Measurement of Engine Exhaust Particle Size

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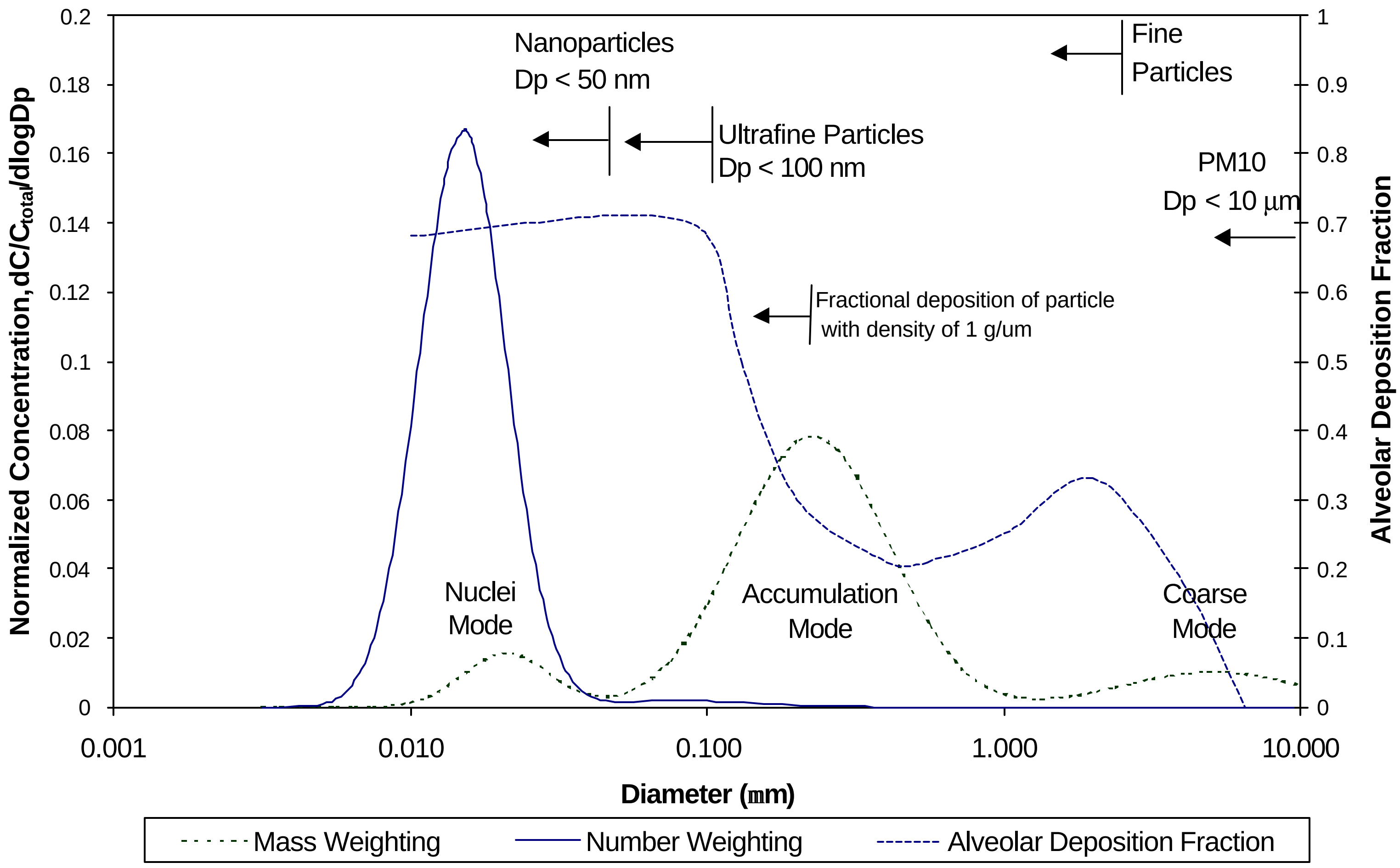
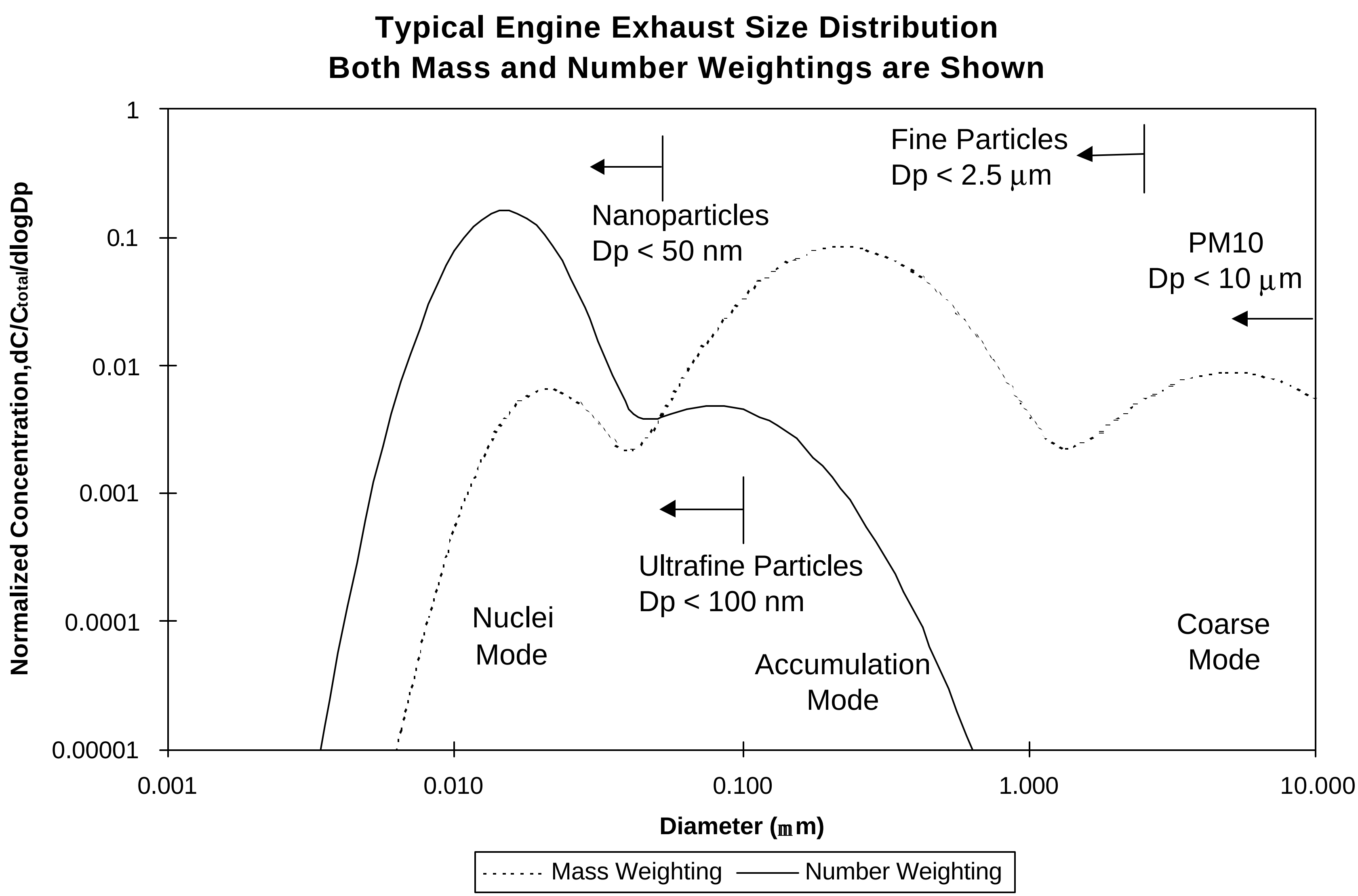
Background

- Current emission standards are mass based. Recently interest in other measures, i.e, size, number, surface, has increased.
- Concerns about particle size
  – New ambient standards on fine particles
  – Special concerns about ultrafine and nanoparticles
  – Indications that reductions in mass emissions may increase number emissions
- Difficulties associated with measurement of ultrafine and nanoparticles
  – Often more than 90% of particle number are formed during exhaust dilution
  – Particle dynamics during sampling and dilution are highly nonlinear - large changes in of particle number may result from small changes dilution and sampling conditions

Typical Diesel Particle Size Distribution



Typical Diesel Particle Size Distribution - Log Scale



Health

- Correlations between fine particles and excess deaths
- Increased asthma in children living near roadways
- Special concerns about ultrafine and nanoparticles

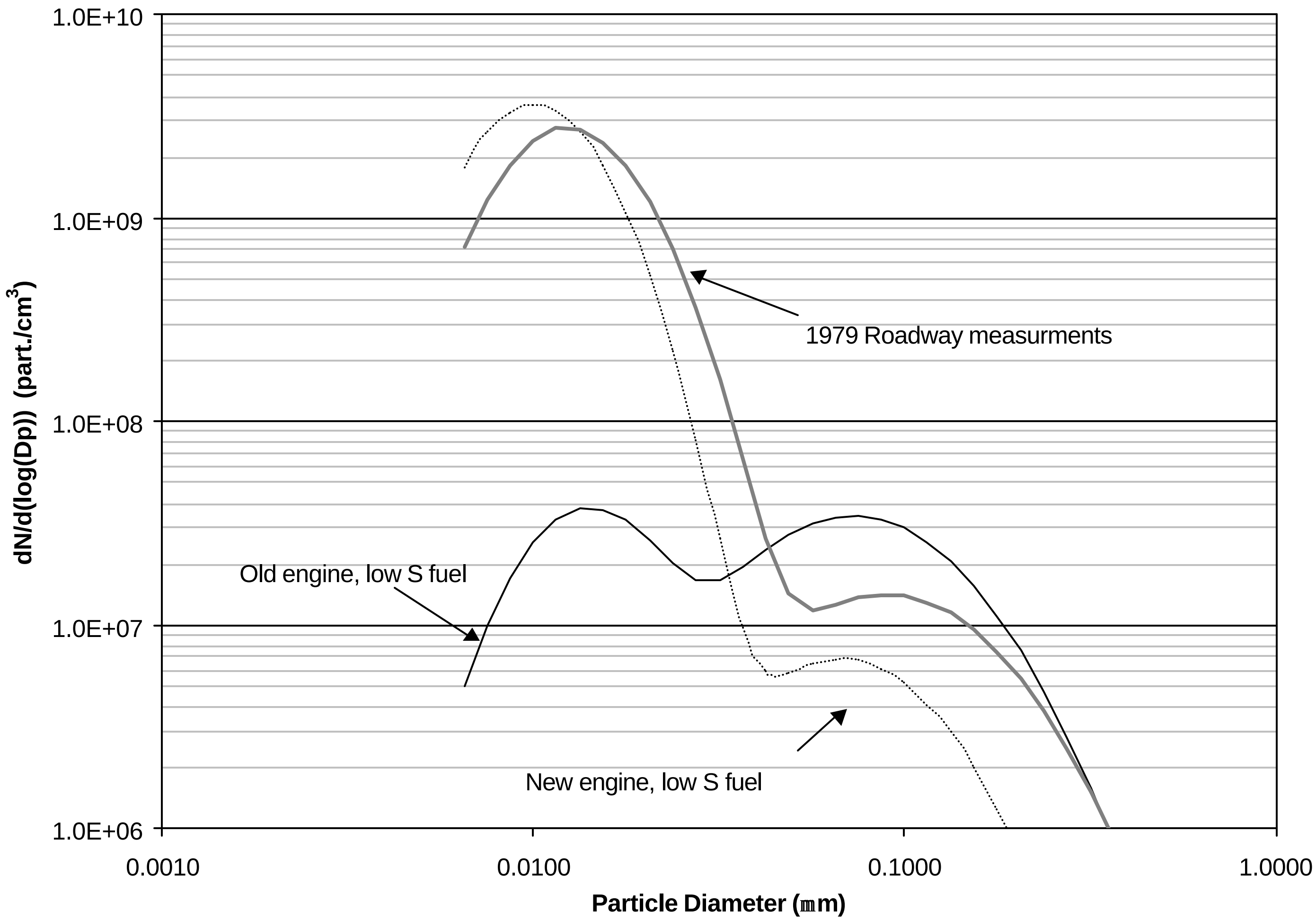
Special Concerns about Nanoparticles and Health

- Increased deep lung deposition
- Increased number and surface area at same mass exposure
- Particles which are non-toxic in µm size range may be toxic in nm range
  - Rats exposed to the same mass of 0.25 and 0.02µm diameter TiO_2 retain more nanoparticles in the interstitial tissue of the lung and develop marked inflammatory response. (Seaton et al., 1995).
  - Comparison of surface free radical activity of ambient PM10 particles, and 0.5 and 0.025 µm diameter TiO_2 showed significant activity for PM10 and much more activity for 0.025 than for 0.5µm TiO_2 (Donaldson et al., 1996).
  - Modest concentrations of 0.03µm Teflon fume particles caused acute pulmonary toxicity in rats (Ferin et al., 1992).

A Recent HEI Study Gave a Surprising Result for a Low Emission Engine

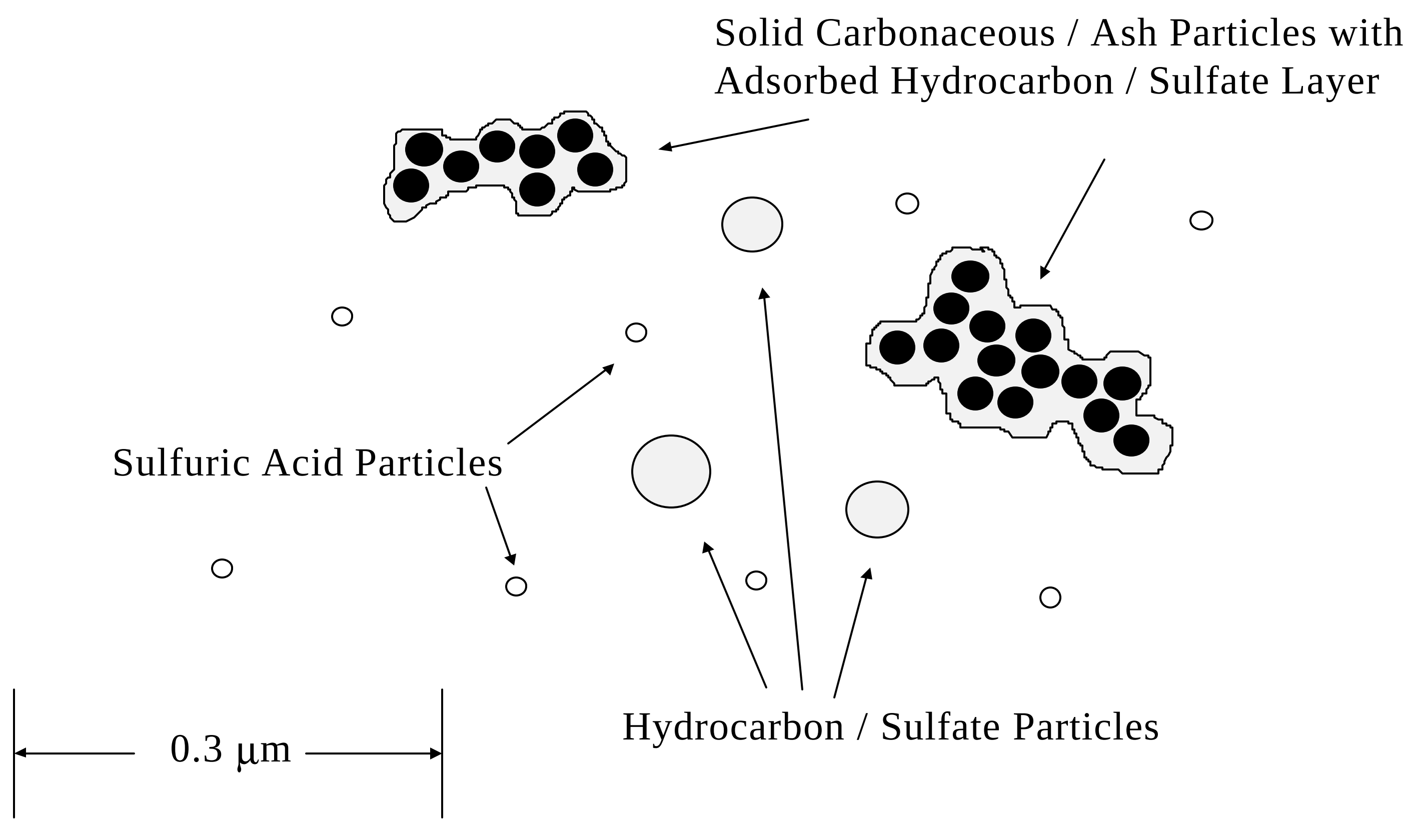
- Particle concentrations and size distributions were measured for a 1988 and a 1991 engine
  - When run on very low sulfur fuel particle number emissions were much higher, 30 -100 times, from the new engine although mass emissions were about 3 times lower
  - The 1988 engine produced high number emissions, but not as high as the 1991 engine when run on a 1988 type fuel (higher sulfur)
  - This raised concerns that new engines might be producing large numbers of nanoparticles while still meeting mass emission standards and focused attention on nanoparticle emissions
- However reviews of measurements made on and near roadways in the 70’s and 80’s show high nanoparticle emissions. **High nanoparticle emissions may be a problem but are not a new development!**

Number Size Distribution Data from HEI Report and 1979 CRC Roadway Study

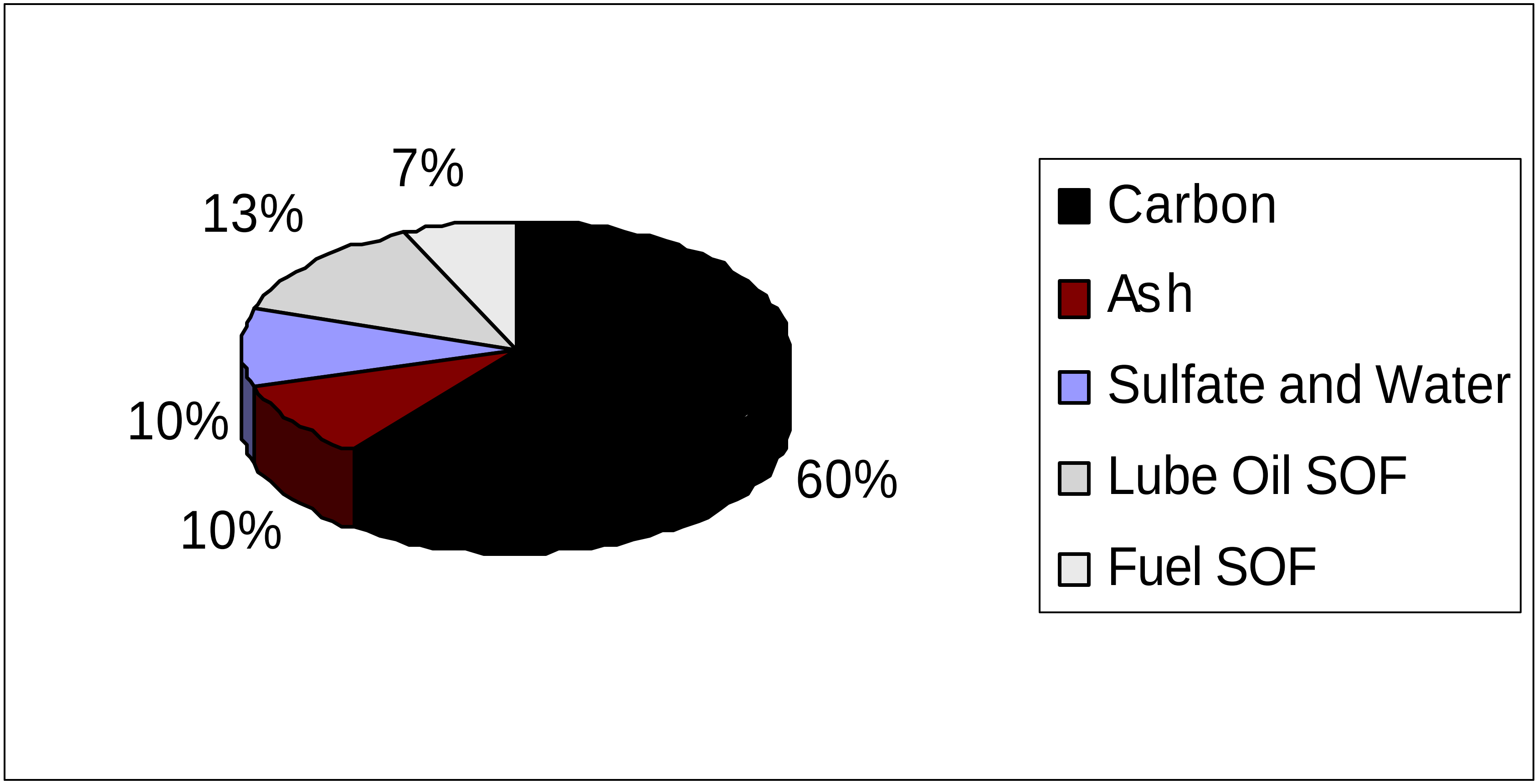


Particle Composition and Structure

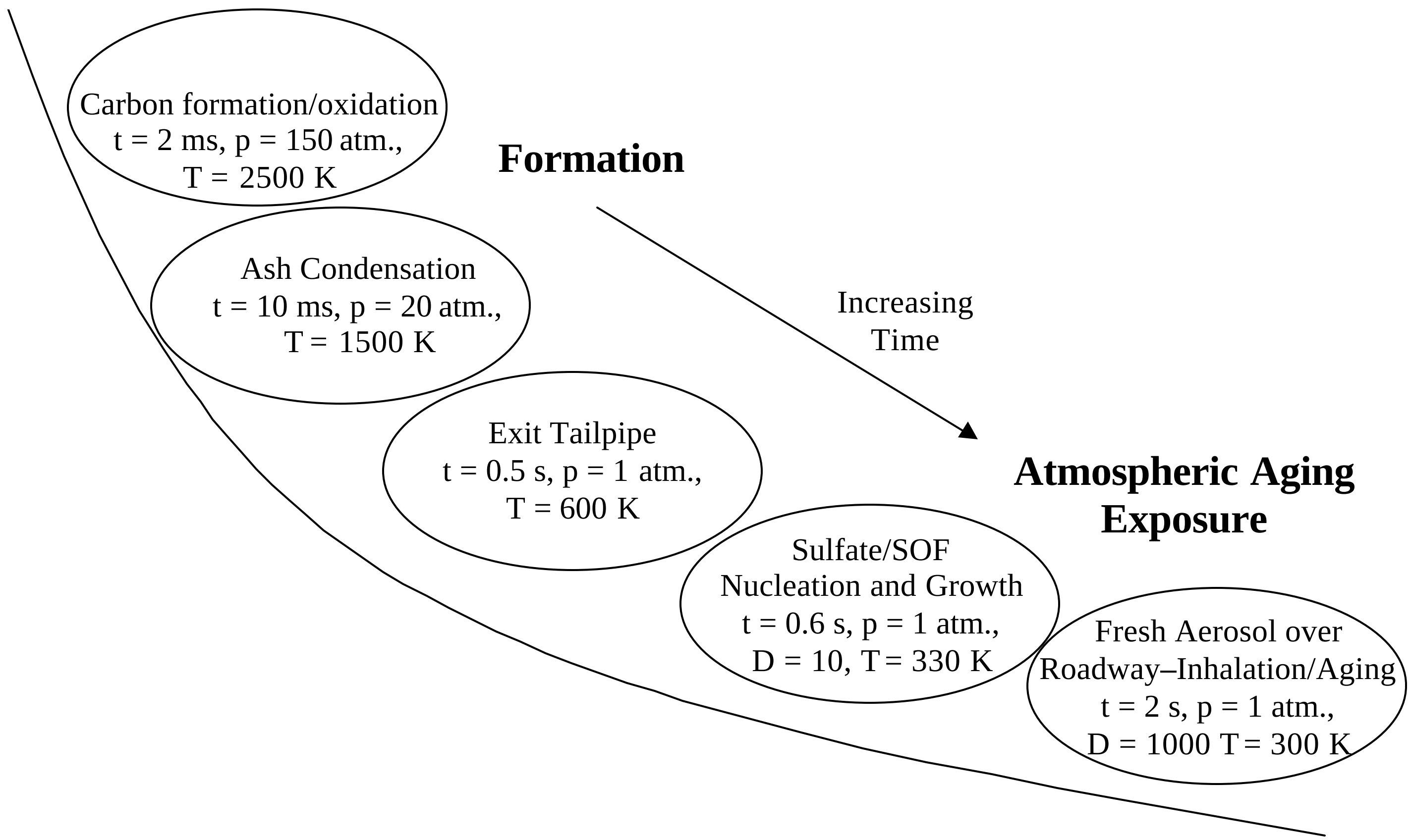
Particles consist mainly of highly agglomerated solid carbonaceous material and ash and volatile organic and sulfur compounds.



Typical Composition of Diesel Particulate Matter: Lube oil contributes to SOF, ash, sulfate



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

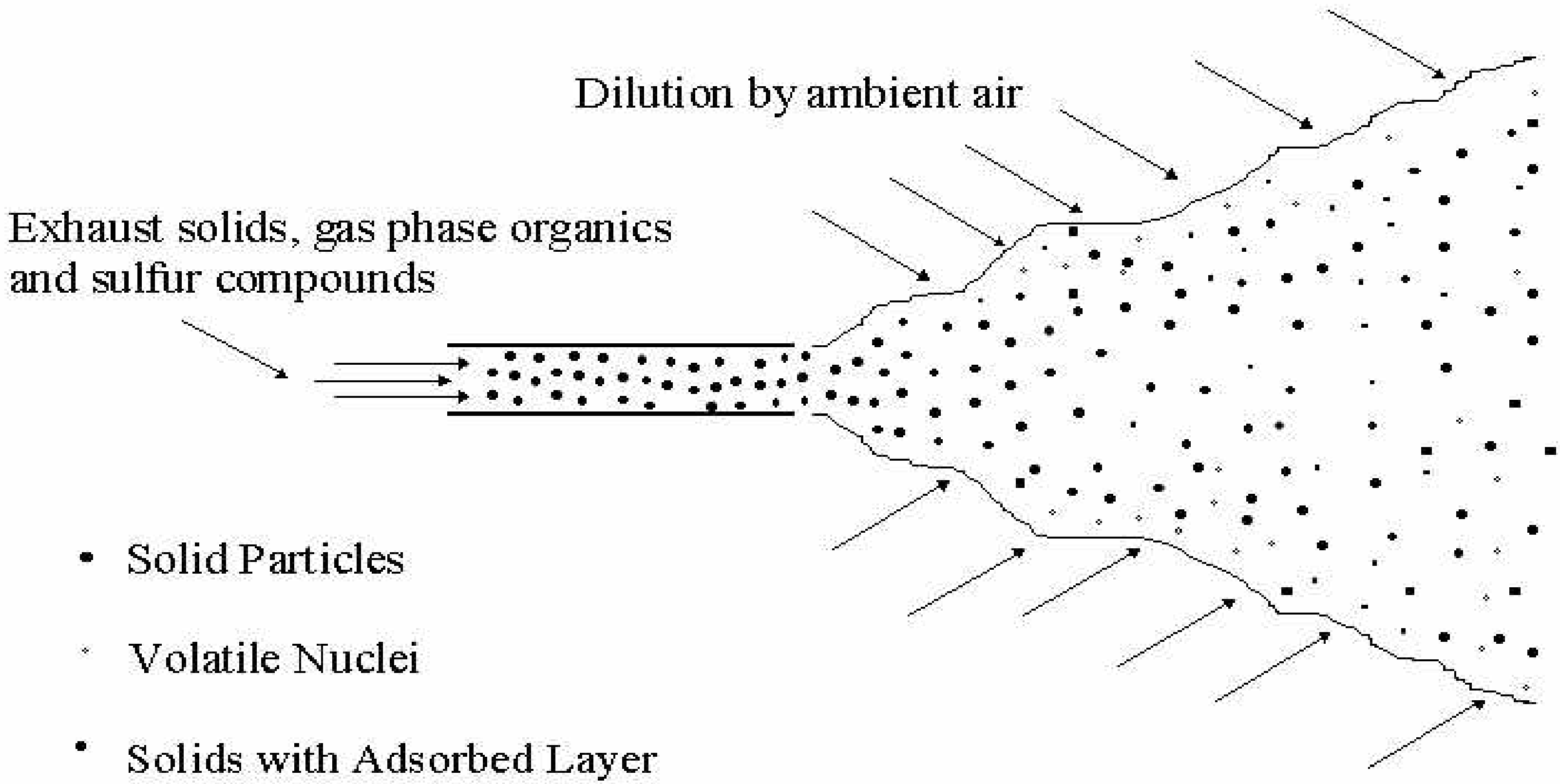


Significant Gas to Particle Conversion Takes Place as the Exhaust Dilutes and Cools

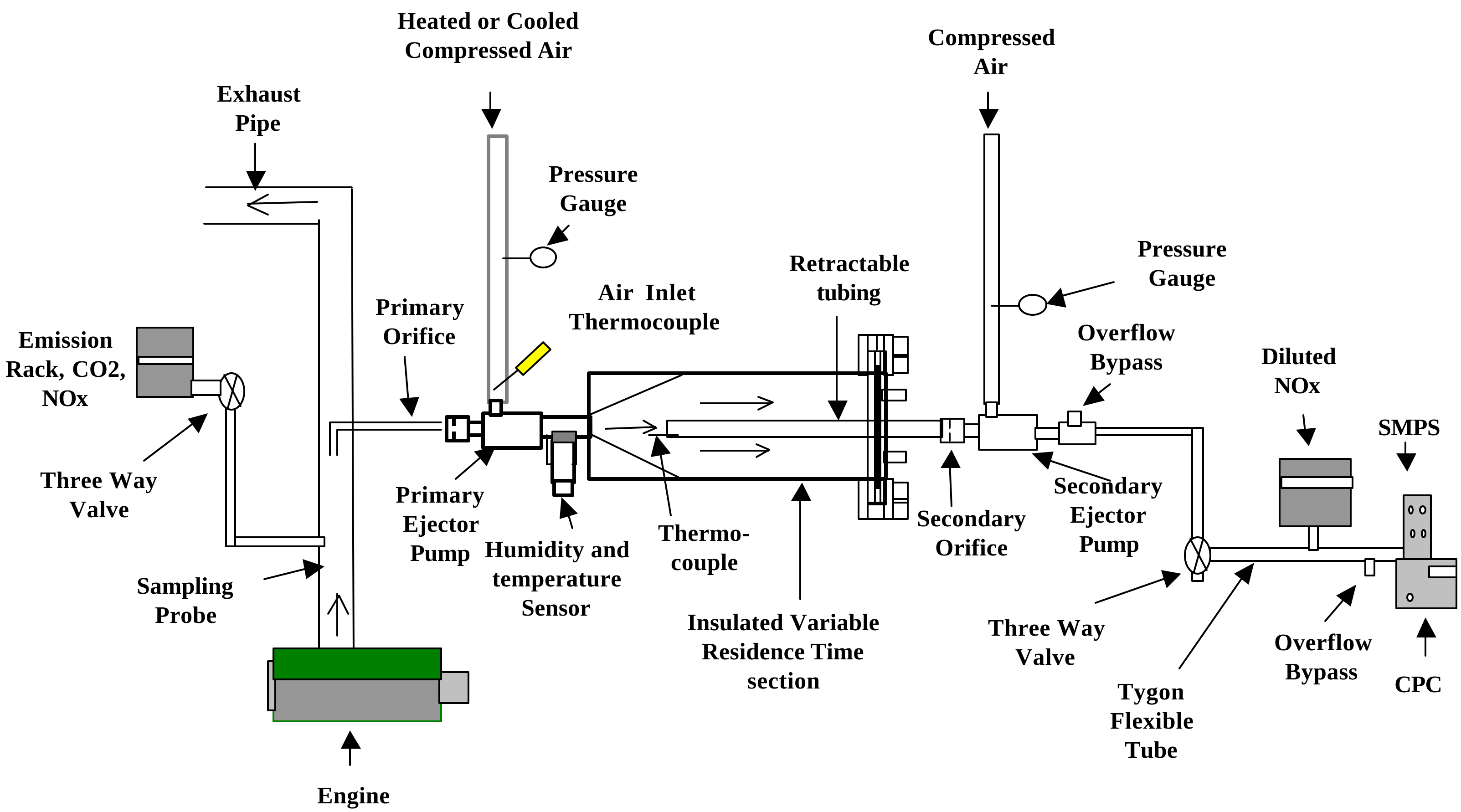
- More than 90% of the particle number may form through homogeneous nucleation of nanoparticles
- From 5 to more than 50% of the particle mass may form through adsorption, absorption, and nucleation
- These processes are *extremely* sensitive to dilution conditions
- Thermodynamics and fluid mechanics of mixing during dilution are very complicated and vary widely

Atmospheric Dilution Leads to Nucleation, Absorption, and Adsorption

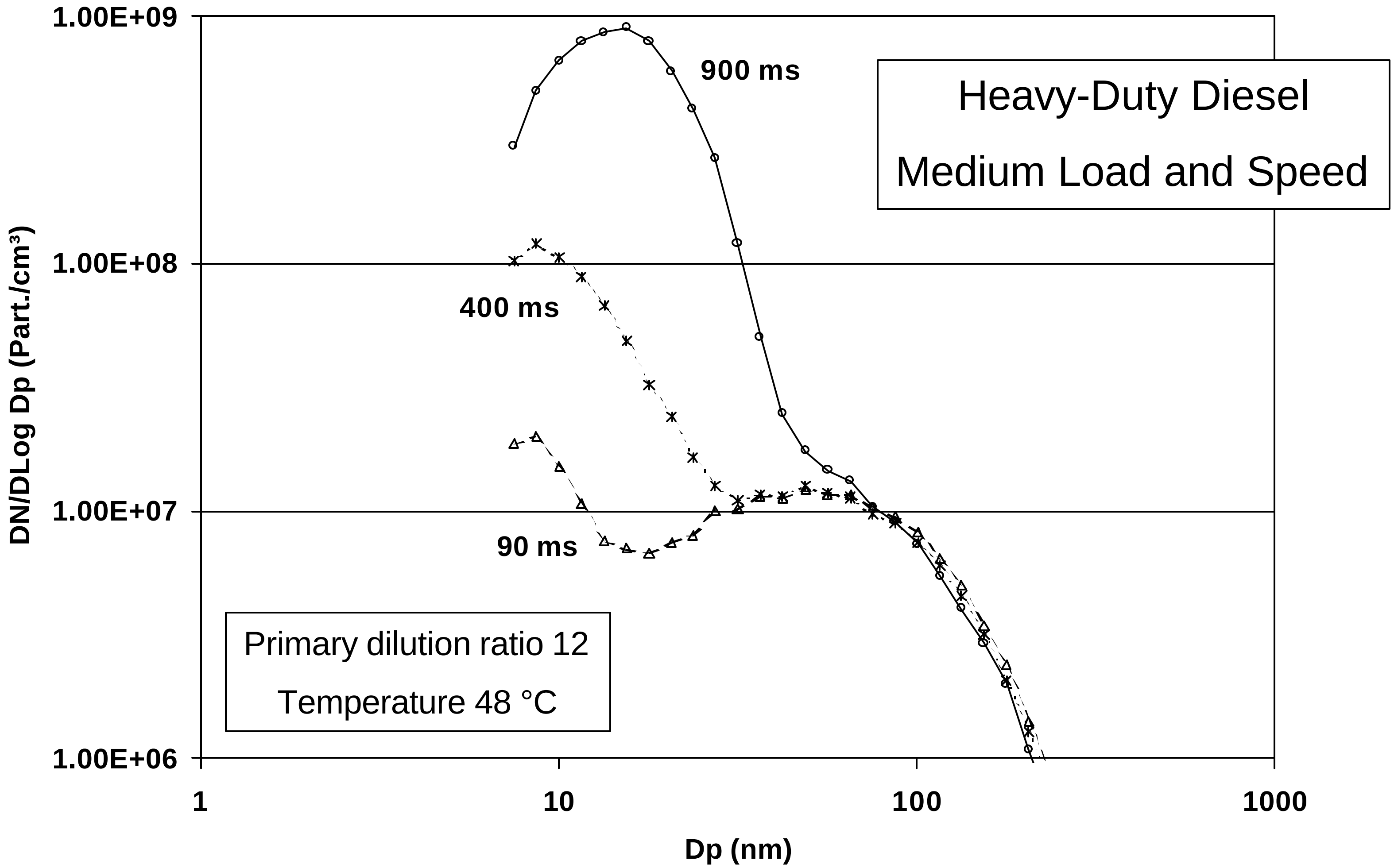
A dilution ratio of 1000 may be reached in 1 - 2 s



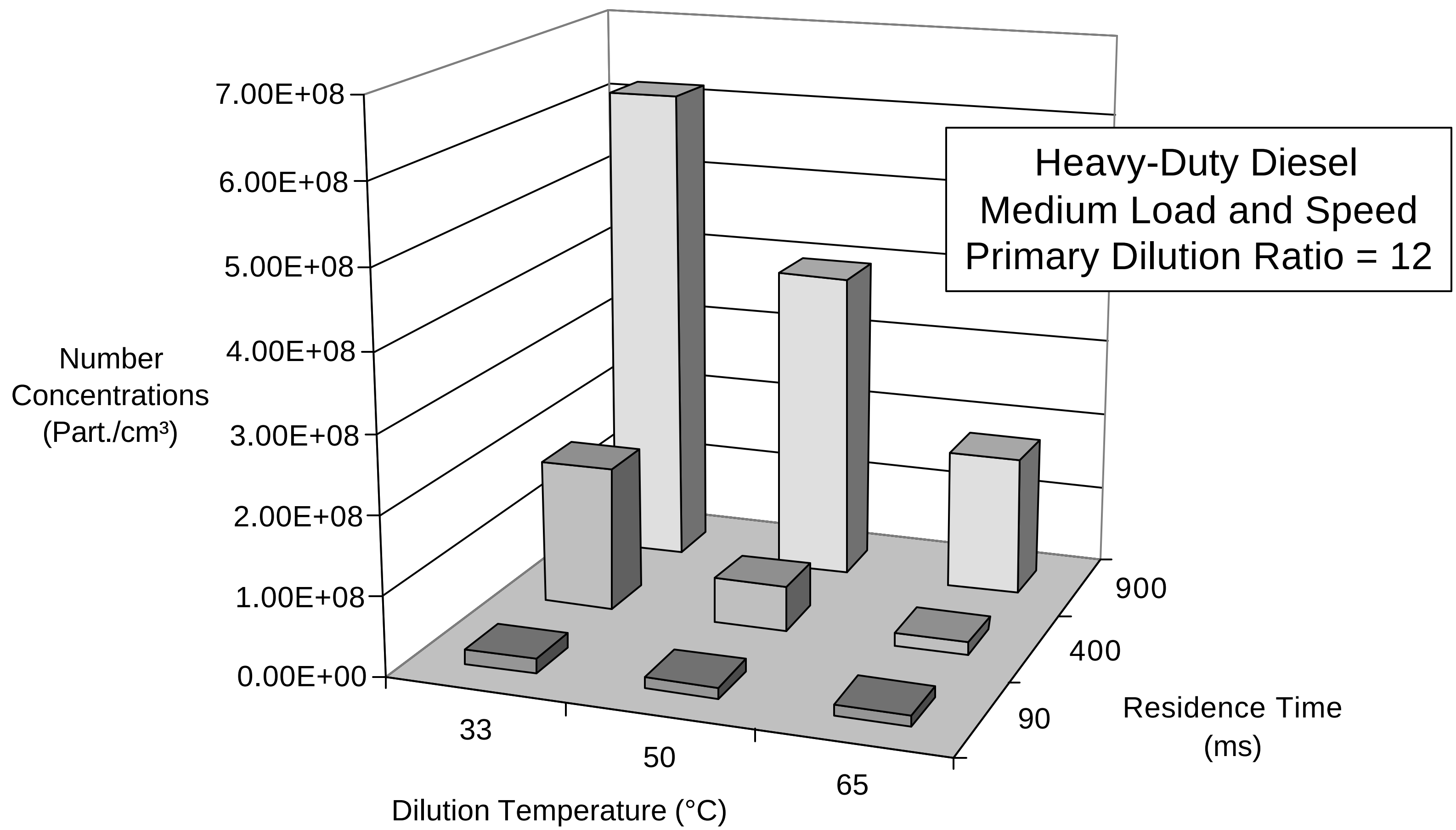
Studies of Diesel Nanoparticle Formation Using a Variable Residence Time Dilution System



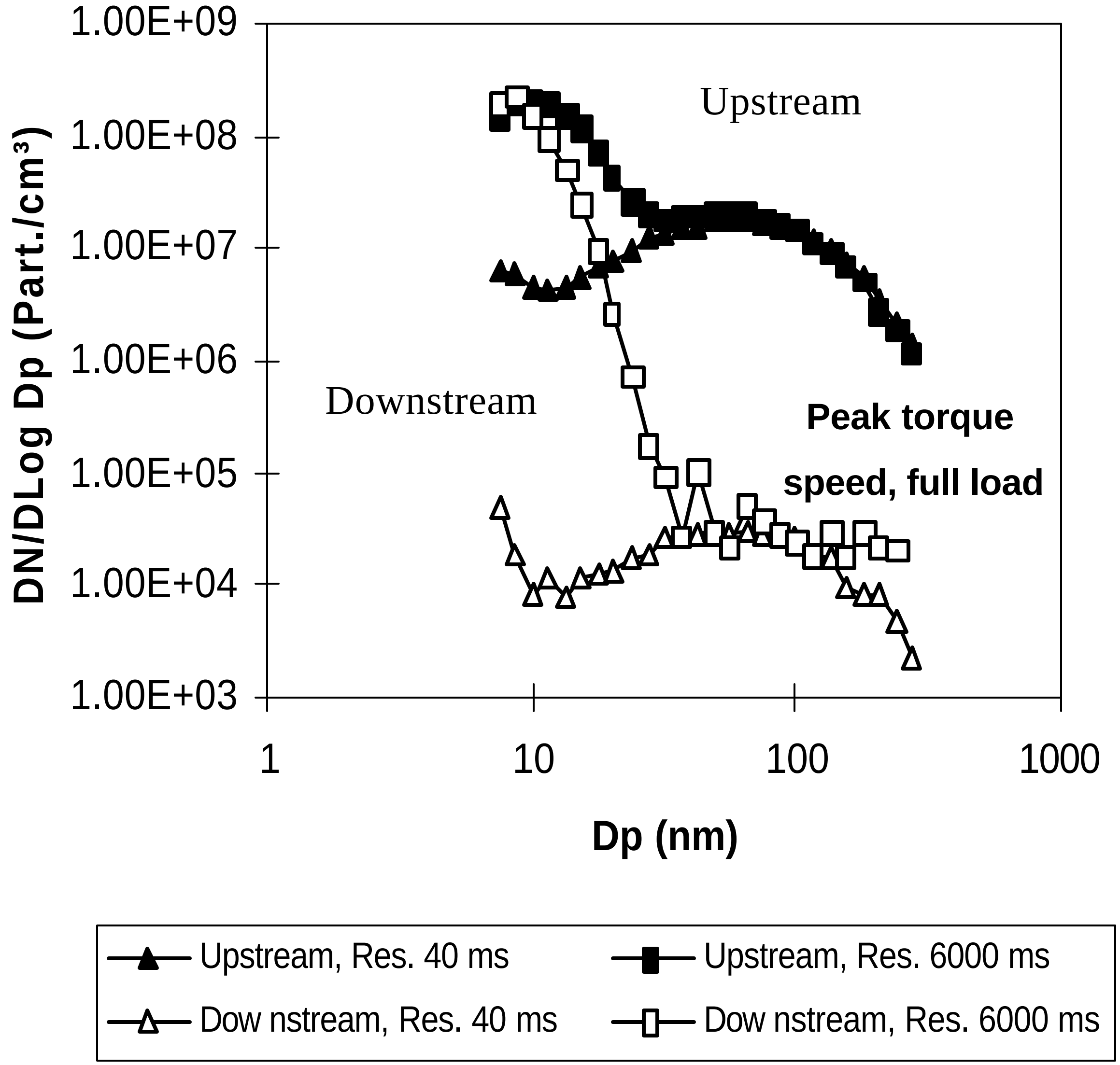
Sensitivity of Diesel Particle Size Distribution to Dilution Conditions - Residence Time Effects



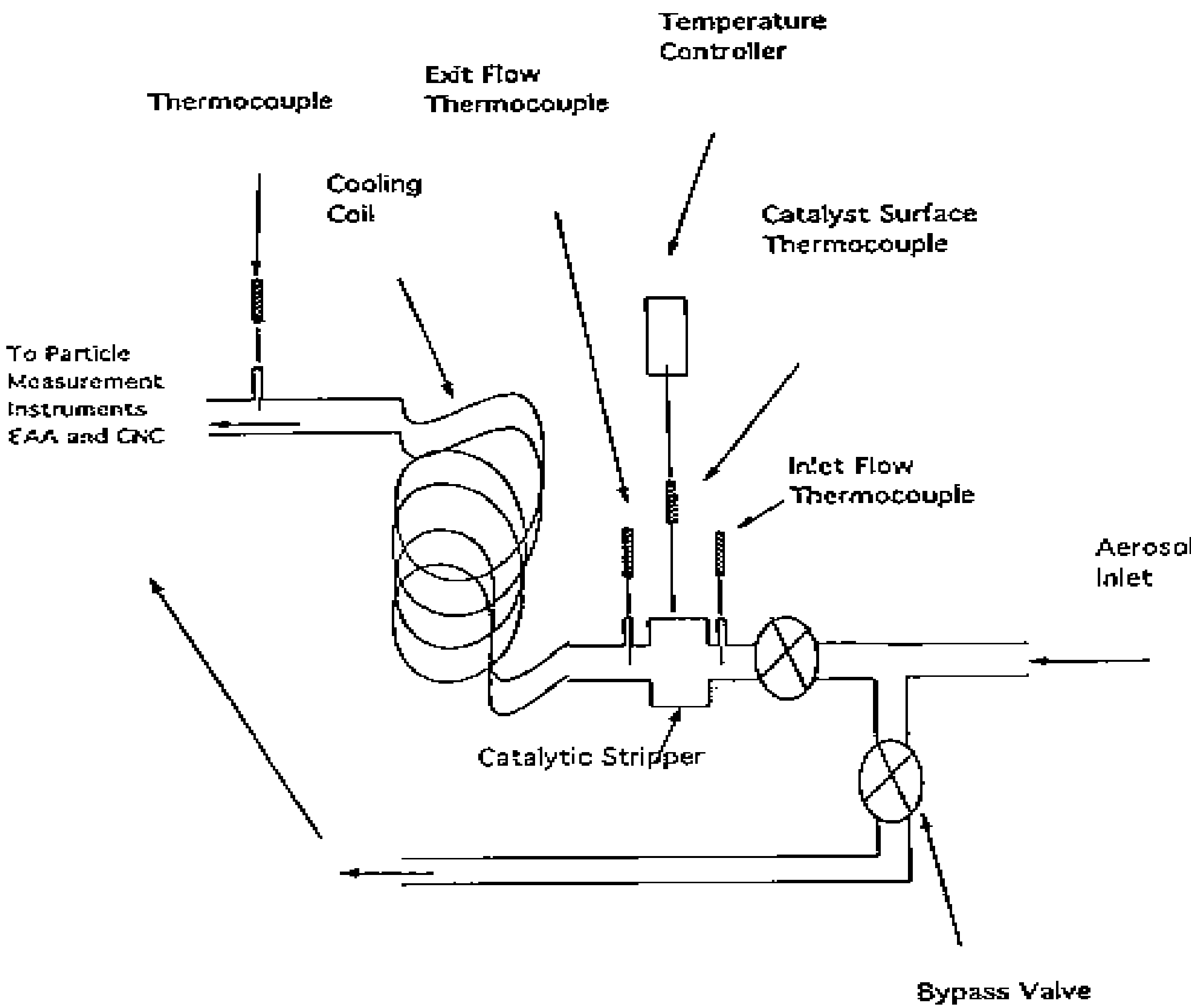
Sensitivity of Diesel Particle Number Emissions to Dilution Conditions - Residence Time and Temperature Effects



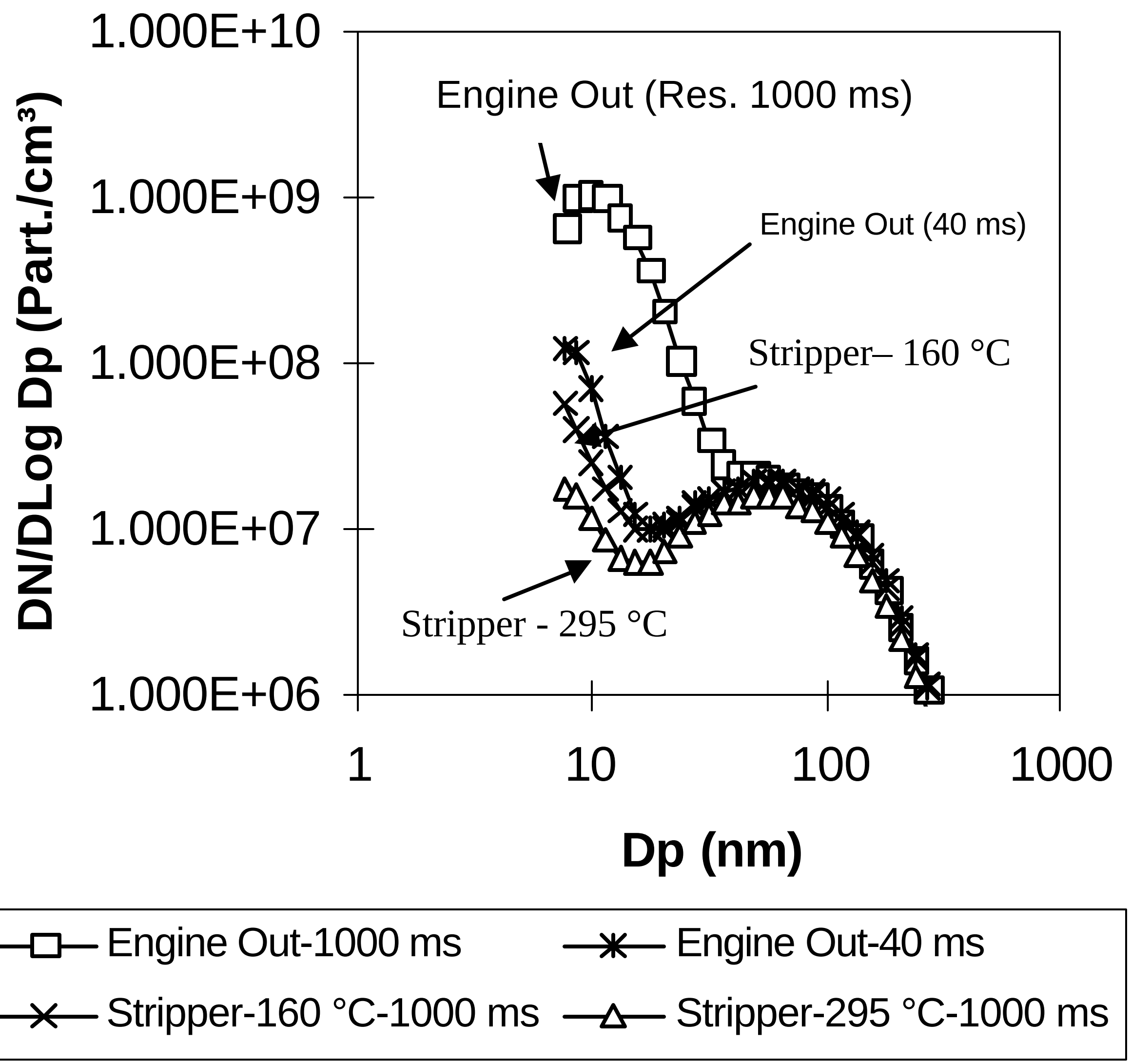
Nanoparticle formation downstream of an exhaust filter may be even more sensitive to dilution conditions



Our results suggest nanoparticles are mainly volatile, we have demonstrated this with a catalytic stripper



Typically more than 99% of the nanoparticles disappear by 300 C (except with metal additives)



How do nanoparticles form during dilution? Driving force for gas-to-particle conversion is saturation ratio

The saturation ratio, S, is defined as:

$$S = \frac{p}{p_v}$$

where p is the partial pressure and p_v is the vapor pressure of the volatile component. The dilution ratio, D, is defined as:

$$D = \frac{Q_{mix}}{Q_{exh}}$$

where Q_{mix} and Q_{exh} refer to the standard volumetric flows of diluted and raw exhaust, respectively. Also:

$$p \propto \frac{1}{D}$$

and

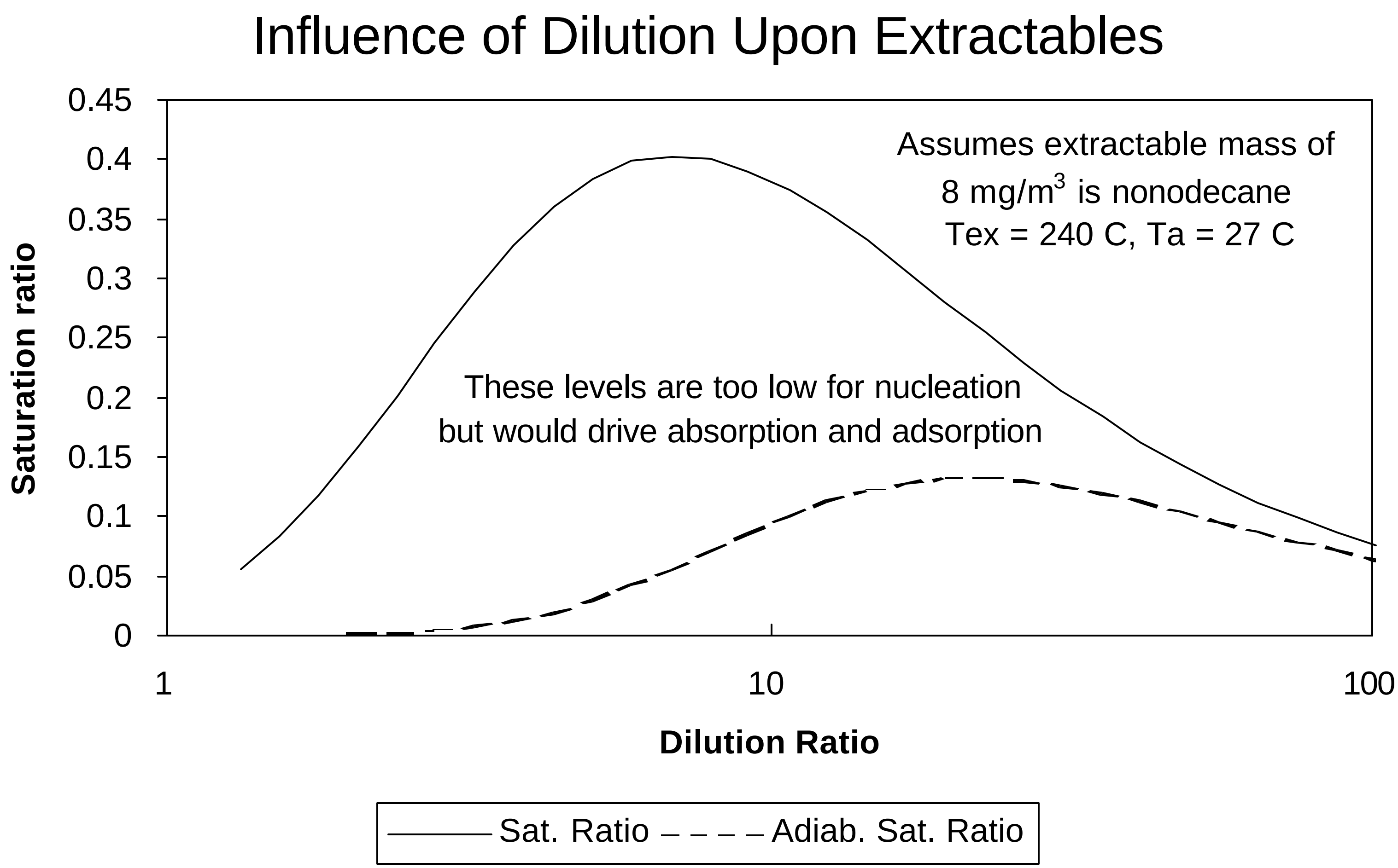
$$p_v \propto e^{\frac{-\Delta H}{RT_{mix}}}$$

so that

$$S \propto \frac{1}{De^{\frac{-\Delta H}{RT_{mix}}}}$$

and for adiabatic dilution.

For typical diesel exhaust conditions, saturation ratio may not be high enough for nucleation, S > ~ 3



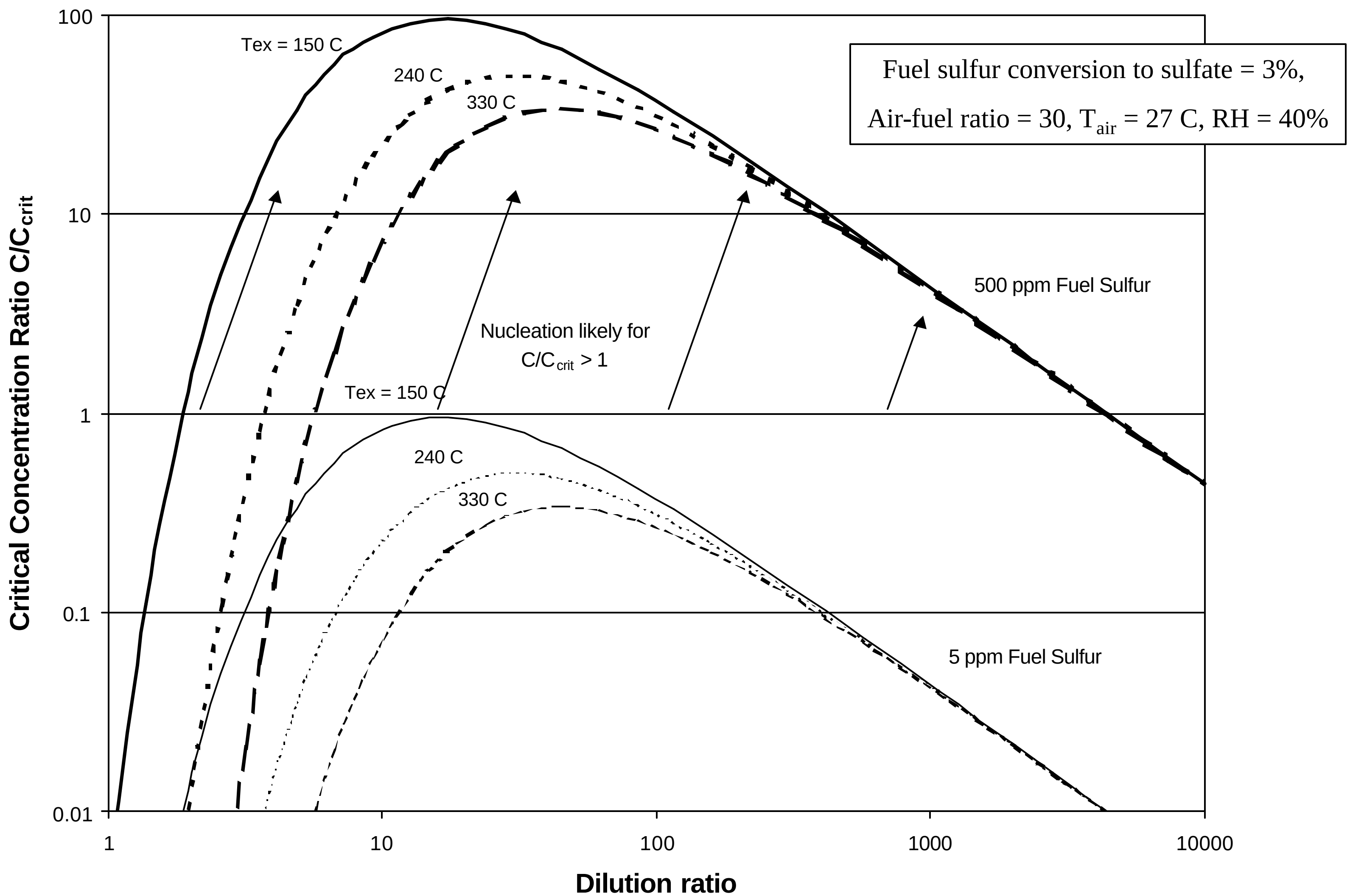
What does nucleate? Consider the threshold for Binary H_2SO_4-H_2O nucleation

- An extreme dependence of the nucleation rate upon temperature, H_2SO_4, and H_2O concentrations makes theoretical predictions of nucleation difficult.
- Seinfeld and Pandis give an empirical expression to predict the onset of nucleation in this system:

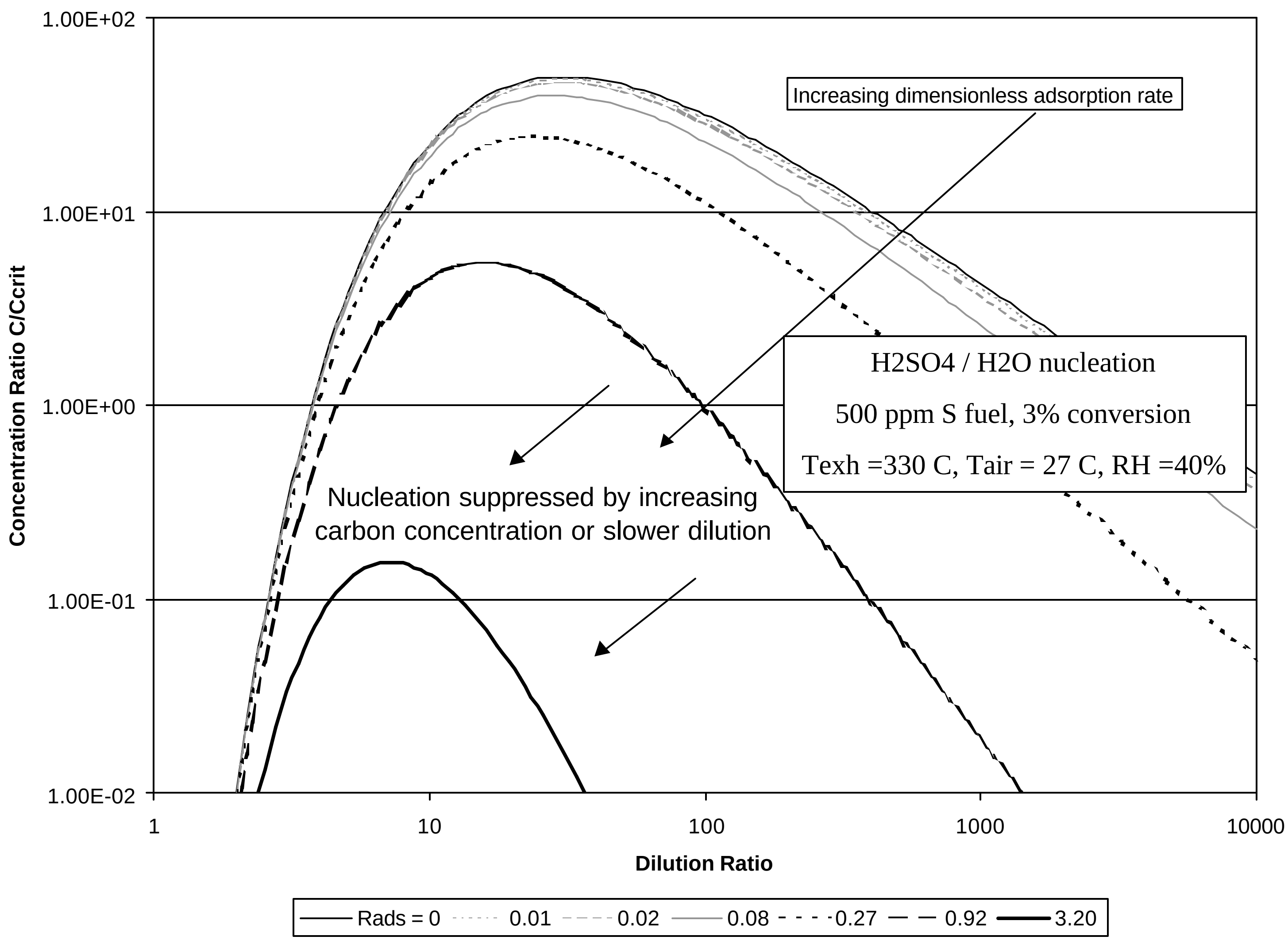
$$C_{crit} = 0.16\exp(0.1T - 3.5RH - 27.7)$$

  where C_{crit} is the threshold H_2SO_4 concentration in $\mu g/m^3$, T is temperature, RH is relative humidity (0 to 1).
- I have used this expression and mass and energy balances applied to the dilution process to predict the ratio of the actual H_2SO_4 concentration to the critical one, C/C_{crit}. When this critical concentration ratio exceeds one, nucleation is likely.

Influence of Fuel and Exhaust Conditions on Sulfuric Acid Nucleation



H_2SO_4 Nucleation Is Suppressed by Adsorption on Carbon Particles



Nanoparticle Nucleation and Growth

- It appears that with current engines binary sulfuric acid - water nucleation triggers the process.
- The initial size 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.

Summary Diesel - 1

- A significant amount of particulate matter (e.g. 90 % of the number and 30% of the mass) is formed during exhaust dilution from material present 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. Soot agglomerates provide a large surface area for adsorption that suppresses nucleation. Thus, engines with low soot mass emissions may have high number emissions.

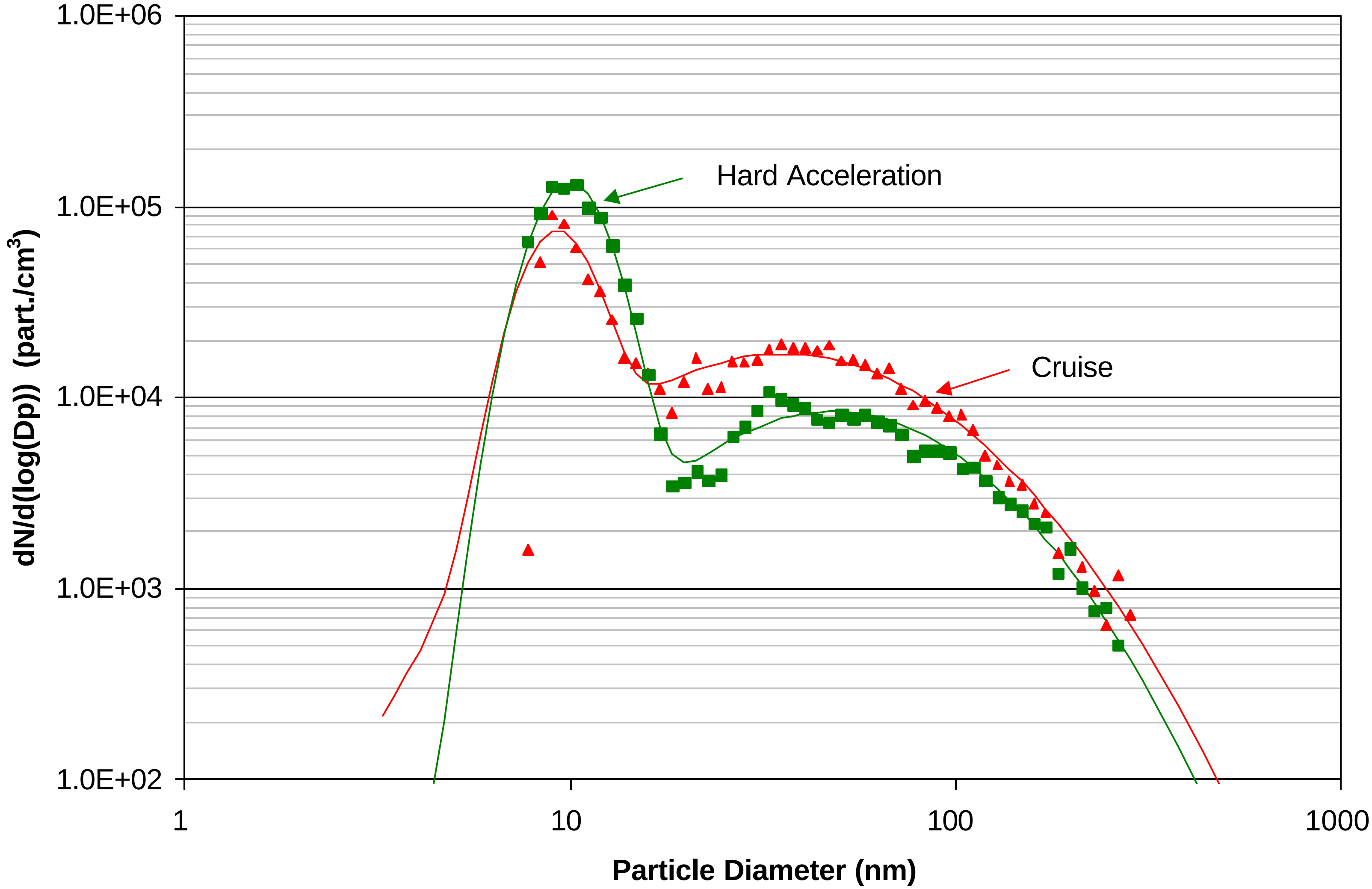
Summary Diesel - 2

- Nanoparticle measurements are very strongly influenced by the sampling and dilution techniques employed.
  - Nucleation, adsorption, absorption, and coagulation during sampling and dilution depend upon many variables, including dilution rate, (or residence time at intermediate dilution ratio), humidity, temperature, and relative concentrations of carbon and volatile matter.
  - Changes of more than two orders of magnitude in nanoparticle concentration may occur as dilution conditions are varied over the range that might be expected for normal ambient dilution, e.g., 0.1 to 2 s dilution time scales.
- Sampling systems should mimic atmospheric dilution to obtain samples representative of the tailpipe to nose process.

The most difficult problem associated with exhaust particle measurement is understanding the dilution process from tailpipe to nose -- this is being examined in the CRC E-43 program

This illustration shows a typical application of the University of Minnesota Mobile Aerosol laboratory developed for the CRC E-43 Program

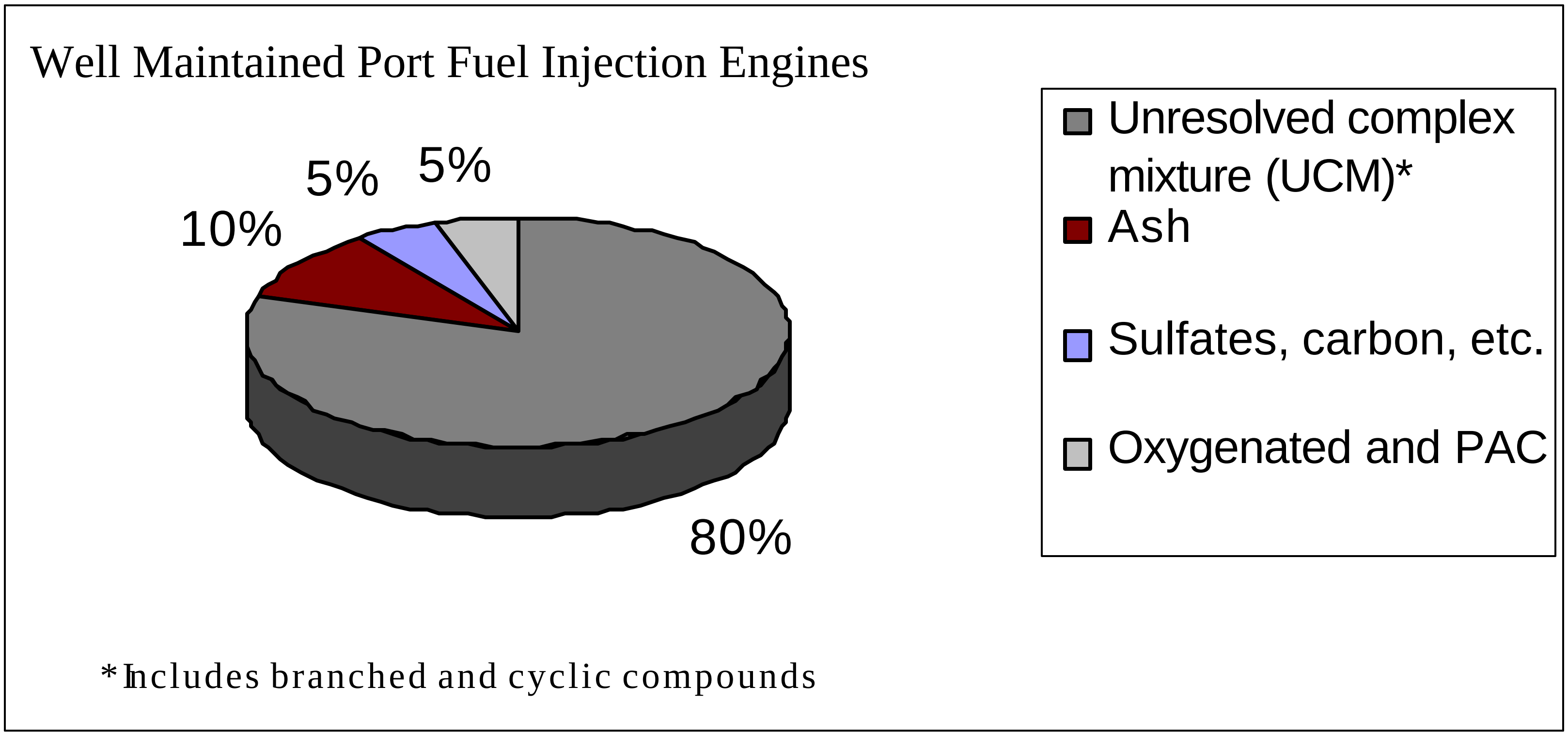
Nanoparticles are produced by new engines, but concentrations may be much lower than feared



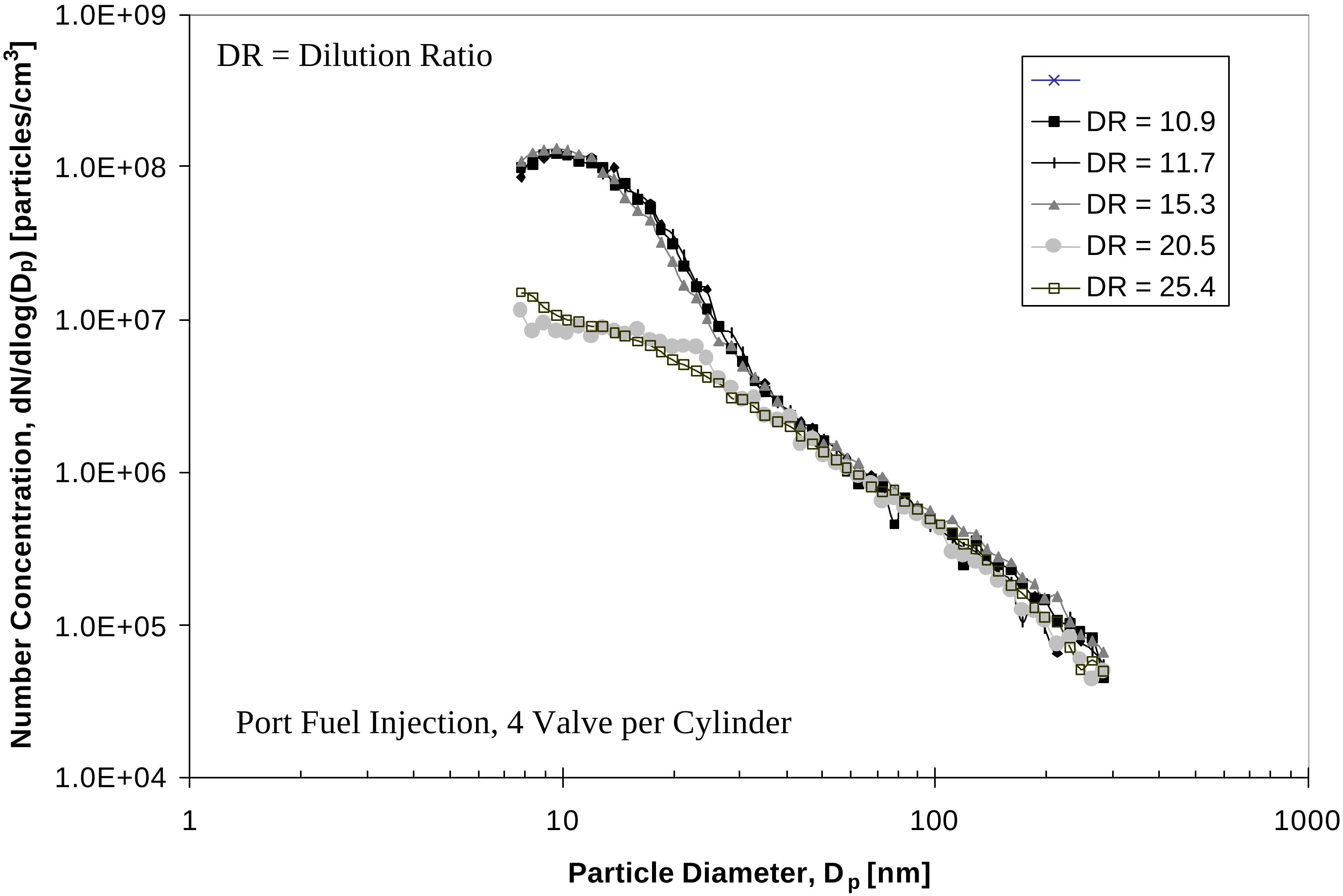
Summary Diesel - 3

- Currently most of the particles in the nanoparticle size range are volatile. However, as engines become cleaner, metallic ash particles from the lubricating oil (or fuel if metallic additives are present) may become more important.
  - Solid particles raise new issues…
  - But they are easy to control with exhaust filters
- Spark ignition engines typically emit smaller particles than diesel engines and are an important source of fine particles and nanoparticles.
  - A recent study in Colorado concluded that up to 2/3 of the fine particle mass emitted by vehicles was from spark ignition engines
  - New gasoline direct injection engines emit much higher particle concentrations than conventional engines and may approach diesel levels under some conditions

Particles from Spark Ignition Engines - Approximate Composition of Exhaust Particulate Matter



Nanoparticle Emissions from Spark Ignition Engines Also Depend upon Dilution Conditions



Port Fuel Injected Spark Ignition Engine - Influence of Load and Additives

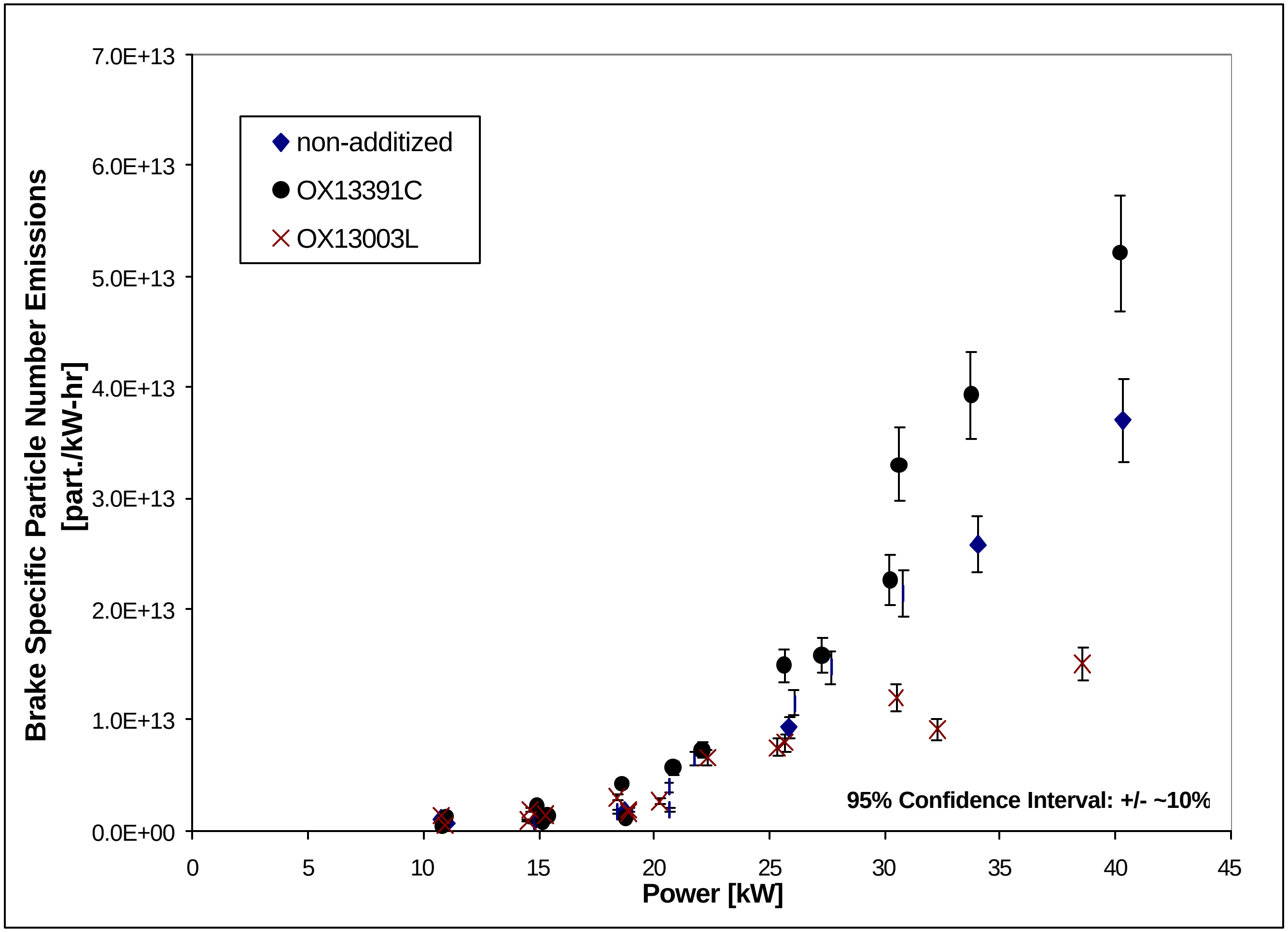


Figure 2. Brake Specific Particle Number Emissions as a Function of Power with 95% Confidence Intervals

Port Fuel Injected Spark Ignition Engine - Influence of Additives on Size Distributions

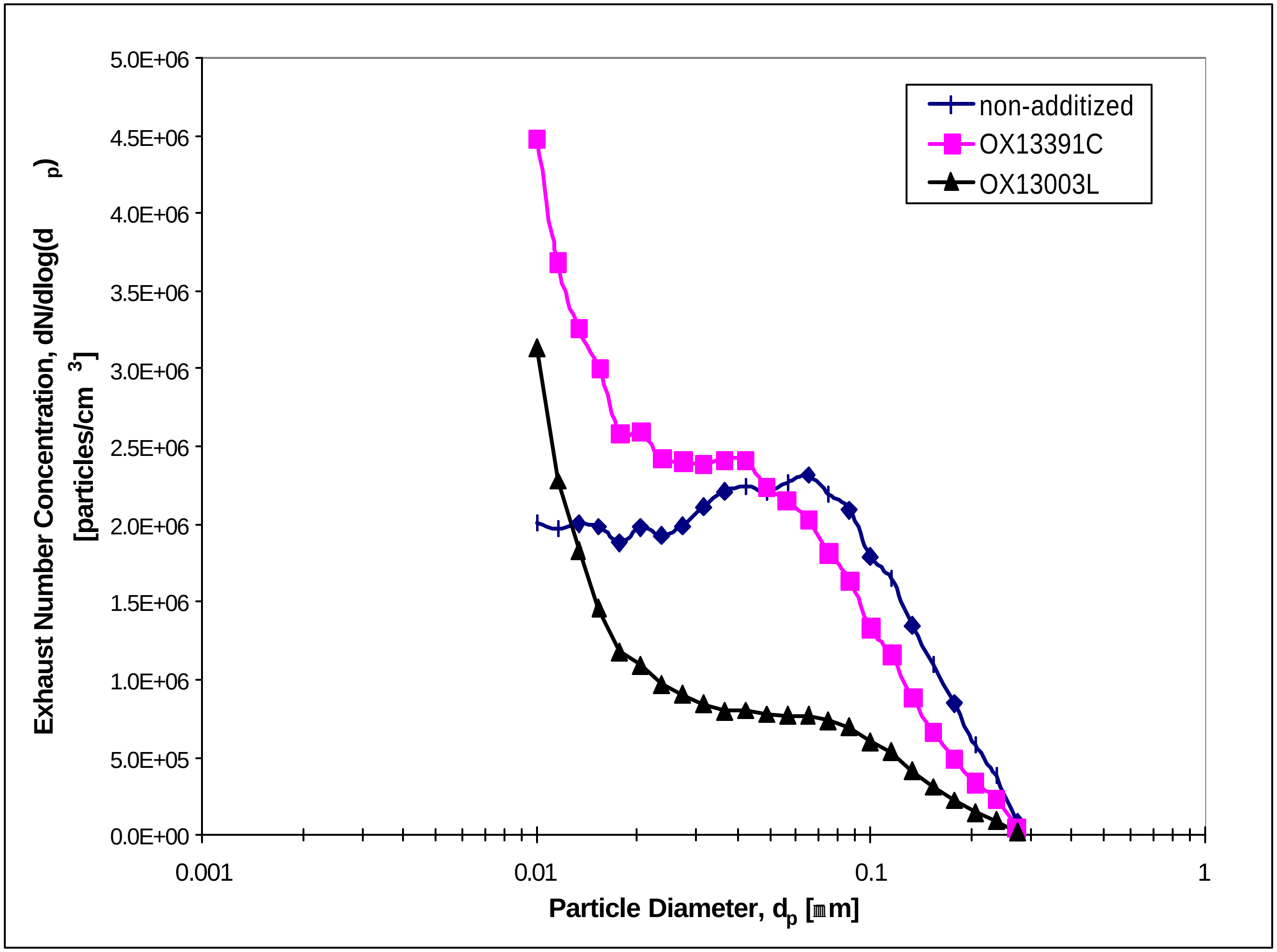
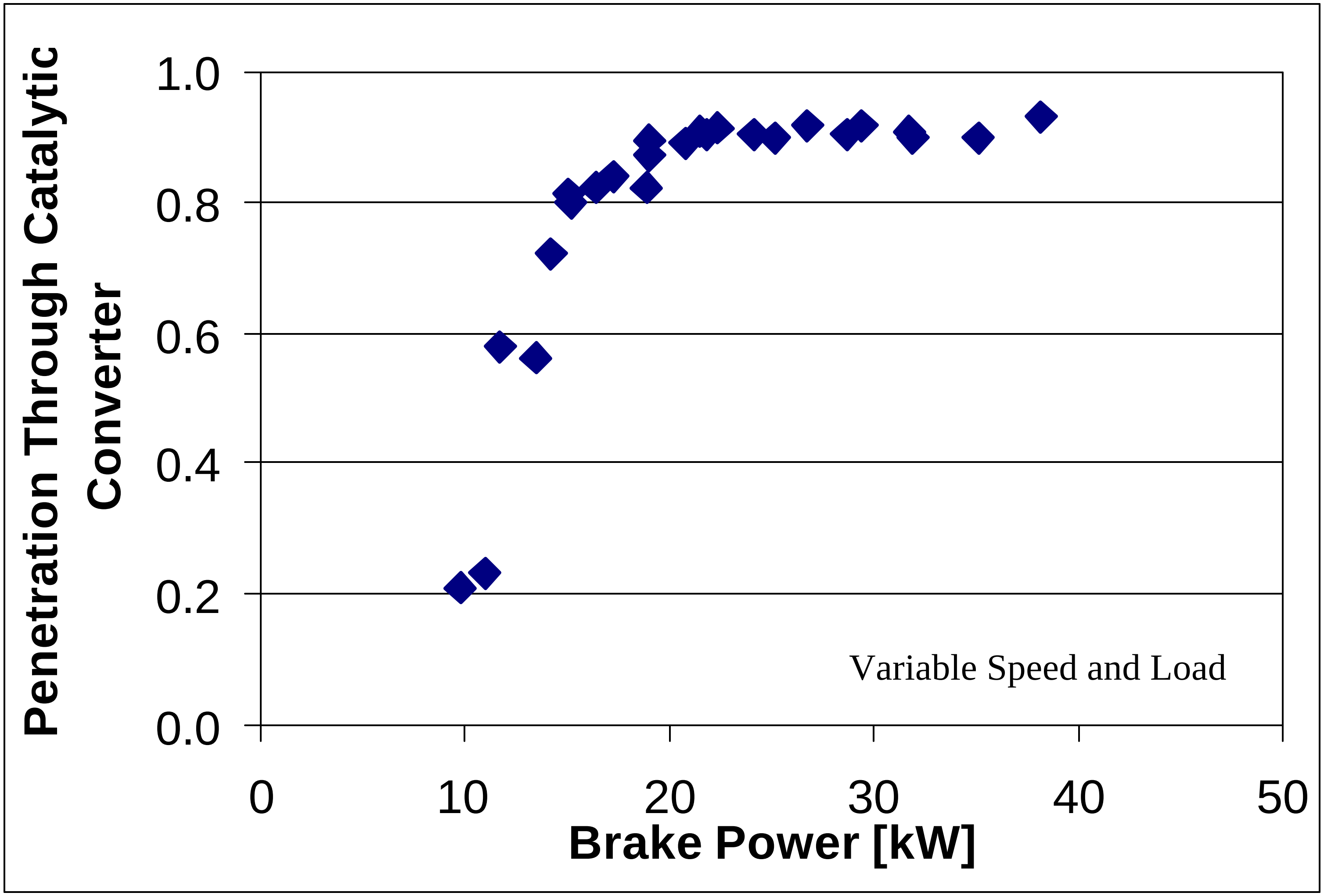


Figure 3. Representative Baseline Size Distributions for the OX13391 and OX13003 Additives [2500 RPM, 90 kPa]

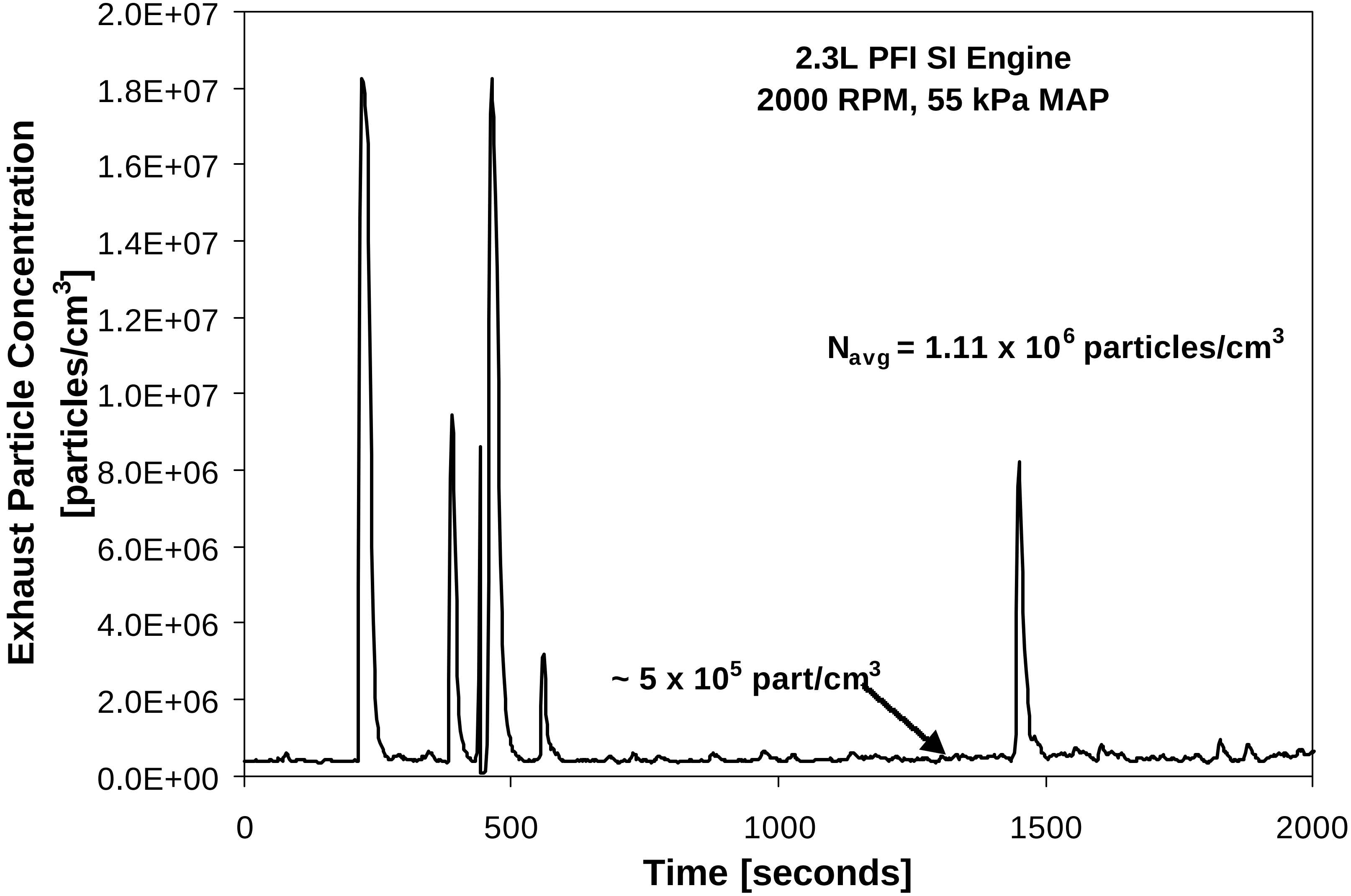
Summary - Particle Emissions from Port Fuel Injection (PFI) Spark Ignition Engines

- PFI engine exhaust particles are quite different from diesel particles
  - They usually smaller
  - They are composed primarily of volatile materials
  - Lube oil may play an important role
- PFI emissions are strongly influenced dilution conditions
  - Thus they are formed from volatile precursors during dilution
  - Sulfuric acid-water nucleation and hydrocarbon absorption likely play a role although direct nucleation of heavy hydrocarbon derivatives may play a role
  - Formation likely to be associated by local inhomogeneous conditions - big droplets, crevices

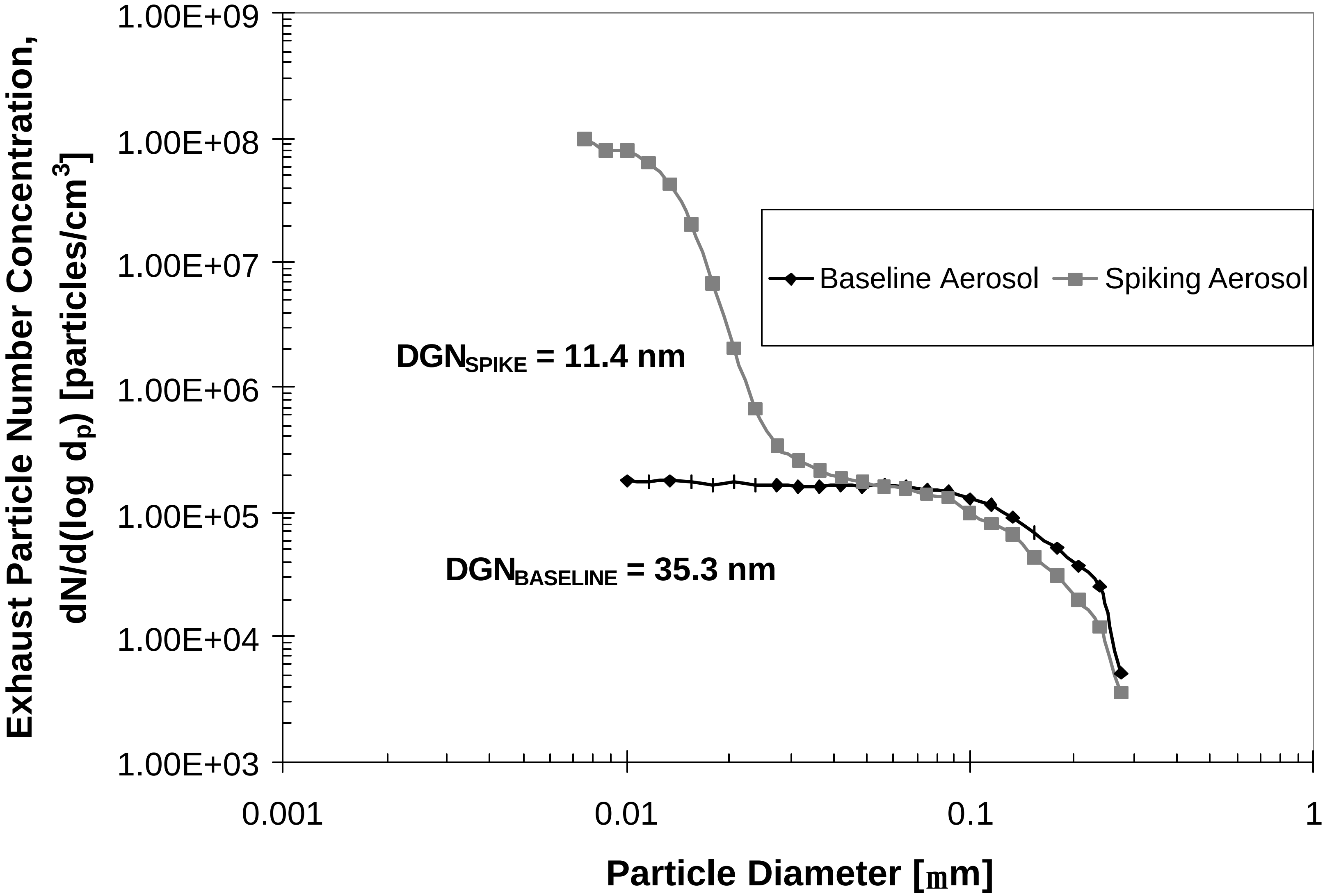
Particle Number Penetration through the Catalytic Converter on a Port Fuel injection Engine



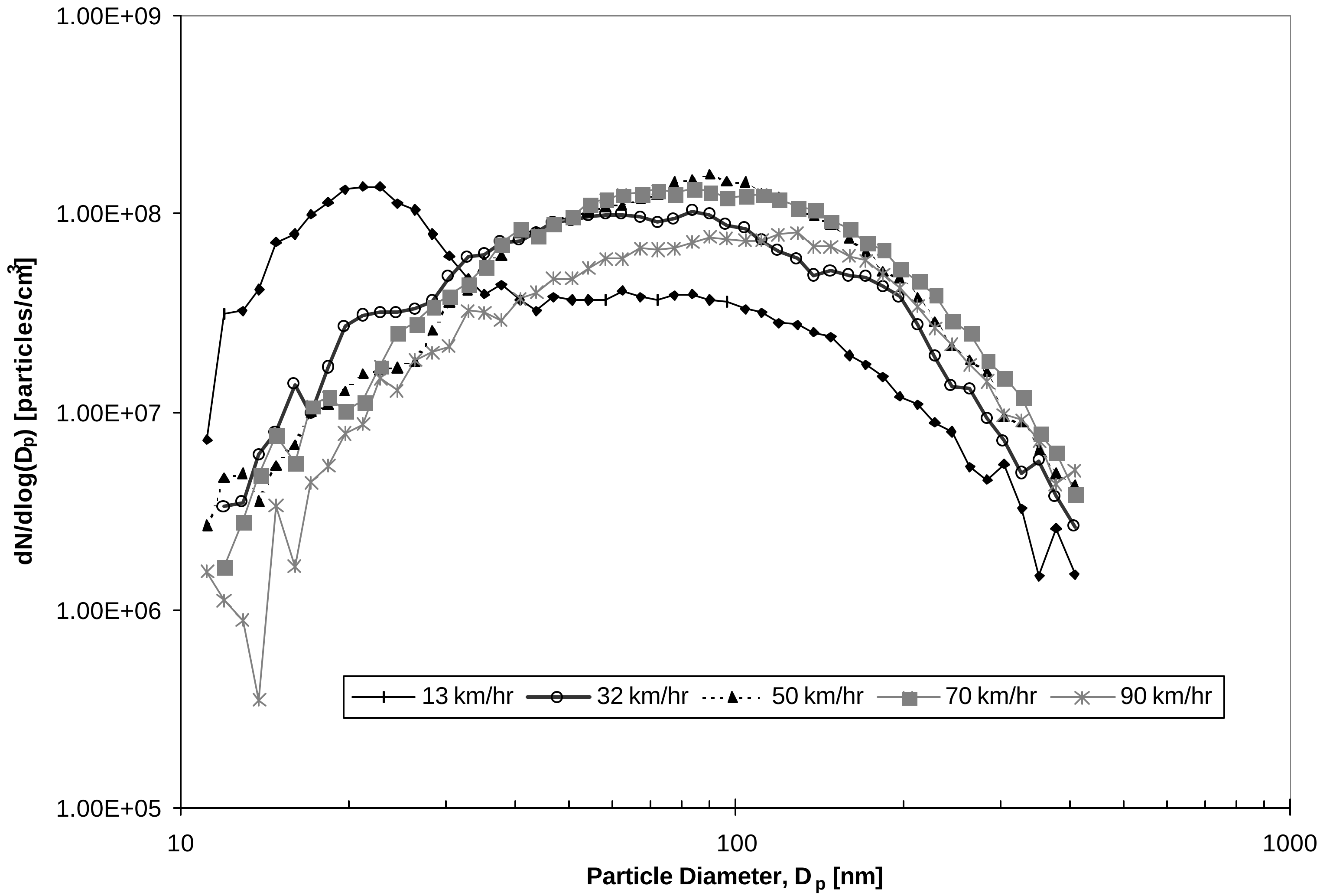
Time-Resolved Polydisperse Number Concentration in an SI engine Under Steady State Operating Conditions



Stable and Unstable (Spiking) Particle Size Distributions from a Spark Ignition Engine



Size Distributions for a GDI Engine



Summary - Particle Emissions from GDI Spark Ignition Engines

- These engines are likely to come into widespread use in Europe and Asia
- **Particles structure and emission rates are much more like those from diesels than PFI engines**
- Only limited studies of fuel and additive effects have been done