

# Formation of Nanoparticles during Exhaust Dilution

David Kittelson and Imad Abdul-Khalek

University of Minnesota, Department of Mechanical Engineering  
EFI Members Conference: "Fuels, Lubricants Engines, & Emissions"  
January 18-20, 1999

## 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. Figure 4 is a plot showing how the presence of solid carbonaceous agglomerates in the exhaust can act to reduce the saturation ratio, the ratio of partial pressure to vapor pressure, of condensable species. 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. The competing processes likely to be involved in the nucleation and growth of nanoparticles are summarized below.

### **Nucleation and growth of nanoparticles during exhaust dilution**

- As exhaust dilutes and cools, the ratio of partial pressure to vapor pressure of condensable species, the saturation ratio, goes through a maximum.
- In most systems the only species that is likely to become super-saturated enough for homogeneous nucleation (gas-to-particle conversion to form new particles) during dilution is sulfuric acid.

*Sulfuric acid / hydrocarbon particles may nucleate and grow by:*

- Heteromolecular nucleation of sulfuric acid – water nuclei
- Growth of nuclei by coagulation (collision with other nuclei)
- Growth of nuclei by absorption of sulfuric acid and water
- Growth of nuclei by absorption of hydrocarbons to form particles of mixed composition?

#### *Mechanisms suppressing nucleation and growth:*

- Adsorption of sulfuric acid and hydrocarbons onto existing carbon particles.
- Coagulation of nuclei with existing carbon particles.

Thus carbon (soot or carbonaceous agglomerates) in the exhaust will tend to suppress the formation and growth of nanoparticles. The potential of an engine to form nanoparticles will depend upon the relative concentrations of volatile particle precursors (sulfuric acid and hydrocarbons) and solid carbon. Consequently, 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 volatile particle precursors. Nucleation is an extremely nonlinear process so that nanoparticle formation is very sensitive to the dilution and cooling process, whether in the atmosphere or in the laboratory. Some experiments to explore this sensitivity are described below.

### 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 5. 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 ratios, 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 6 shows the influence of residence time on number weighted size distribution for a dilution temperature 48 °C and dew point of 1 °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 7 shows the influence of dilution temperature at a fixed residence time of 400 ms and a dew point of 1 °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 8 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 9 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 10 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 4 °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.

### MODELING THE INFLUENCE OF SOLID PARTICLES ON PARTICLE NUCLEATION AND GROWTH

The influence of solid particles on homogeneous nucleation and growth of particles from volatile particle precursors depends upon the relative concentrations of carbon and precursors, temperature, and the time scale of the dilution process. In order for solid particles to significantly influence the saturation ratio and thus nucleation

and growth, the characteristic time for adsorption of particle precursors onto existing particles must be of the same order or less than the residence time in the critical dilution ratio range from about 5 to 50 where saturation ratios are highest (as shown in Figure 4). Table 1 below shows adsorption time constants and residence times in the critical dilution ratio range.

<b>Table 1 – Adsorption and Dilution Characteristic Times</b>			
Characteristic Adsorption Times			
Technology	Exhaust Solid Carbon Concentration (mg/m <sup>3</sup> )	Time Constant, raw exhaust (ms)	Time Constant @ D=18 (ms)
Older Heavy-Duty	20	16	290
Modern Medium-Duty	10	32	580
Modern Heavy-Duty	3	110	1900
Characteristic Dilution Times			
		Residence Times (ms)	
Dilution Tunnel			500 - 2000
Ejector Dilutor			10 - 100
Roadway (time in D = 5 to 50 range)		5 - 50	

Table 1 shows that for concentrations in the range of 10 to 20 mg/m<sup>3</sup> time constants in diluted exhaust are shorter than residence times in typical dilution tunnels. Thus the solids will suppress the saturation ratio and nucleation and growth rates. On the other hand for the carbon concentration characteristic of modern heavy duty engines, the adsorption time constant in the dilution tunnel is long enough that the saturation ratio may not be suppressed enough to significantly reduce nucleation and growth.

Ejector dilutor systems unless used with a flow reactor like that described above have very short residence times. While these times are so short that little adsorption is likely, there is also little time for significant nucleation and growth.

The residence times in the critical range for atmospheric dilution are very short, however in this case dilution is a continuous process starting with D = 1 and rapidly increasing. It is probably more appropriate to compare these times with the raw exhaust time constants. For the higher exhaust concentrations, time constants are in the same range as the longer atmospheric residence times so suppression of nucleation would be expected. The shorter residence times would be expected to lead to little suppression. Atmospheric data shows that even the older engine technologies exhibit large nuclei modes, suggesting significant nucleation. A question that arises from Table 1 is how the short atmospheric residence times in the critical dilution ratio regime can give rise to the significant nucleation observed, especially in view of the relatively longer times required above in Figures 6 – 8. These results were obtained under very low humidity conditions and sulfuric acid nucleation increases with humidity. Most roadway data have been collected under moderate humidity conditions where nucleation could be faster.

## MODELING NUCLEATION DURING DILUTION

Figures 11 and 12 show results of modeling of sulfuric acid nucleation in a dilution tunnel for conditions similar to those shown in Table 1. Doyle (1961) predicted that homogenous nucleation between sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and H<sub>2</sub>O may be triggered in the atmosphere with a minute partial pressure of H<sub>2</sub>SO<sub>4</sub> of 10<sup>-9</sup> Torr at 50 % relative humidity and a temperature of 298 K. This was also supported in the work of Mirabel and Katz (1974) and Hamill (1976). They also predicted a critical cluster size of about 0.7 nm. In a typical Diesel exhaust without any after-treatment device, sulfuric acid concentration may range from 5-20 PPM (this is based on 0.04 % sulfur mass in fuel). This concentration of H<sub>2</sub>SO<sub>4</sub> is sufficiently high to trigger nucleation during dilution and cooling. Baumgard (1996) used a similar approach to Mirabel and Katz and predicted rapid nucleation of sulfuric acid in a dilution tunnel with a dilution ratio of 10. This work is being expanded by Abdul-Khalek (1999, PhD thesis), and these modeling calculations are based on his work. Figure 11 shows nuclei concentration as a function of time in the dilution tunnel at a dilution ratio 18. The presence of solid particles can suppress nucleation by nearly two orders of magnitude. It is likely that sulfuric acid water droplets are the first nuclei to form and these subsequently absorb

hydrocarbons and additional sulfuric acid and water. Figure 12 shows the growth of nucleus size with time due to both sulfuric acid and hydrocarbon absorption. Here it may be seen that the soot adsorbs the volatile matter fast enough to significantly reduce diameter growth. In the case of the highest solid particle loading the nuclei grow to no more than 3 nm diameter, too small to be detected by most measurement systems. These are preliminary results. We are currently examining these growth mechanisms in detail.

## 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 13 shows transient measurements of total exhaust particle number concentrations after transition from stabilized idle to full power and Figure 14 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. There is another possible explanation for this behavior, however. It has been reported that in many cases it takes on the order of twenty minutes for engine oil consumption to stabilize when there is a major shift in engine operating conditions. Lubricating oil is an important contributor to the volatile particle precursors present in diesel exhaust so a temporary increase in oil consumption may contribute to these transient nanoparticle emissions.

## 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.

## REFERENCES

- Bagley, S. T., K.J. Baumgard, L.D. Gratz, J.H. Johnson, and D.G. Leddy. 1996. Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions. Health Effects Institute Research Report No. 76, 88 pp.
- Baumgard, K., "The effect of Fuel and Engine Design on Diesel Exhaust Particle Size Distributions", Ph.D Thesis, Michigan Technological University, 1995.
- Doyle, G.J., "Self-Nucleation in the Sulfuric Acid-Water System," J. Chem. Phys., 35, 795-799, 1961.
- Hamill, P., "The Nucleation of H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O Solution Aerosol Particles in the Stratosphere", J.Atmo. Sci., Vol. 34, PP. 150-162, 1976.
- Kittelson, D. B., et al. 1988. Characterization of Diesel Particles in the Atmosphere. Coordinating Research Council AP-2 Project Group Final Report.
- Mirabel, P., J.L. Katz, "Binary homogeneous nucleation as a mechanism for the formation of aerosols", J. Chem. Phys., Vol. 60, No. 3, PP. 1138-1144, 1974.
- Weingartner, E., et al. 1997(a). Aerosol Emission in a Road Tunnel. Atmosph. Environ. 31(3):451-462.
- Whitby, K. T. and B. K. Cantrell. 1975. Atmospheric Aerosols - Characteristics and Measurement. ICESA Conference Proceedings, IEEE #75-CH 1004-1 ICESA, paper 29-1, 6 pp.
- Whitby, K. T., et al. 1975. Characterization of California Aerosols - 1. Size Distributions of Freeway Aerosol. Atmosph. Environ. 9:463-482.
- Wilson, W. E., et al. 1977. General Motors Sulfate Dispersion Experiment: Summary of EPA Measurements. JAPCA 27(1):46-51.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge the support of this work by Perkins Technology and Caterpillar, Inc.

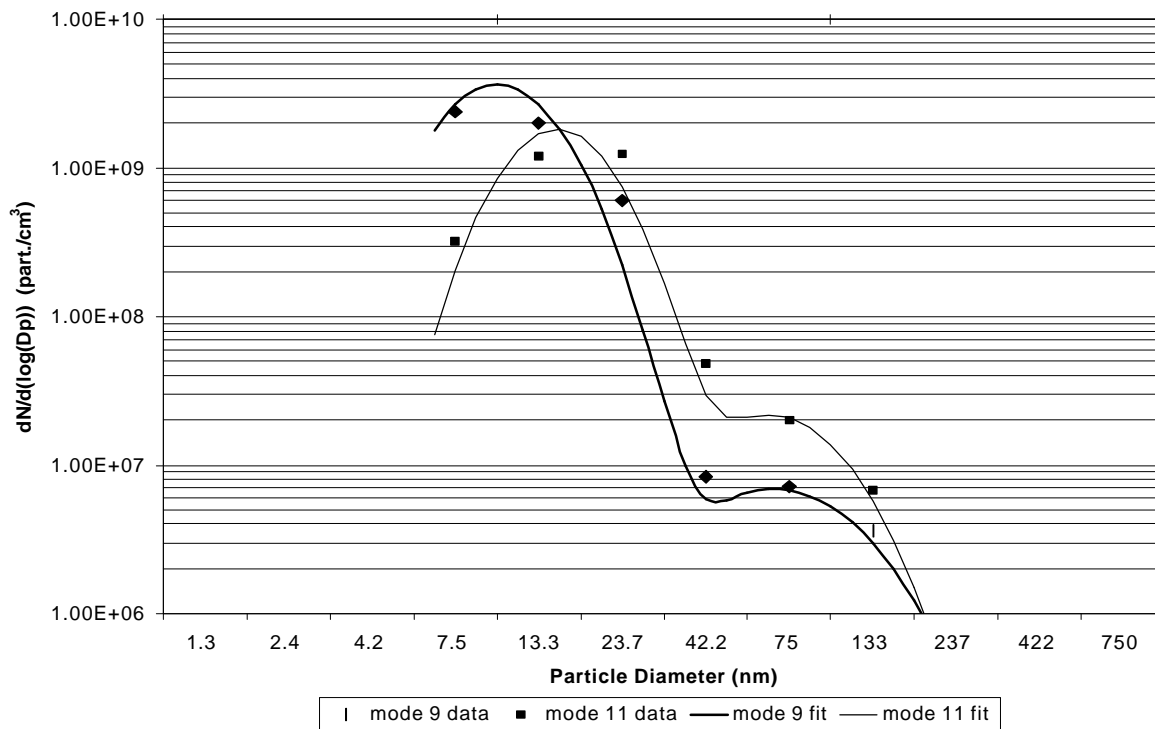


Figure 1 - Number Weighted Size Distribution from HEI Report, 1991 Engine (Bagley, et al., 1996)

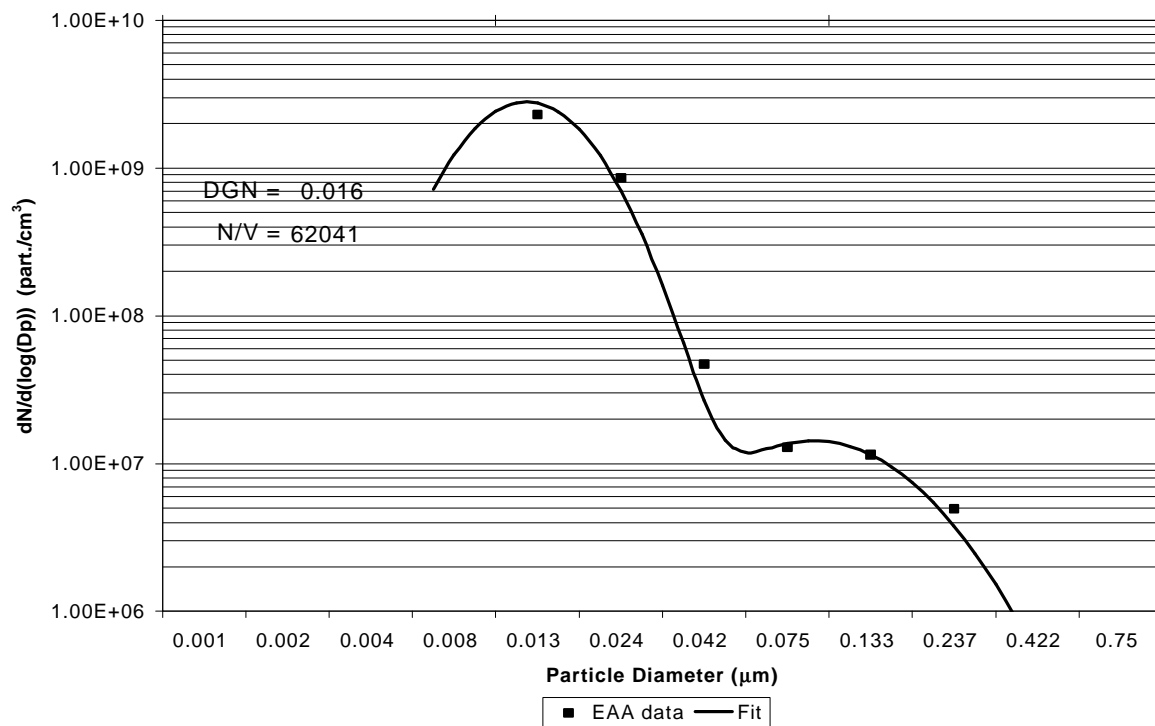
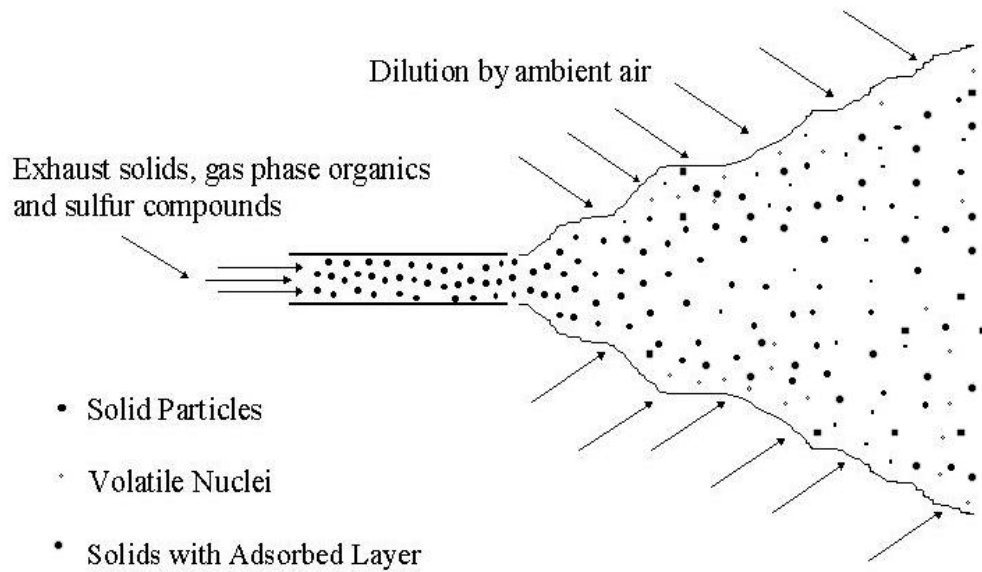
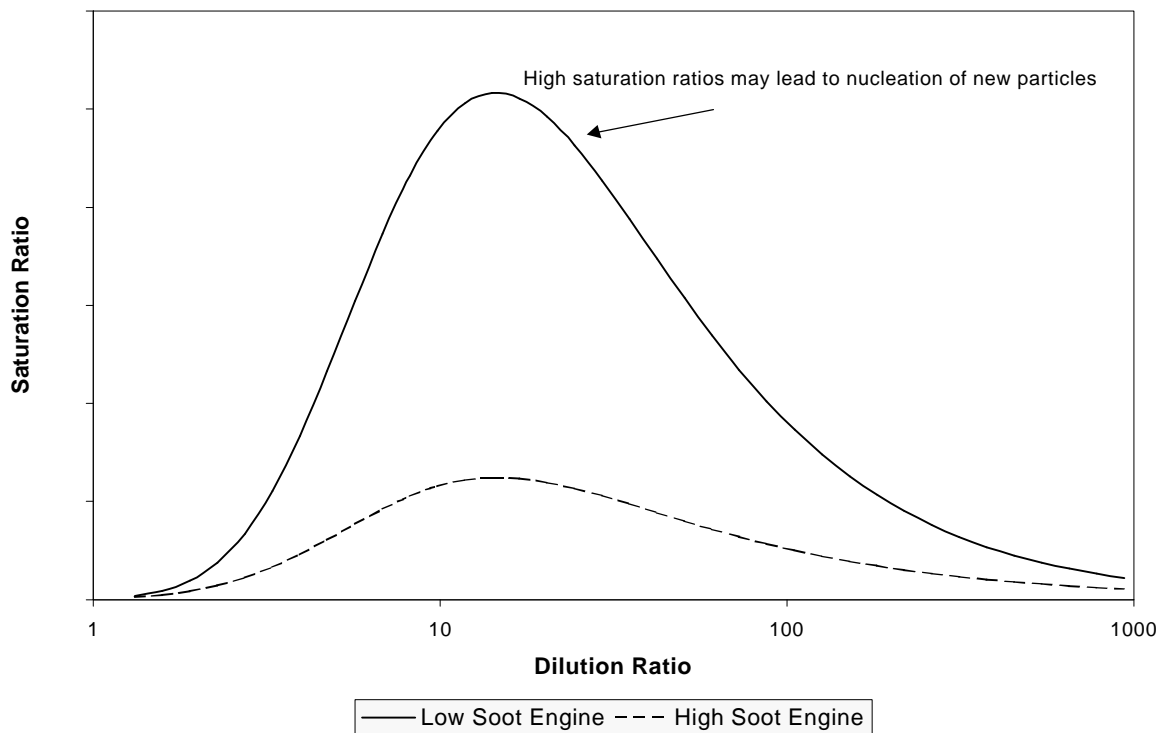


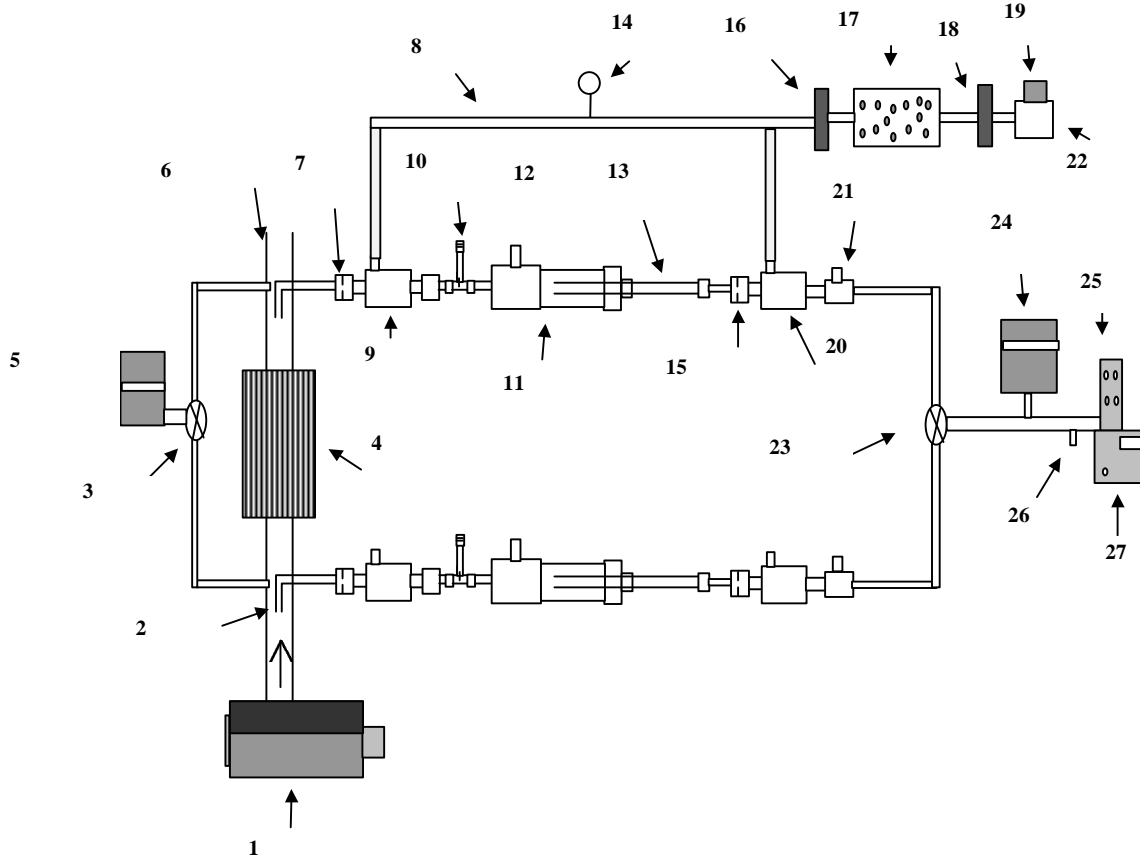
Figure 2 - Number Weighted Size Distribution Recalculated from Roadway Data (Kittelson, et al., 1988). Measurements Made on a Highway in the Plume of a Heavy-Duty Highway Tractor-Trailer.



**Figure 3 - Illustration of Particle Formation during Dilution**

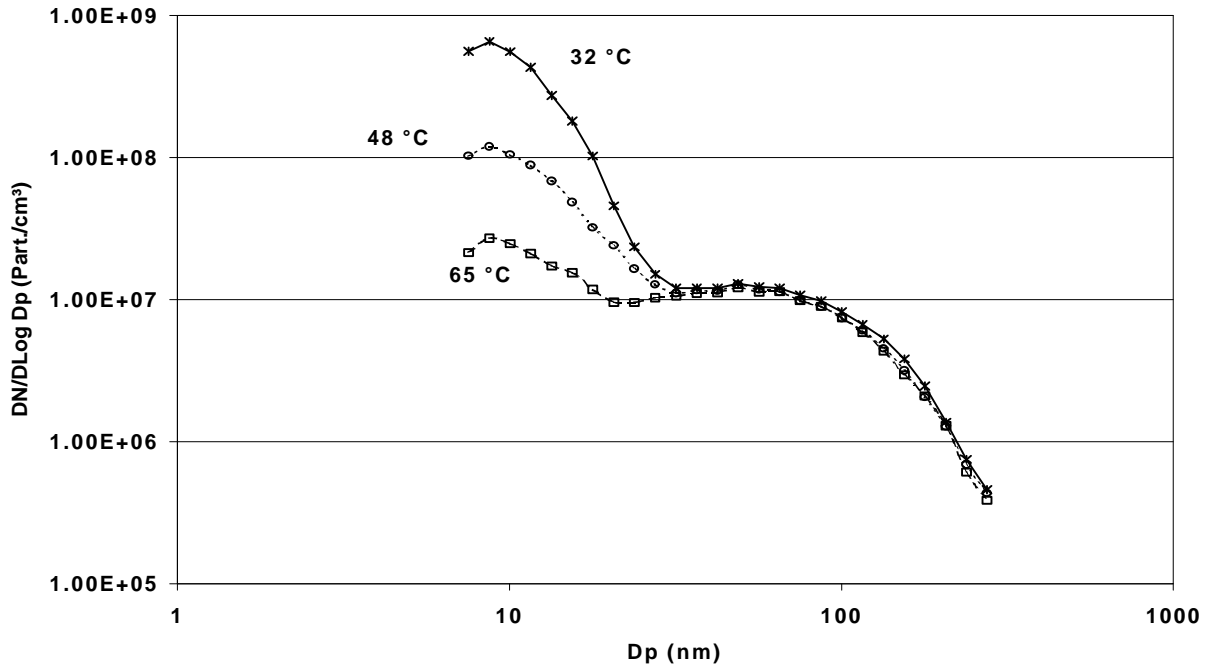


**Figure 4 – Influence of Solid Particles on Saturation Ratio during Adiabatic Dilution**

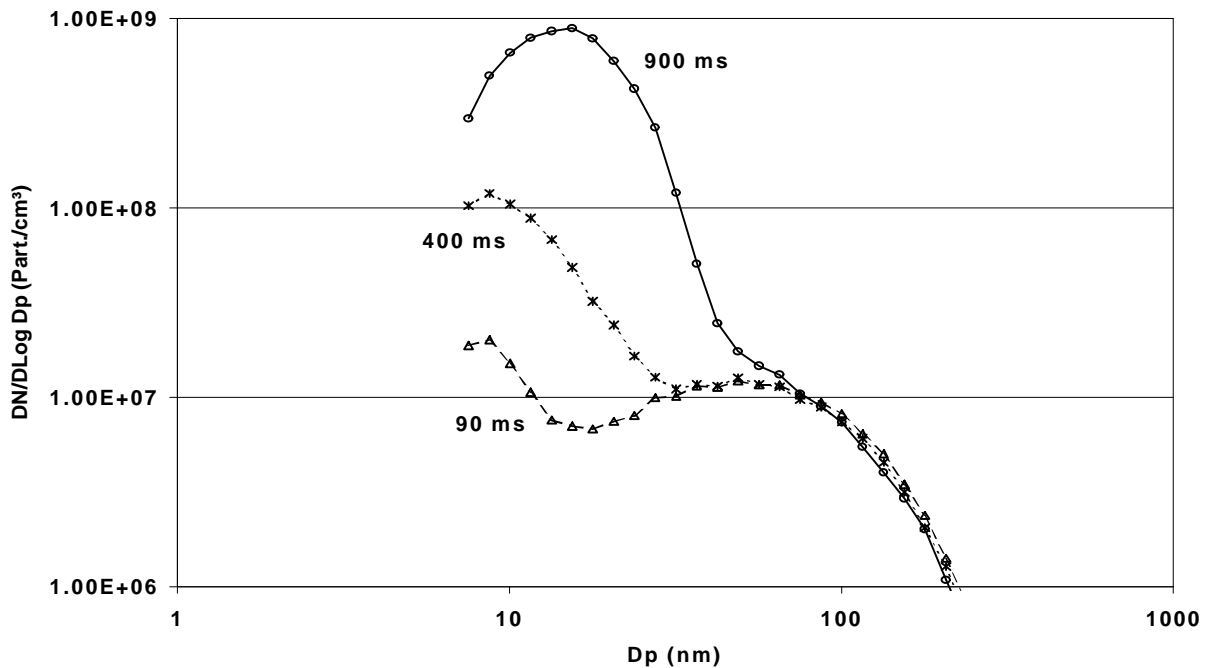


1- Engine: Perkins Phaser T4.40; 2- Sampling Probe; 3- Three Way Valve; 4- Ceramic Filter Trap; 5- Emissions Rack, CO<sub>2</sub>, NO<sub>x</sub>; 6- Exhaust Pipe; 7- Primary Ejector Orifice; 8- Air Supply Tube; 9- Primary Ejector Pump; 10- Thermocouple; 11- Variable Residence Time Dilution Section; 12- Overflow Bypass Section; 13- Retractable Tube; 14- Pressure Gauge; 15- Secondary Ejector Orifice; 16- HEPA Filter; 17- Silica Gel Dryer; 18- HEPA Filter; 19- Pressure Regulator; 20-Secondary Ejector; 21- Overflow Bypass; 22- Compressed Air Inlet; 23- Three Way Valve; 24- Diluted NO<sub>x</sub>; 25- Condensation Nucleus Counter; 26- Overflow Bypass; 27- Scanning Mobility Particle Sizer

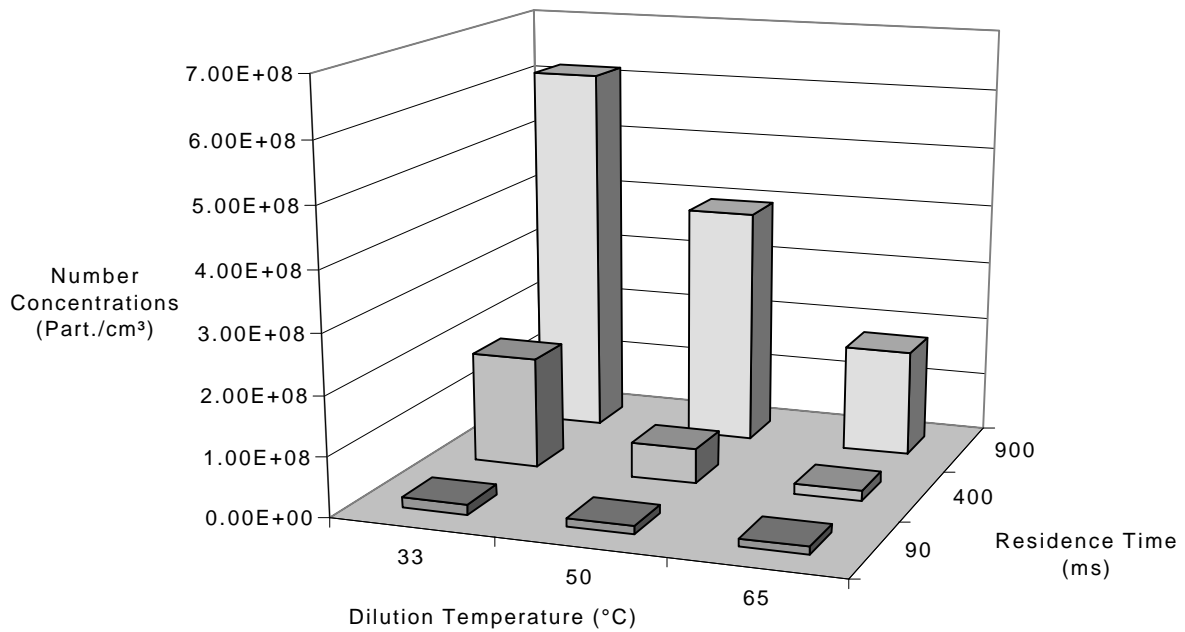
**Figure 5- Typical Experimental Setup with Two Identical Variable Residence Time Micro Dilution Systems Allowing Measurements Upstream and Downstream of Aftertreatment Device**



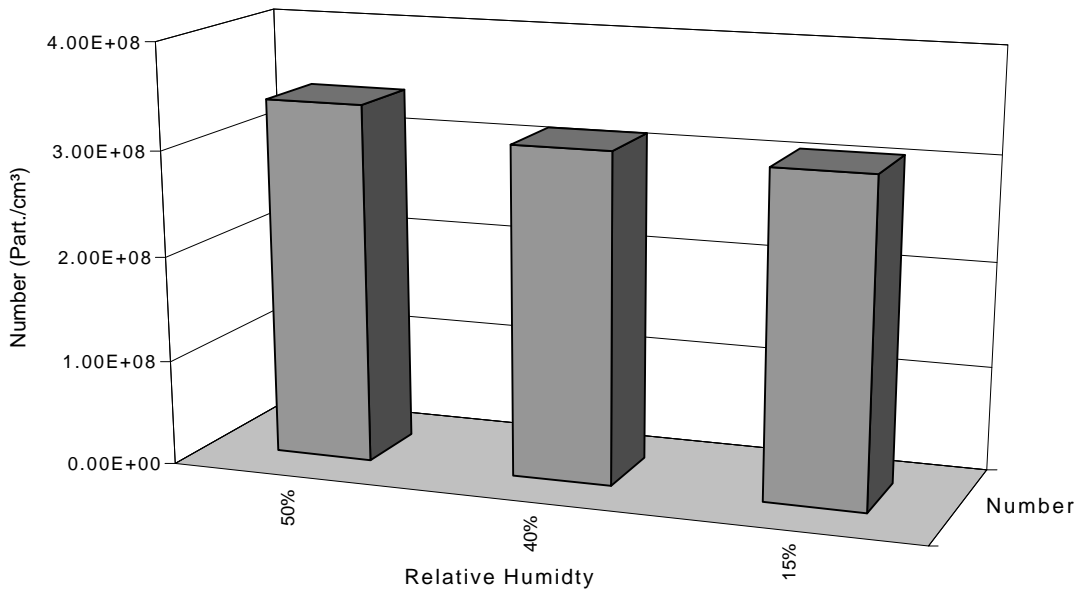
**Figure 6 – Influence of Residence Time in Primary Dilution Stage on Particle Size Distribution Measured with SMPS, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 50% load. Primary Dilution Temperature 48 °C, Dew Point, 1 °C.**



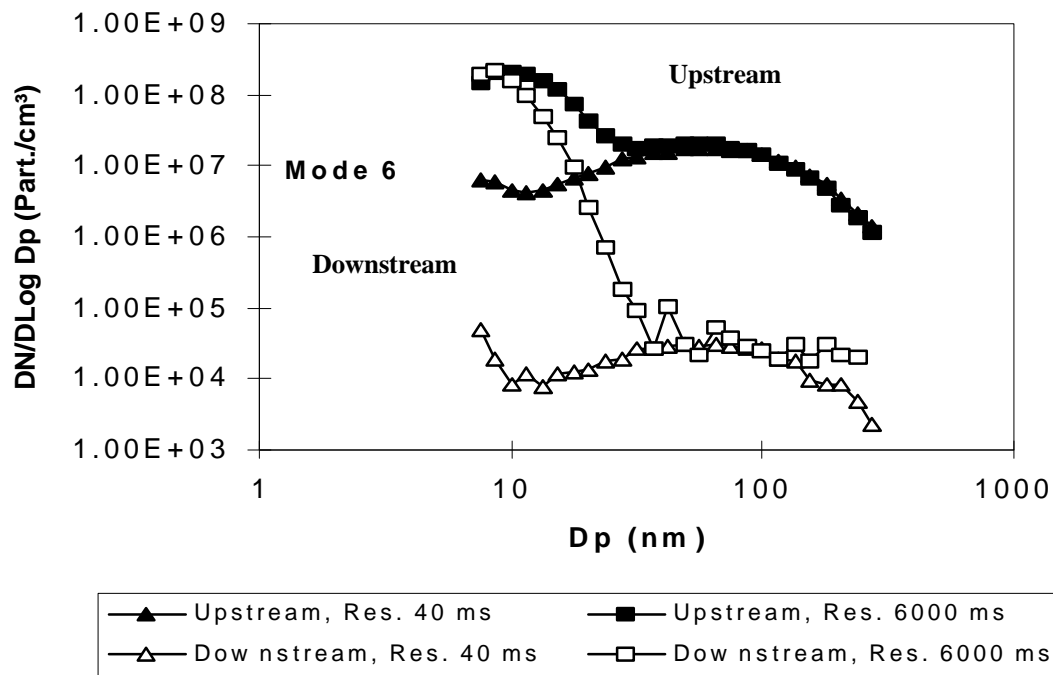
**Figure 7 – Influence of Temperature in Primary Dilution Stage on Particle Size Distribution Measured with SMPS, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 50% load. Primary Dilution Residence Time 400 ms, Dew Point, 1 °C.**



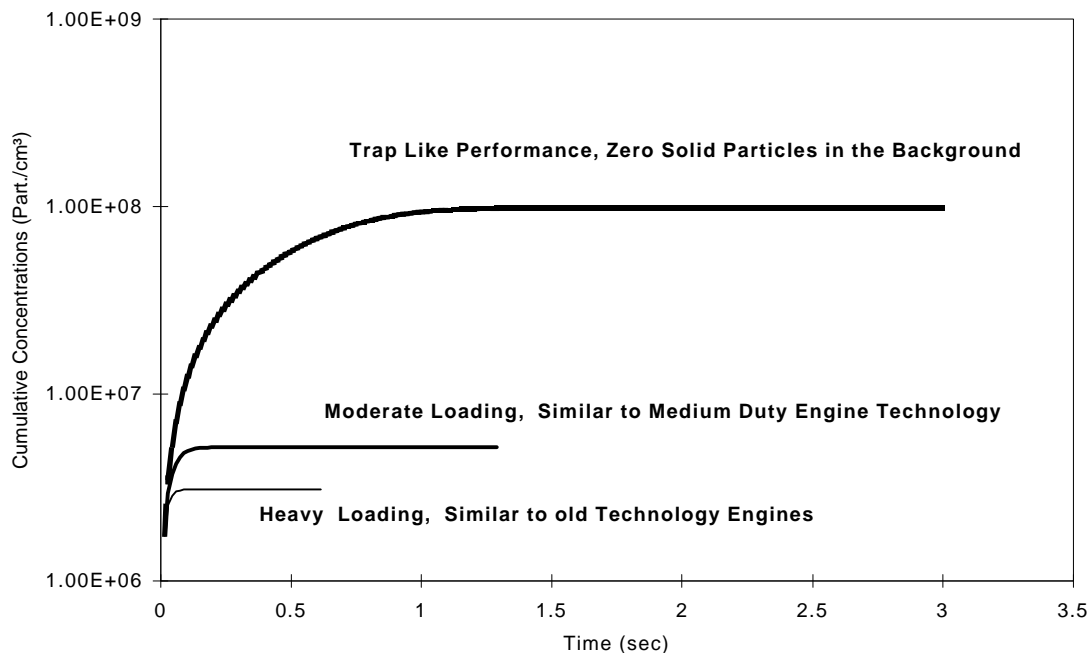
**Figure 8 - Influence of Temperature and Residence Time in Primary Dilution Stage on Total Particle Number Concentration Measured with SMPS, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 50% load. Primary Dilution Dew Point, 1 °C.**



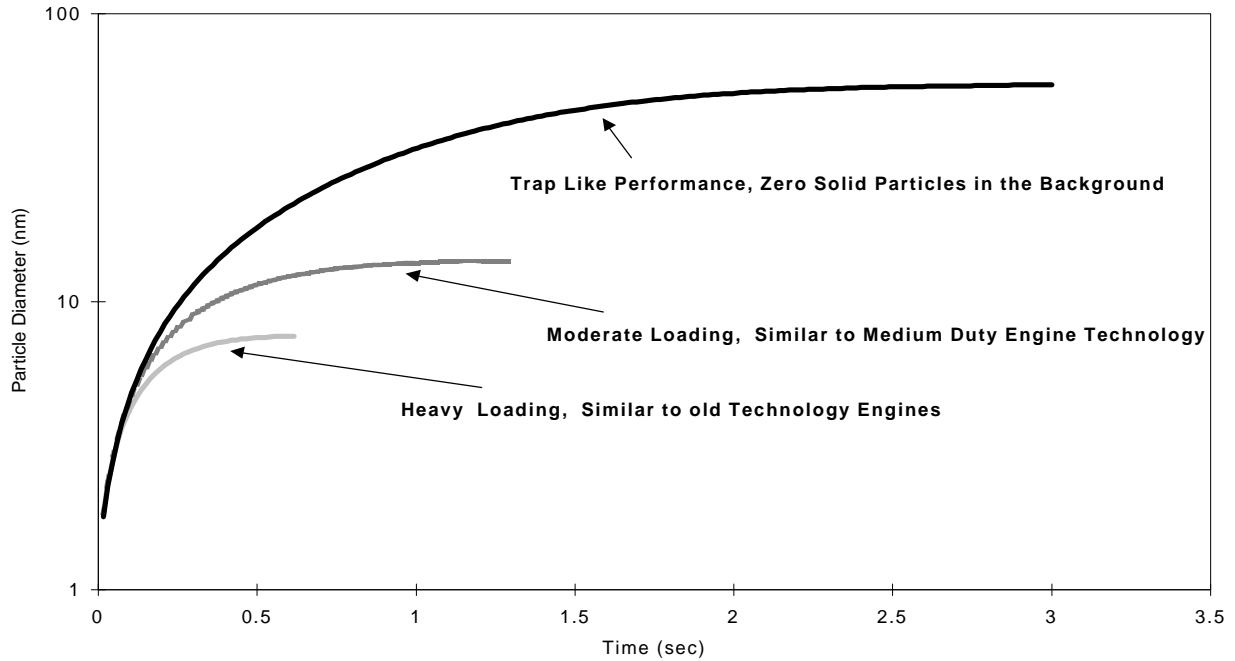
**Figure 9 - Influence of Relative Humidity on Total Particle Number Concentration Measured with SMPS, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 50% load. Primary Dilution Temperature 30 °C, Residence Time 300 ms.**



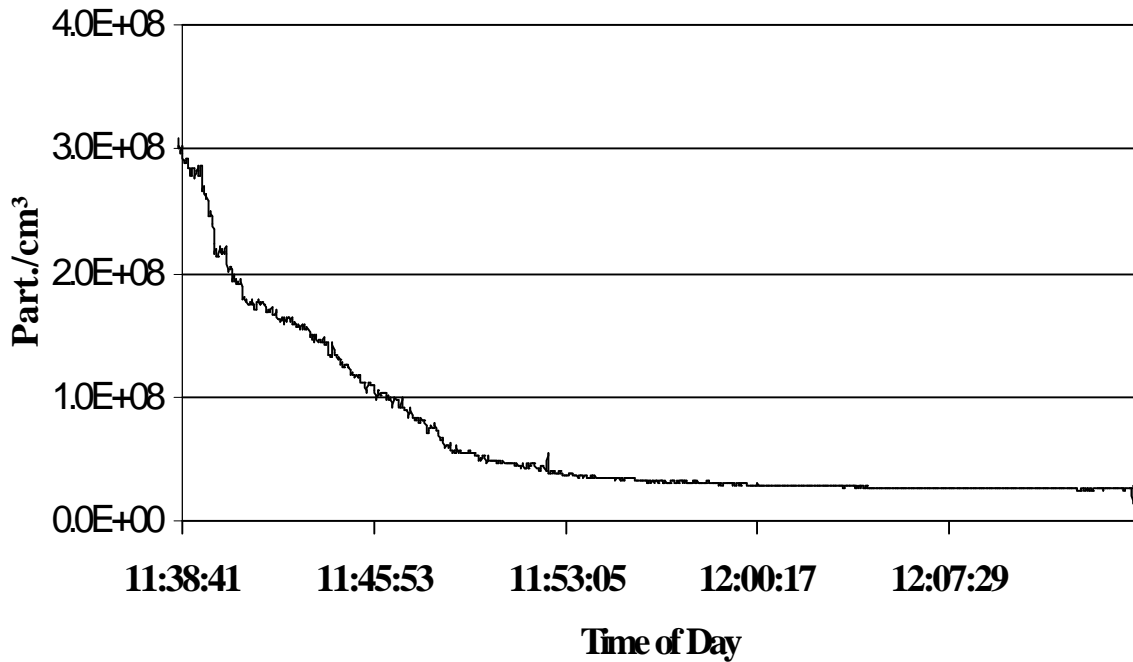
**Figure 10 - Influence of Residence Time in Primary Dilution Stage on Particle Size Distribution Measured with SMPS Upstream and Downstream of Exhaust Filter, Primary Dilution Ratio 12, Secondary Dilution Ratio 60. Engine Operated at 1600 rpm, 100% load. Primary Dilution Temperature 50 °C, Dew Point, 4 °C.**



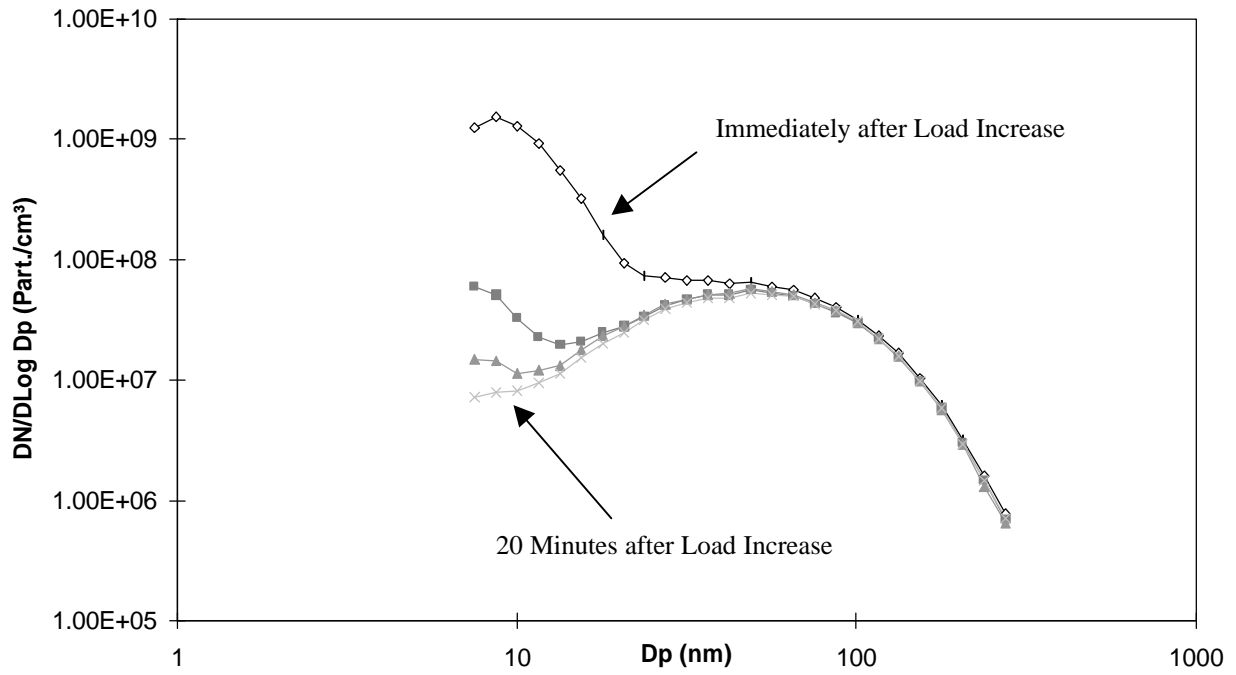
**Figure 11 – Calculated Influence of Primary Dilution Residence Time and Solid Carbon Loading on Sulfuric Acid Nucleation. Primary Dilution Ratio, 18; Temperature, 42 °C; Dew Point, -3 °C, 0.03% S Fuel, 4% Conversion to SO4.**



**Figure 12 – Calculated Influence of Residence Time and Solid Carbon Loading on Sulfuric Acid / Hydrocarbon Nuclei Growth. Primary Dilution Ratio, 18; Temperature, 42 °C; Dew Point, -3 °C, 0.03% S Fuel, 4% Conversion to SO<sub>4</sub>, 1 ppm C<sub>20</sub> in Exhaust.**



**Figure 13 - Transient Measurements of Total Particle Number Concentration Measured with CPC after Transition from Stabilized Idle to Full Power, 2600 rpm, Full Load.**



**Figure 14 - 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**