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BACKGROUND

A recent Health Effects Institute (HEI) study (Bagley, et al., 1996) showed dramatic increases in nanoparticle emissions for a 1991 engine compared to 1988 engine, both running on very low sulfur fuel. This has raised great concerns about very high nanoparticle emissions from modern, low particle mass emission engines. However it is important to recognize that the 1988 engine also produced high nanoparticle emissions when it was run on a 0.3% fuel similar to what it would have been operated on when it was new. Furthermore, diesel exhaust size distribution measurements made during 70's and 80's often showed high nanoparticle emissions and roadside measurements have nearly always shown a large nuclei (nanoparticle) mode (Whitby and Cantrell, 1975; Whitby, et al., 1975; Wilson, et al., 1977; Kittelson, et al., 1988; Weingartner, et al., 1997). Figures 1 and 2 show size distributions from the HEI study, and from a roadway measurement made in the early 80's in the plume of an engine of the same make as that used in the HEI study. The size distributions are surprisingly similar. Thus, high nanoparticle emissions are not a new development. What is new, and unexpected, is that nanoparticle emissions may not decrease along with mass emissions, but may actually increase. Nanoparticles are mostly volatile, except those formed from metallic additives. Most of these volatile nanoparticles are formed during exhaust dilution. The number formed is very sensitive to the nature of the dilution process.

PARTICLE FORMATION DURING DILUTION

Nearly all of the particulate matter found in the tailpipe before dilution is present as solid carbonaceous agglomerates and a small amount of metallic ash. However there also may be a significant quantity of volatile organic and sulfur compounds (particle precursors) in the gas phase at exhaust temperatures that are transformed to diesel particulate matter (DPM) by nucleation, adsorption, and condensation as the exhaust dilutes and cools. Most of the mass of volatile material that is transformed into DPM during dilution and cooling adsorbs onto the surface of existing carbonaceous agglomerates, however a small amount may undergo homogeneous nucleation to form new particles in the nanometer diameter range. This process is illustrated in Figure 3. Homogeneous nucleation of volatile matter to form nanoparticles becomes more likely when the concentration of carbonaceous agglomerates is reduced by aftertreatment or cleaner combustion. Thus nanoparticle formation may be more likely with clean, low carbon emission engines, especially when the concentration of carbon has been reduced more markedly than that of particle precursors. The carbonaceous agglomerates may be thought of as "sponges" that "soak up" volatile particle precursors and prevent them from reaching the level of super-saturation necessary to produce nucleation. Nucleation is a very nonlinear process so that nanoparticle formation is very sensitive to the dilution and cooling process, whether in the atmosphere or in the laboratory.

INFLUENCE OF DILUTION CONDITIONS ON NANOPARTICLE FORMATION

We have constructed a micro-dilution system to explore the sensitivity of nanoparticle formation to dilution and cooling conditions. It is shown in Figure 4. It utilizes two-stage dilution. The primary stage is designed to produce dilution ratios in the range of about 5 to 50. This is the range most likely to produce high saturation ratio, and thus nucleation. Temperature, humidity, and residence time in this stage may be varied to examine the sensitivity to these variables. The secondary stage is designed to dilute quickly to a high enough dilution ratio to stop nucleation and slow coagulation. Results shown below are for a primary dilution ratio of 12. The results are not very sensitive to secondary dilution ratio; a value of about 60 was used here. A medium-duty, low emission engine (meeting 1995 U.S. on-highway standards) running on standard D2 fuel (0.03% S) was used as a particle source for these experiments. The particle size distributions shown below were measured using a SMPS (scanning mobility particle sizer) and number concentrations were measured with a condensation particle counter (CPC), a TSI model 3020. Figure 5 shows the influence of residence time on number weighted size distribution for a dilution temperature 48 °C and dew point of 10 °C. The engine was operated at 50% load at 1600 rpm. The concentrations of particles in the nanoparticle range, smaller than 50 nm, change by nearly two orders of magnitude as the residence time is varied from 90 to 900 ms, but the concentrations of larger particles (which are presumably carbonaceous agglomerates) are essentially unchanged. Figure 6 shows the influence of dilution temperature at a fixed residence time of 400 ms and a dew point of 10 °C. The concentrations of particles in the nanometer range are increased by more than an order of magnitude as the dilution temperature is decreased from 65 to 32 °C. Again there is little influence on larger particles. Figure 7 summarizes the effects of residence time and temperature on total particle number concentration (most of the number is in nanoparticles). The total number concentration increases by two orders of magnitude between the short residence time, high temperature case and the long residence time, low temperature case. This illustrates the extreme sensitivity of nanoparticle concentration to dilution conditions.
Figure 8 shows the effect of relative humidity on total number concentration. The dilution temperature is 30 °C, the residence time 300 ms, the engine at 50% load, 1600 rpm. The concentration increases modestly, 10 – 20 % as the relative humidity is raised from 15 to 50%. The sensitivity of nanoparticle formation to dilution conditions may be even stronger when most of the carbonaceous agglomerates are removed from the exhaust. Tests have been done with an uncatalyzed, wall-flow particle filter fitted to the engine. Figure 9 illustrates the sensitivity of nanoparticle formation to residence time both upstream and downstream of the filter. The engine was run at 1600 rpm, 100% load with a dilution temperature of 50 °C and a dew point of 10 °C. Residence times of 40 ms and 6 s were used. At the short residence time particle concentrations are 3 orders of magnitude lower downstream of the filter across the entire size range. However, significant nucleation occurs with the long residence time. The concentration of 10 nm particles downstream of the filter increases by 4 orders of magnitude and ends up higher than the concentration in this size range upstream of the filter.

STORAGE AND RELEASE OF VOLATILE PARTICLE PRECURSORS

Volatile particle precursors may collect in the exhaust and sampling system during low exhaust temperature operating modes and be released during high temperature excursions.
Figure 10 shows transient measurements of total exhaust particle number concentrations after transition from stabilized idle to full power and Figure 11 shows several size distributions taken during this transient. Particle number concentration immediately after the load increase is ten times higher than the stabilized concentration that is reached after about 20 minutes. The size

distributions taken during this transient show that essentially all of the changes in number are taking place in the nanometer diameter range. This suggests that the engine is producing an essentially steady concentration of carbonaceous agglomerates that mainly comprise the accumulation mode. Volatile particle precursors, likely stored on engine and sampling system surfaces during the idle mode, are released at the high temperatures produced by the full power condition lead to nanoparticle formation. For this condition, it appears that about 20 minutes are required to drive off these materials and come to a new stable operating condition.

CONCLUSIONS

Most nanoparticles form by homogeneous nucleation of volatile particle precursors as the exhaust dilutes and cools. Although nanoparticle formation may be favored by certain laboratory dilution procedures, the well-documented existence of a large nuclei (nanoparticle) mode in the air above and near roadways, shows that their formation is not a laboratory artifact. Their formation may be favored when solid carbon emissions are relatively low compared to emissions of volatile particle precursors. Nanoparticle formation depends on 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.

Even greater sensitivity to dilution may be observed with exhaust filters or low emission engines that produce very low exhaust carbon concentrations. Thus, accurate simulation of the atmospheric dilution process will be necessary to make laboratory measurements representative of actual human exposures to nanoparticles on and near roadways.

ACKNOWLEDGMENTS

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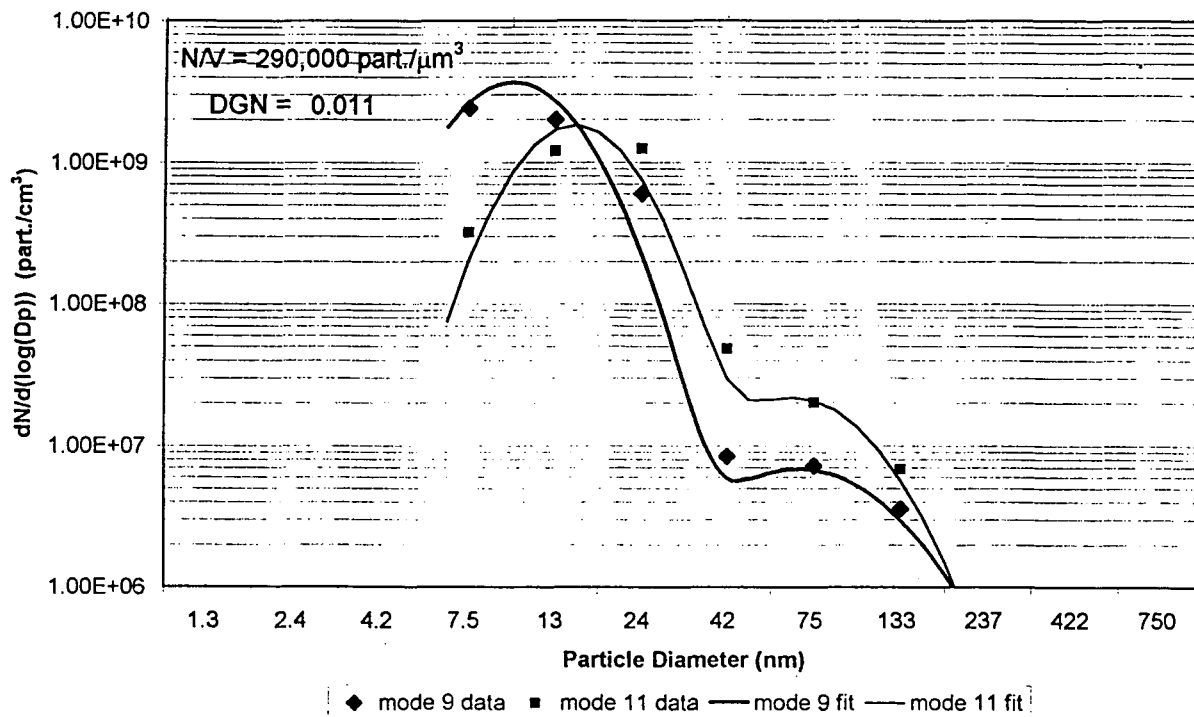
Figure 1 - Number Weighted Size Distribution from HEI Report (Bagley, et al., 1996)
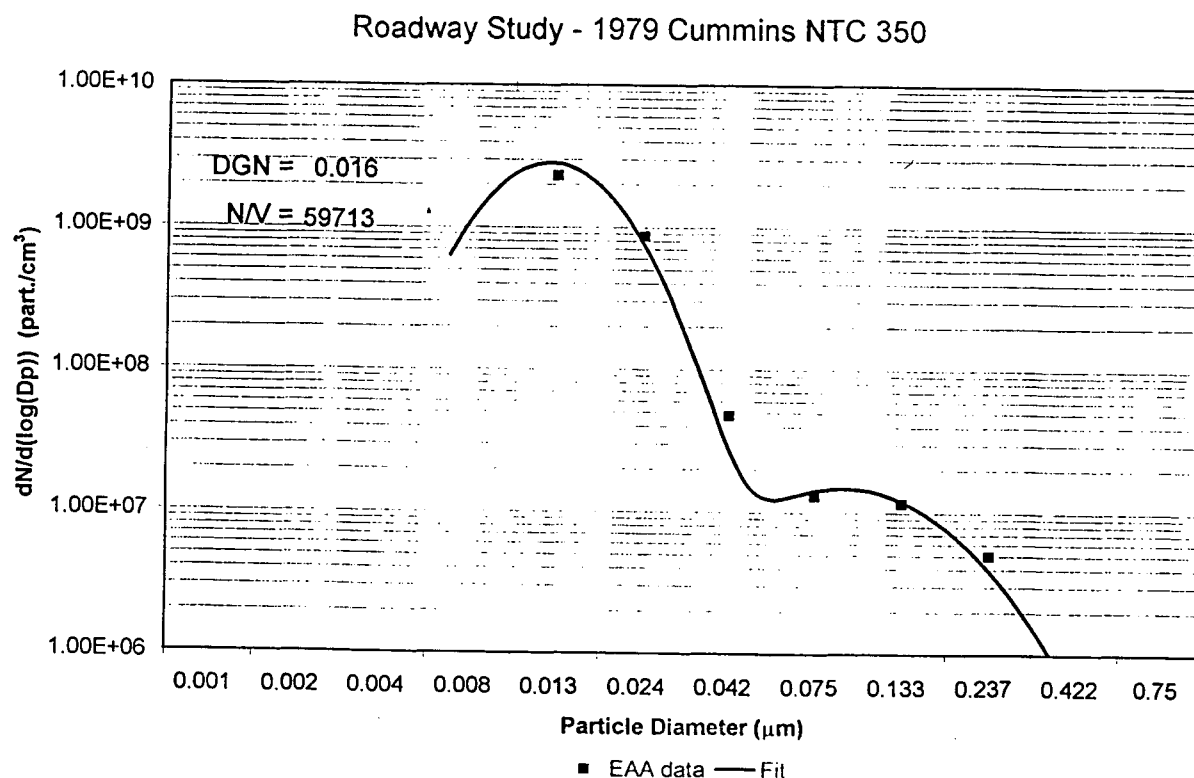

Figure 2 - Number Weighted Size Distribution Recalculated from Roadway Data (Kittelson, et al., 1988). Measurements Made on a Highway in the Plume of a Heavy-Duty Highway Tractor-Trailer.
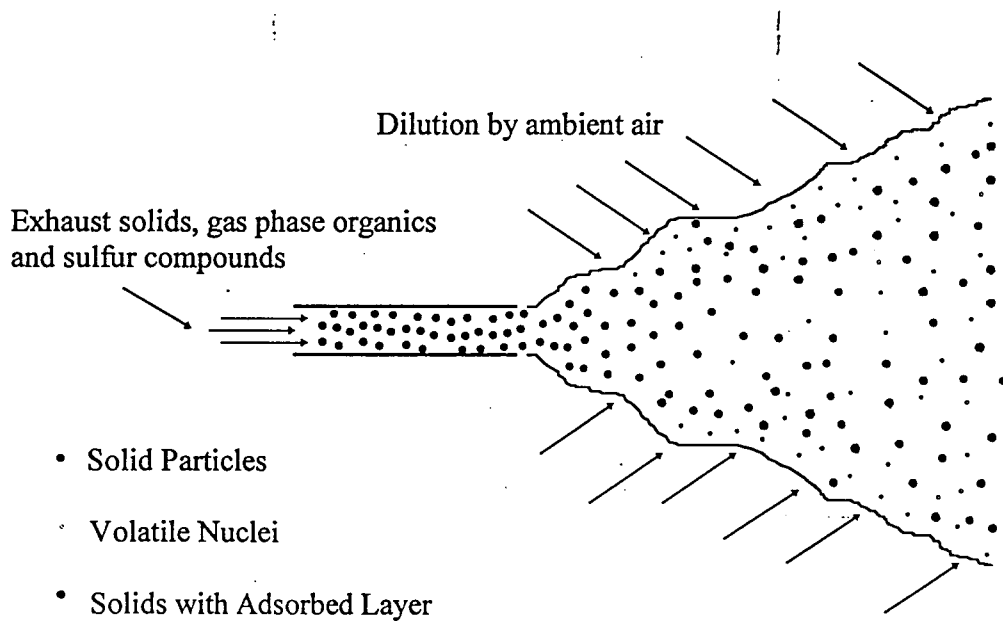
Dilution by ambient air

Exhaust solids, gas phase organics
and sulfur compounds

- Solid Particles

- Volatile Nuclei

- Solids with Adsorbed Layer

Figure 3 - Illustration of Particle Formation during Dilution

Air Supply
Line

Pressure Gauge

HEPA
Filter

Silica Gel
Dryer

HEPA
Filter

Pressure
Regulator

Exhaust
Pipe

Primary
Orifice

Thermo-
couple

Overflow
Bypass

Retractable
Tube

Overflow
Bypass

Diluted
NOx

Compressed
Air Inlet

Emission
Rack, CO2,
NOx

SMPS

Primary Ejector
Pump

Variable
Residence
Time section

Secondary
Orifice

Secondary
Ejector Pump

Three Way
Valve

Three
Way
Valve

Exhaust
Particulate
Trap

Overflow
Bypass

CNC

Sampling
Probe

Engine:Perkins
Phaser T4.40

Figure 4 - Micro Dilution System
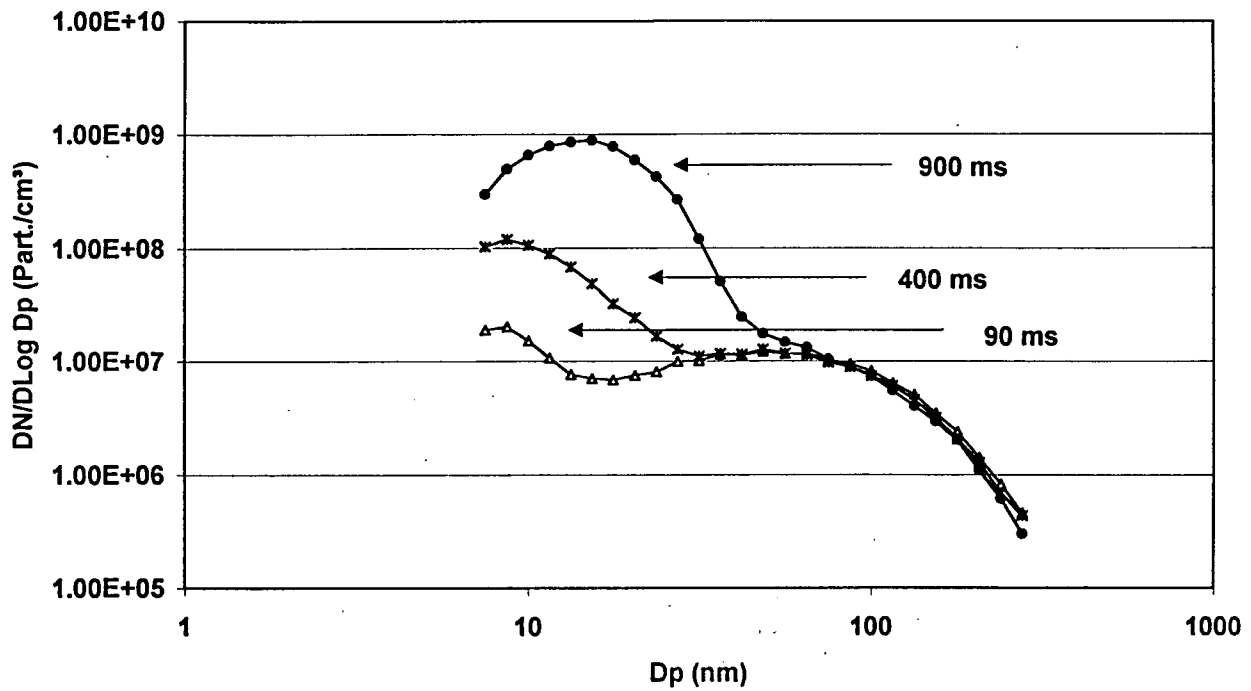
Figure 5 – Influence of Residence Time in Primary Dilution Stage on Particle Size Distribution Measured with SMPS, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 50% load. Primary Dilution Temperature 48 °C, Dew Point, 10 °C.
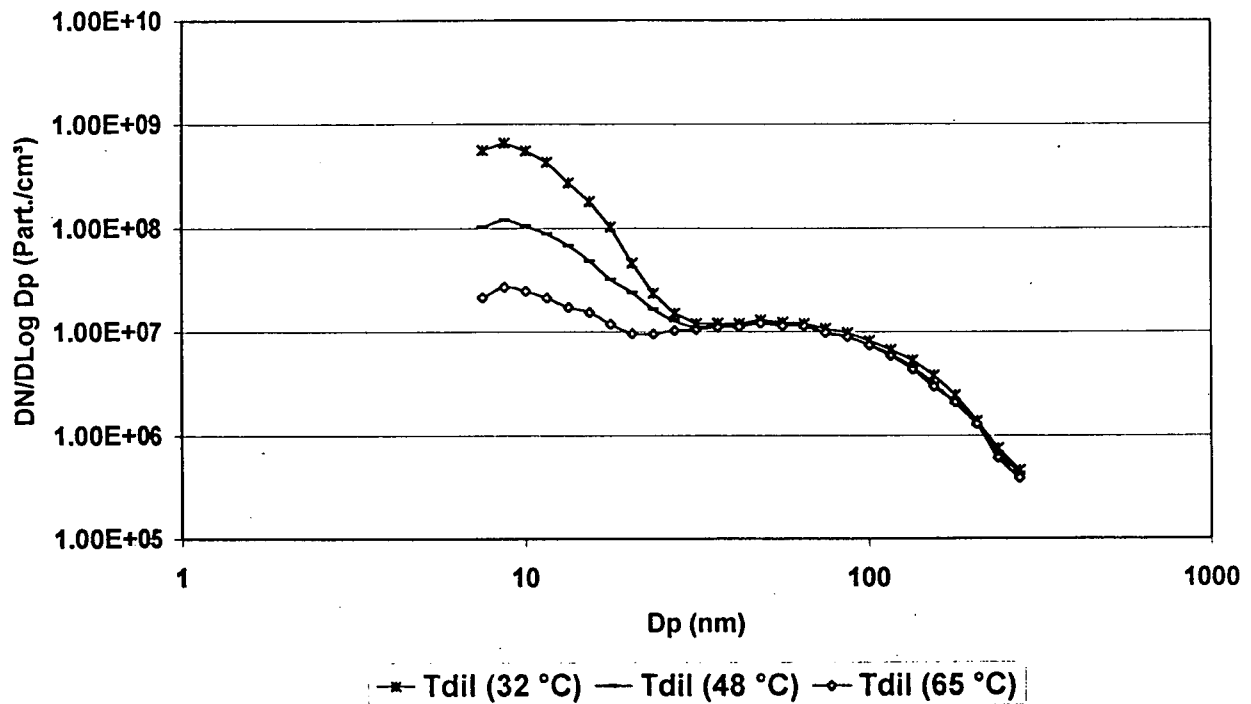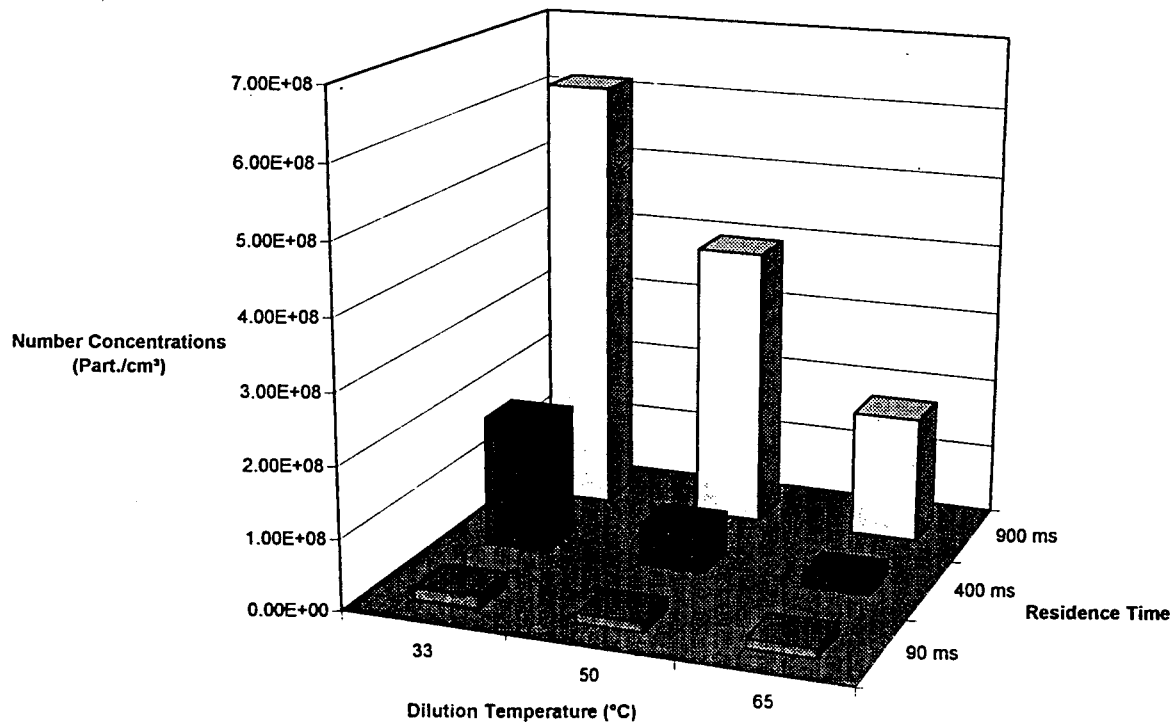

Figure 6 – Influence of Temperature in Primary Dilution Stage on Particle Size Distribution Measured with SMPS, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 50% load. Primary Dilution Residence Time 400 ms, Dew Point, 10 °C.

Figure 7 - Influence of Temperature and Residence Time in Primary Dilution Stage on Total Particle Number Concentration Measured with SMPS, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 50% load. Primary Dilution Dew Point, 10 °C.
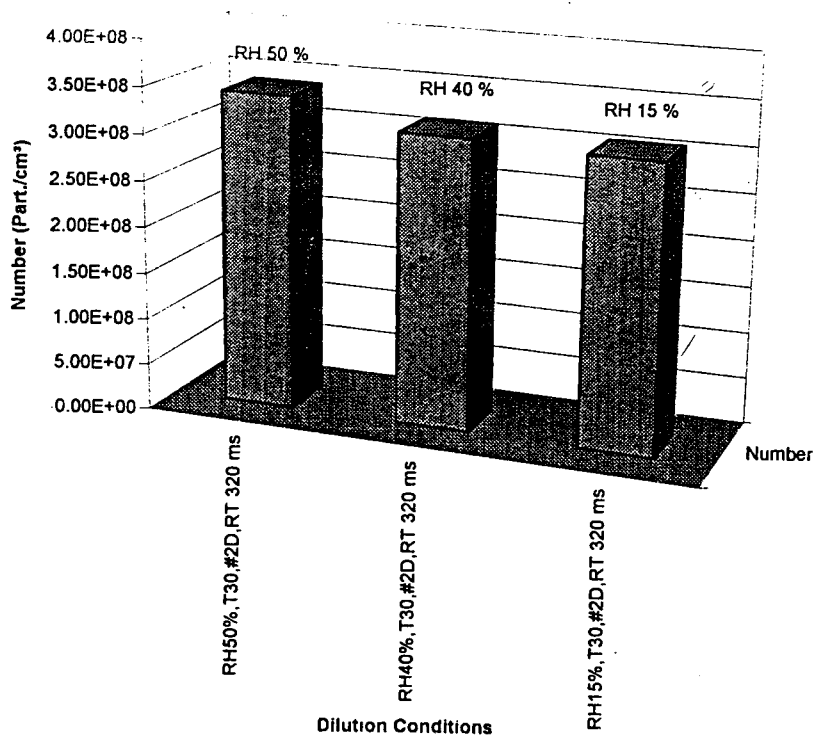

Figure 8 - Influence of Relative Humidity on Total Particle Number Concentration Measured with SMPS, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 50% load. Primary Dilution Temperature 30 °C, Residence Time 300 ms.
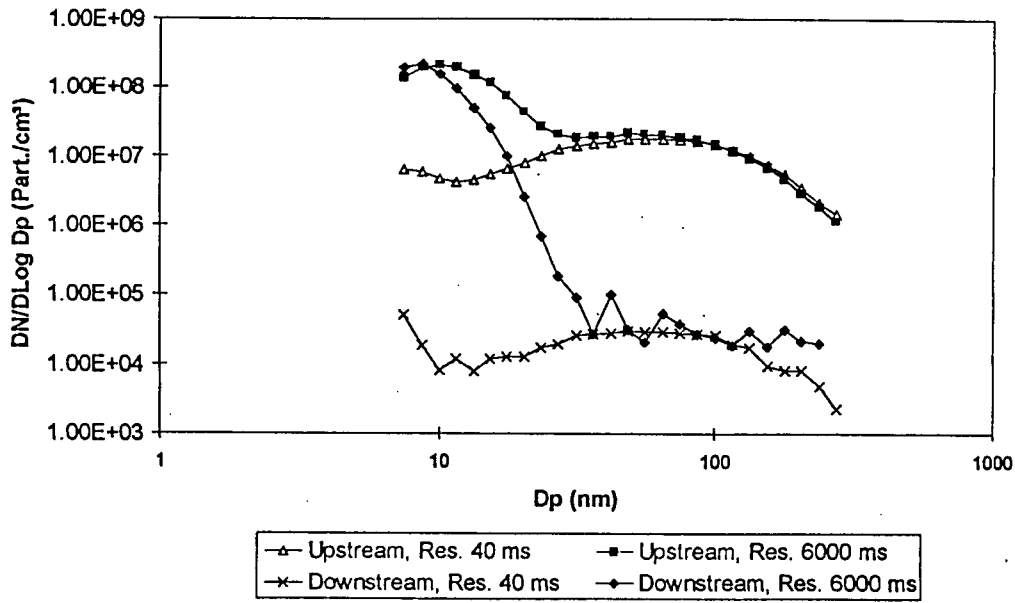
Figure 9 - Influence of Residence Time in Primary Dilution Stage on Particle Size Distribution Measured with SMPS Upstream and Downstream of Exhaust Filter, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 100% load. Primary Dilution Temperature 50 °C, Dew Point, 10 °C.
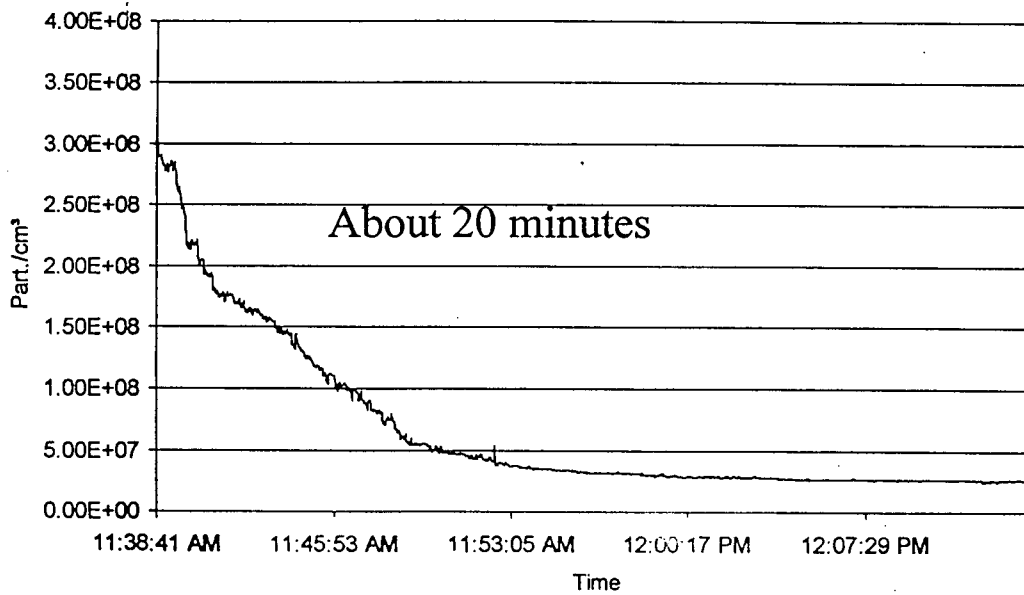
Figure 10 - Transient Measurements of Total Particle Number Concentration Measured with CPC after Transition from Stabilized Idle to Full Power, 2600 rpm, Full Load.
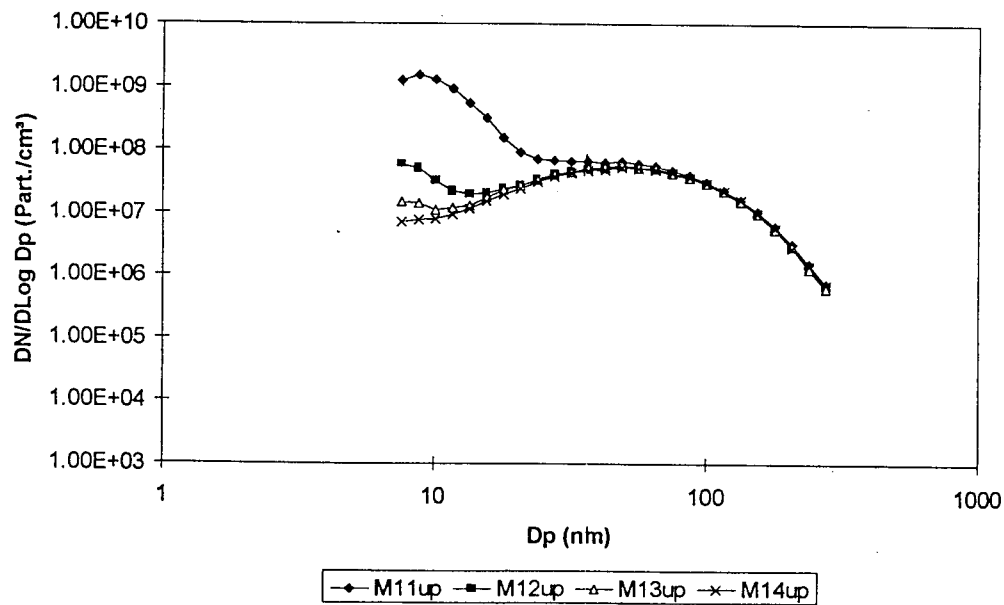

Figure 11 - Particle Size Distributions Measured with SMPS after Transition from Stabilized Idle to Full Power, 2600 rpm, Full Load. Measured at 5-6 Minute Intervals after Transition, M11 is Shortly after Transition, M14 after 20 Minutes.