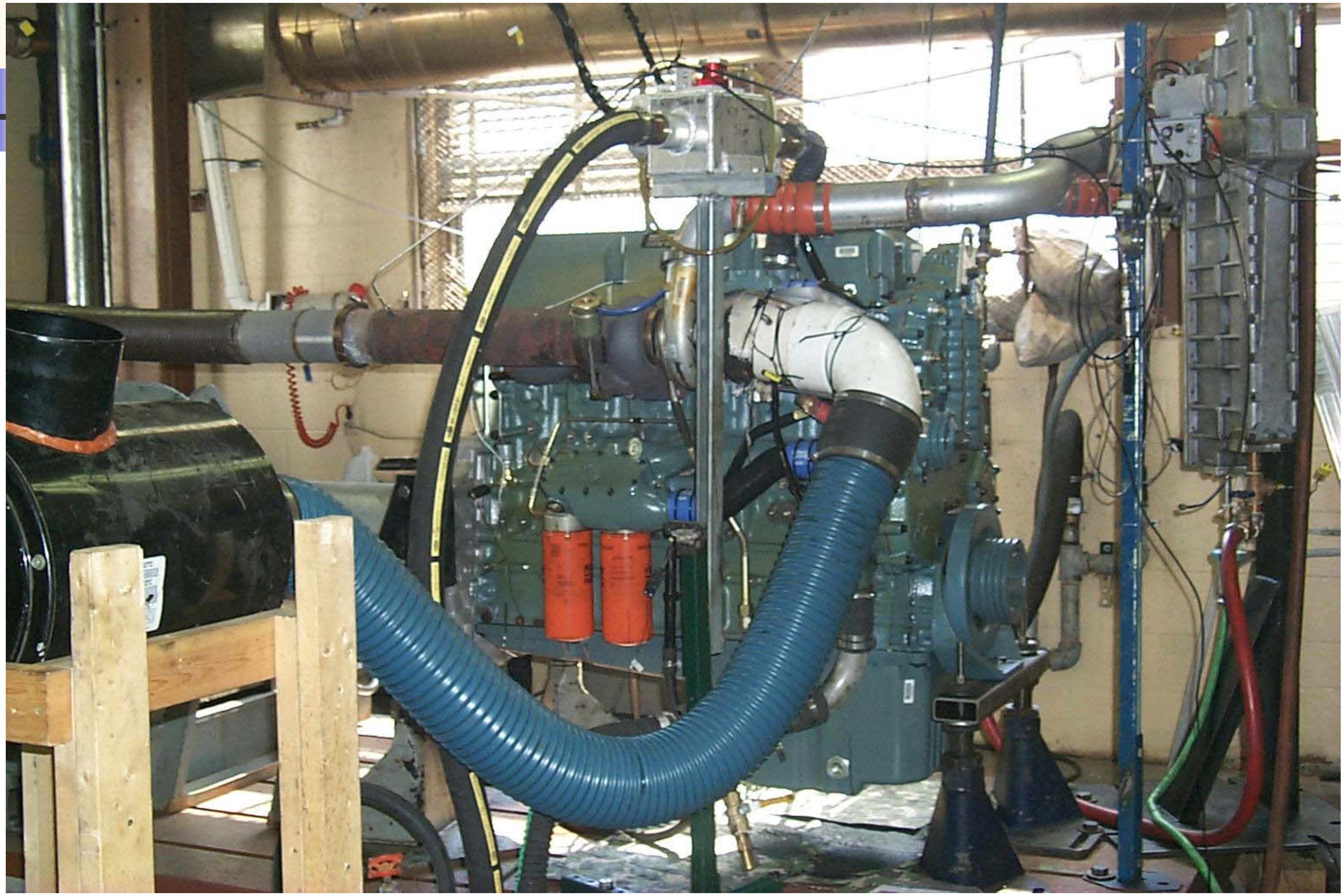
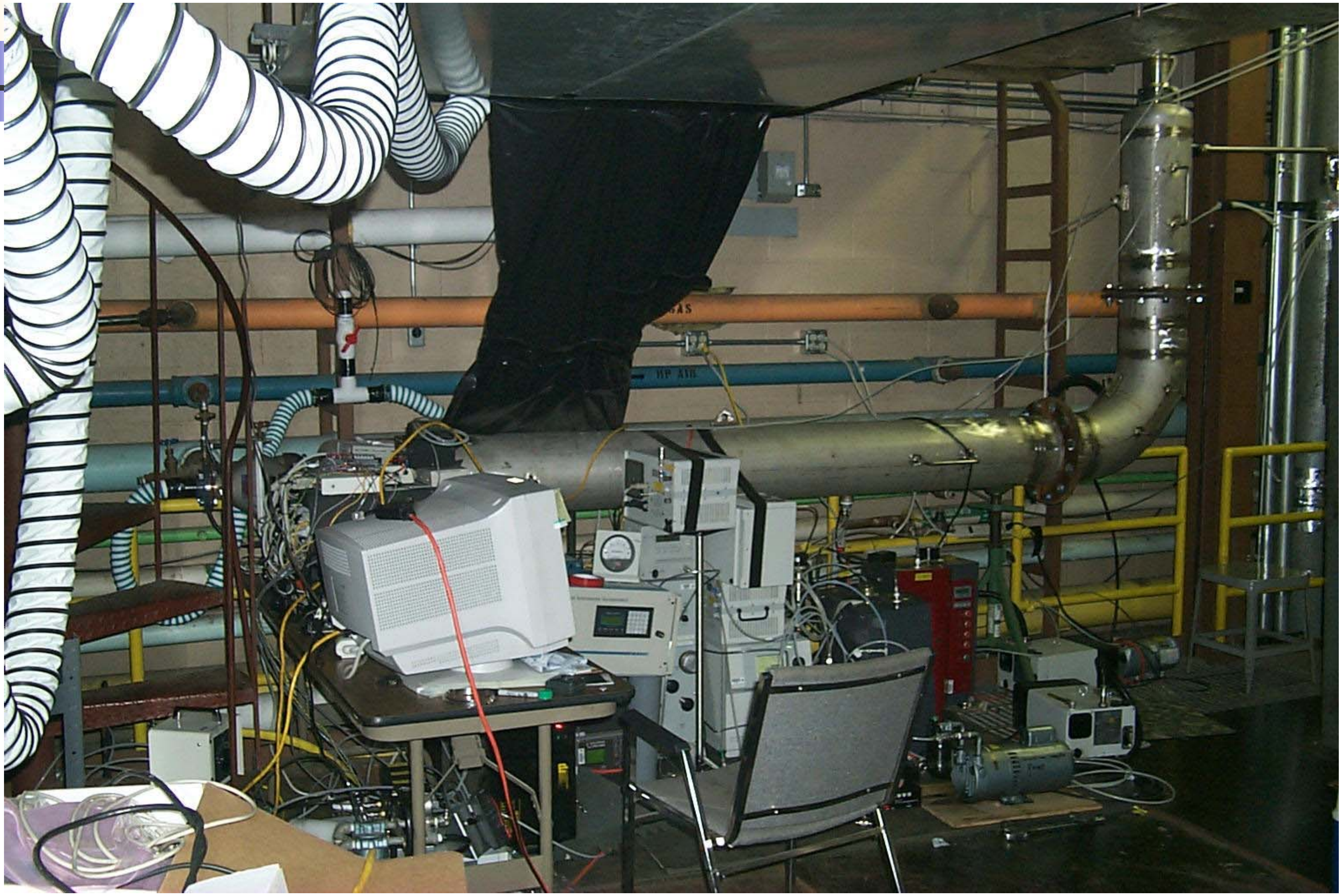
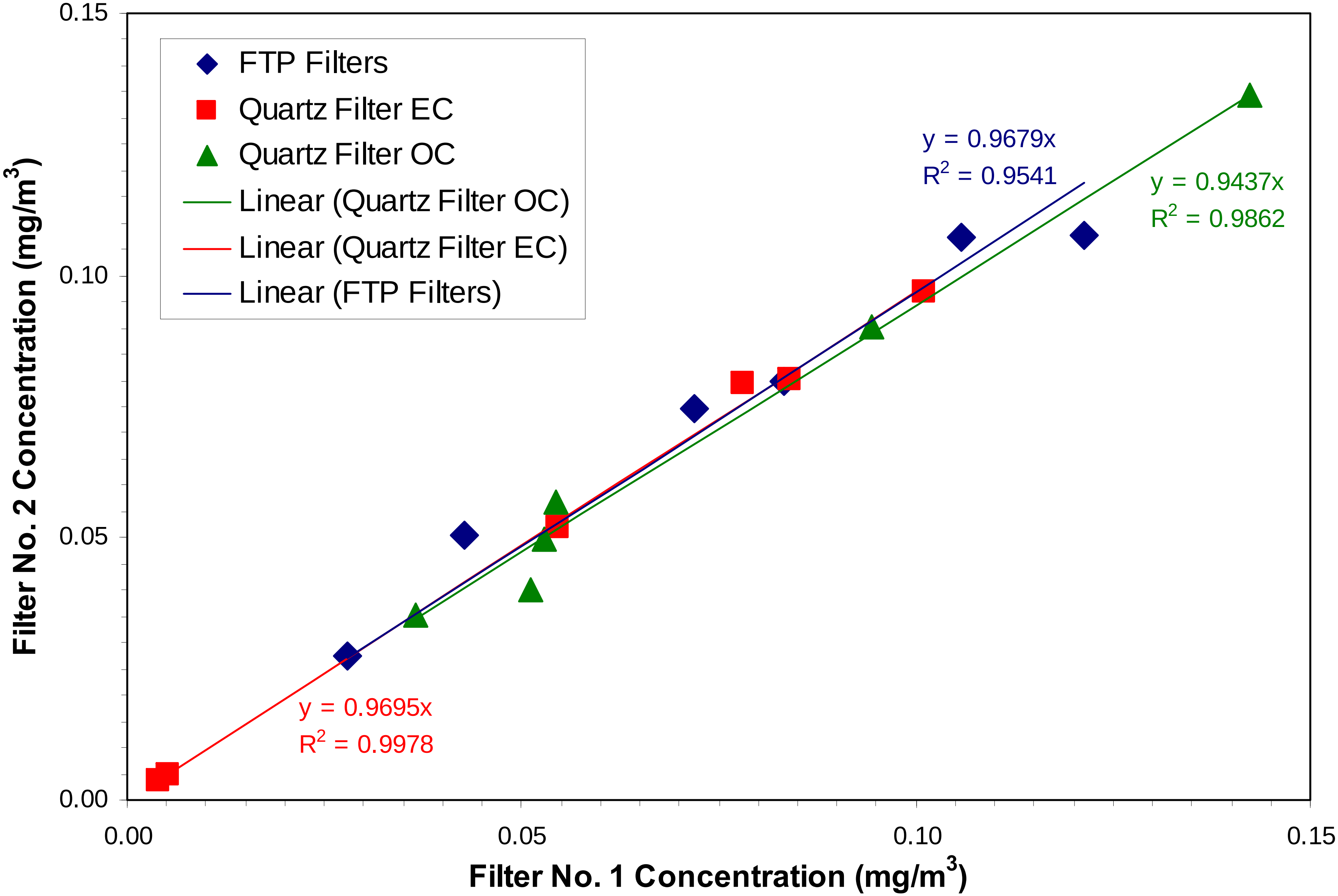
DD 60 on Engine Dynamometer



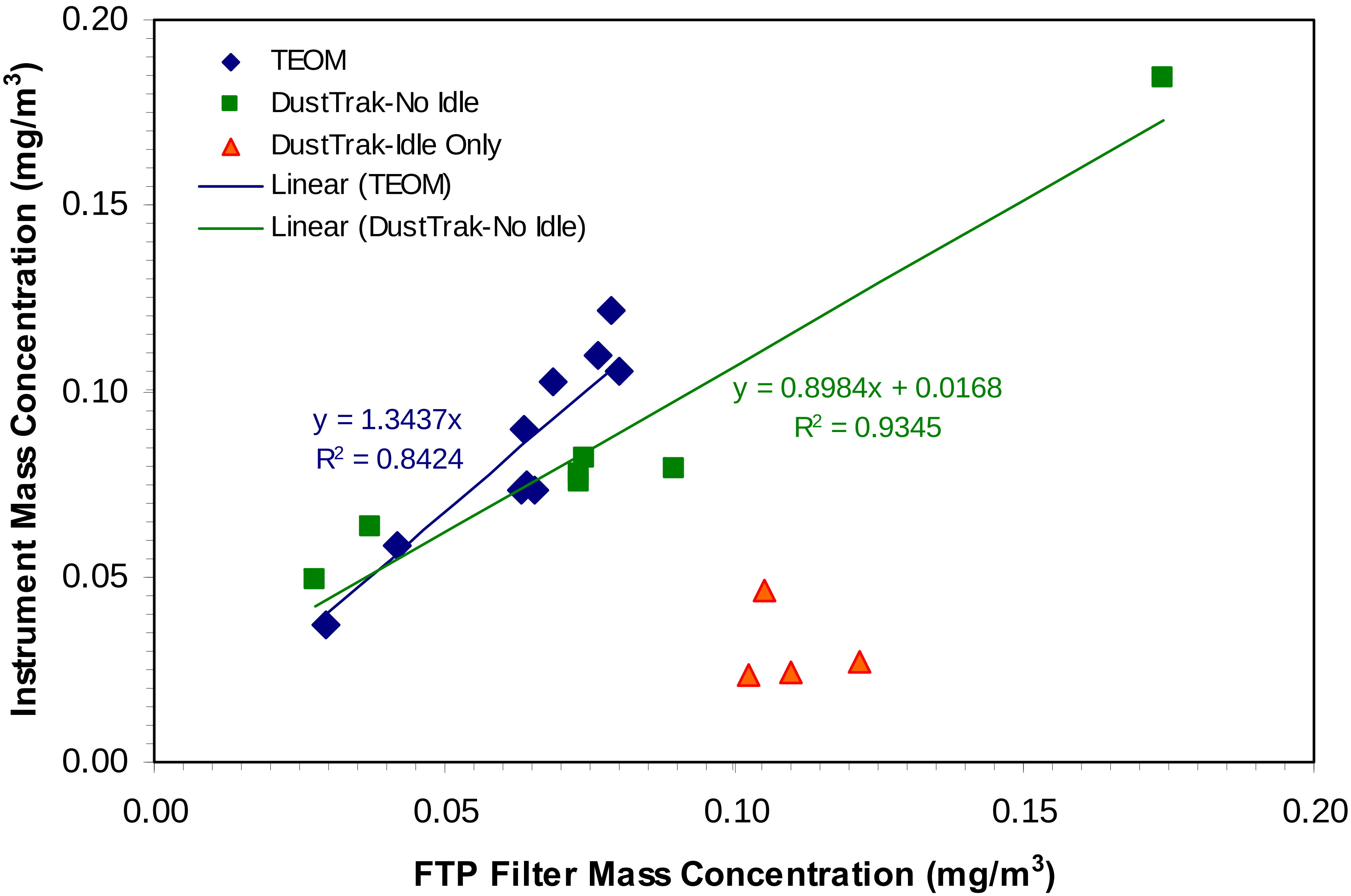
Secondary Tunnel and Instruments



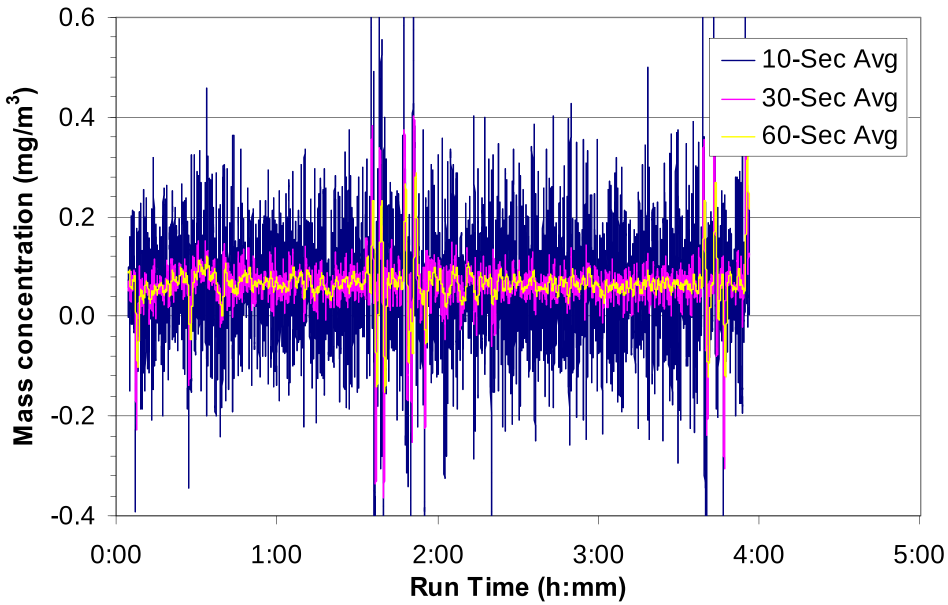
Comparison of Paired Filter Samples

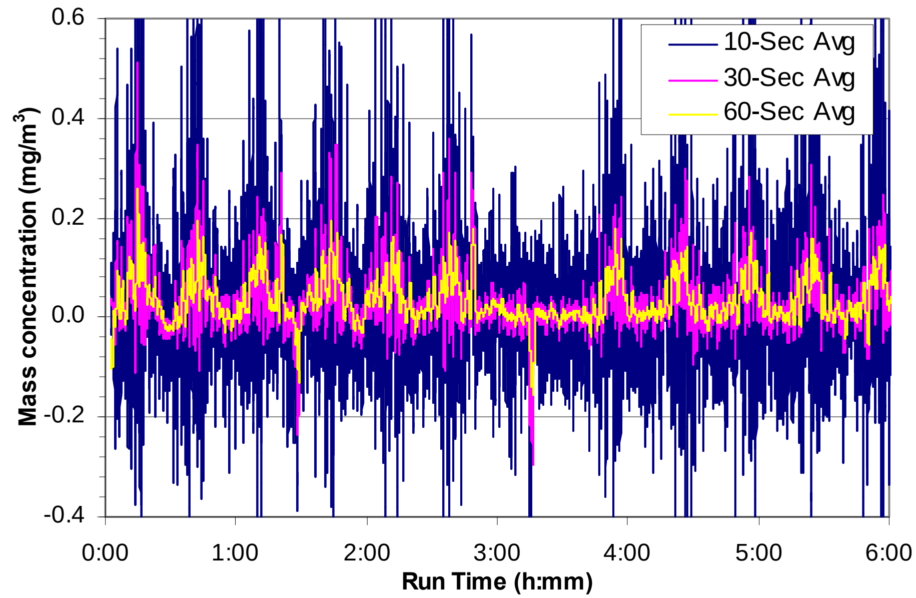


Values for TEOM, DustTrak, and Filter Samplers



Time for Steady-State and Cyclic Operation

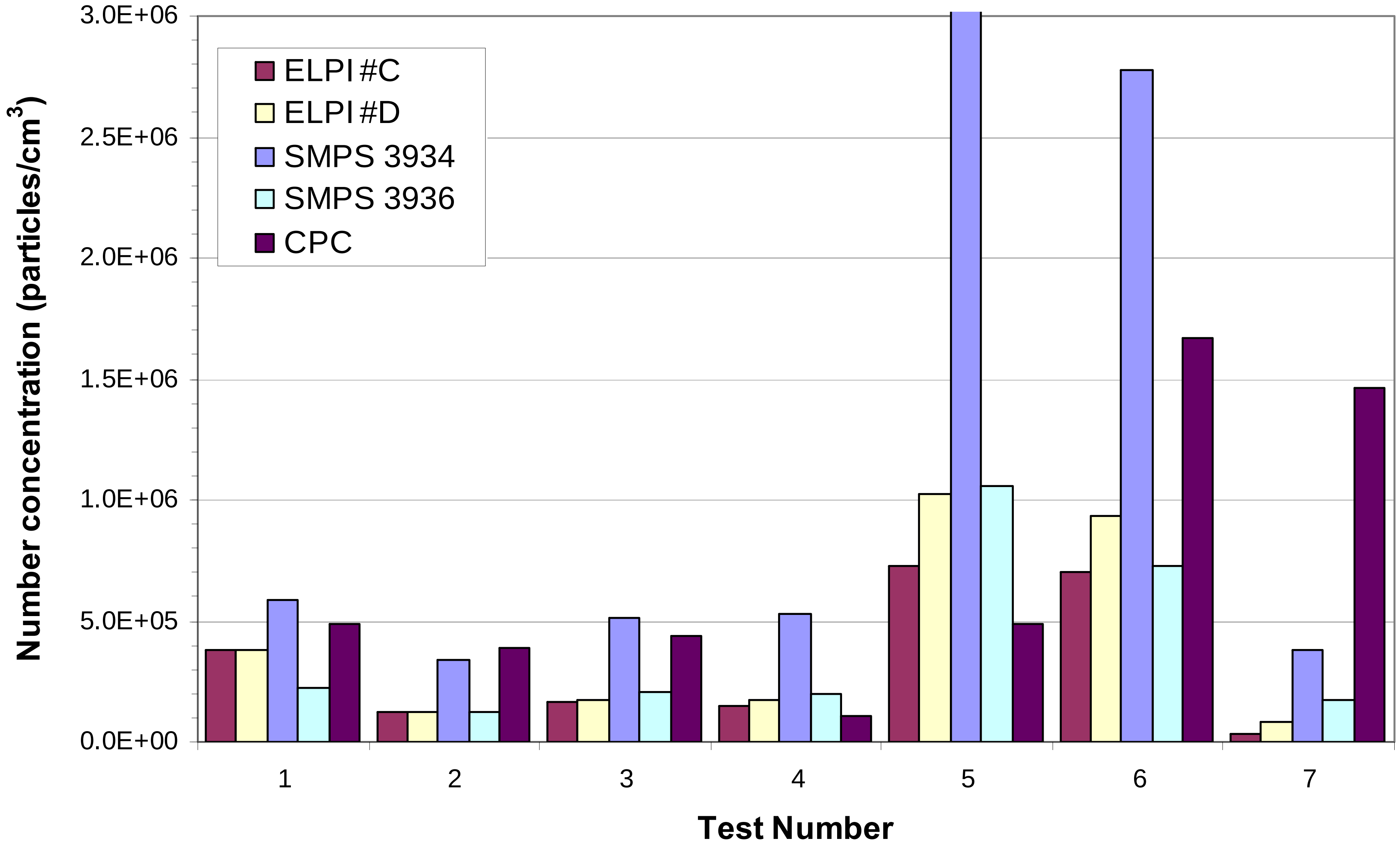




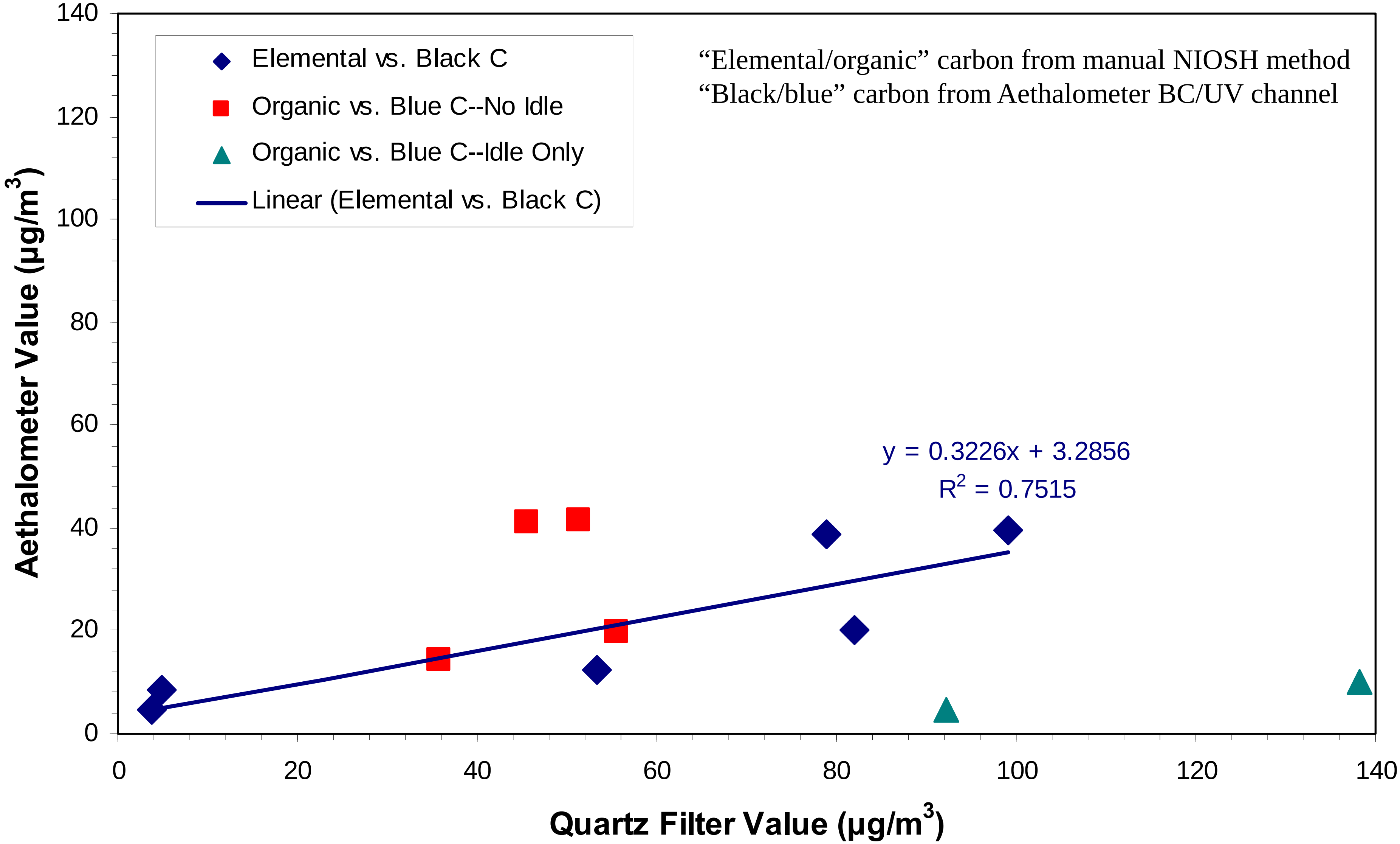
200 HP; Steady-State (Test 4)

FTP Cycles (Test 7)

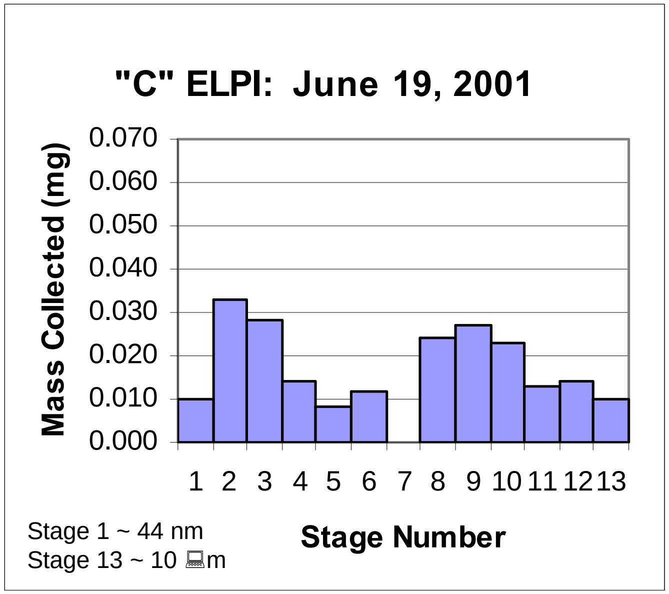
Particle Number Concentration as Measured by Different On-Line Instruments

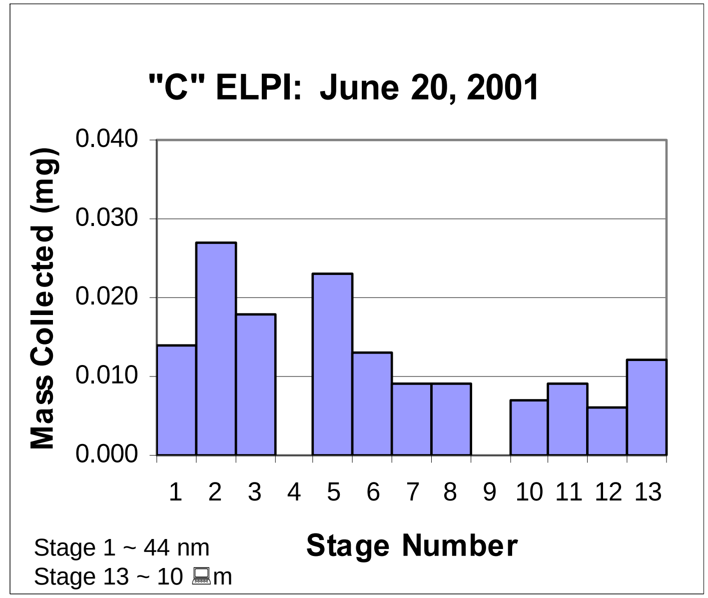


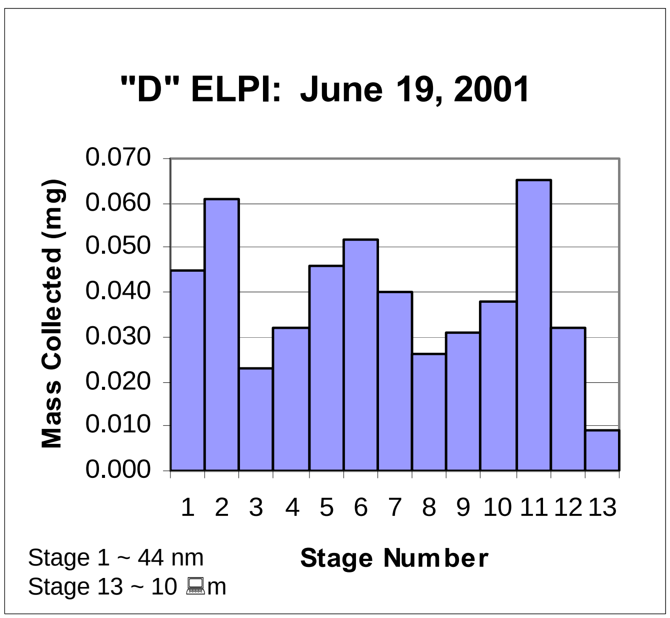
Quartz Filters vs. Aethalometer Measurements

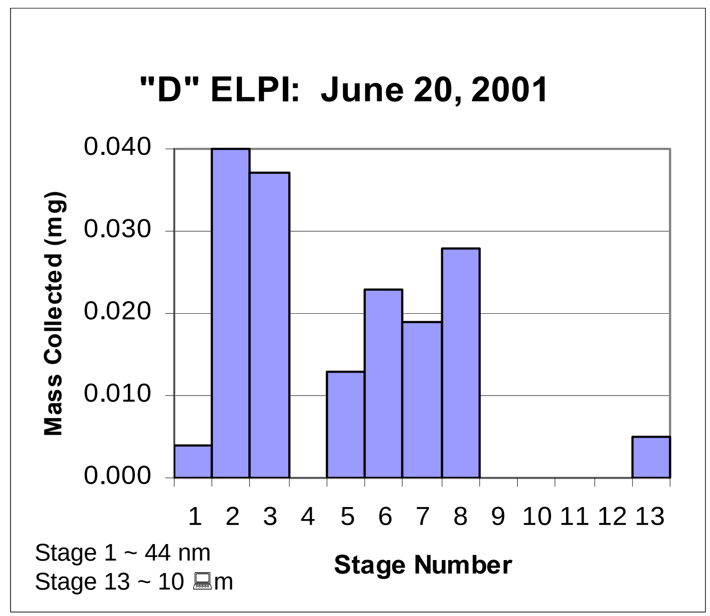


ELPI Mass Distribution Comparison: 200 HP

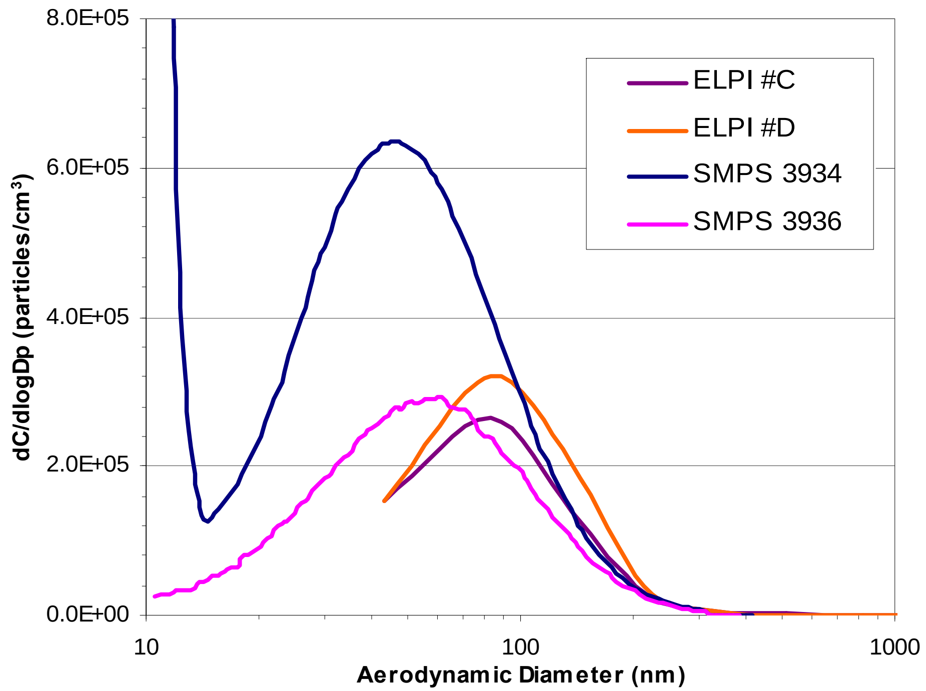


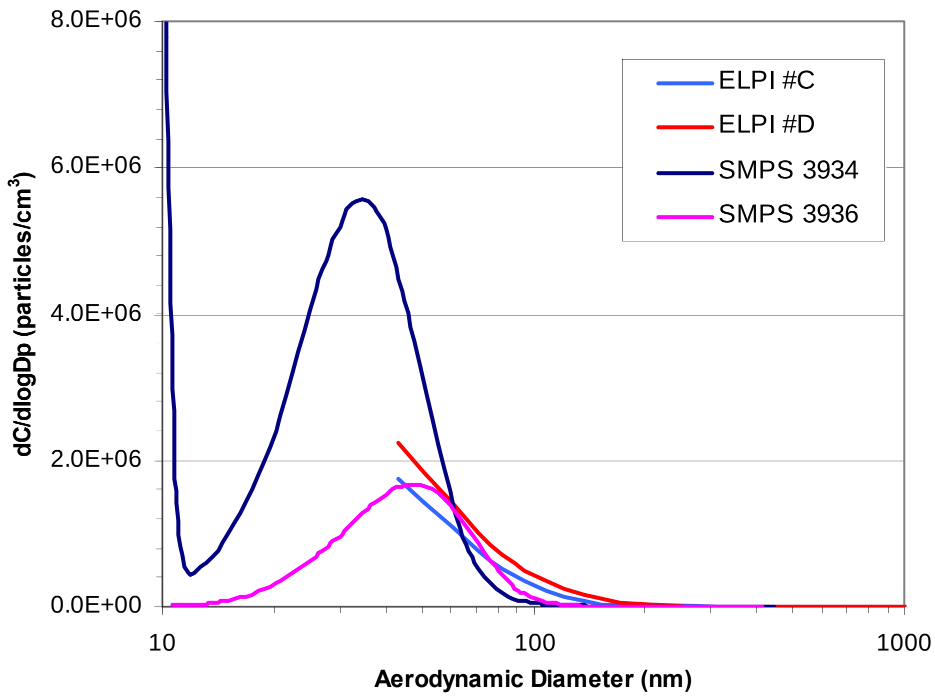






Example ELPI and SMPS Size Distributions

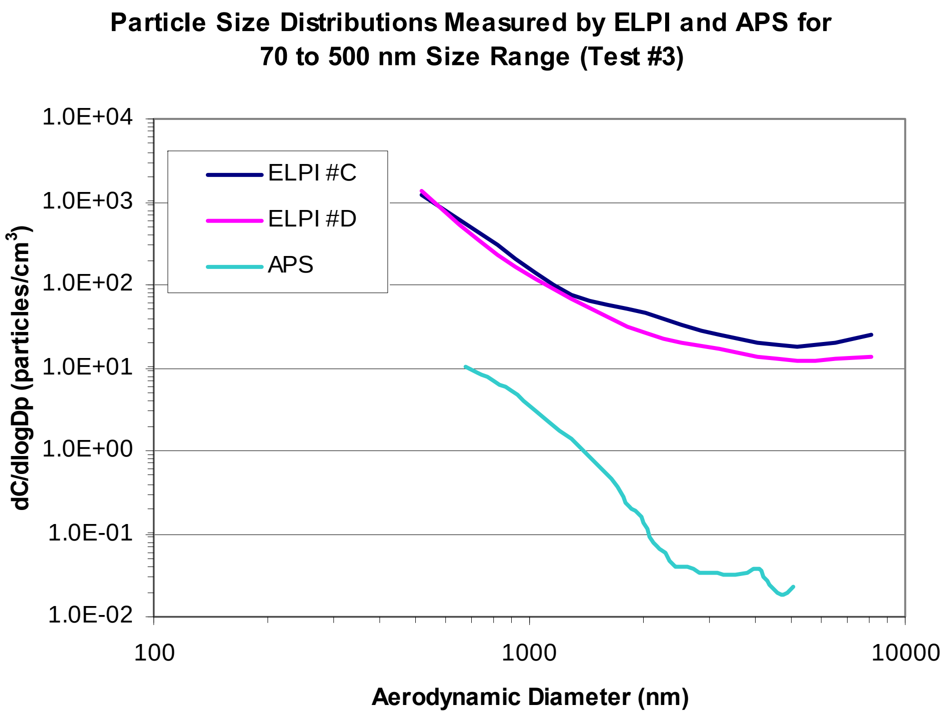




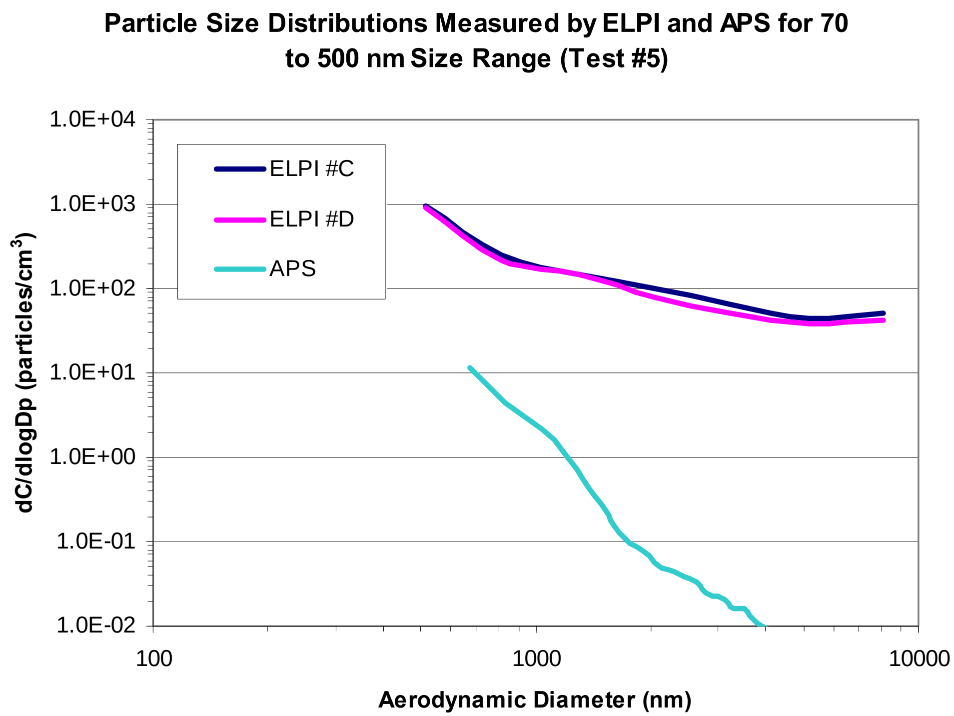
200 HP; Steady-State (Test 4)

Fast Idle (Test 6)

Example ELPI and APS Particle Size Distributions (0.7 to 5 µm Aerodynamic Diameter)



200 HP; Steady-State (Test 3)



Fast Idle (Test 5)

Current Findings (1)

- Good precision was achieved during the analysis of filter catches for split samples.
- Comparison of manual vs. automated methods showed mixed results--some instruments (e.g., TEOM) correlated reasonably well, whereas others (e.g., DustTrak) were highly dependent on engine operating conditions.
- Certain types of paired analyzers (e.g., SMPS) exhibited different response characteristics and/or produced substantially different results.
- The 1105a TEOM provided a highly variable data output with many negative values—data are generally not useful for averaging times less than one minute.

Current Findings (2)

- Chemical analysis of the ELPI samples were not conducted due to:
  - low sample weights;
  - inconsistencies in the gravimetric results between the two instruments; and
  - Problems with lost samples due to poor collection substrate preparation.
- Both PAH analyzers were found to be malfunctioning after being returned to the manufacturer for post-test calibration.
- Easy, inexpensive, and field-capable calibration methods/equipment are needed for all analyzer types to assure high quality data collection.
- Second round of testing scheduled for November 2002 at WVU