Characteristics and Measurement of Nanoparticles from Engines

Presented by

Prof. David Kittelson*

Center for Diesel Research
University of Minnesota
Department of Mechanical Engineering
Minneapolis, MN

Chairman's Air Pollution Seminar, California EPA,

Sacramento, CA

Monday, March 18, 2002

*The work described has involved many investigators including Professor Peter McMurry, Dr. Hiromu Sakarai, Dr. Win Watts, Mr. Jason Johnson and Mr. Kihong Park of the University of Minnesota and Professor Paul Ziemann of the University of California, Riverside.

Ongoing research on engine generated particulate matter at the University of Minnesota

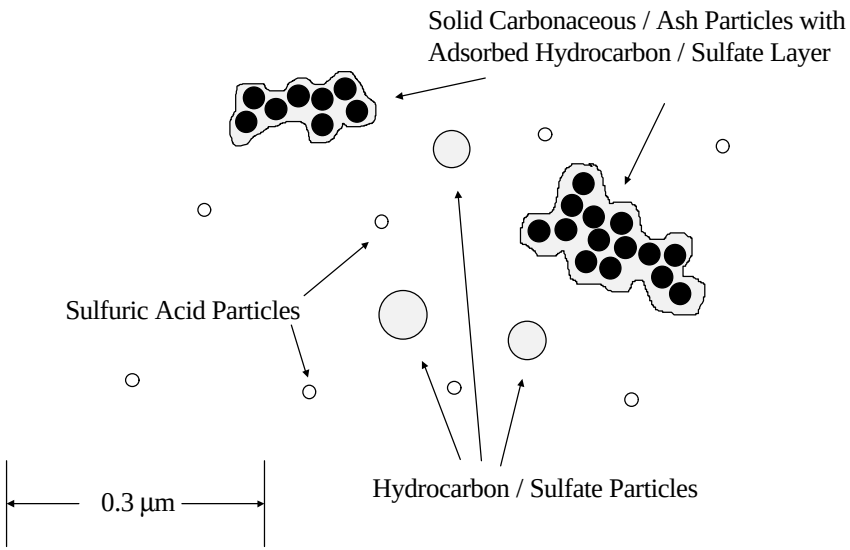
- CRC E-43 - Diesel Aerosol Sampling Methodology
  - Sponsors: CRC, DOE, EMA, SCAQMD, CARB, Cummins, Caterpillar, and Volvo.
- Gasoline Vehicle Exhaust Particle Sampling Study
  - Sponsor: DOE
- Nanoparticles on Minnesota Highways
  - Sponsor: Minnesota Department of Transportation
- Chemical Analysis of Diesel Nanoparticles Using a Nano-DMA/Thermal Desorption Particle Beam Mass Spectrometer
  - Sponsor: CARB – U of M is subcontractor, Ziemann's group at UC Riverside prime
- Density, Volatility, and Hygroscopicity of Diesel Particles
  - Sponsor: EPA, DOE – Peter McMurry's group lead
- Characterization of Diesel Exhaust Aerosols – Sampling, Fuel, Lube, and Aftertreatment Issues
  - Sponsors: Caterpillar, Cummins, Volkswagen, Johnson-Matthey, BP, Corning

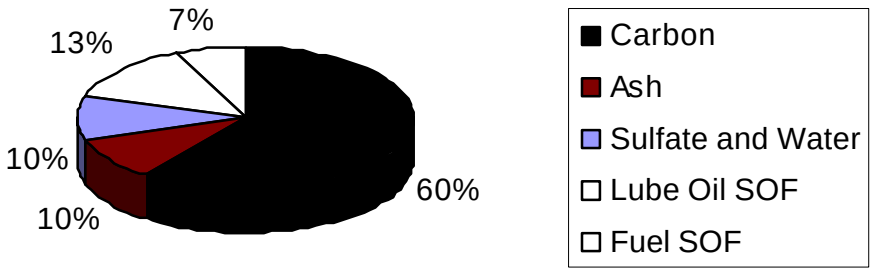
Outline

- In recent years many concerns have been raised about ultrafine and nanometer sized particles from engines.
- This presentation will discuss physical and chemical properties of the two main submicron size modes – the nuclei and accumulation mode
  - Structure and Size
  - Where they are found
  - How they form
  - Likely composition
  - New measurement methods

Typical Composition and Structure of Diesel Particulate Matter

- Solid particles are typically carbonaceous chain agglomerates and ash and usually comprise most of the particle mass
- Volatile or semi-volatile matter (sulfur compounds and organics) typically constitutes 30% (5-90%) of the particle mass, 90% (30-99%) of the particle number
- Carbon, sulfur compounds, and organics derive from fuel
- Organics, ash, sulfur compounds, and carbon derive from oil
- Most of the volatile and semi-volatile materials undergo gas-to-particle conversion as exhaust cools and dilutes



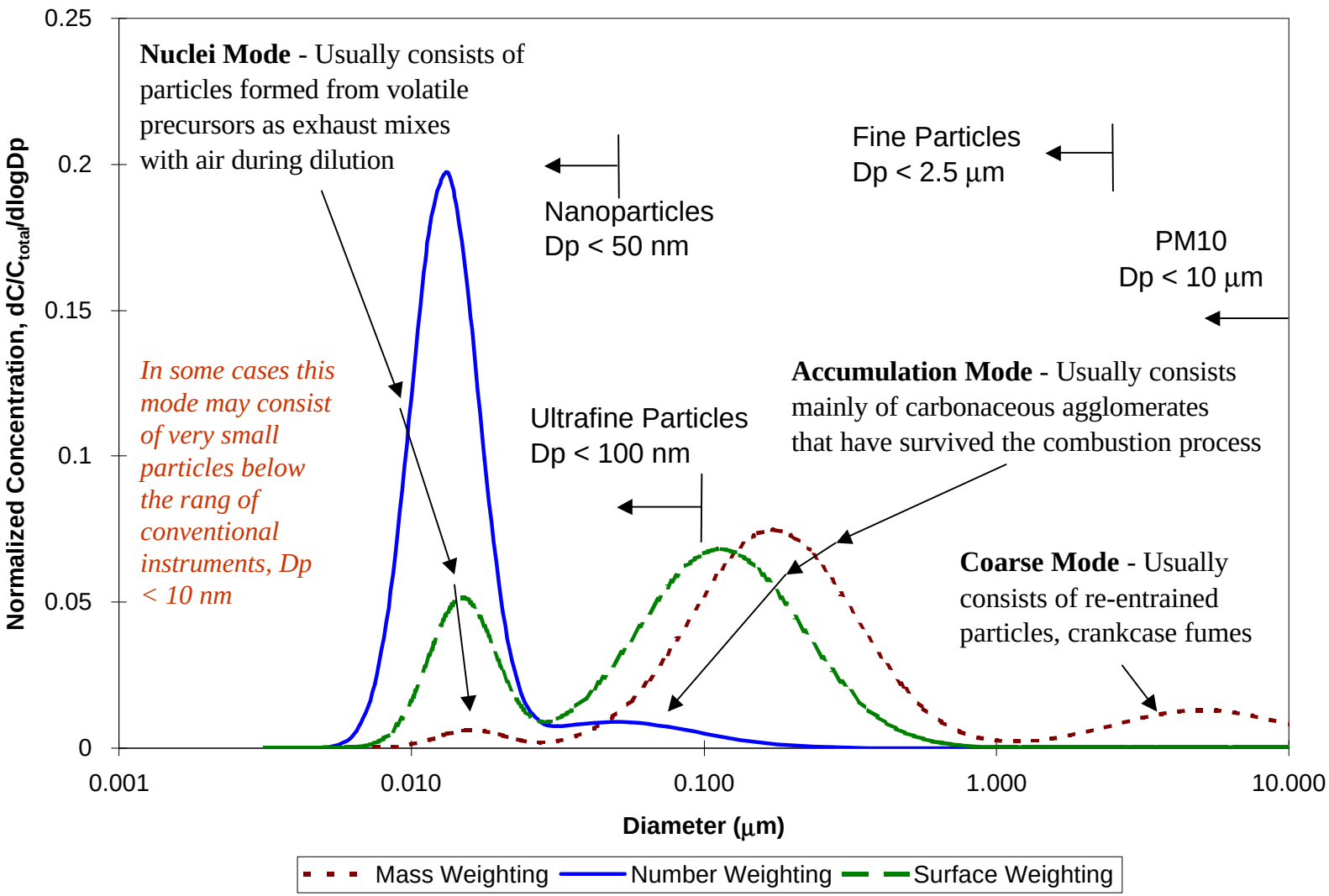


TDPBMS measures the volatility and mass spectra of the volatile fraction of *all* the particles in selected size ranges between 15 and 300 nm - Summary Results

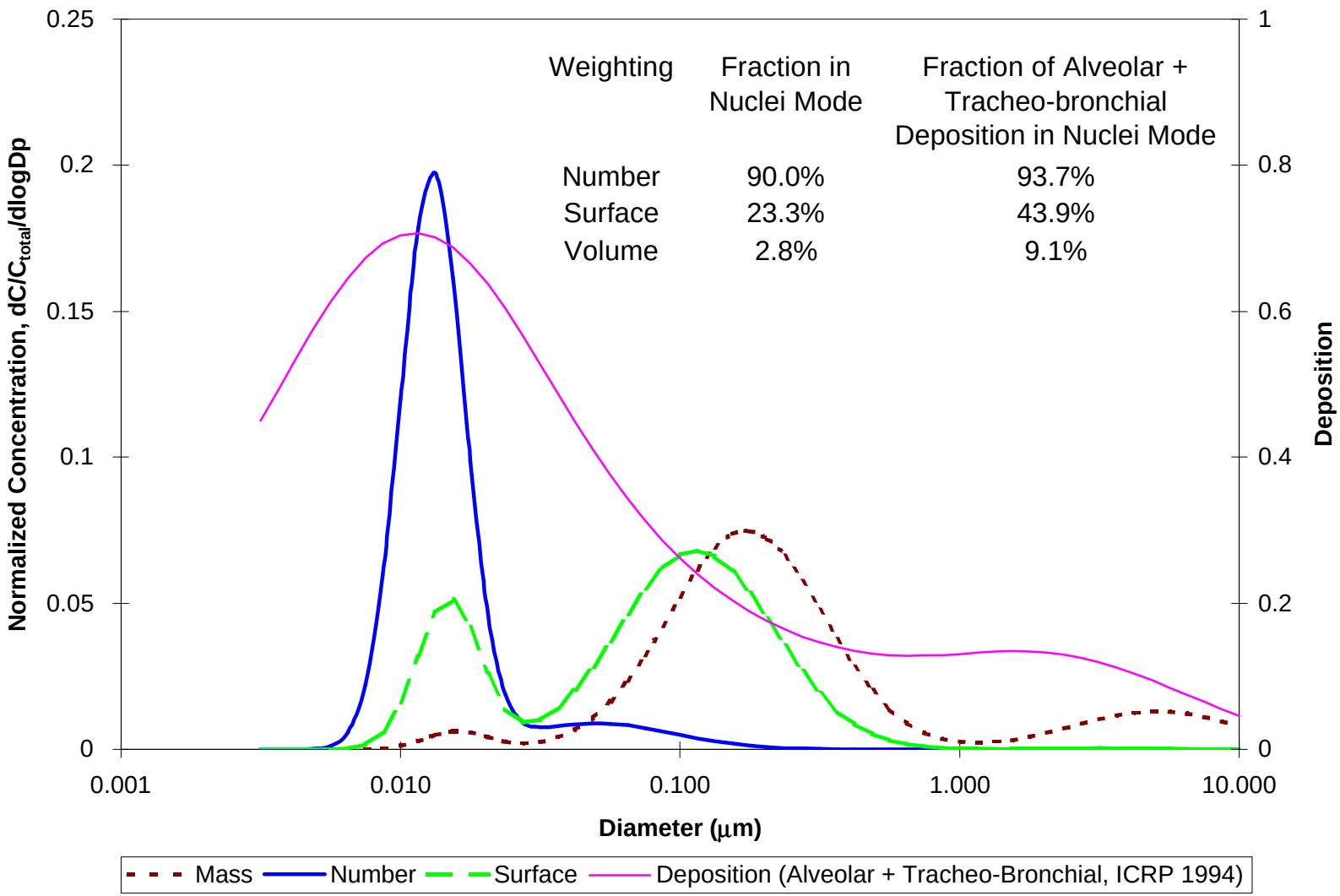
- Engines
  - Deere 4045T medium-duty
  - Caterpillar C12 heavy-duty
  - Cummins ISM
- Fuels
  - Federal pump fuel, 360 ppm S
  - California pump fuels, 50 and 96 ppm S
  - Fischer-Tropsch, < 1 ppm S
- Test conditions
  - Light and medium load

- Composition of volatile fraction
  - Organic component of total diesel particles and nanoparticles appears to be mainly unburned lubricating oil
  - Major organic compound classes are alkanes, cycloalkanes, and aromatics
  - Low-volatility oxidation products and PAHs have been found in previous GC-MS analyses, but are only a minor component of the organic mass
  - Nanoparticles formed with higher S Federal pump fuel contain small amounts of sulfuric acid but those formed with the lower S fuels show no evidence for sulfuric acid

Typical Diesel Particle Size Distributions, Number, Surface Area, and Mass Weightings Are Shown



Particles in the Nuclei Mode Play a Larger When Respiratory Deposition is Considered



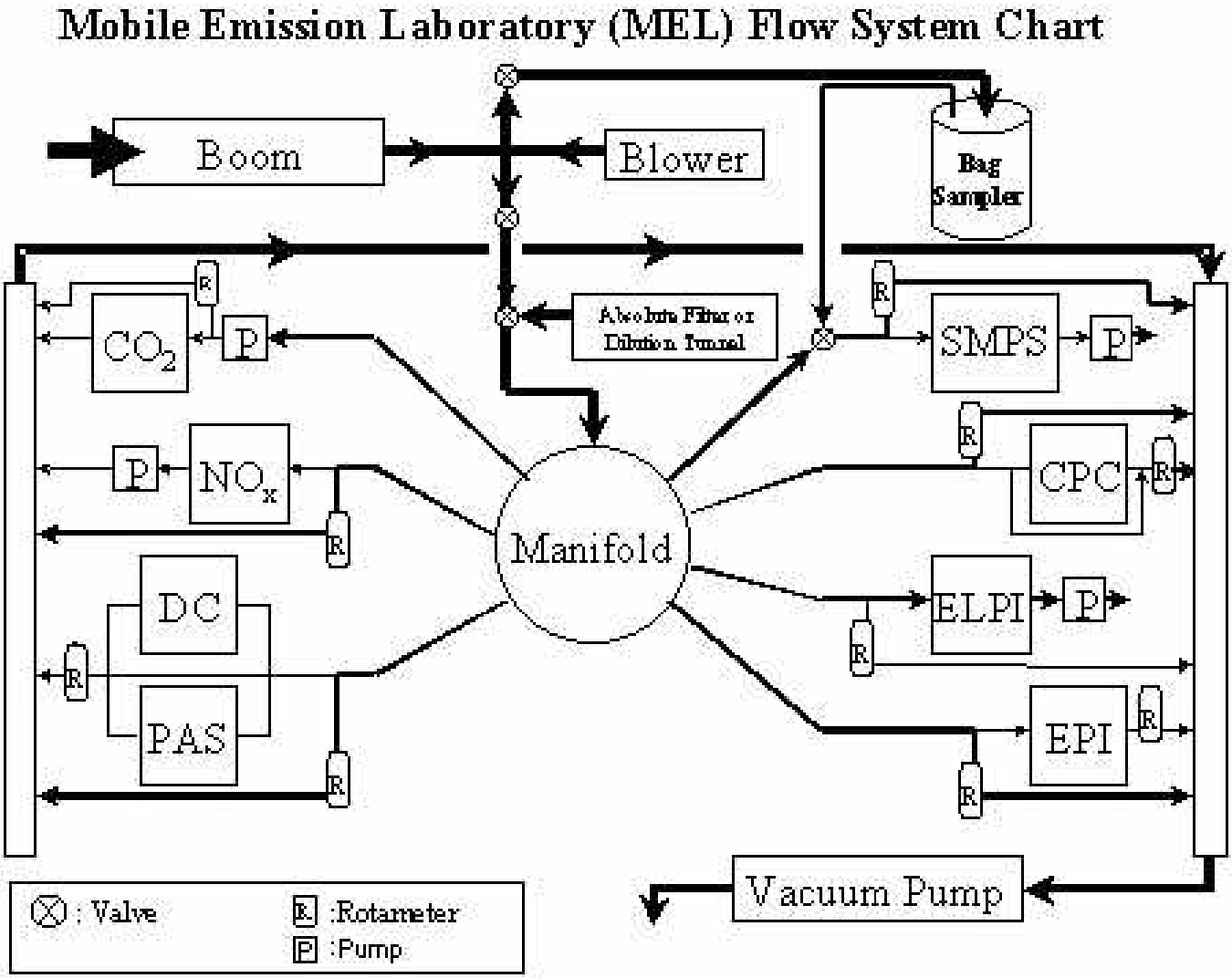
Nuclei Mode Particles Exist in Large Concentrations over Roadways

- Measurements made with University of Minnesota Mobile Laboratory
- Large concentrations observed in presence of both Diesel and spark ignition traffic
- The nuclei mode forms rapidly in the diluting plumes of vehicles – time scale seconds
- Nuclei mode decays rapidly downwind of roadway – time scale minutes

- The focus here is on nucleation in diluting exhaust plumes, nucleation also occurs in the atmosphere as a result formation of low vapor species by atmospheric chemistry but usually on a longer time scale

U of M Mobile Laboratory built to study formation of nanoparticles in the atmosphere for the CRC E-43 project

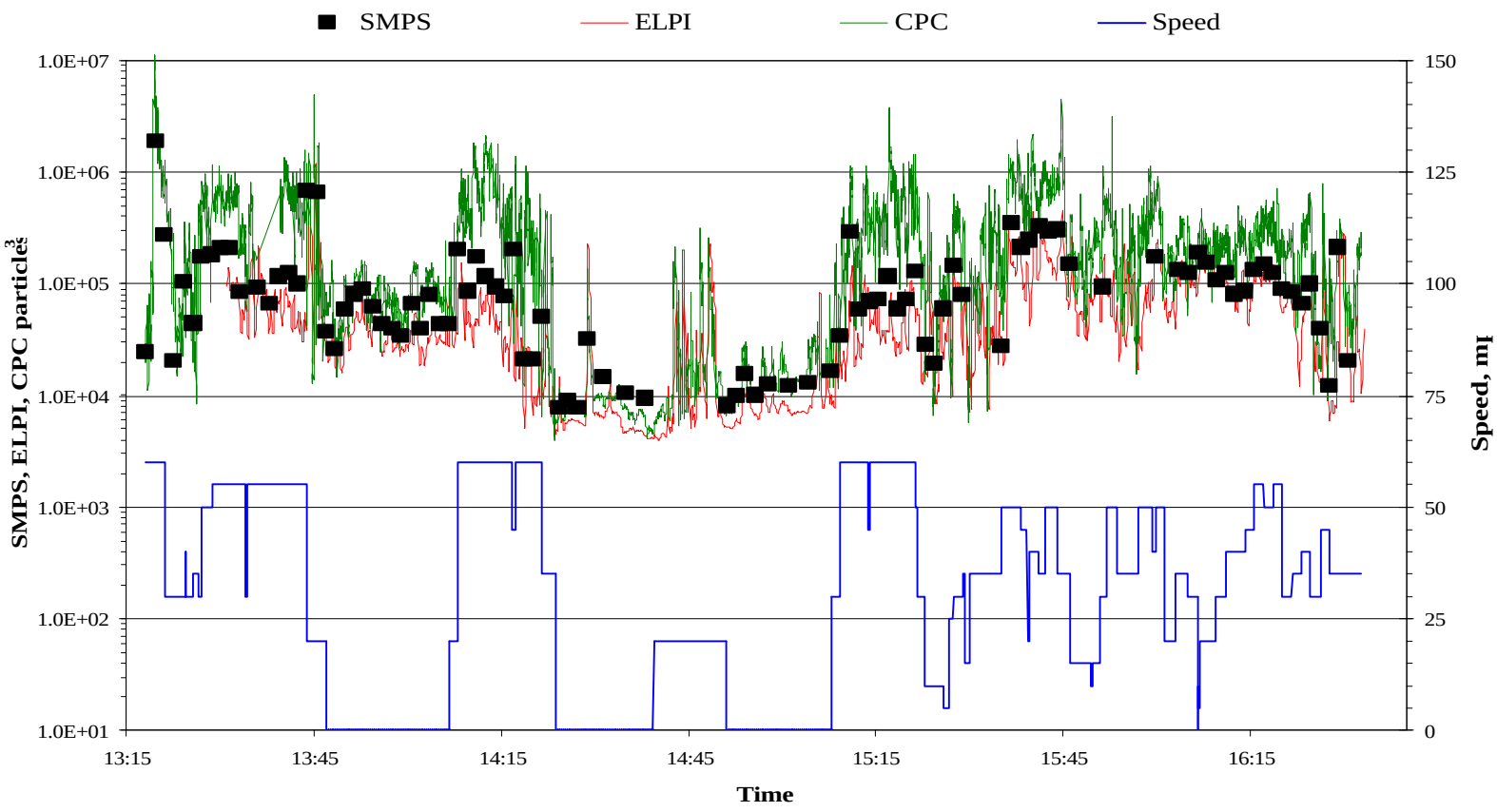
Instrument and Sampling Arrangement in Mobile Emission Laboratory



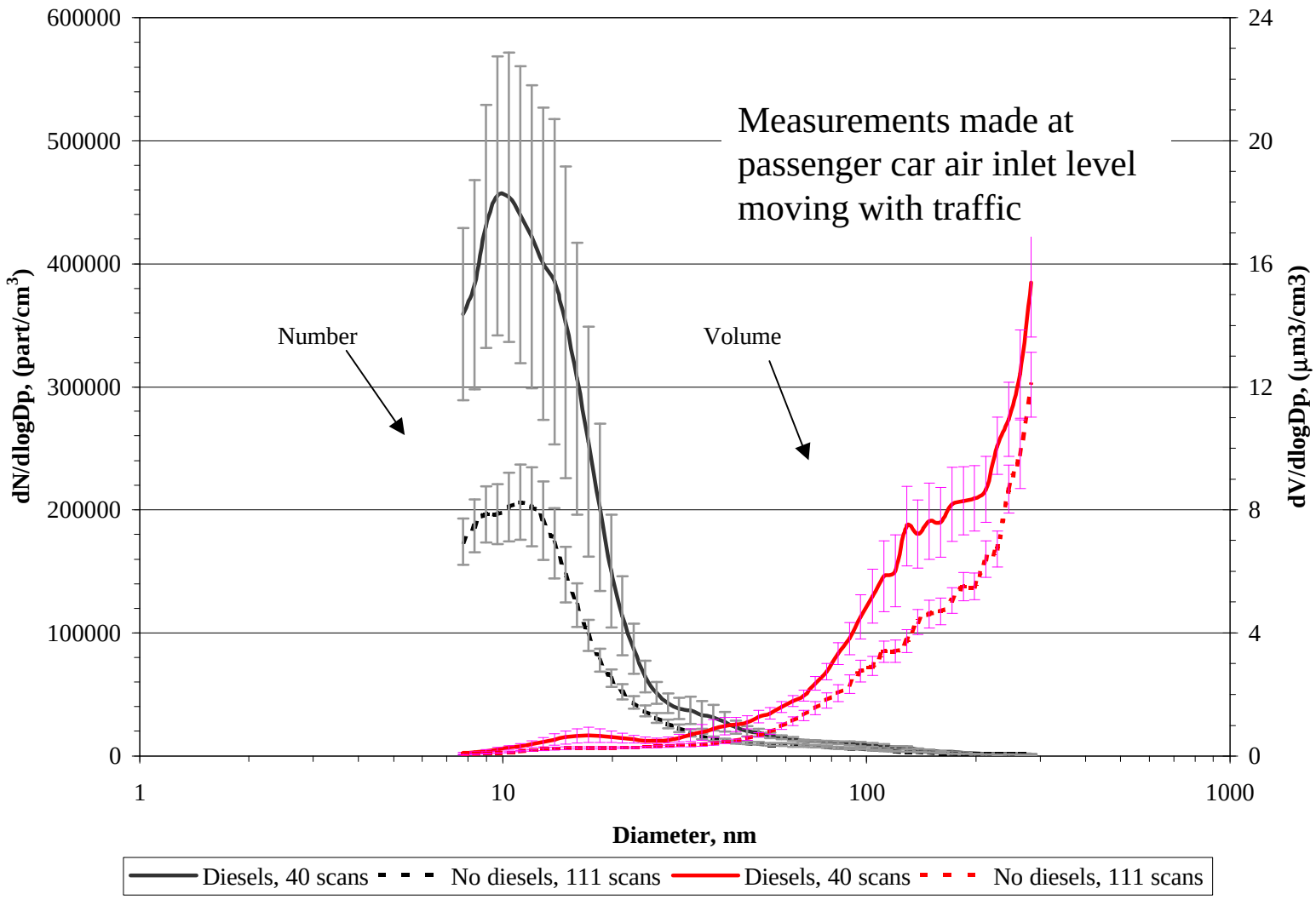
Principal Instruments in MEL

- SMPS to size particles in 9 to 300 nm size range
- ELPI to size particles in 30 to 2500 nm size range
- CPC to count all particles larger than 3 nm
- Diffusion Charger to measure total submicron particle surface area
- Epiphaniometer to measure total submicron particle surface area
- PAS to measure total submicron surface bound PAH equivalent
- CO_2 , CO, and NO analyzers for gas and dilution ratio determinations

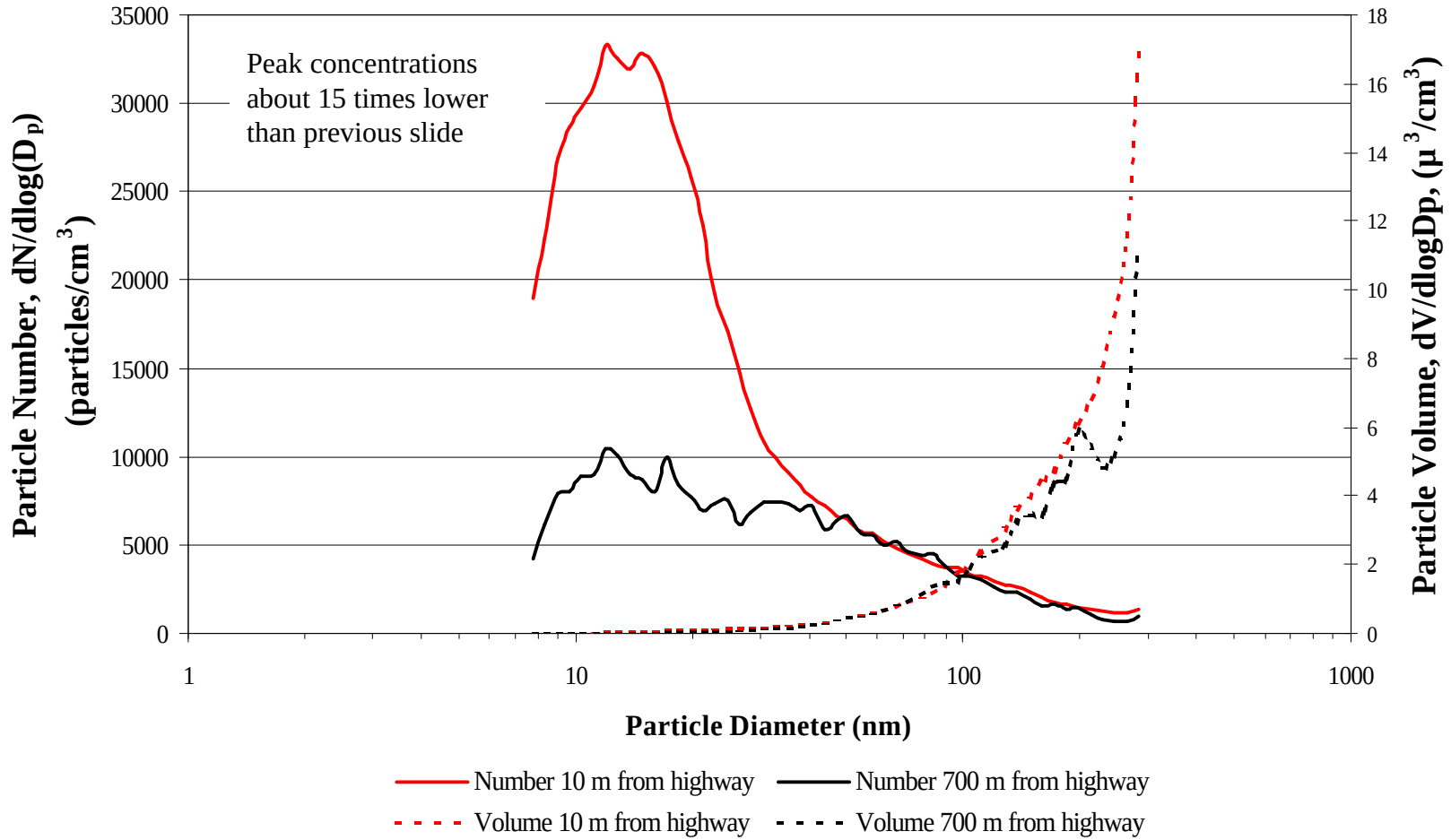
Typical Roadway Data



Nanoparticles exist over Minnesota highways – both with and without significant Diesel traffic

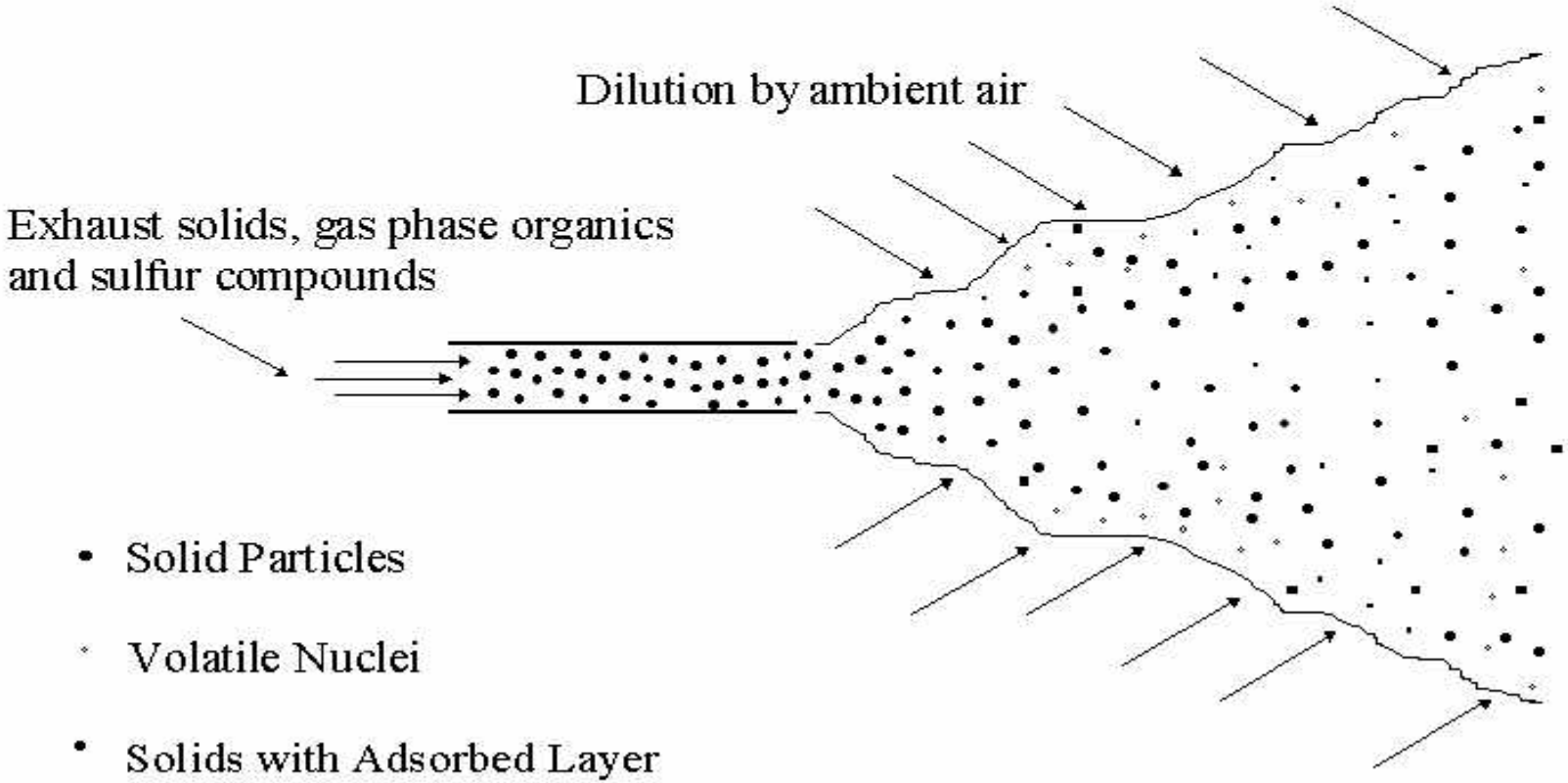


Nuclei Mode Decays Rapidly Downwind of Roadways

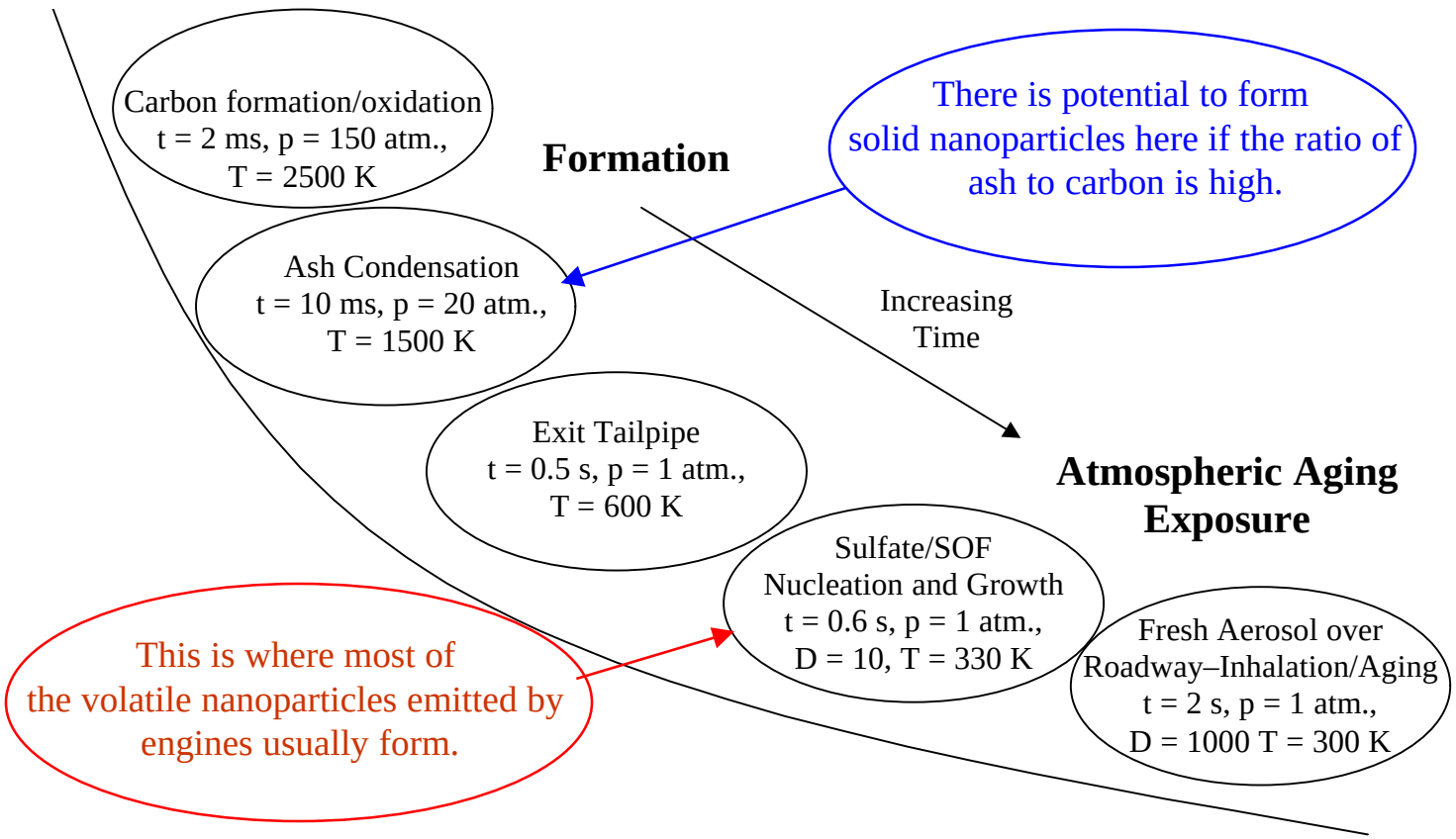


Atmospheric dilution leads to nucleation, absorption, and adsorption - in excess of 90 % of the particle number may form as the exhaust dilutes

A dilution ratio of 1000 may be reached in 1 - 2 s



Particle Formation History: From the Start of Combustion to the Nose



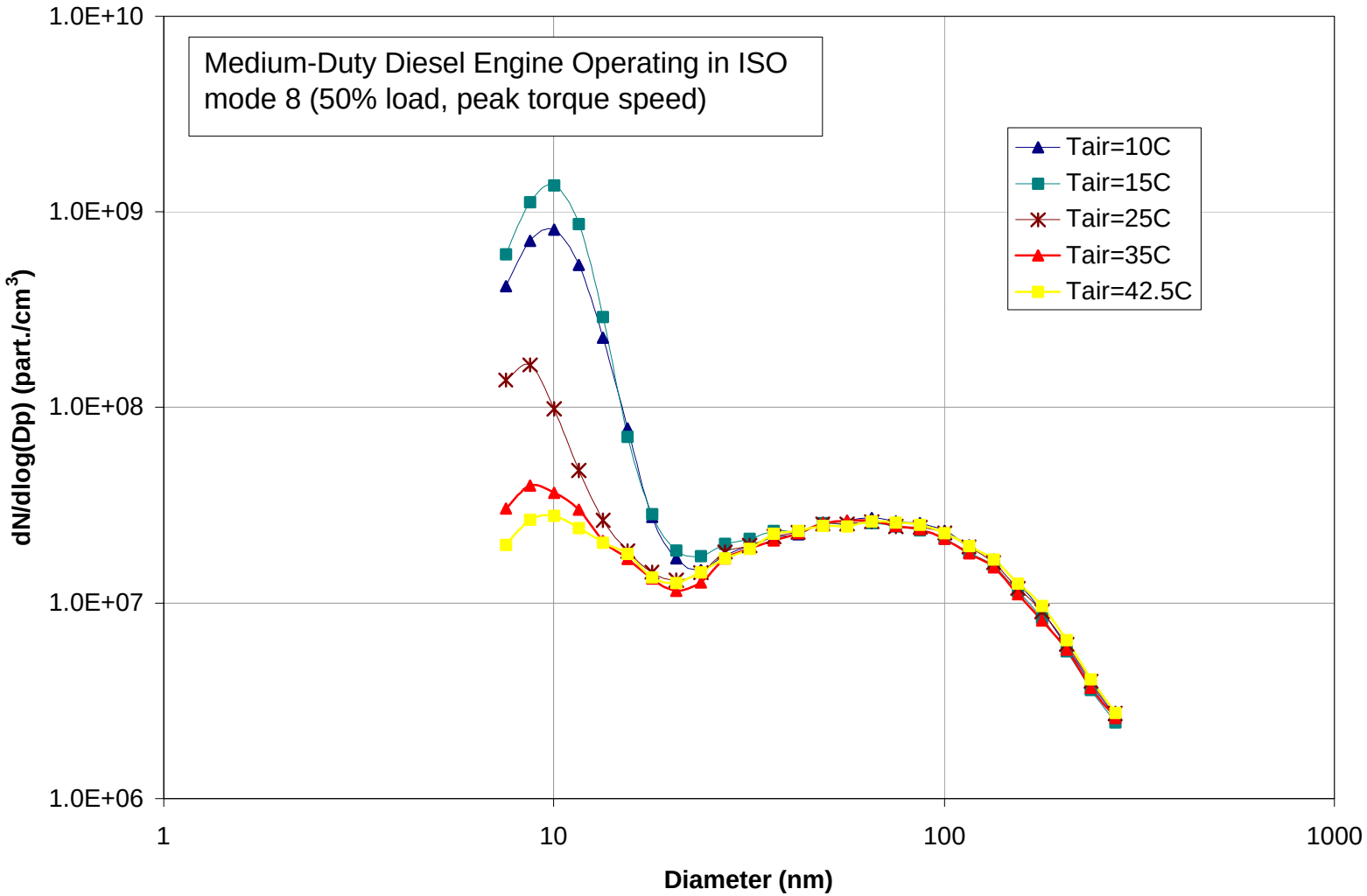
Gas and Particle Partitioning during Dilution

- A significant amount of particulate matter (e.g. 90 % of the number and 30% of the mass) is formed during exhaust dilution from particle precursors that are in the vapor phase in the tailpipe (e.g., sulfuric acid, fuel and oil residues).
  - New particles are formed by nucleation. This is likely to be the source of most of the ultrafine and nanoparticles (and particle number) associated with engine exhaust.
  - Preexisting particles grow by adsorption or condensation.
  - Nucleation and adsorption are competing processes. Carbon agglomerates provide a large surface area for adsorption that suppresses nucleation.
  - Rapid dilution and low concentrations of carbon agglomerates favor nucleation. However if dilution is too rapid there will be little time for growth and significant amounts of low vapor pressure species may remain in the gas phase
  - Thus, engines with low carbon mass emissions may have high number emissions of volatile, but NOT solid particles.

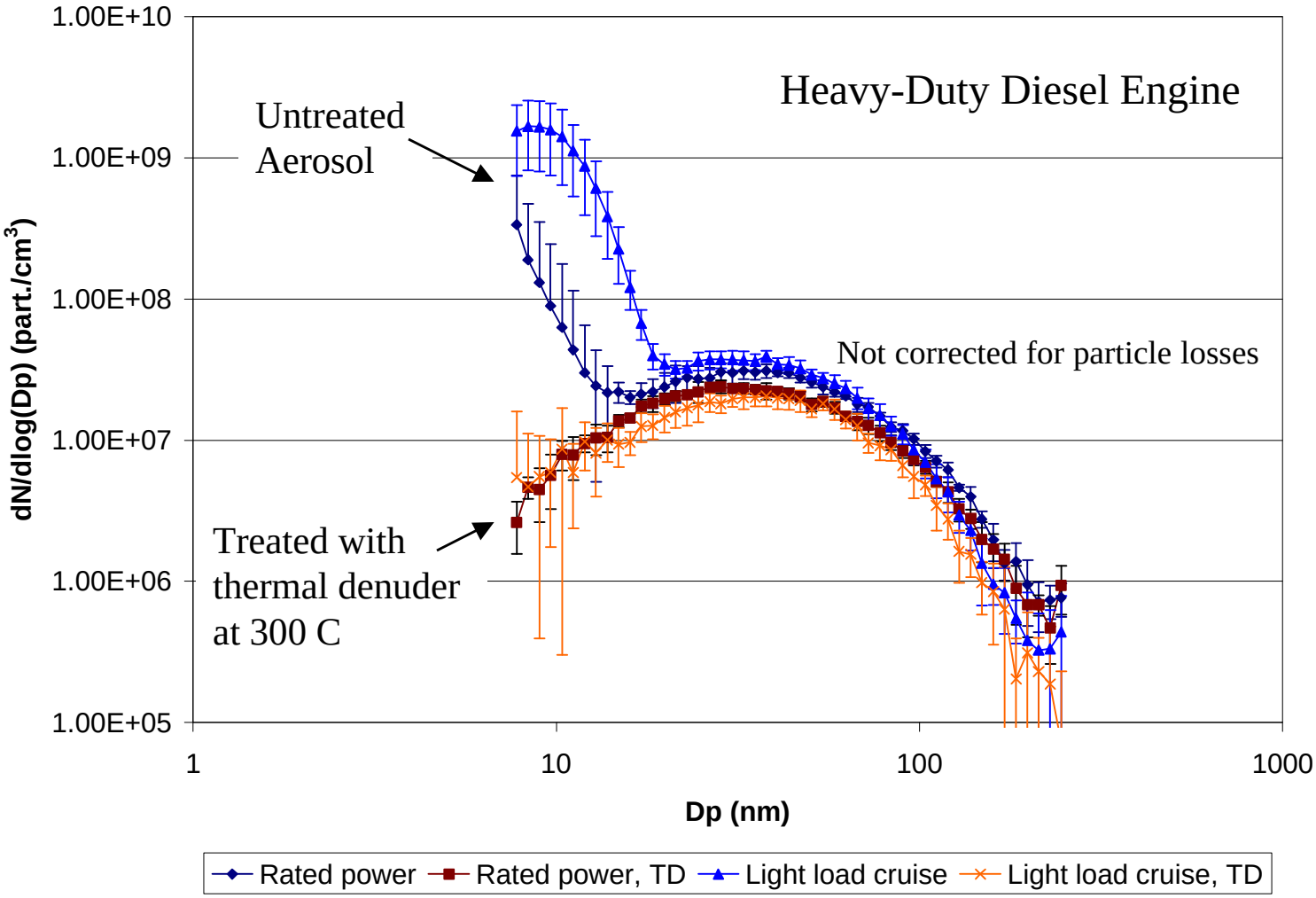
Most nuclei particles are volatile and form from precursors during dilution

- Evidence
  - Their formation depends on dilution conditions
    - » In the laboratory
    - » Over roadways
  - They are readily removed by heating

Influence of Temperature in a Single-Stage Dilution Tunnel on Nuclei Mode Formation



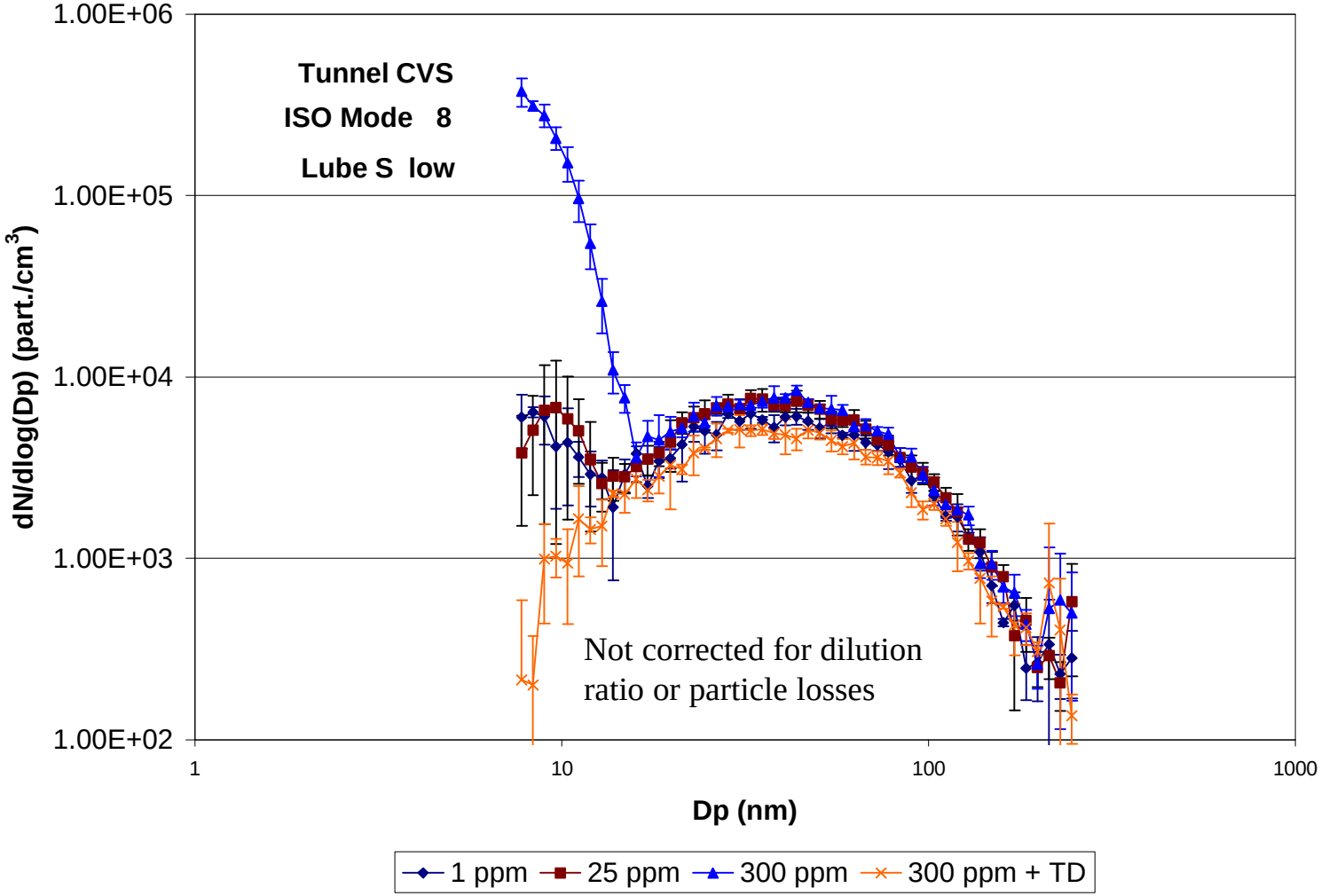
Particles in the Nuclei Mode Are Removed by Moderate Heating



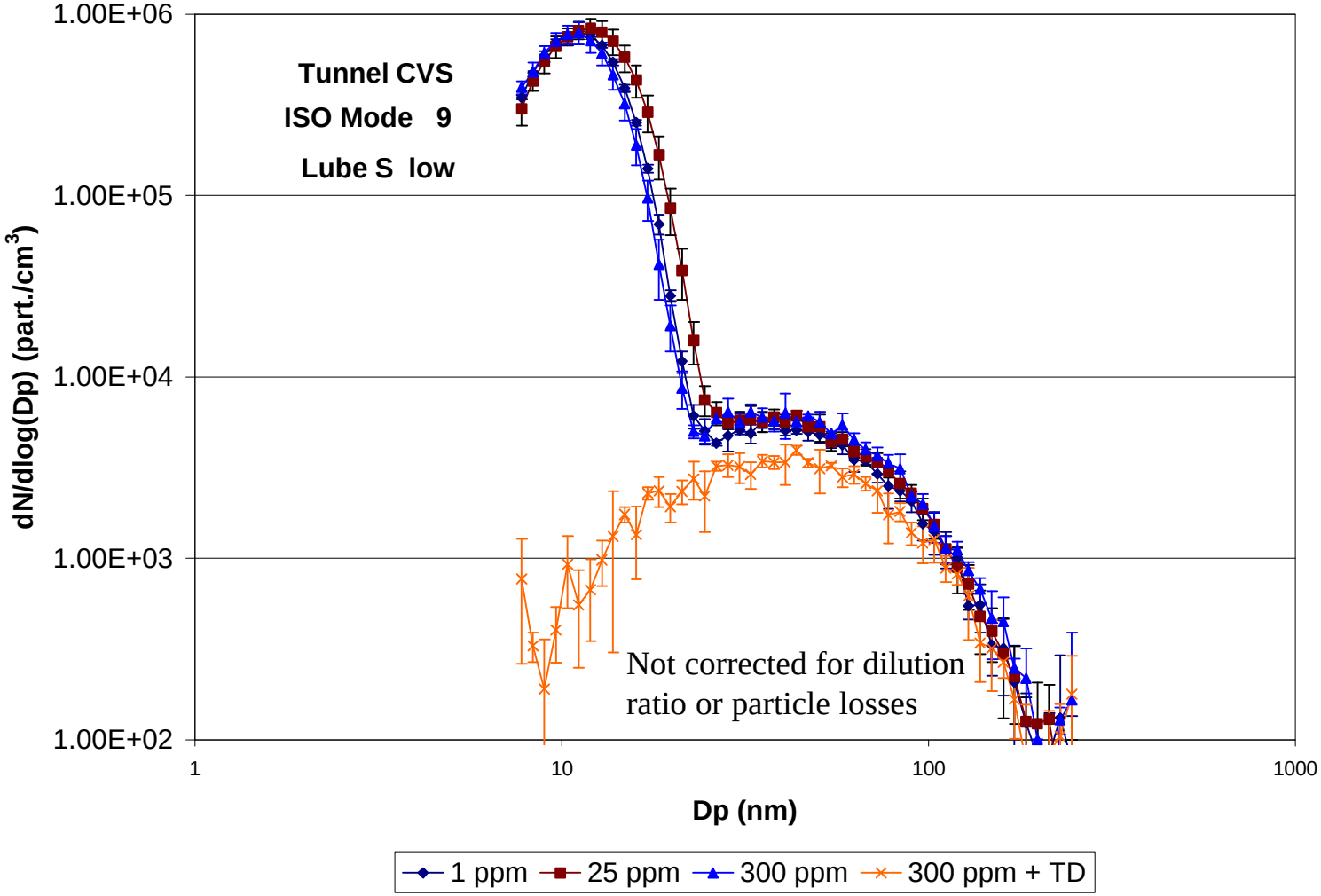
Nuclei Mode Composition

- Very few size resolved composition measurements in the nuclei mode range have been made
- It is well established that nuclei mode particles are volatile (except in the presence metallic ash)
- It has been suggested that they are mainly sulfuric acid and water
  - Most are removed by heating to 100 C or less
  - **Often their formation depends strongly on the sulfur content of fuel and lube oil**
- However recent measurement suggest that hydrocarbons, likely the heavy ends of lube oil, are important constituents
  - Some engines and conditions show little sensitivity to sulfur in the fuel
  - Growth rates observed in our 2-stage tunnel are 5-10 times too fast to be explained by sulfuric acid-water
  - TDPBMS measurements suggest that they are mainly heavy hydrocarbons likely to form from lubricating oil (Ziemann, et al., UC Riverside, Minnesota)
  - Ongoing tandem DMA measurements indicate little growth of nuclei mode particles when humidified. Similar experiments show that they disappear on heating like C30 normal alkane. (McMurry, et al., Minnesota)

Influence of Fuel Sulfur with Heavy-Duty Diesel Engine, 1200 RPM, 50% load



Influence of Fuel Sulfur with Heavy-Duty Diesel Engine, 1200 RPM, 25% Load



Nanoparticle Nucleation and Growth

- In most cases with current engines and fuels binary sulfuric acid - water nucleation triggers the process.
- The initial size (theory) of these nuclei is about 1 nm.
- In most cases there is not enough sulfuric acid present in the exhaust to explain the observed rates of particle growth.
- Hydrocarbons normally associated with the soluble organic fraction apparently are absorbed by the concentrated sulfuric acid nuclei leading to the observed growth rates.
- Nanoparticle formation with very low sulfur fuels suggests that in some cases high molecular weight hydrocarbons may nucleate.

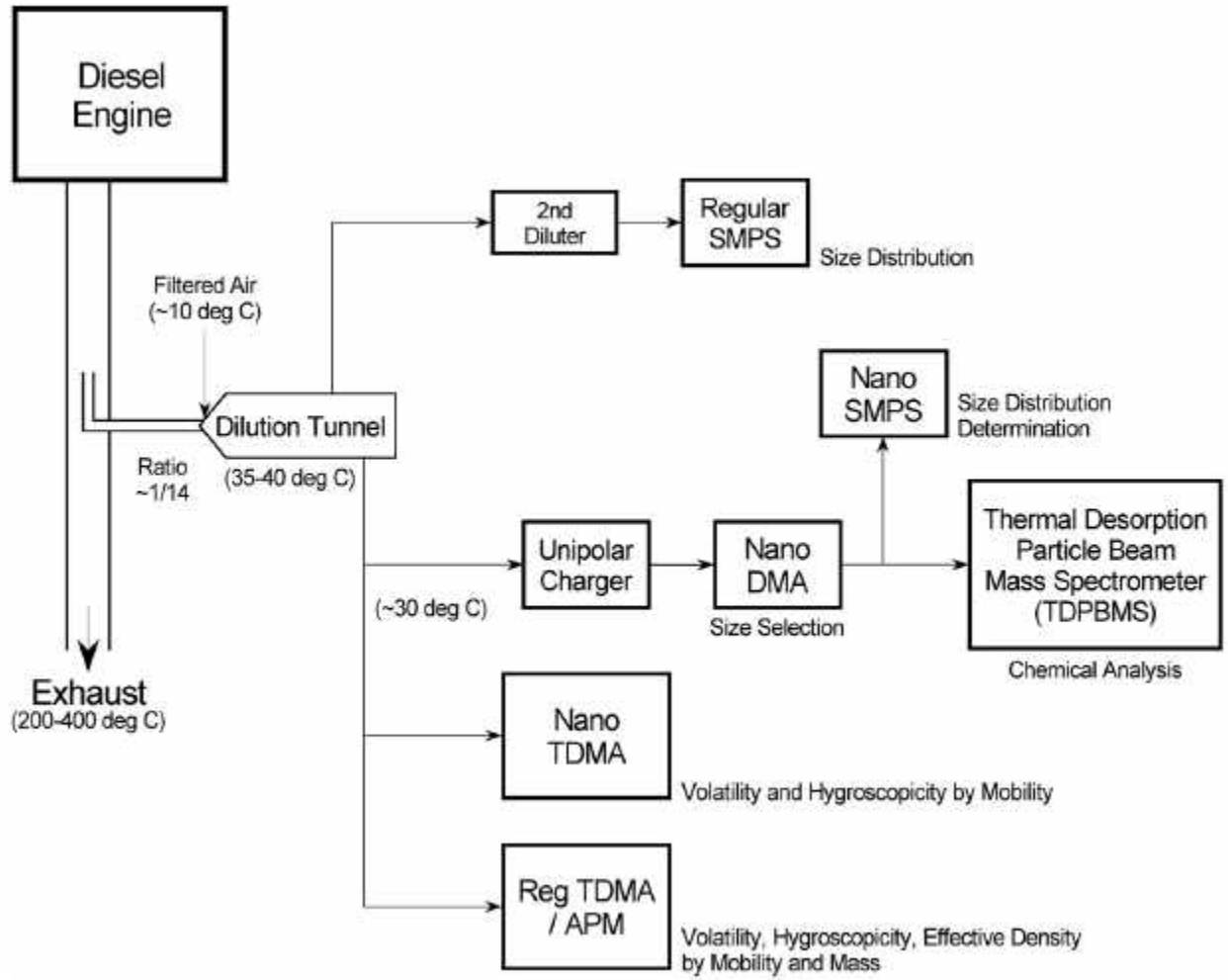
Current Understanding of the Composition of Nuclei Mode Particles

- Most nuclei mode particles formed by current engines appear to be volatile
  - Range of solubility ….
  - Insoluble or slightly soluble – heavy hydrocarbons like heavy ends of lubricating oil ….
  - Soluble – sulfuric acid/water ….
- There is a very small solid residue in this size region
  - Carbon residue
  - Ash from lubricating oil
  - Ash from fuel / fuel additives
  - Metal compounds could be an issue

What about the Accumulation Mode?

- By number and surface weightings most of the accumulation mode is in the ultrafine range
- Most of the mass of the accumulation mode consists of carbonaceous agglomerates with significant amounts of adsorbed hydrocarbons, sulfuric acid, water
  - Most of the soluble organic fraction (SOF) is found in the accumulation mode
  - The lower size range of the accumulation mode is a mix of solid and volatile particles
  - The density of accumulation mode particles decreases with increasing size

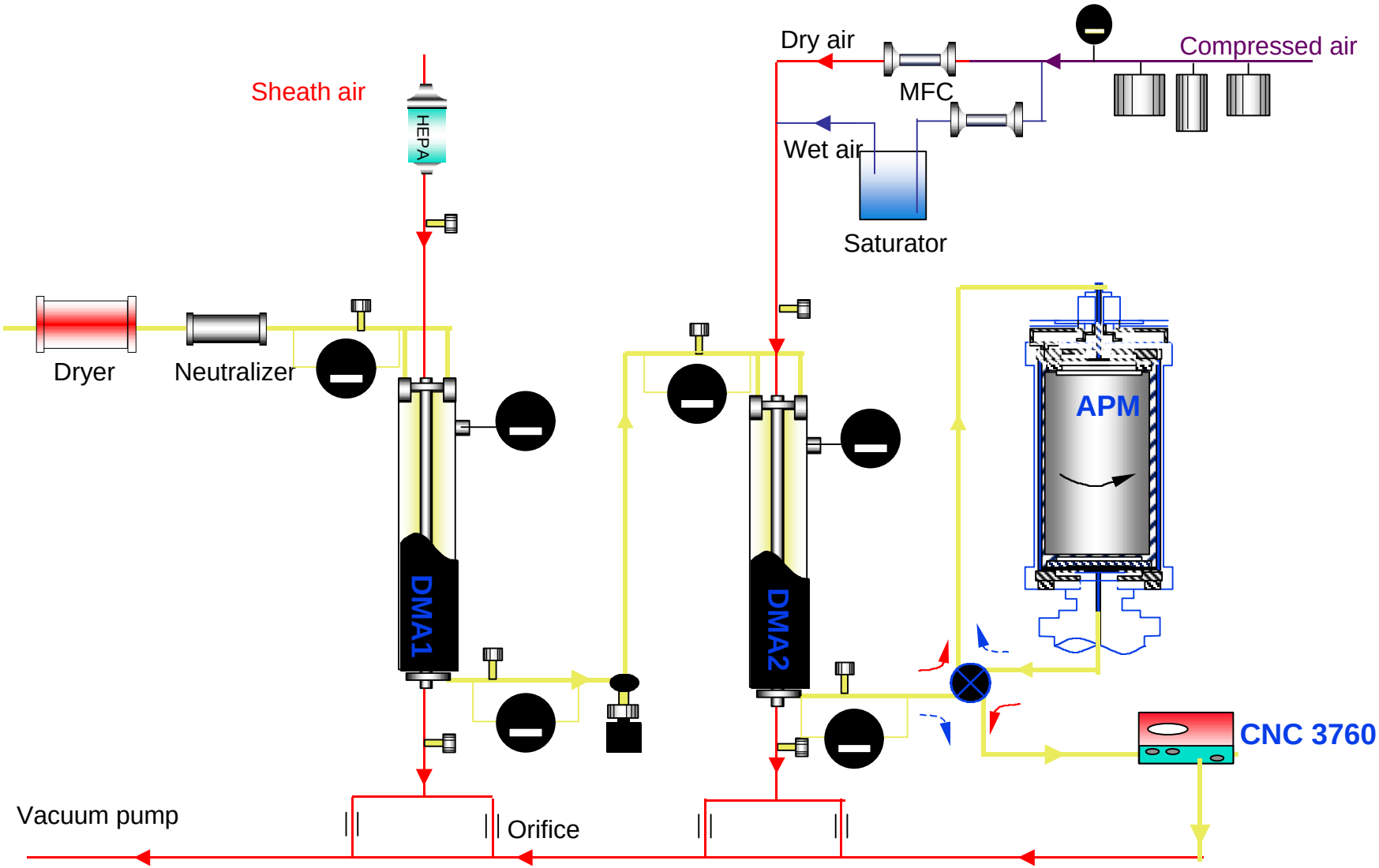
Applying advanced particle characterization methods to Diesel aerosols – ongoing work by McMurry, Kittelson, Ziemann (UC Riverside), Sakurai, and Park



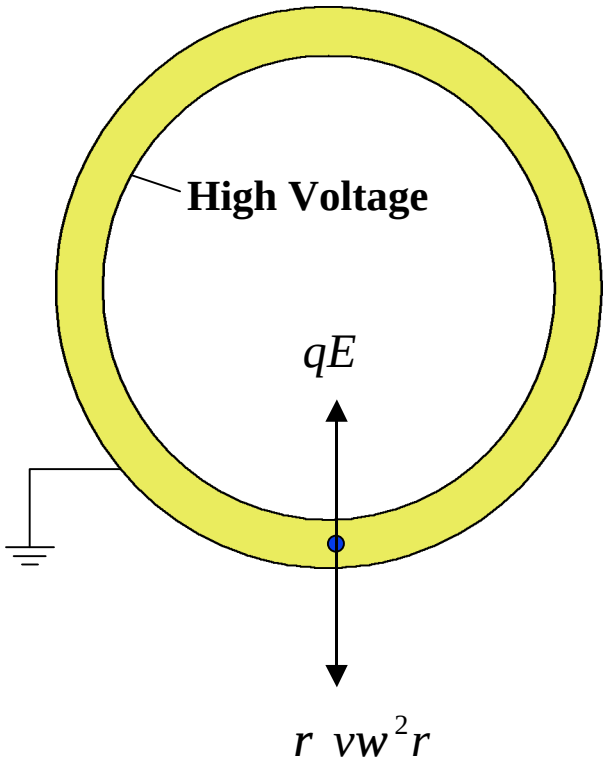
Applying advanced particle characterization methods to Diesel aerosols – types of measurements to be described

- Density measurements
  - Select single particle size with DMA
  - Measure particle mass with APM
  - Calculate effective density = mass/volume
- Volatility measurements
  - Select single particle size with DMA
  - Heat
  - Observe diameter change and relate to volatility
- Hygroscopicity measurements
  - Select single particle size with DMA
  - Humidify
  - Observe diameter change and relate to content of hygroscopic material

Density measurements with TDMA-APM system

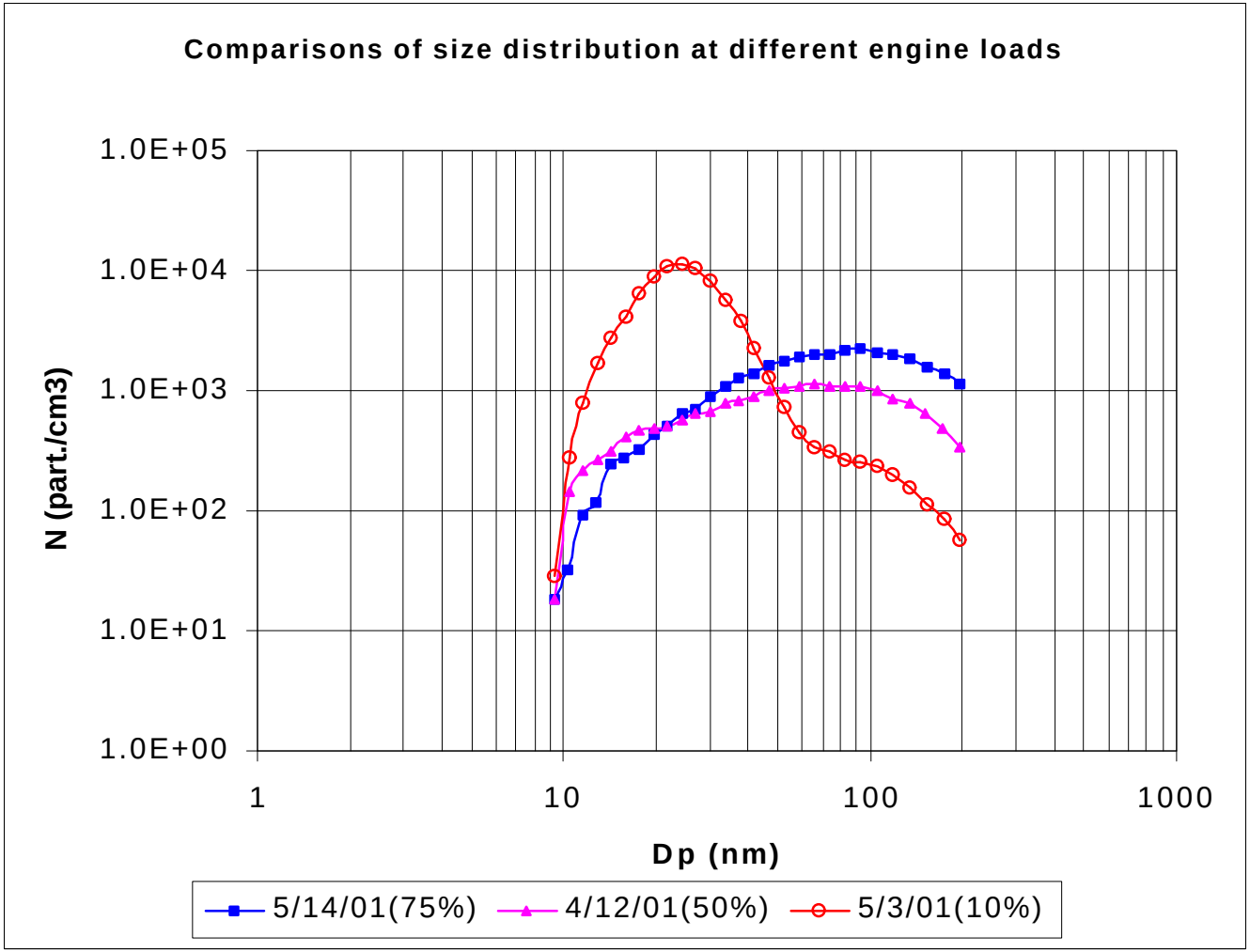


APM theory

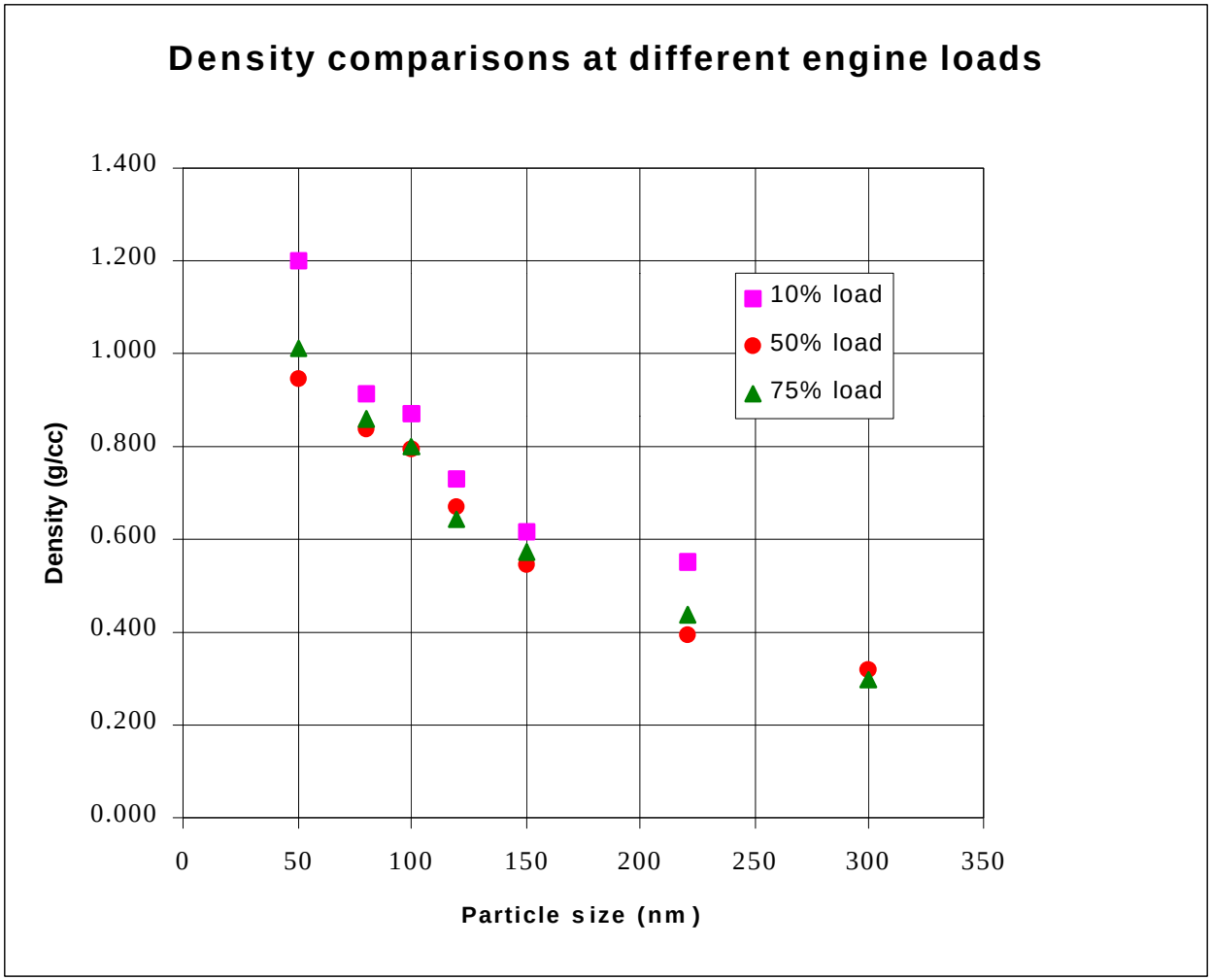


$$mrw^2 = \frac{pd_{ve}^{\ 3}}{6} r_{true} rw^2 = neE_{APM}$$

Density measurement made for a variety of engine condition giving very different size distributions

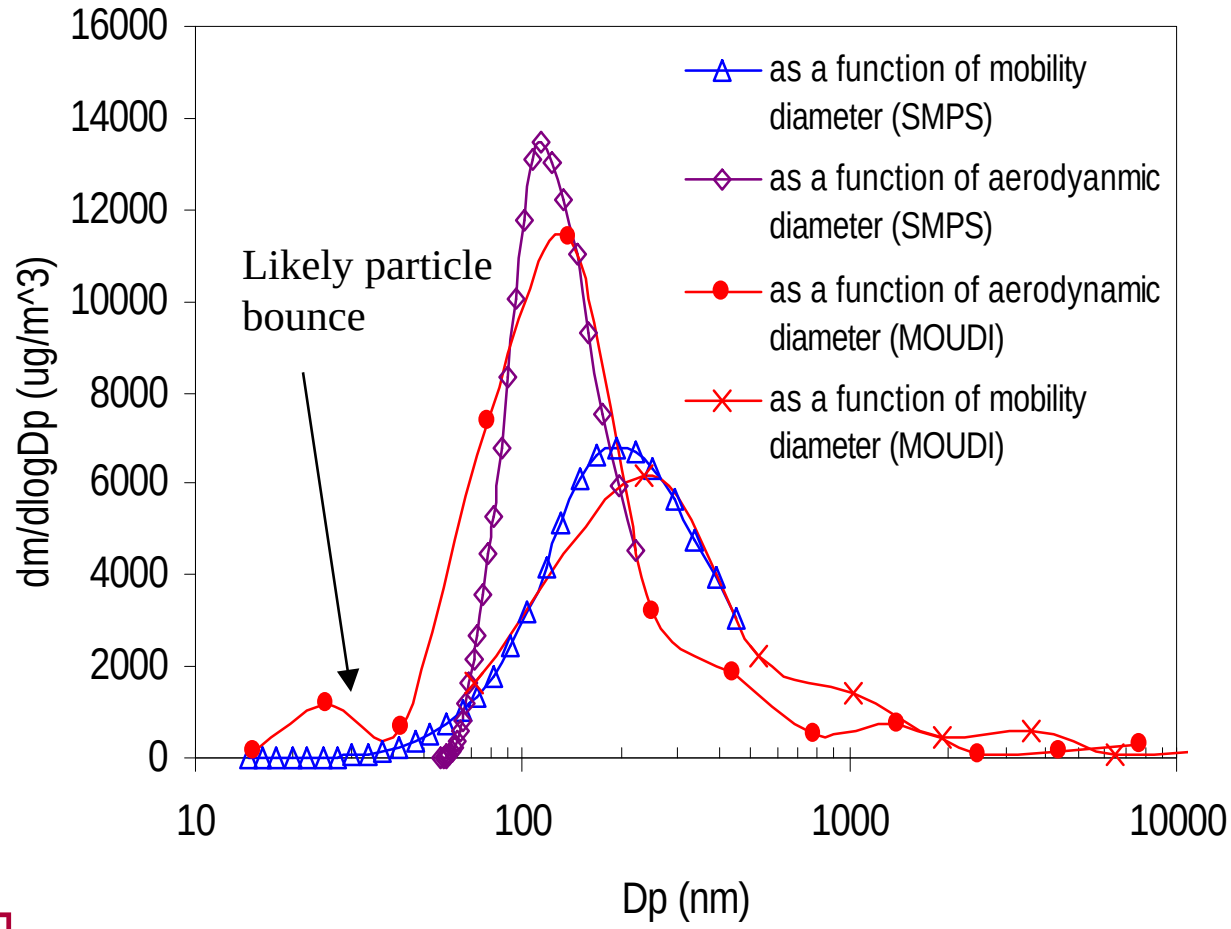


Comparison of density at different engine loads, 10%, 50%, and 75% at 1000 rpm, Deere engine



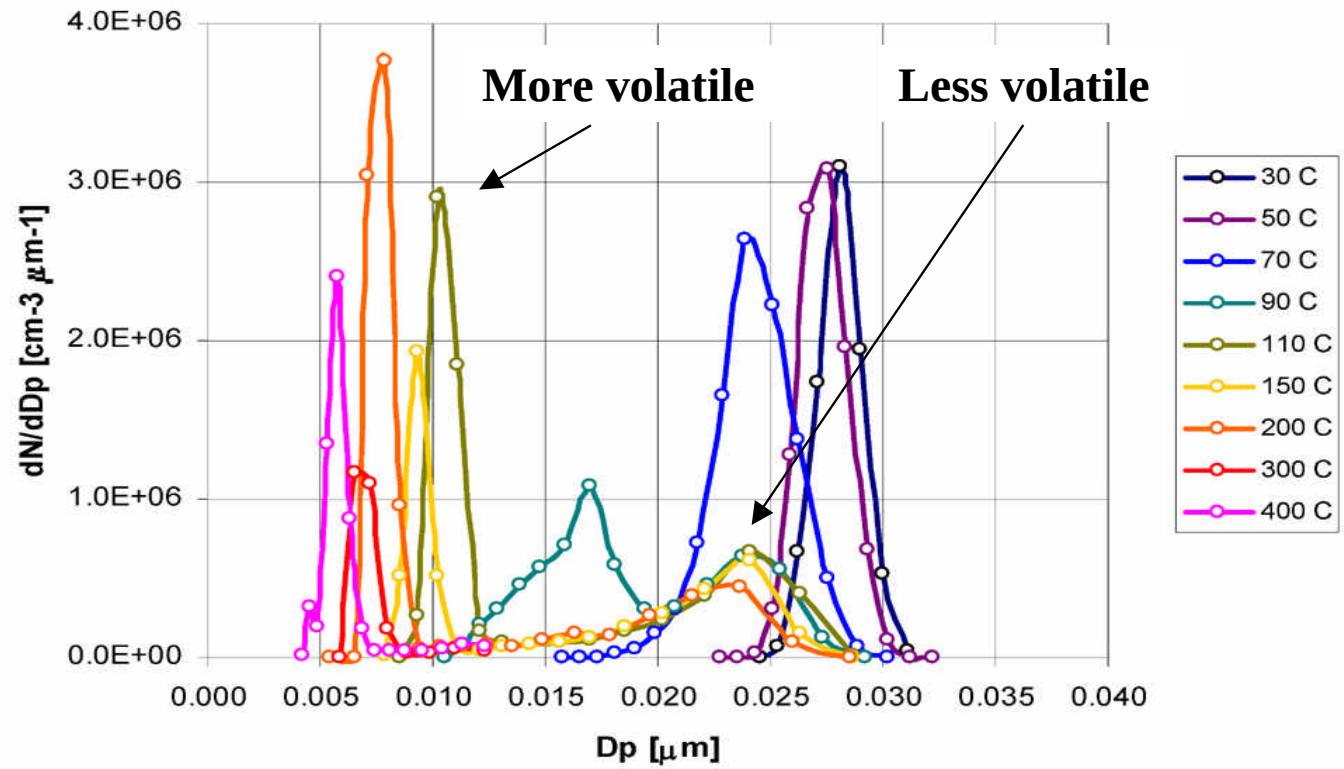
Mass size distributions obtained from SMPS and nano-MOUDI, Deere engine running at 1000 rpm and 50% load

Density measurements used to relate mobility and aerodynamic diameters



Volatility of diesel nanoparticles (30 nm)

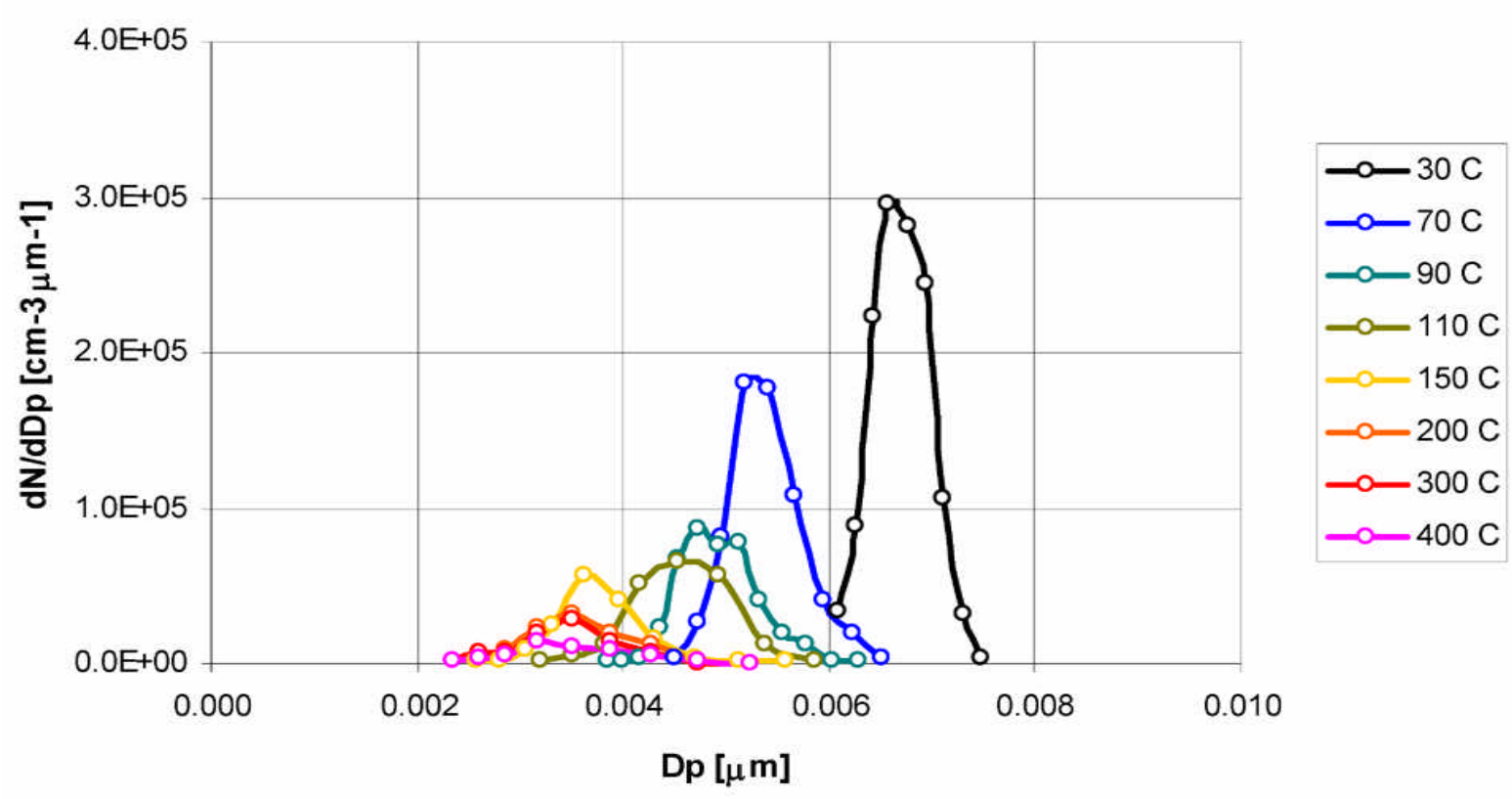
Cummins ISM, pump fuel (350 ppm S), 1400 rpm , medium load



- Two particle types of different volatilities present.
- Volatile particles more abundant
- Significant shrinkage occurred when temperature was in the range of 50- 110 °C

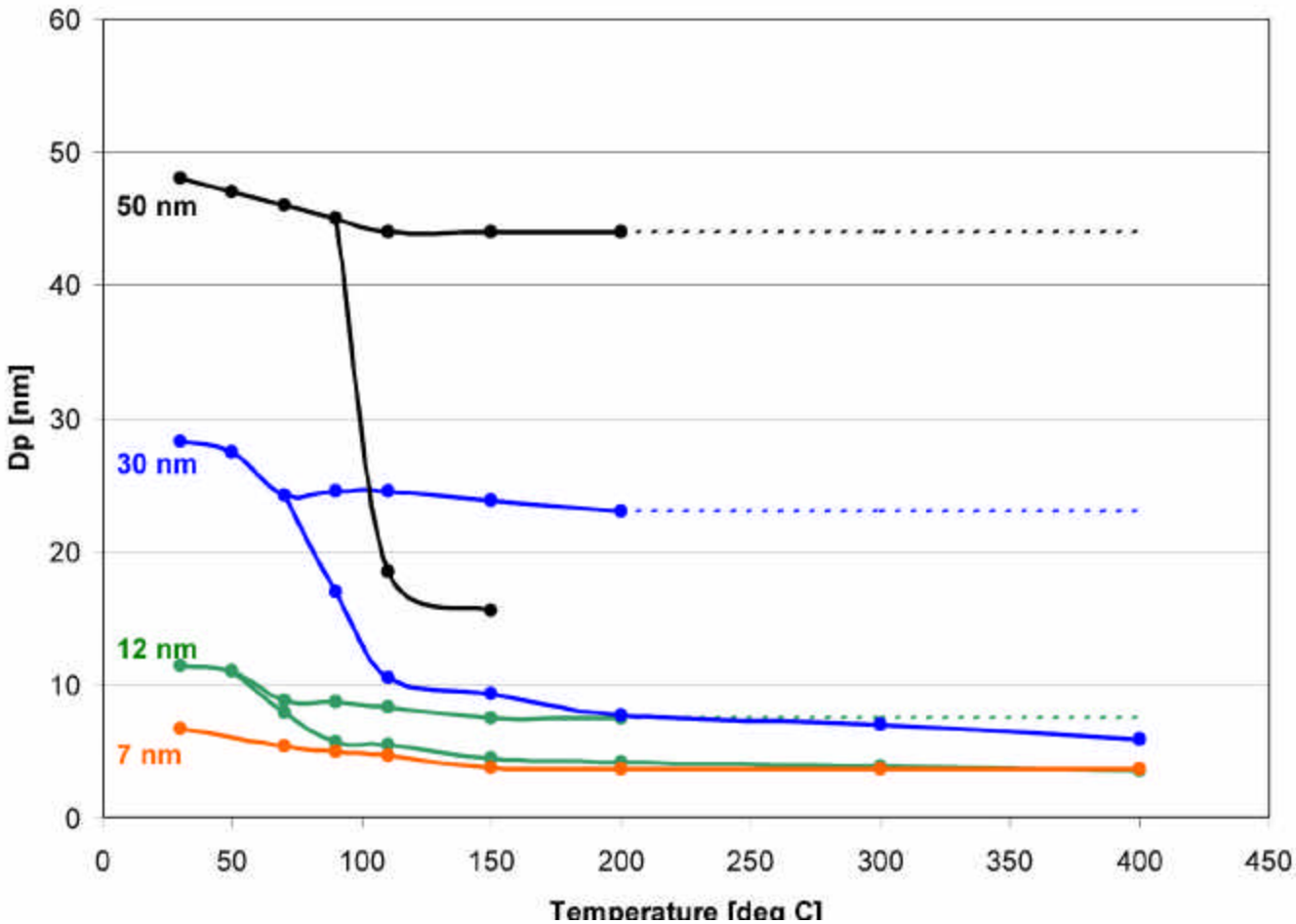
Volatility of diesel nanoparticles (7 nm)

Cummins ISM, pump fuel (350 ppm S), 1400 rpm , medium load

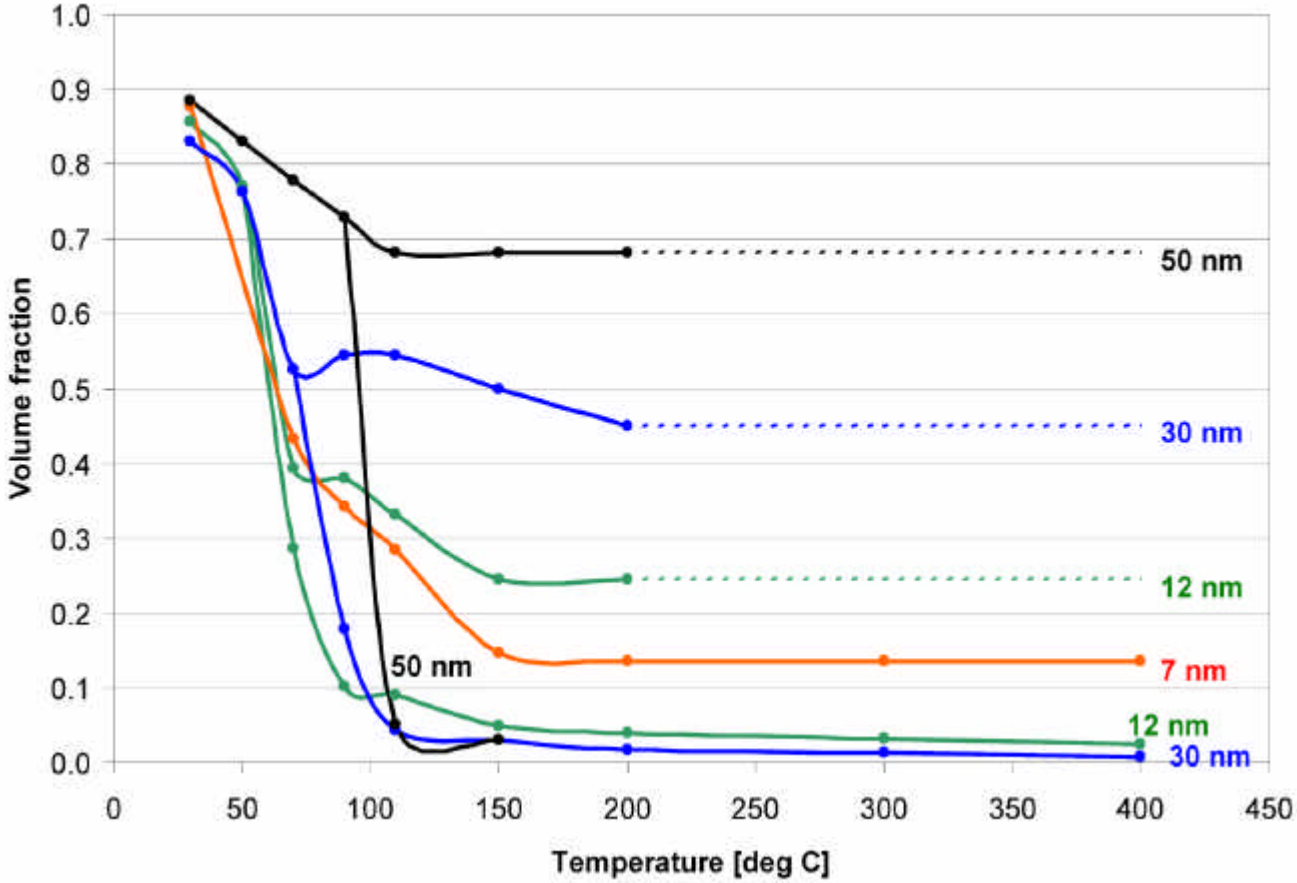


- For these very small particles only one particle type, volatile, was observed
- No detectable solid core

Volatility of diesel nanoparticles – plot of peak diameter shifts during heating. All but the smallest sizes consist of two particle types

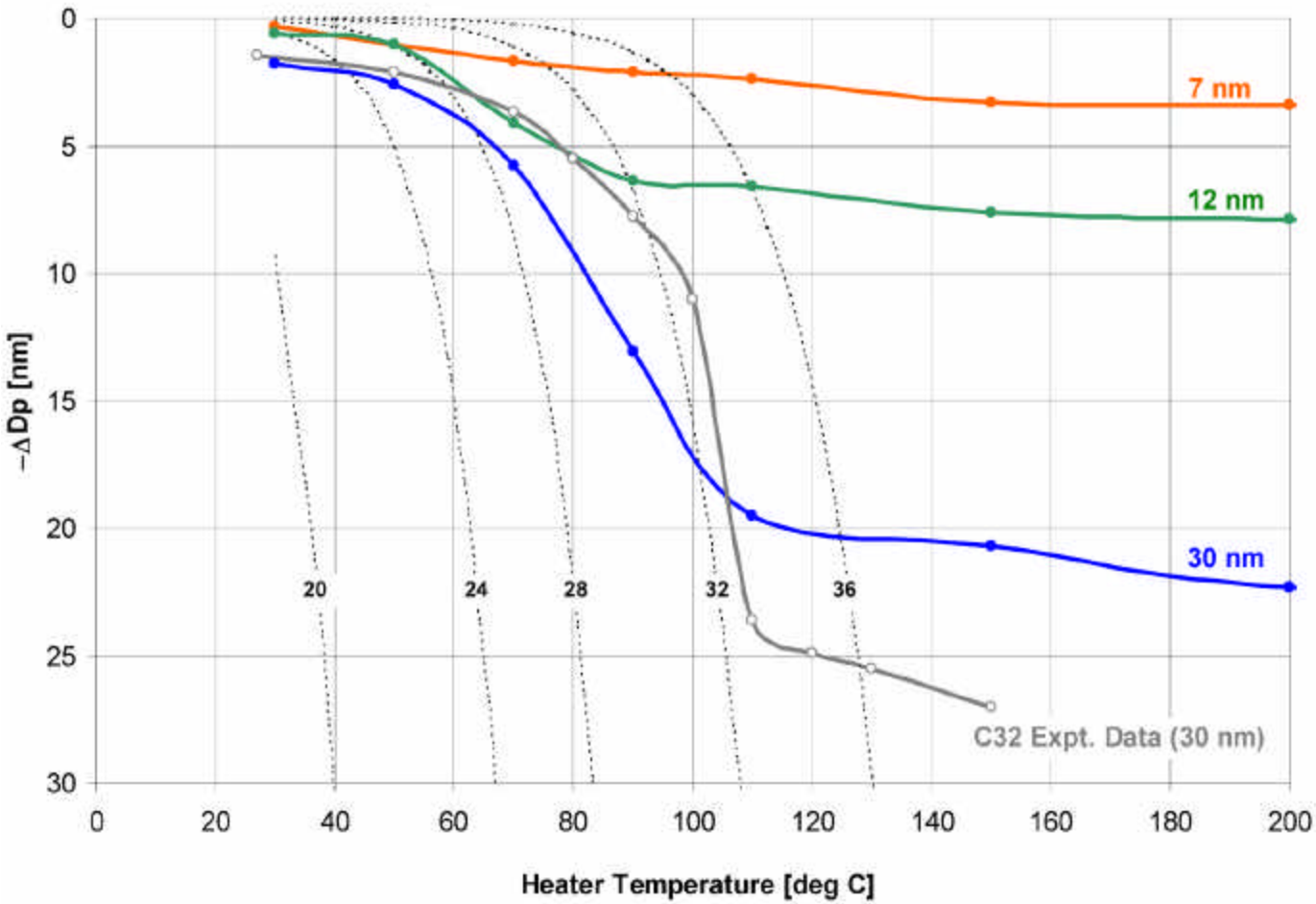


Volatility of diesel nanoparticles - volume change due to evaporation of volatile components

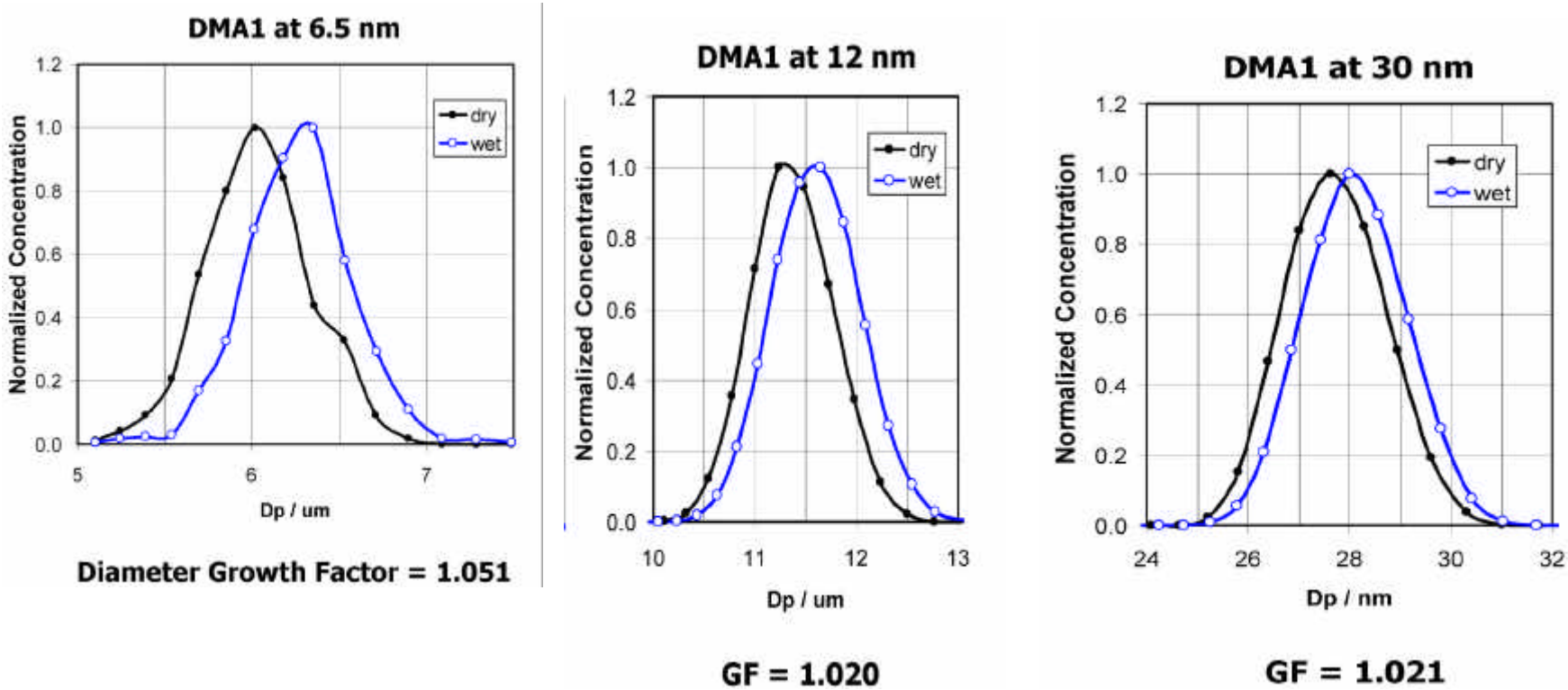


•Volume fraction of non-volatile components as little as 2- 3% for particles initially 12- 30 nm.

Evaporative shrinkage of n-alkane and Diesel nanoparticles. Diesel nanoparticles behave like C28-C32 – lube oil?



Hygroscopicity of diesel nanoparticles – ISM engine pump fuel (350 ppm S) medium load



•Similar water uptake was observed light engine load with pump fuel

•With CA fuel (96 ppm S), no water uptake was observed either at medium or light engine load.

Hygroscopicity of diesel nanoparticles – 350 ppm S fuel

		H_2SO_4 + H2O (6% RH)		H_2SO_4 only		
Diameter [nm]	Growth Factor	Volume Fraction	Equivalent Diameter [nm]	Volume Fraction	Mass Fraction	Equivalent Diameter [nm]
6.5 nm	1.051	11%	3.1	9.4%	19%	3.0
12 nm	1.020	3.2%	3.8	2.8%	6.0%	3.6
30 nm	1.021	2.6%	8.9	2.3%	5.0%	8.5

Note: The Kelvin effect was taken into account. For the mass fraction calculation, the densities of 1.8 and 0.8 g/cm^3 were assumed for sulfuric acid and organics, respectively.

Estimated sulfuric acid contents in other studies

TDPBMS (Tobias et al., Environ. Sci. Technol. 2001, 35, 2233- 2243)

1.2- 5.3% in mass fraction or 7- 12 nm in diameter for 41 nm MMD particles

0.7- 2.3% in mass fraction or 8- 13 nm in diameter for 58 nm MMD particles

ELPI sampler (Shi and Harrison, Environ. Sci. Technol. 1999, 33, 3730- 3736)

6% in mass fraction for 30- 73 nm particles

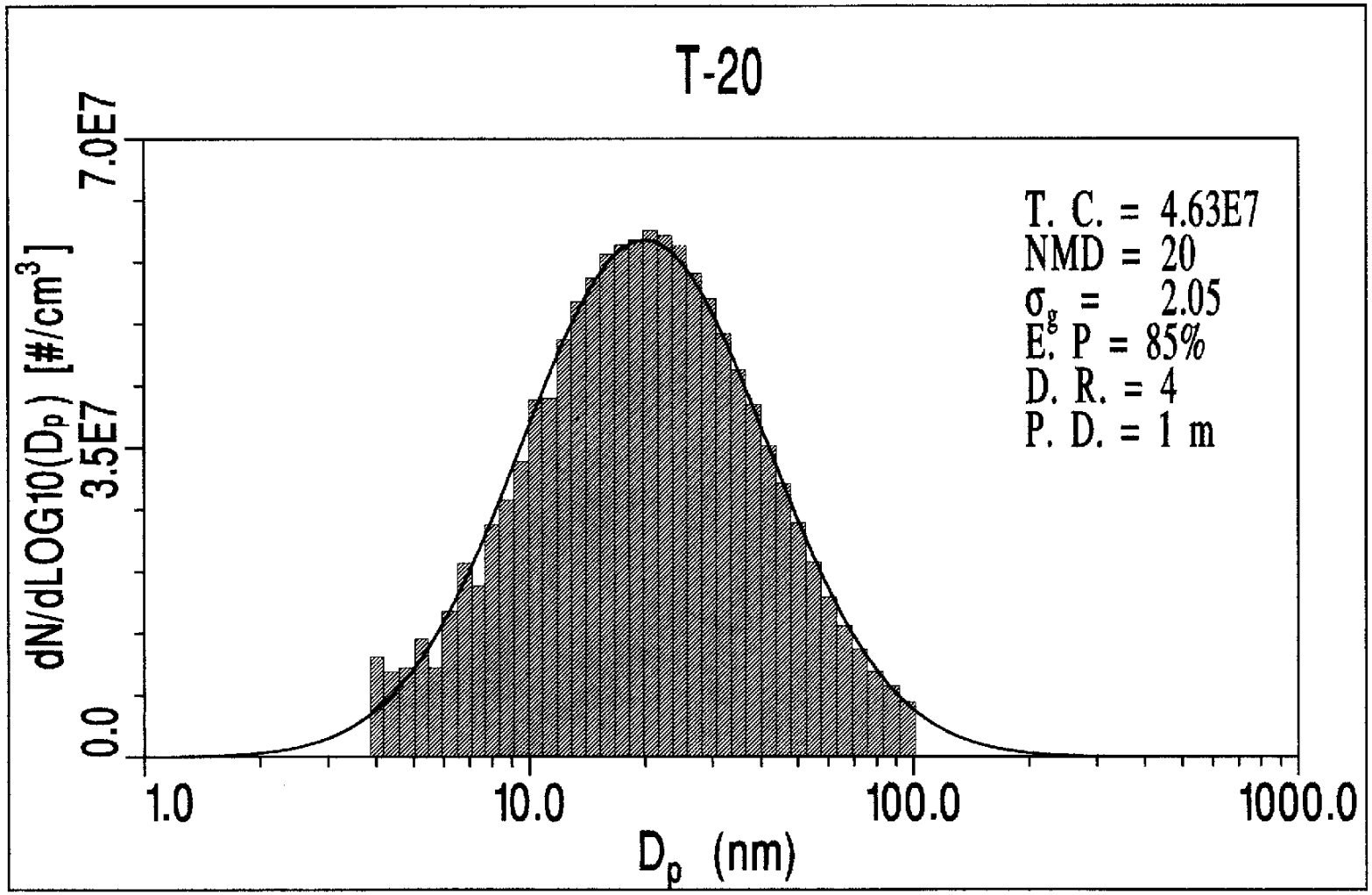
Model calculation (Khalek et al., SAE Technical Paper Ser. 2000, 2000- 01- 0515)

8 nm of H_2SO_4/H_2O nucleus in diameter after 1 sec of growth following nucleation

Conclusions – properties of Diesel particles

- Nuclei mode particles consist mainly of volatile materials, mainly heavy hydrocarbons, sulfuric acid
  - Concentrations of these particles are much higher on and near roadways – a “hotspot” issue?
  - Their formation is very dependent on dilution conditions, especially dilution rate and dilution air temperature
  - The are volatile and sometimes hygroscopic
  - Although these particles are volatile they may be relatively insoluble, e.g., lube oil – this could influence their behavior in biological systems
  - Their formation may be favored by low carbon concentrations in the exhaust
  - In some cases there is a tiny solid residue in the nuclei mode range that is *likely* to consist of carbon and metallic ash
- The density decreases with size in the accumulation mode
  - Densities are less than one in most of the size range falling to about 0.3 g/cm^3 at 300 nm
  - Thus mobility diameters are larger than aerodynamic diameters

Future Issues

- Future Diesel engines fitted with traps should largely eliminate solid particle emissions
  - Volatile nuclei mode particles are formed downstream of traps under some conditions
  - Some trap systems utilize metallic fuel additives to assist regeneration. This could lead to metallic nanoparticle emissions in the unlikely event of trap failure
- Nanoparticle formation is driven mainly by volatile particle precursors like heavy hydrocarbons and sulfuric acid – these must be controlled
  - Reduced lube oil consumption
  - Oxidizing catalysts and traps
  - Very low S fuel and lube oil
- Future low emission engine concepts without traps have potential to for significant nanoparticle emissions mainly associated with heavy hydrocarbons and metallic ash in the lubricating oil
  - Spark ignition engines
  - Gaseous fuel engines
  - Homogeneous charge compression ignition engines (HCCI)
- Recent measurements of aircraft nanoparticles show emission factors higher than Diesel (NASA, Pui U of M)

Another Nanoparticle "Hotspot" Might Be near Airports: T-38 Size Distribution (from: Han, Chen and Pui)