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10/14/97

Draft of paper submitted to AAAR Journal

INTRODUCTION

Particles produced by diesel and spark ignition engines are of concern to engine builders because they influence engine performance and wear and because of their impact on the environment. They may be associated with the formation of combustion chamber and intake valve deposits, fouling of the exhaust gas recirculation (EGR) and positive crankcase ventilation (PCV) systems, and increased engine wear when they are recycled to the engine via the EGR and PCV systems. However, the main concerns about these particles are environmental, namely, adverse health effects, decreased visibility, and soiling of buildings. Recently, much attention worldwide has been given to the influence of fine particles in the atmosphere on human health. This has led to proposed new standards (Raber, 1997) on fine particles in the atmosphere from the United States Environmental Protection Agency (USEPA). These standards would maintain allowed levels of $50 \mu\text{g}/\text{m}^3$ annual average concentration of PM₁₀ (particles smaller than $10 \mu\text{m}$ aerodynamic diameter) and add an annual average standard of $15 \mu\text{g}/\text{m}^3$ of fine particles (particles smaller than $2.5 \mu\text{m}$ aerodynamic diameter). These standards are the result of many studies (see for example Dockery et al., 1993 or Pope et al., 1995) that have shown an association between adverse health effects and the concentration of fine particles in the atmosphere. Engines, especially diesel, are major sources of fine particles. This paper will describe the principal physical characteristics of these particles, historical trends, and some recent concerns related to particle size. The discussion will focus primarily on particles emitted by diesel engines, because particulate mass emissions from diesel engines typically are 10-100 times higher than those from spark ignition engines. However, if very tiny particles or number emissions become an issue, spark ignition engines may also be a concern.

PARTICLE COMPOSITION AND STRUCTURE

Diesel exhaust particles consist mainly of highly agglomerated solid carbonaceous material and ash, and volatile organic and sulfur compounds. The structure is illustrated schematically in Figure 1. Solid carbon is formed during combustion in locally rich regions. Much of it is subsequently oxidized. The residue is exhausted in the form of solid agglomerates. A tiny fraction of the fuel and atomized and evaporated lube oil escape oxidation and appear as volatile or soluble organic compounds (SOF) in the exhaust. The SOF contains polycyclic aromatic compounds containing oxygen, nitrogen, and sulfur (Farrar-Khan et al., 1992). Most of the sulfur in the fuel is oxidized to SO_2 , but a small fraction is oxidized to SO_3 that leads to sulfuric

acid and sulfates in the exhaust particles. Metal compounds in the fuel and lube oil lead to a small amount of inorganic ash. Figure 2 shows typical composition of the particulate matter for a current technology diesel engine tested using the U.S. Heavy Duty Transient Test. The sulfuric acid/sulfate fraction is roughly proportional to the fuel sulfur content. The fraction associated with unburned fuel and lube oil (soluble organic fraction or SOF) varies with engine design and operating condition. It can range from less than 10% to more than 90% by mass. SOF values are highest at light engine loads when exhaust temperatures are low.

The USEPA defines diesel particulate matter as the mass collected on a filter from exhaust that has been diluted and cooled to 52 °C or below (SAE, 1993). The composition of exhaust particles depends upon where and how they are collected. As the exhaust is diluted and cooled, nucleation, condensation, and adsorption transform volatile materials to solid and liquid particulate matter. In the tailpipe, where temperatures are high, most of the volatile materials are in the gas phase. The details of the dilution and cooling processes determine the relative amounts of material that adsorb or condense on existing particles and nucleate to form new particles.

PARTICLE SIZE

Figure 3 shows idealized diesel exhaust particle number and mass weighted size distributions. The distributions shown are trimodal, lognormal in form. Lognormal distributions usually fit actual data very well. The concentration of particles in any size range is proportional to the area under the corresponding curve in that range. Most of the particle mass exists in the so-called accumulation mode in the 0.1 to 0.3 μm diameter range. This is where the carbonaceous agglomerates and associated adsorbed materials reside. The nuclei mode typically consists of particles in the 0.005 to 0.05 μm diameter range. This mode usually consists of volatile organic and sulfur compounds that form during exhaust dilution and cooling, and may also contain solid carbon and metal compounds. The nuclei mode typically contains 1-20% of the particle mass and more than 90% of the particle number. The coarse mode contains 5-20% of the particle mass. It consists of accumulation mode particles that have been deposited on cylinder and exhaust system surfaces and later reentrained. Also shown in Figure 3 are some size range definitions for atmospheric particles: PM₁₀, diam. < 10 μm ; fine particles, diam. < 2.5 μm ; ultrafine particles, diam. < 0.10 μm ; and nanoparticles diam. < 0.05 μm or 50 nm. Note that by number, nearly all of the particles emitted by a diesel engine (the same is true for a spark ignition engine) are nanoparticles.

SIGNIFICANCE OF PARTICLE SIZE

Particle size influences the behavior of particles within the engine itself (for example in EGR and PCV systems) and in the environment. We will focus on the latter. However it is worthwhile noting one engine related particle size effect: performance of aftertreatment devices. Exhaust filters (or traps) and catalysts may be used to reduce diesel particulate emissions. Both show size dependent performance (Mayer, 1995). Traps are most effective at removing solid accumulation mode particles, while catalysts remove mainly organic compounds that will contribute to the SOF and nuclei mode.

Particle size influences the environmental impacts of engine exhaust particles in several ways: it influences the atmospheric residence time of the particles, the optical properties of the particles, the particle surface area and ability to participate in atmospheric chemistry, and the health effects of the particles.

The residence time of particles in the atmosphere is maximum for particles in the 0.1 to 10 μm diameter range and is typically about one week. Larger particles are removed from the atmosphere quite quickly by settling and smaller ones by diffusion and coagulation. A typical residence time for 10 nm particles is only about 15 minutes (Harrison, 1996). The main mechanism for removal of these tiny particles is coagulation with particles in the accumulation mode. Thus, although they lose their identity as individual particles, they remain in the atmosphere for essentially the same time as the larger accumulation mode particles.

The optical properties of exhaust particles influence atmospheric visibility and soiling of buildings. These properties depend on particle size, shape, and composition (Scherrer and Kittelson, 1981, Kittelson et al., 1988). Particles interact with light by absorption and scattering. For diesel particles absorption is much stronger than scattering and is relatively independent of particle size for light in the visible range. The absorption is due to the carbon content of the particles and is in the range of 9 m^2/g of elemental carbon. Light scattering is strongly dependent on particle size and is maximum for particles a few tenths of a micron in diameter. Scattering cross sections for typical diesel exhaust particles vary from about 1.5 to 4 m^2/g . The scattering is due mainly to particles in the accumulation mode size range. Ultrafine and nanoparticles scatter very weakly.

The specific surface area of diesel exhaust particles is typically in the range of 100 m^2/g (Jakab et al., 1992). This corresponds to the specific surface area of a 0.03 μm carbon sphere. This suggests that nearly all of the surface area of the individual nuclei that comprise the agglomerates is available for adsorption. Thus the surface area of diesel particles is probably more a function of the size of the individual nuclei in the agglomerates rather than the agglomerate size. This surface area may be available for atmospheric reactions. In the atmosphere, various atmospheric constituents will compete with exhaust constituents for this surface area.

The aspect of particle size that is attracting the greatest current attention is the influence of fine and ultrafine particles on human health. The USEPA proposed fine particle standards are based on studies that link fine particles with adverse health effects. Many of these studies show that the correlation between health effects and atmospheric particle concentration is improved when fine particle concentration rather than the concentration of PM₁₀ is used (Dockery et al., 1993, Pope et al., 1995). Thus adverse health effects seemed to be linked with smaller particles. A number of factors may be involved here. The number of particles and particle surface area per unit mass increases with decreasing particle size. Currently all pollution standards are mass based so that the dose by number or area will increase as size decreases. The efficiency of deposition in the human respiratory tract depends upon particle size (ICRP, 1984). In particular, pulmonary deposition increases with decreasing particle size. Recently special concerns have

been raised for particles in the ultrafine and nanoparticle diameter range. 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 0.02 μm 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 0.5 μm TiO_2 (Donaldson et al., 1996). Modest concentrations of 0.03 μm Teflon fume particles caused acute pulmonary toxicity in rats (Warheit et al., 1990). These and many similar studies have raised significant concern about particles in the fine, ultrafine, and nanoparticle size range.

The size distribution shown in Figure 3 shows that nearly all of the mass emitted by engines is in the fine particle range and nearly all the number is in the nanoparticle diameter range. Emission inventories suggest that engines and vehicles are the principal contributor of fine particles to the atmosphere in urban areas. For example, Schauer et al., (1996) estimate that 51-69% of the fine particles in downtown Los Angeles in 1982 were vehicle related. Roughly one-quarter of these fine particles were fugitive dust and not directly engine related. Harrison (1996) estimates that approximately 90% of the PM10 particles emitted in greater London in 1990 were road transport related. Emission inventories are not available for nanoparticles, but measurements made near roadways suggest that engines are an important source. For example, Harrison compares size distributions measured near roadways and aged background aerosols and shows that concentrations of nanoparticles are much higher near roadways.

TRENDS IN ENGINE PARTICLE EMISSIONS

Diesel engines have been subject to increasingly stringent tailpipe emission standards. Table 1 shows trends in USEPA heavy-duty engine emission standards. Note that these standards are based on the total mass of particulate matter collected during the test cycle.

Table 1 - U.S. Heavy-Duty Emission Standards		
Standard	Particulate Matter (g/kWh)	NO_x (g/kWh)
1988 On-Highway	0.80	8.0
1991 On-Highway	0.34	6.7
1994 On-Highway	0.13	6.7
1998 On-Highway	0.13	5.4
1997 Off-Highway (75-130 kW)	0.7	9.2

Current on-highway engines are required to emit no more than one sixth the particle mass allowed for 1988 engines and probably less than one tenth that of an uncontrolled engine. Emission standards do not address particle size.

Some trends in particle volume and number concentrations and size are given below. Before presenting those results here are some useful definitions. Let n be the number of particles, then the number concentration, N is:

$$N = \frac{\text{number of particles}}{\text{volume of gas}} = \frac{n}{\text{volume of gas}} \left(\frac{\text{particles}}{\text{cm}^3} \right)$$

Let v be the volume of particulate matter, then the volume concentration, V is:

$$V = \frac{\text{volume of particulate matter}}{\text{volume of gas}} = \frac{v}{\text{volume of gas}} \left(\frac{\mu\text{m}^3}{\text{cm}^3} \right) \quad \text{Then:}$$

$$\frac{N}{V} = \frac{\text{number of particles}}{\text{volume of particulate matter}} = \frac{n}{v} \left(\frac{\text{particles}}{\mu\text{m}^3} \right)$$

Current air quality and emission standards are based on total particulate mass, m , but recently concerns have been raised about the number of particles, n .

$$n = v \left(\frac{n}{v} \right) = \frac{m}{\rho} \left(\frac{n}{v} \right) = \frac{m}{\rho} \left(\frac{N}{V} \right)$$

Here ρ is the average density of the particulate matter. For spherical particles:

$$v = \sum_i n_i \pi \frac{D_i^3}{6} = \pi \frac{D_{av}^3}{6} \sum_i n_i = \pi \frac{D_{av}^3}{6} n$$

Where n_i and D_i are, respectively, the number and diameter of particles of size class, i , and D_{av} is the diameter of average volume. Then

$$\frac{n}{v} = \frac{N}{V} = \frac{6}{\pi D_{av}^3} \quad \text{and} \quad D_{av} = \left(\frac{6}{\pi \left(\frac{N}{V} \right)} \right)^{1/3}$$

An example is useful to help to understand the scale of these quantities. For particles with a diameter of average volume of 50 nm, or 0.05 μm , we have

$$\frac{N}{V} = \frac{6}{\pi (0.05)^3} = 15,000 \left(\frac{\text{particles}}{\mu\text{m}^3} \right)$$

The number of spherical particles in 1 g of this particulate matter, assuming an average density of 1 g/cm^3 , is

$$n = \frac{m}{\rho} \left(\frac{N}{V} \right) = \frac{1 \text{ g}}{1 \frac{\text{g}}{\text{cm}^3} 10^{-12} \frac{\text{cm}^3}{\mu\text{m}^3}} 15,000 \frac{\text{particles}}{\mu\text{m}^3} = 15 \times 10^{15} \text{ particles!}$$

The results shown below were obtained using electrical aerosol analyzers (EAA) as the primary instrument for measuring particle size and volume concentrations. Number concentrations have been measured using the EAA and condensation nucleus counters (CNC). In most cases the CNC and EAA number concentrations were found to be in reasonable agreement. These

instruments are designed to measure typical atmospheric particle concentrations. Consequently it was necessary to dilute exhaust samples prior to measurement. Dilution ratios in the range of 1000 were typically used. These brought concentrations into a convenient measurement range and simulated the atmospheric dilution process (Kittelson et al., 1988). All concentrations are corrected to ambient temperature and pressure. Key features of these measurements are given in by Abdul-Khalek and Kittelson (1995), Baumgard and Kittelson (1985), and Dolan et al. (1980). All measurements were made at the University of Minnesota, except those taken from a recent Health Effects Institute (HEI) report (Bagley et al., 1996) which were made at Michigan Technological University. The results shown reflect changes in engine technologies as well as in fuels. The 1991 and 1995 diesel engines were operated on low sulfur (< 0.05%) fuels while the older engines were operated on fuels with a sulfur content of about 0.3%.

Figure 4 shows plots of particle volume concentration against fuel-air equivalence ratio, ϕ , the ratio of the engine fuel-air ratio to the chemically correct fuel-air ratio, for some representative of diesel and spark ignition engines. For diesel engines the load is roughly proportional to the equivalence ratio. Most modern spark ignition engines run at an equivalence ratio of 1.0, however, higher equivalence ratios are used during cold starts, warm-up, and high loads. In general, exhaust volume concentrations increase with increasing ϕ . Higher values of ϕ lead to higher local fuel-air ratios in the engine which increase the rate of carbon formation and decrease the rate of oxidation. The trend lines are significantly lower for the newer engines, with the 1995 engine more than a factor of 10 lower than the older engines. Since mass concentrations are proportional to volume concentrations, these decreases are in keeping with trends in tailpipe emission standards.

Results for two spark ignition (SI) engines are shown in Figure 4. Modern fuel injected, catalyst equipped, SI engines are much cleaner than older carbureted, non-catalyst engines. At $\phi = 1$, the 1993 SI engine emits volume concentrations about 1 and one half orders of magnitude lower than the 1995 diesel. On the other hand, the particle volume emitted by the SI engine depends very strongly on ϕ . Under cold start conditions SI engines operate at value of ϕ in excess of two. Under these conditions particle concentrations similar to modern diesels may be produced.

Figure 5 show exhaust number concentrations plotted against ϕ . Here the trends are different from those of volume concentrations. For the diesel engines the number concentrations drop with increasing equivalence ratio through most of the operating range and only increase at the highest loads. Most of the particle number is in the nuclei mode which usually consists mainly of SOF and sulfates (Abdul-Khalek and Kittelson, 1995). At light loads, and thus low ϕ , the exhaust temperatures are low and unburned fuel and oil are not effectively oxidized. When the exhaust is diluted and cooled, these materials nucleate and form large numbers of tiny particles in the nuclei mode. These particles lead to large number concentrations, but because of the small particle size, they do not usually contribute significantly to the volume or mass concentrations. As load is increased, the exhaust temperature increases and the SOF is more effectively oxidized causing the exhaust number concentrations to fall. At fairly high loads the increase in carbon formation with increasing load offsets the decrease in the SOF nuclei and the number concentration starts increase. The 1995 diesel engine shows lower number concentrations than

the older engines, but the difference is much less pronounced than in the case of volume concentration.

The 1991 diesel engine tested for the HEI study (Bagley et al., 1996) show exceptionally high number concentrations, more than an order of magnitude higher than the older engines and two orders of magnitude higher than the 1995 engine. The HEI engine is of very modern design with a very high pressure, precisely controlled fuel injection system. It has been suggested that the very high number concentrations are due to breakup of agglomerates by oxidation (Hunter, 1996). However, the engine produced very high values of SOF (60-75%) for the test conditions of the HEI report. The combination of high SOF and relatively low solid carbon mass may have caused extensive nucleation of the SOF to form a very large nuclei mode and very large number concentrations. These results are of special concern because the fuel injection system used on the 1991 engine may be more representative of future heavy-duty applications than that of the 1995 engine, which uses a moderately high pressure, mechanically controlled fuel injection system.

The SI engine shows continuously increasing number concentration with ϕ . This suggests that increases in carbon formation at higher ϕ may be the dominant factor, but other factors may be involved. As with volume, number concentrations are much lower than for diesel engines.

Figure 6 shows plots of N/V ratios for the engines for which both number and volume concentrations were measured. For the diesel engine, the number to volume ratios are much higher at light loads where high number concentrations are produced by nucleation. Over much of the operating range the N/V ratio for the 1995 diesel is higher than for the older engines. This indicates that the newer engine is emitting smaller particles. This is confirmed in Figure 7 which shows average volume diameters. The exception to this general trend is the 1988 engine which forms very small particles at light loads. This engine has a very high SOF fraction at light loads (Abdul-Khalek and Kittelson, 1995).

Again the 1991 engine used for the HEI report shows exceptional values with N/V ratios one to two orders higher than the other engines. These high N/V ratios are associated with the very small particles diameters shown in Figure 7.

The SI engine also produces very small particles, with average volume diameters smaller than most of the diesel cases (except the HEI engine) throughout its operating range.

Figures 8 - 11 compare typical size distributions from the engine tested for the HEI report with size distributions from the 1995 engine that we have been testing. Figure 8 shows a volume weighted size distribution from the HEI engine while Figure 9 shows a comparable distribution from the 1995 DI engine. Note that the accumulation modes in the two plots are nearly identical, the scales are the same, but that the HEI engine has a nuclei mode with nearly the same volume as the accumulation mode, while the 1995 DI engine has essentially no nuclei mode. The HEI engine has a SOF for this condition of about 60%. Kittelson et al. (1988) and Abdul-Khalek and Kittelson (1995) show a strong correlation between the SOF and the volume fraction in the nuclei mode. This suggests that the large nuclei mode observed for the HEI engine is largely

SOF. Figures 10 and 11 show the same size distributions in a number weighting. The enormous number of particles in the nuclei mode of the HEI engine is much more evident in these plots. The scale for the HEI engine is 150 times larger than for the 1995 DI engine. The number weighted geometric mean diameter, DGN, is also much smaller, 0.011 μm , compared to 0.043 μm .

Table 2 - N/V Ratios Calculated from Various Sources				
1 part/ μm^3 corresponds to 10^{12} particles/g for spherical particles with a density of 1 g/cm ³				
Condition	SOF	N/V part/μm^3	Source	Reference
Roadway dilution	0.13	62,000	1979 DI diesel, Cummins	Kittelson et al., 1988
Roadway dilution	0.38	57,000	1979 DI diesel, Detroit Diesel	Kittelson et al., 1988
Atmospheric dilution	~0	3,700	1979 DI diesel, Caterpillar endurance test stand	Kittelson et al., 1988
Rural freeway	0.24	26,000	Mixed traffic	Kittelson et al., 1988
Rural background	0.14	4,300	Background	Kittelson et al., 1988
Chassis dynamometer - lab dilution	na	56,000	SI non-catalyst - In use vehicles	Hildemann et al., 1991 N/V calculated from their data.
Chassis dynamometer - lab dilution	na	46,000	SI catalyst - In use vehicles	Hildemann et al., 1991 N/V calculated from their data.
Engine dynamometer	na	400,000	1995 DI diesel, ox. catalyst in sulfate forming mode	Work in progress, University of Minnesota
Engine dynamometer	na	25,000	4-stroke DI diesel, iron additive	Work in progress, University of Minnesota
Engine dynamometer	na	2,900	4-stroke DI diesel, baseline	Work in progress, University of Minnesota

The HEI report raises concerns about new diesel engine technology leading to increases in emissions of nanoparticles. The relative emissions of tiny particles are well represented by N/V ratios. Table 2 is a tabulations of N/V ratios determined from published data not included in Figures 4-7.

It is clear from Table 2 that N/V ratios and thus the number of particles emitted per unit mass of particulate matter is highly variable. The results suggest that N/V ratios in the range of 50,000 to 60,000 part/ μm^3 (or, assuming spherical, unit density particles, 5 to 6 x 10¹⁶ particles per gram of emitted particle mass) are probably not uncommon for older diesel and SI engines under highway cruise conditions. This is consistent with the N/V ratio of 26,000 observed over a rural freeway under mixed traffic conditions. This ratio is lower than sources levels because of

dilution and coagulation. The values of 120,000 to 360,000 observed in the HEI work (Figure 6) are significantly higher than reported for other engine types. The only way we could produce such a high N/V ratio in our laboratory was to operate a diesel engine equipped with a catalyst in an off-design, high load condition that led to significant sulfate formation. This led to an N/V ratio of 400,000.

DISCUSSION AND CONCLUSIONS

Concerns about possible adverse health effects of particles from engines are leading to a reexamination of particulate emission standards and measurement protocols. The new engine technology represented by the engine used in the HEI study, while markedly reducing particle mass emissions, led to sharp increases in number emissions of tiny particles. These particles may include: hydrocarbons (SOF), carbon fragments, sulfates, and metallic ash. Hydrocarbons and carbon fragments are probably the main source of tiny particles for engines running under normal conditions with low sulfur fuels. Possible reasons for the formation of large concentrations of these particles by low emission engines include nucleation of SOF enhanced by a reduction of total soot mass and extensive carbon oxidation in the engine leading to fragmentation of agglomerates. As engine exhaust dilutes and cools, the SOF may pass from the gas phase to the particle phase by two paths: nucleation to form new particles and adsorption on existing particles. Nucleation is favored if there is little surface area on which to adsorb. This may be the case for the HEI engine where the mass of particles in the accumulation mode that could adsorb SOF has been significantly reduced when compared to older engines. On the other hand, the 1995 engine tested at the University of Minnesota has a similarly low concentration of particles in the accumulation mode, but formed no significant nuclei mode. However, this engine has significantly lower SOF values (around 30%). Thus, since nucleation is a highly non-linear process, (Friedlander, 1977) the concentration of condensable species may not go high enough during the dilution process to cause significant nucleation. If this interpretation is correct, the formation of tiny particles by future engines will depend upon the relative amounts of condensable species and solid surface on which to condense or adsorb.

Some other issues should be considered if emission of tiny particles by engines continue to be a concern. If these particles are primarily composed of volatile materials, they are formed as the exhaust dilutes and cools. The number formed and their size will depend upon the details of the dilution process. Thus, atmospheric dilution should be simulated to make representative measurements. Coagulation of these tiny particles will cause them to disappear quickly into the accumulation mode size range during atmospheric aging. Thus, the highest exposures will occur on or near roadways where particles are young.

Current emission standards are mass based. Mass tends to be conserved during the dilution and sampling process. On the other hand, particle number is not conserved and may be changed significantly by coagulation. This in turn may change particle size, especially if a number weighted size is used. Thus, any changes in, or additions to, current mass based emission standards will lead to significant sampling and measurement challenges.

Concern about particle emissions from vehicles tends to focus on those powered by diesel engines, because of their much higher mass emissions. However, if nanoparticles are a problem, not only diesel, but also spark ignition engines may be important sources.

REFERENCES

Abdul-Khalek, I.S. and D.B. Kittelson, "Real Time Measurement of Volatile and Solid Exhaust Particles Using a Catalytic Stripper," SAE Paper No. 950236, SAE International Congress & Exposition, Detroit, MI, February 17-March 2, 1995.

Bagley, S.T., K.J. Baumgard, L.G. Gratz, J.H. Johnson, and D.G. Leddy, "Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions," Health Effects Institute (HEI), Research Report No. 76 (September 1996), p. 24..

Baumgard, K.J. and D.B. Kittelson, "The Influence of a Ceramic Particle Trap on the Size Distribution of Diesel Particles," SAE Paper No. 850009, U.S. Bureau of Mines Best Paper Award for 1985, 1985 Transactions of the SAE (1986).

Dockery, D.W., A. Pope III, X. Xu, J.D. Spengler, J.H. Ware, M.E. Fay, B.G. Ferris, Jr., and F.E. Speizer, "An Association Between Air Pollution and Mortality in Six U.S. Cities," J. of Medicine, Vol. 329, No. 24 (December 9, 1993), p. 1753-1759.

Dolan, D.F., D.B. Kittelson and D. Pui, "Diesel Exhaust Particle Size Distribution Measurement Technique," SAE Paper No. 800187 (1980).

Donaldson, K., P.H. Beswich, and P.S. Gilmour, "Free Radical Activity Associated with the Surface of Particles: A Unifying Factor in Determining Biological Activity?" Toxicology Letters 88 (1966) pp. 293-298, Elsevier.

Farrar-Khan, J.R., G.E. Andrews, P.T. Williams, K.D. Bartle. "The Influence of Nozzle Sac Volume on the Composition of Diesel Particulate Fuel Derived SOF. SAE Paper 921649, p. 12, 1992.

Friedlander, S.K., Smoke, Dust and Haze: Fundamentals of Aerosol Behavior, John Wiley and Sons, New York (1977)

Harrison, R.M., "Airborne Particulate Matter in the United Kingdom," Third Report of the Quality of Urban Air Review Group, R.M. Harrison, chair, The University of Birmingham, Edgbaston, England, prepared at the request of the Department of the Environment, UK (May 1996).

Hildemann, L.M., Markowski, G.R., Jones, M.C., and Cass, G.R., "Submicrometer Aerosol Mass Distributions from boilers, fireplaces, Automobiles, Diesel Trucks, and Meat Cooking Operations," Aero. Sci. Tech. 14, pp. 138-152, (1991)

Hunter, Gary, "Particle Formation from Engines and Impact of Design Features on Particle Formation," Oral presentation at Health Effects Institute "Workshop on Particle Characterization," Cambridge, MA, Dec. 3-4, (1996)

"ICRP Task Group Model," Ann. Am. Conf. Ind. Hyg., Vol. 11 (1984)

Jakab, G.J., T.H. Risby, D.R. Hemenway, "Use of Physical Chemistry and in Vivo Exposure to Investigate the Toxicity of Formaldehyde to Carbonaceous Particles in the Murine Lung," Health Effects Institute, Res. Rep. No. 53 (1992)

Kittelson, D.B., P.A. Kadue, H.C. Scherrer, and R. Lovrien, "Characterization of Diesel Particles in the Atmosphere," Final Report, Coordinating Research Council, March 1988.

Mayer, A., et al. "Particle Size Distribution Downstream Traps of Different Design, SAE Paper 950373, 1995.

Pope III, C.A., M.J. Thun, M.M. Namboodiri, D.W. Dockery, J.S. Evans, F.E. Speizer, and C.W. Heath, Jr., "Particulate Air Pollution as a Predictor of Mortality in a Prospective Study of U.S. Adults," Am. J. Respir. Crit. Care Med., Vol. 151 (1995) pp. 669-674.

Raber, L.R., "EPA's Air Standards," Chem. & Engr. News, April 14, 1997, p10-18.

SAE, "Chemical Methods for the Measurement of Nonregulated Diesel Emissions," 1993 SAE Handbook, Vol. 3, "Engines, Fuels, Lubricants, Emissions, & Noise, p.25.38, 1993,

Seaton, A., W. MacNee, K. Donaldson, D. Godden, "Particulate Air Pollution and Acute Health Effects," The Lancet, Vol. 345 (January 21, 1995, excerpt from section on -- How particles may cause harm, p. 177.

Schauer, J.J., W.F. Rogge, L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit, "Source apportionment of airborne particulate matter using organic compounds as tracers," Atmospheric Environment 30, 3837-3855, 1996.

Scherrer, H.C. and D.B. Kittelson, "Light Absorption Cross Sections of Diesel Particles," SAE Paper No. 810181, 1981 Transactions of SAE (1982).

Warheit, D.B., W.C. Seidel, M.C. Carakostas, and M.A. Hartsy, "Attenuation of Perfluoropolymer Fume Pulmonary Toxicity: Effect of Filters, Combustion Method, and Aerosol Age," Pulmonary Toxicity of Perfluoropolymer Fumes, Academic Press, 1990, pp. 309-329.

Figure 1 - Particle Composition and Structure

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

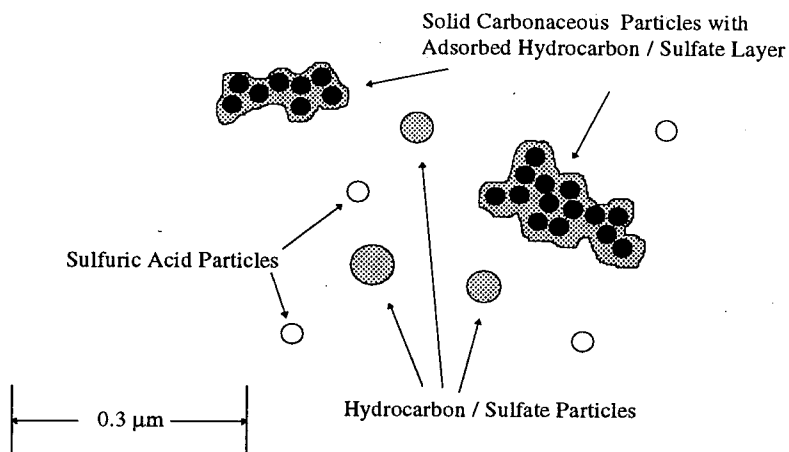


Figure 2 - Typical Particle Composition, Heavy-Duty Diesel Engine Tested in the Heavy-Duty Transient Cycle

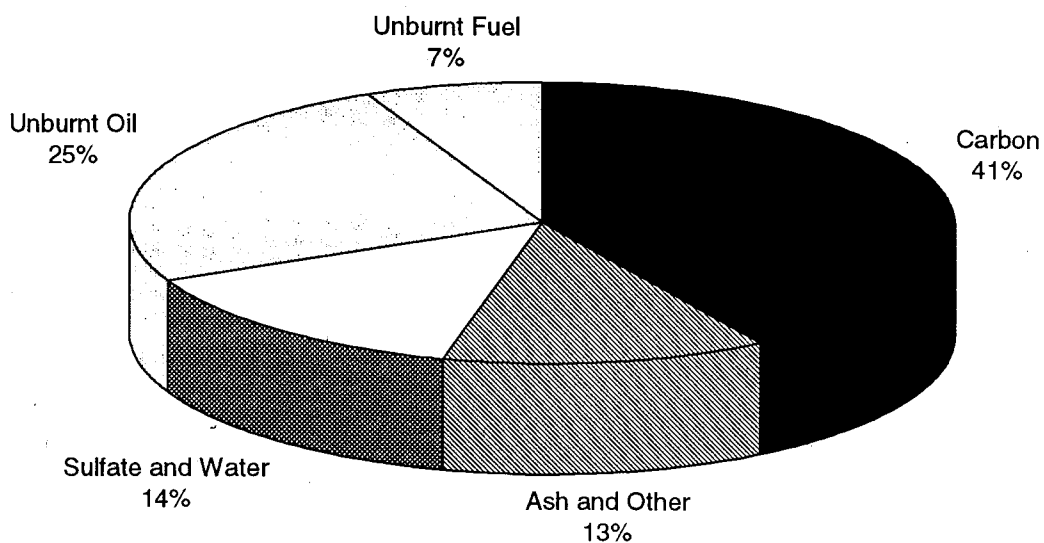


Figure 3 - Typical Engine Exhaust Size Distribution. Both Mass and Number Weightings are Shown.

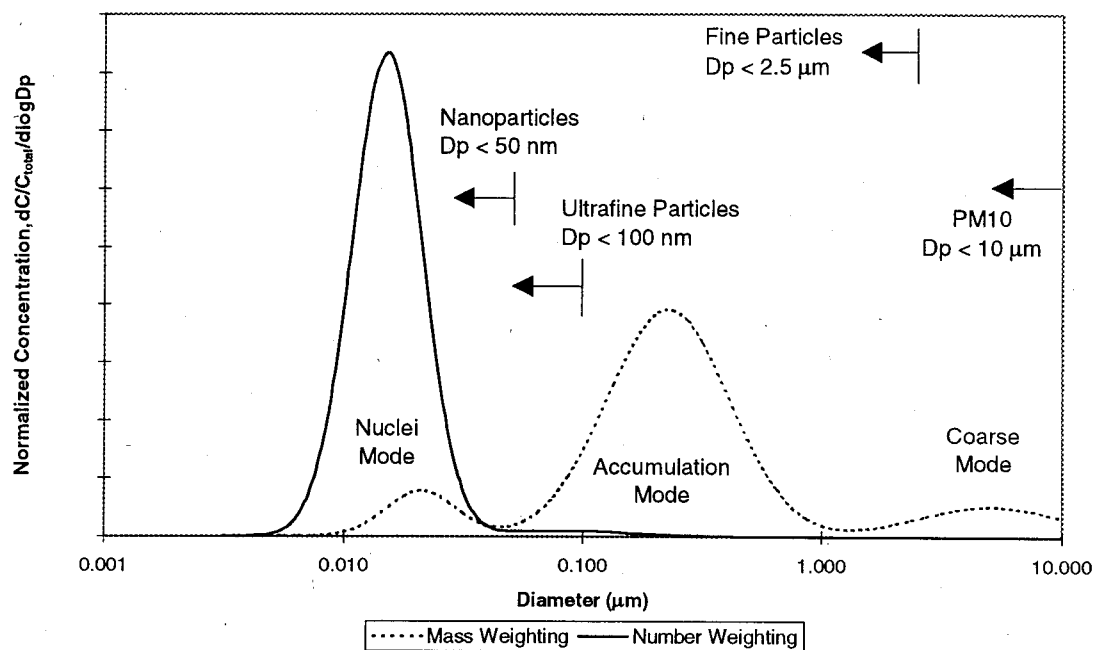


Figure 4 - Engine Exhaust Particle Volume Concentrations Measured with Electrical Aerosol Analyzers for a Range of Engines and Operating Conditions. All Data are from University of Minnesota, Except HEI which are from Bagey, et al., 1996. DI and IDI Denote Direct and Indirect Injection, Respectively.

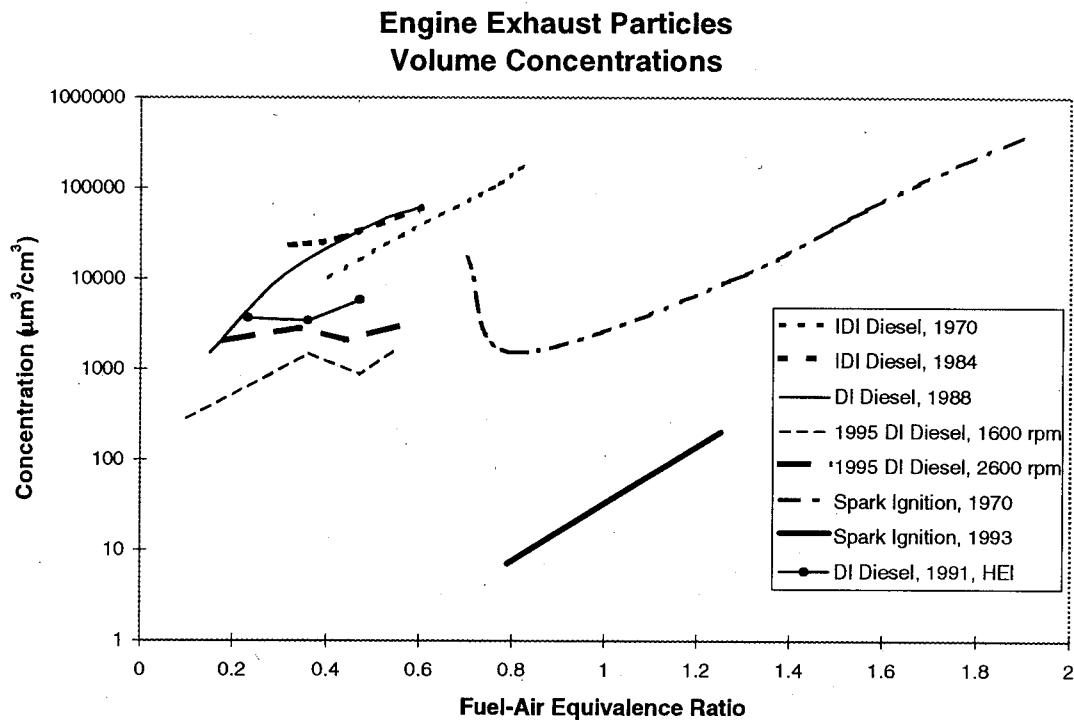


Figure 5 - Engine Exhaust Particle Number Concentrations Measured with Electrical Aerosol Analyzers for a Range of Engines and Operating Conditions. All Data are from University of Minnesota, Except HEI which are from Bagey, et al., 1996. DI and IDI Denote Direct and Indirect Injection, Respectively.

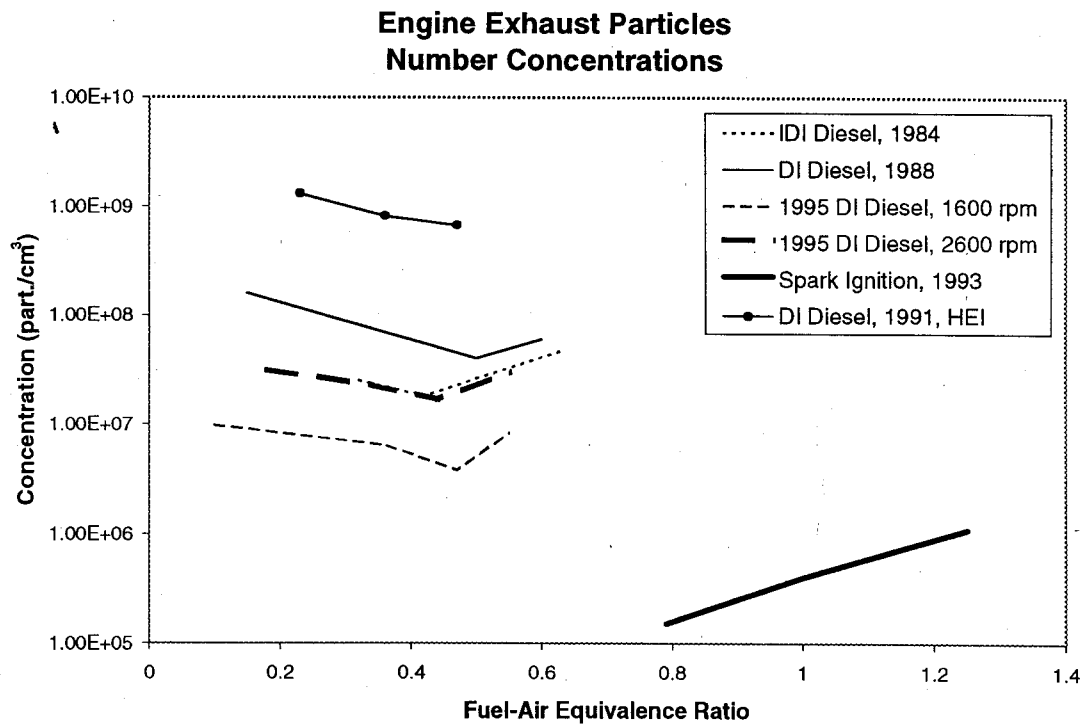


Figure 6 - Ratios of Particle Number to Volume Concentrations Calculated from Data in Figures 4 and 5.

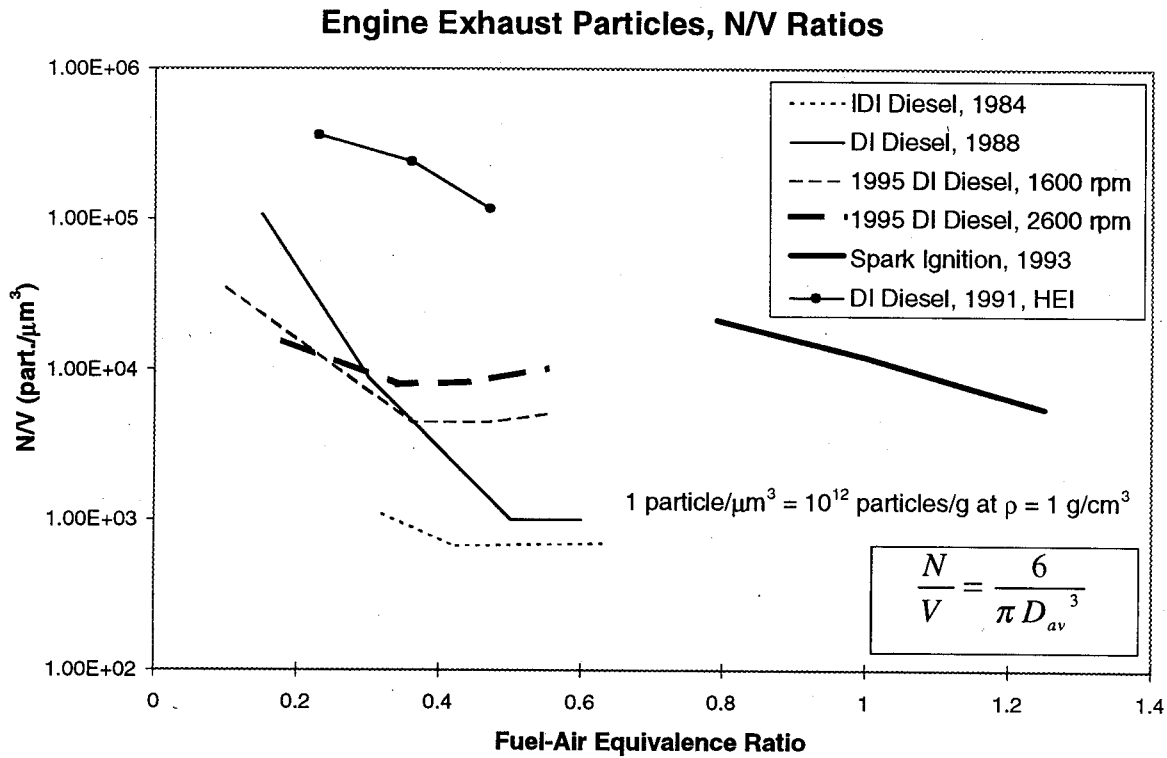


Figure 7 - Diameter of Average Volume Calculated from N/V Ratios in Figure 6. Spherical Particles are Assumed.

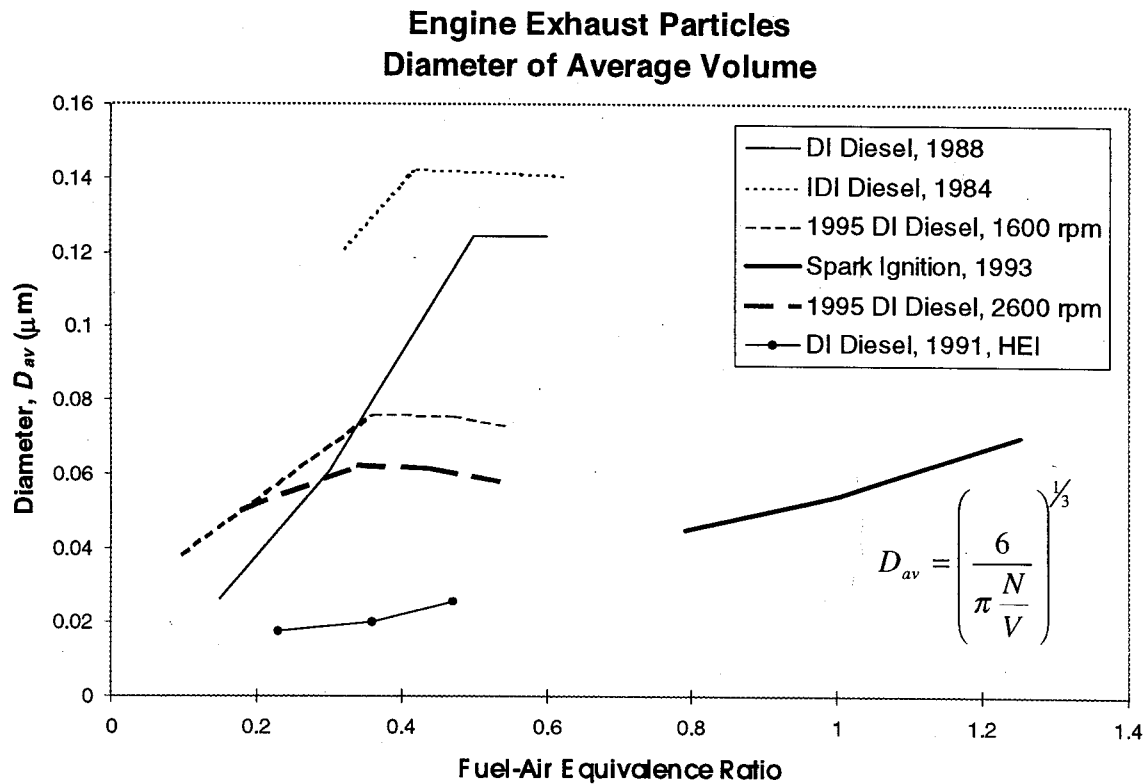


Figure 8 - Volume Weighted Size Distribution for 1991 Diesel Engine Tested for HEI Report. (Bagley, et al., 1996). DGV Denotes Geometric Volume Mean Diameter.

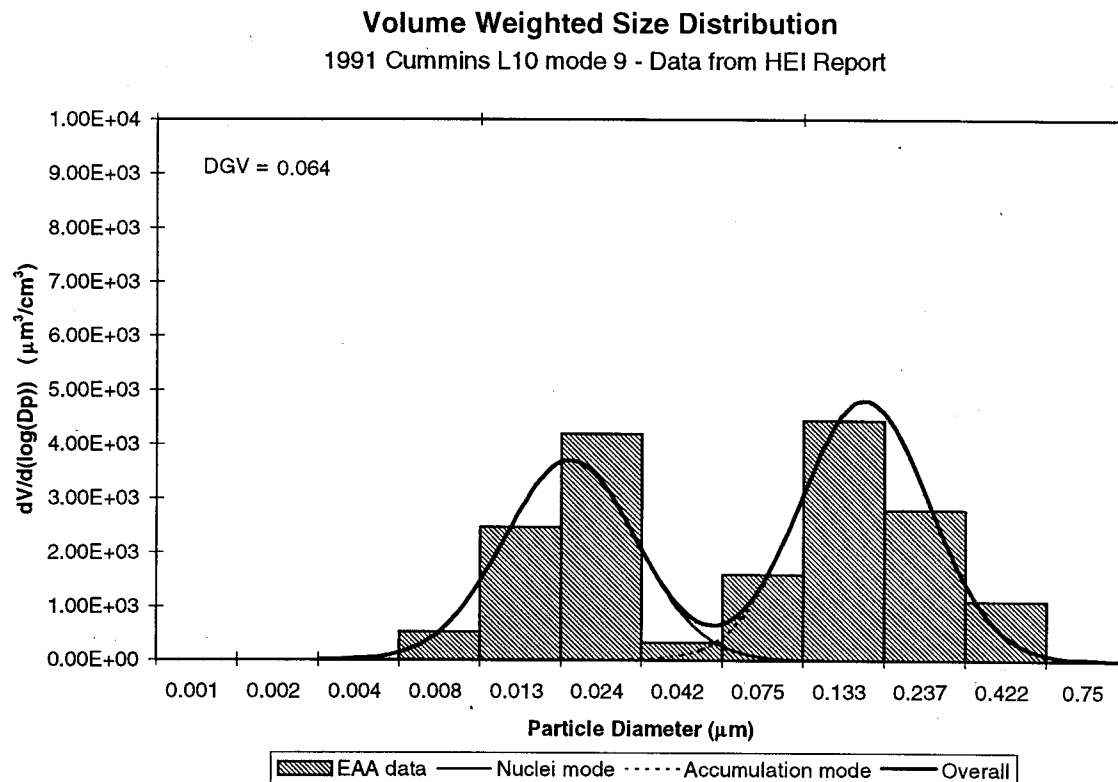


Figure 9 - Volume Weighted Size Distribution for 1995 Diesel Engine Tested at University of Minnesota. DGV Denotes Geometric Volume Mean Diameter.

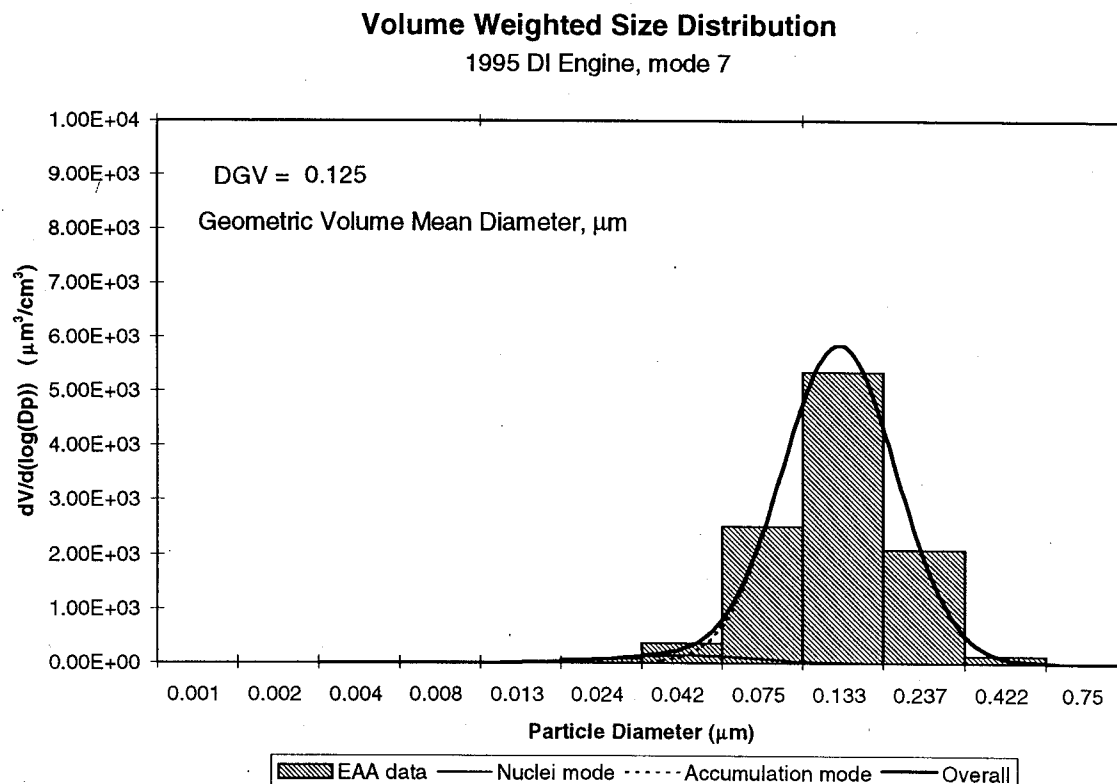


Figure 10 - Number Weighted Size Distribution for 1991 Diesel Engine Tested for HEI Report. (Bagley, et al., 1996). DGN Denotes Geometric Number Mean Diameter.

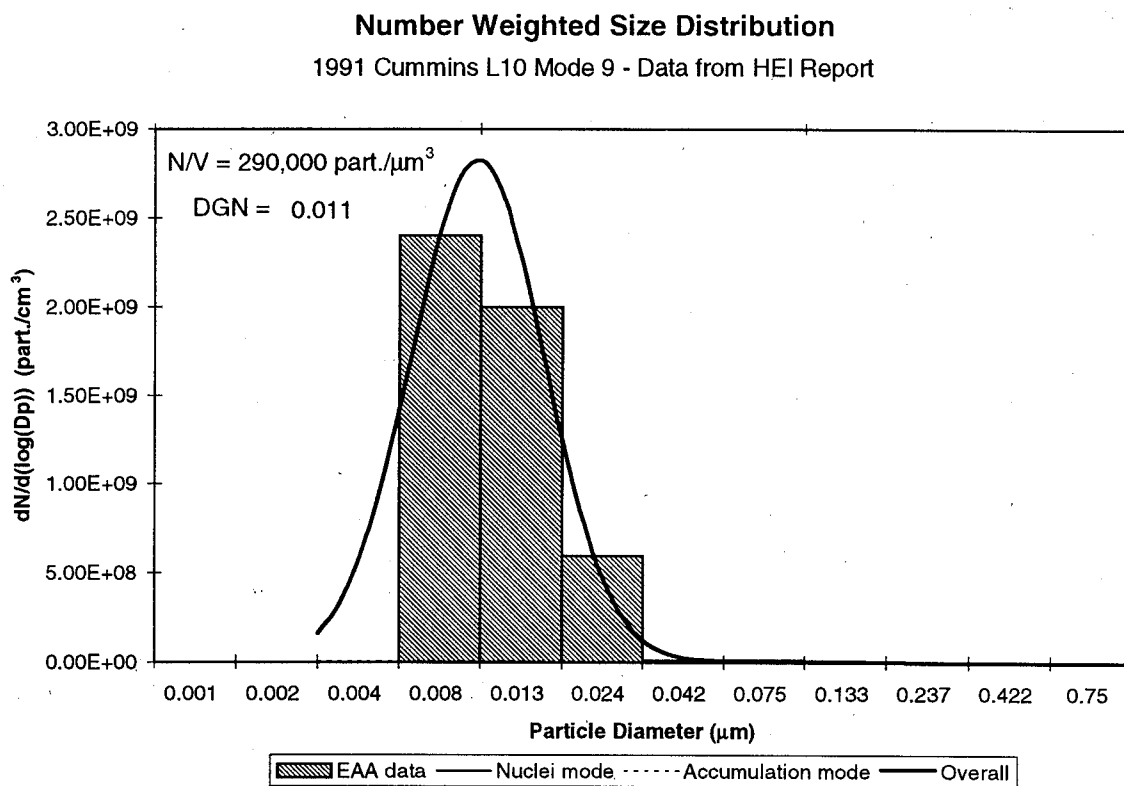


Figure 11 - Number Weighted Size Distribution for 1995 Diesel Engine Tested at University of Minnesota. DGN Denotes Geometric Number Mean Diameter.

