DieselNet Technology Guide

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Diesel Exhaust Particle Size

Abstract: Diesel particulates have a bimodal size distribution which includes small nuclei mode particles and larger accumulation mode particles. Most of diesel particle mass is contained in the accumulation mode but most of the particle number can be found in the nuclei mode. Although the exact composition of diesel nanoparticles is not known, it is believed that they are composed primarily of condensates (hydrocarbons, water, sulfuric acid). The amount of these condensates and the number of nanoparticles depends very significantly on the particulate sampling conditions, such as dilution ratios, which were applied during the measurement. It was also found that spark ignited engines emit numbers of small particles which are comparable to those from diesel engines.

Diesel Particle Size Distribution

Since the mid-1990's, particle size distributions from internal combustion engines have been receiving increased attention due to possible adverse health effects of fine and ultrafine particulates. Diesel emission control strategies, based on both engine design and aftertreatment, are being examined and re-evaluated for their effectiveness in the control of the finest fractions of diesel particulates and particle number emissions. However, a fair performance assessment of various control technologies can be possible only if the research community reaches a consensus on the definition and the measurement techniques of the smallest fractions of diesel particulates. The determination of particle sizes and numbers is much more sensitive to the measuring techniques and parameters than the quantification of particulate mass emissions. Dilution and sampling methods are key variables that must be taken into consideration to ensure accurate and repeatable results. On the other hand, particle sizing instruments exist that have significantly better sensitivities than the gravimetric measurement, thus presenting an attractive alternative for the PM emission measurement in future engines, provided standardized measuring methods are developed.

Ambient particulate matter is divided by most authors into the following categories based on their aerodynamic diameter (the aerodynamic diameter is defined as the diameter of a 1 g/cm^3 density sphere of the same settling velocity in air as the measured particle):

- *PM_{10}*—particulates of an aerodynamic diameter of less than 10 µm
- *Fine particles* of diameters below 2.5 µm
- *Ultrafine particles* of diameters below 0.1 µm or 100 nm
- *Nanoparticles*, characterized by diameters of less than 50 nm.

A typical size distribution of diesel exhaust particulates is shown in Figure 1 (note that a logarithmic scale is used for particle aerodynamic diameter). Nearly all diesel particulates have sizes of significantly less than 1 µm. As such, they represent a mixture of fine, ultrafine, and nanoparticles. Due to the current PM sampling techniques (diluted exhaust, temperature <52°C), diesel particulate matter includes both solids, such as elemental carbon and ash, and liquids, such as condensed hydrocarbons, water, and sulfuric acid. Formation of particulates starts with nucleation, which is followed by subsequent agglomeration of the nuclei particles. The nucleation occurs both in the engine cylinder (carbon, ash) and in the dilution tunnel (hydrocarbons, sulfuric acid, water), through homogeneous and heterogeneous nucleation mechanisms.

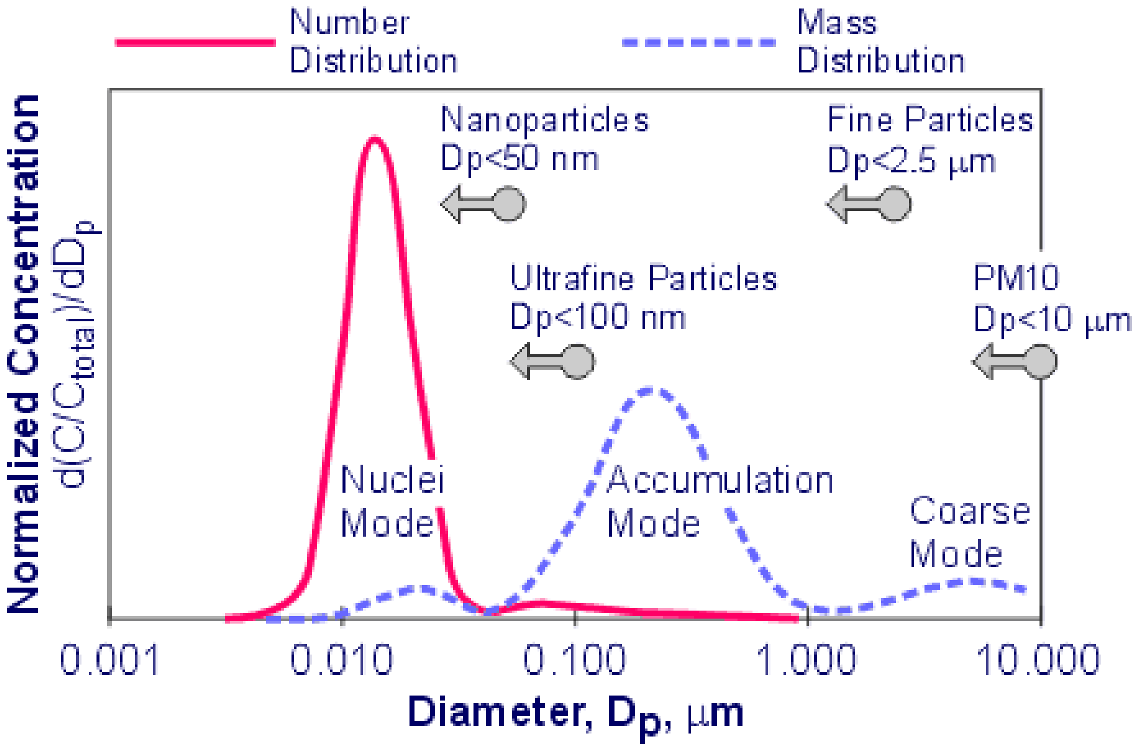


Figure 1. Diesel Particulate Size Distribution

Size distributions of diesel particulates have a well established bimodal character which corresponds to the particle nucleation and agglomeration mechanisms, with the corresponding particle types referred to as the *nuclei mode* and the *accumulation mode*. Size distributions are usually presented using either particle mass or particle number weighting. In each representation normal-logarithmic distribution curves are produced, as shown in Figure 1. Both the maximum particle concentration and the position of the nuclei and accumulation mode peaks, however, depend on which representation is chosen. In mass distributions, the majority of the particulates (i.e., the particulate mass) is found in the accumulation mode. In number distributions, on the other hand, most particles are found in the nuclei mode. In other words, diesel particulate matter is composed of numerous small particles holding very little mass, mixed with relatively few larger particles which contain most of the total mass. A small fraction of diesel particulates reside in a third, coarse mode (Figure 1). These three particle modes can be characterized as follows:

- **Nuclei mode**: The diameter of the original nucleus, such as formed during sulfuric acid nucleation, is about 1 nm [Abdul-Khalek 1999]. Today’s measuring techniques are capable of detecting a minimum particle size of approximately 3 nm. According to various definitions, the diameters of nuclei mode particles were generally less than 40-50 nm (0.04-0.05 µm). Based on particle size research in the 1990’s technology heavy-duty diesel engines, it has been postulated that the nuclei mode extends through sizes from 3 to 30 nm (0.003-0.03 µm) [Kittelson 2002][Hall 2001]. All of the above size ranges place nuclei mode particles entirely within the nanoparticle range. The maximum concentration of nuclei mode particles occurs at 10-20 nm. The nuclei mode, depending on the engine technology and particle sampling technique, typically contains only 0.1-10% of the total PM mass, but it often includes more than 90% of the total particle count. Sometimes the nuclei mode particles present as much as 99% of the total particulate number. Nuclei mode particles are composed mostly of volatile condensates (hydrocarbons, sulfuric acid) and contain little solid material.
- **Accumulation mode**: The accumulation mode is made of sub-micron particles of diameters ranging most often from 30 to 500 nm (0.03-0.5 µm nm) [Kittelson 2002], with a maximum concentration between some 100-200 nm (0.1-0.2 µm). As shown in Figure 1, the accumulation mode extends through the fine, ultrafine, and the upper end of the nanoparticle range. Accumulation mode particles are made of solids (carbon, metallic ash) intermixed with condensates and adsorbed material (heavy hydrocarbons, sulfur species).
- **Coarse mode**: These particles with aerodynamic diameters above 1 µm (1000 nm) contain 5-20% of the total PM mass and practically no contribution to particle numbers [Kittelson 2002]. The coarse particles are not generated in the diesel combustion process. Rather, they are formed through deposition and subsequent re-entrainment of particulate material from walls of the engine cylinder, exhaust system, or the particulate sampling system.

Other particle weightings that may be used include particle surface (which would produce a curve located between the mass and number weightings in Figure 1) and particle volume weighting, which is proportional to the mass weighting.

Particle Distributions from New Diesel Engines

Interest in particulate size distributions and nanoparticle emissions from diesel engines was sparked by reports that newer technology engines—designed for low PM mass emissions—may still generate high particle numbers. The most significant study indicating such possibility, involving measurement of particle size distributions from an older and a newer generation heavy-duty diesel engine, was published by the Health Effects Institute (HEI) [Bagley 1996]. As indicated by later research based on more comprehensive data from several engine models, old and new technology engines produce in general nuclei modes of similar magnitude and the PM mass reductions in new engines are due to smaller accumulation modes [Kittelson 2002]. It is believed that emissions from the new engine in the HEI study—an experimental 1991 design—have not reflected general emission trends in new technology engines. That study, however, must be credited with prompting quality research by the diesel industry, academia, and governments, leading to a greatly increased understanding of particulate emissions from internal combustion engines.

The HEI study compared two 10 liter Cummins engines—a 1988 model year LTA 10-300 engine with a 1991 LTA10-310 [Baumgard 1996]. The 1991 engine had a higher injection pressure, a higher turbo boost pressure, and a larger intercooler than its 1988 counterpart. The engines were operated at several steady-state modes. Modes #9 and #11, which are referenced here, were at rated speed and at 75% and 25%, respectively, of the maximum torque. Figure 2 illustrates particle size distribution measured from both engines at Mode 9, presented in the volumetric units of $\mu m^3/cm^3$.

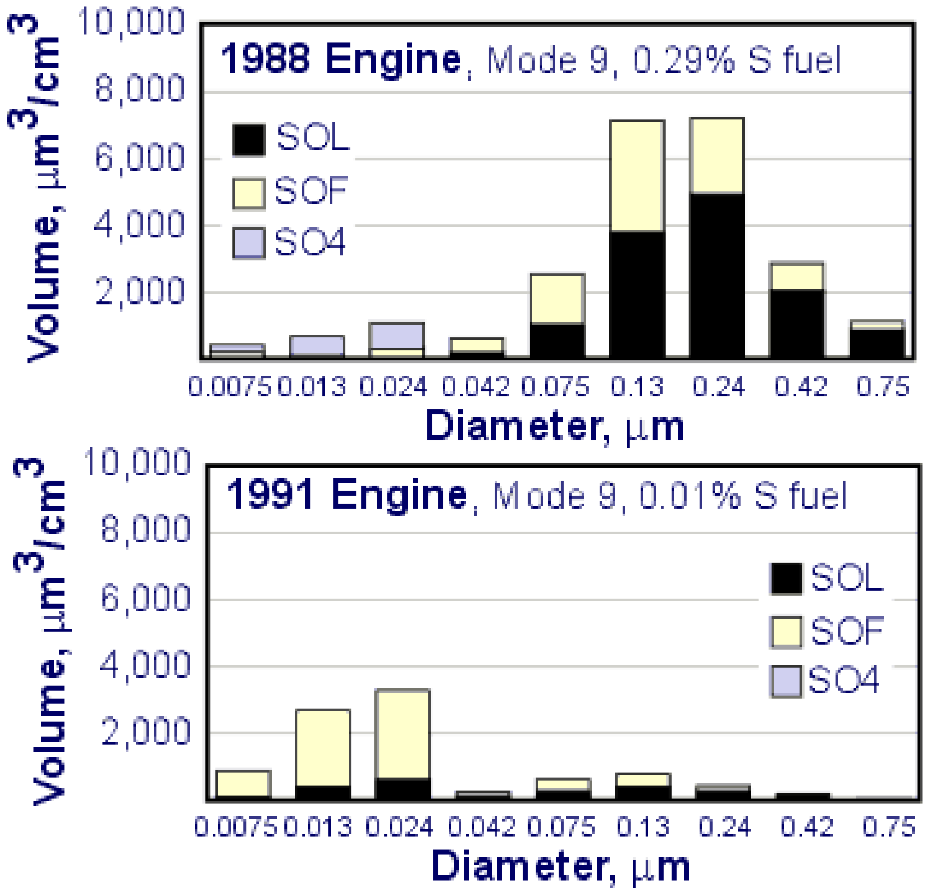


Figure 2. Particle Size Distribution from Two Diesel Engines (HEI Study)

Particle size distributions from both engines showed the bimodal character typical for diesel particulates. The peak concentrations for nuclei and accumulation mode particles were at about 0.02 µm and at about 0.2 µm, respectively. In the 1988 engine, most of the generated particulates were in the accumulation mode. The 1991 engine showed over 90% PM mass emission reduction in the accumulation mode relative to the 1988 engine, however, its nuclei mode was greatly increased, up to as much as 40% of the total particle volume at certain conditions.

Particle numbers emitted from each engine in Modes 9 and 11 are compared in Table 1 (all data with 0.01% S fuel). Even though the total PM volume (as well as mass) was reduced in the new engine by about 80%, a significant increase in the total number of particles was measured at both test modes. In Mode 11 the particle number from the new engine were more than 2 orders of magnitude higher than that from the old engine. One important reason for the high particle numbers was high SOF content in the 1991 engine, which resulted in the formation of nuclei mode hydrocarbon particles.

Table 1

Number of Particles from Two Diesel Engines (HEI Study)

	88 Engine	**91 Engine**
Mode 9		
Total particles (particles/cm^3)	$3.75\cdot10^7$	$1.26\cdot10^9$
Total volume (µm^3/cm^3)	$2.42\cdot10^4$	$3.58\cdot10^3$
Number fraction in nuclei mode	0.58	0.99
Volume fraction in nuclei mode	0.018	0.41
NMD* in nuclei mode	0.011	0.011
NMD* in accumulation mode	0.30	0.17
Mode 11		
Total particles (particles/cm^3)	$4.58\cdot10^7$	$6.69\cdot10^9$
Total volume (µm^3/cm^3)	$2.56\cdot10^4$	$5.76\cdot10^3$
Number fraction in nuclei mode	0.44	0.99
Volume fraction in nuclei mode	0.022	0.44
NMD* in nuclei mode	0.015	0.017
NMD* in accumulation mode	0.16	0.12
*NMD - number mean diameter, µm		

Increased particle numbers were also reported by some other studies. However, in most cases the observed increases in number emissions were not as dramatic as those shown in Table 1. For instance, two Liebherr diesel engines were compared in the VERT study—an old 914 TI (6.11 liter, 2000 rpm, 105 kW, DI, turbocharged) and a new 924 TI-E (6.64 liter, 2000 rpm, 140 kW, DI, turbocharged and intercooled) [Mayer 1998]. In most operating modes increases in particle numbers between 15 and 50% were reported, with a six-fold increase under one operating mode. The maximum particle concentrations were in the order of 10^7 particles/cm^3.

Investigation of particle numbers from heavy-duty engines was a part of the comprehensive diesel aerosol sampling study E-43, funded by the US Coordinating Research Council (CRC) [Kittelson 2002]. A particle number comparison from various engine technologies complied by the study is shown in Figure 3. The three E-43 sets of data (Cummins ISM and CAT 3406) were collected in highway chase experiments, where a mobile emission laboratory was following a diesel truck on a road, sampling air behind its exhaust plume. The chart also includes a curve representing the composite from the HEI data for the 1991 engine discussed above. The comparison shows that the model year 1999-2000 engines in the E-43 study produced fewer nanoparticles than the 1991 HEI engine.

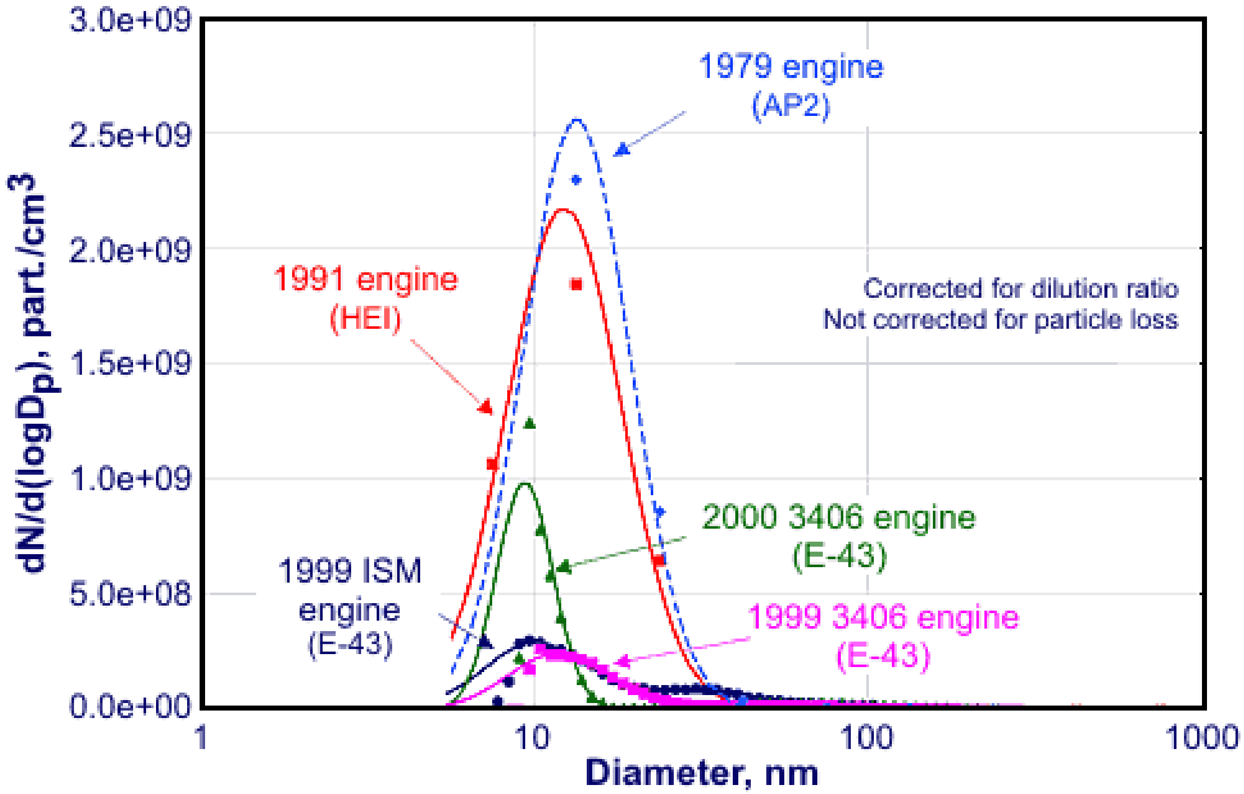


Figure 3. Comparison of Particle Number Emissions from Different Engines

AP2: 1979 Cat NTC350 engine, 3000 ppm S fuel; HEI: 1991 Cummins LTA10-310, 100 ppm S; E-43: 1999 Cummins ISM (California calibration), 1999 Cat 3406E (CA), 2000 Cat 3406E (EPA), 326-406 ppm S

To put things into better historical perspective, the chart also shows a set of data collected in another CRC study (AP2), involving a chase experiment with a model year 1979 engine [Kittelson 1998b]. Particle numbers produced by the 1979 engine were somewhat higher than those in the 1991 HEI engine—a clear indication that nanoparticle emissions have been on the roads for a long time, and are not a new phenomenon caused by new technology engines.

Generally decreasing particle number trends with advanced engine technology were reported in Euro I, Euro II, and Euro III engines when tested over regulatory emission test cycles [Wedekind 2000] [Andersson 2001]. Comparisons of particle number emissions were also conducted in older and newer technology diesel passenger cars in studies funded by ACEA [ACEA 2002]. It was found, based on steady-state and ECE+EUDC cycle tests, that the size distribution of diesel particulates was similar in the older and more advanced technology vehicles. It was also shown that particulate mass could be correlated with particle numbers.

Diesel particle counts reported in different studies span a wide range of approximately 1×10^6 - 1×10^9 particles/cm^3. These results would suggest that there is large variability in particle counts between different engine technologies. However, due to lack of standard measuring methods, comparisons of data from different laboratories has only limited validity. Until sampling and measuring procedures mature, valid particle number comparisons should be based on data generated within a single research program, using the same set of measuring techniques and equipment. Comparing data from different laboratories may require a number of corrections, such as for different dilution ratios, and is not always possible.

Spark Ignited Engines

At first, particulate emission research focused on the characterization and control of diesel PM emissions. This was due to the fact that PM mass emissions from spark ignited (SI) engines were small when compared to those from diesel engines. Prior to the introduction of diesel PM legislation in the 1990’s, the SI engines used to have PM emissions in the order of 1% of diesel particulate emissions. However, recent trends to shift focus from particle mass to particle numbers resulted in renewed interest in particulate emissions from SI engines.

Research on the characterization of the SI particulate emissions [Graskow 1999] and on comparison of diesel and SI particles [Greenwood 1996][Graskow 1998] seems to be reaching a consensus on the following issues:

- SI engine particulates, such as those produced by port fuel injected (PFI) gasoline engines, are composed of much smaller particles than those from diesel engines. In some reports, the SI engine particles were found practically entirely in the nanoparticle range (<50 nm).
- Particle numbers in the SI engines are about 2 orders of magnitude lower than those in diesel engines when measured at low engine speeds or over standard engine test cycles. The particle number emissions increase significantly at rich air-to-fuel ratios, e.g. during high speed highway cruising. At such conditions, comparable particle numbers may be emitted from SI and diesel engines.
- SI particulate numbers, when plotted over time, show repeated patterns of high concentration “spikes”, while the diesel engines emit steady numbers of particles. This would indicate a different mechanism of particle formation in both types of engines.

- SI engine particles appear to be composed of ash (calcium, magnesium, copper, iron, sodium, ...), lube oil, and other volatile components [Andrews 1999]. Their elemental carbon content is low in comparison to diesel.
- Three-way catalytic converters decrease the concentrations of the smallest particles. Different types of fuel additives may either increase or decrease the particulate number concentrations.

A comparison of data from different literature reports, expressed in number emissions per kilometer, shows that automotive diesel engines emitted between about 2.4×10^{14} and 8×10^{13} particles/km, while emissions between 1.2×10^{14} and 3×10^{10} particles/km were observed from gasoline engines [Graskow 1998][CONCAWE 1998]. Expressed per unit of gas volume, new PFI SI engines emit number concentrations from about 1×10^5 particles/cm^3 (low load) to 1×10^7 particles/cm^3 (high load), while older SI engines can emit concentrations in excess of 10^8 particles/cm^3 [Graskow 1999a].

A large study to compare diesel and gasoline particulate number emissions was conducted by CONCAWE [CONCAWE 1998][Hall 1998]. In that study 4 diesel cars (DI and IDI) and 3 gasoline PFI cars were tested using a matrix of 3 diesel and 2 gasoline fuels. The vehicles were tested on several constant speed conditions and over the ECE+EUDC test cycle. Example results are shown in the following figures. Figure 4 illustrates the total particle counts averaged over the tested fuels at selected test modes. These results are in agreement with the above listed characteristics of SI engine particles. Indeed, the SI particle numbers increase significantly at high speed driving, while diesels tend to emit constant particle numbers.

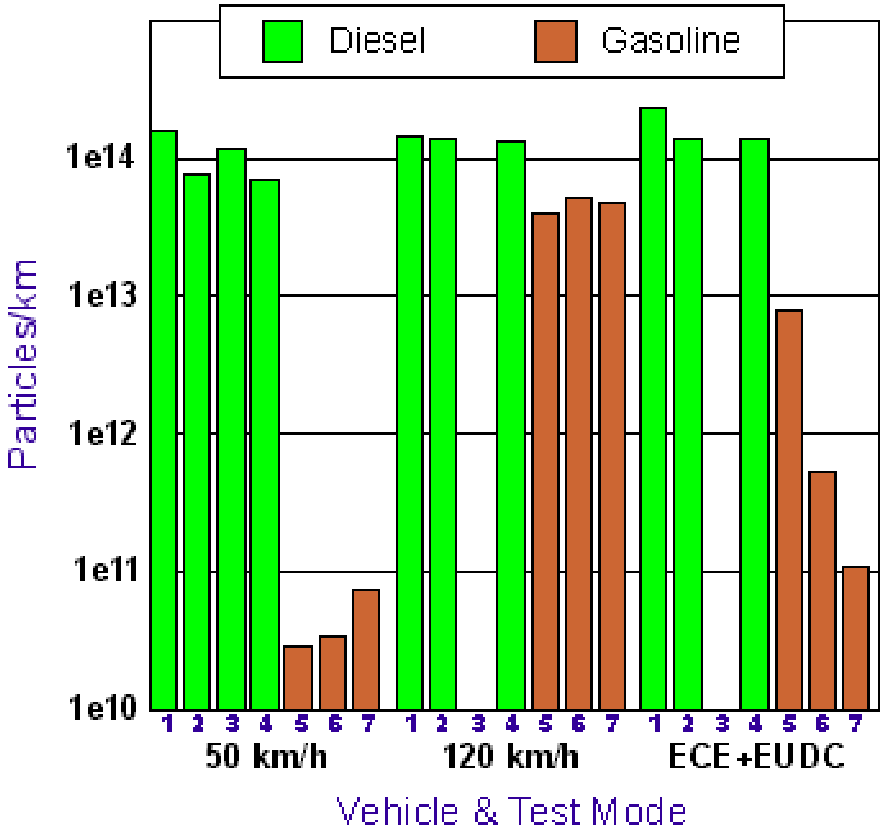


Figure 4. Particulate Number Emissions from Diesel and Gasoline Cars

Figure 5 presents selected number-weighted distributions for diesel and gasoline cars. The particular lines reflect variability for different cars and fuels. Gasoline engine particulates are characterized by generally smaller sizes than those from diesel engines.

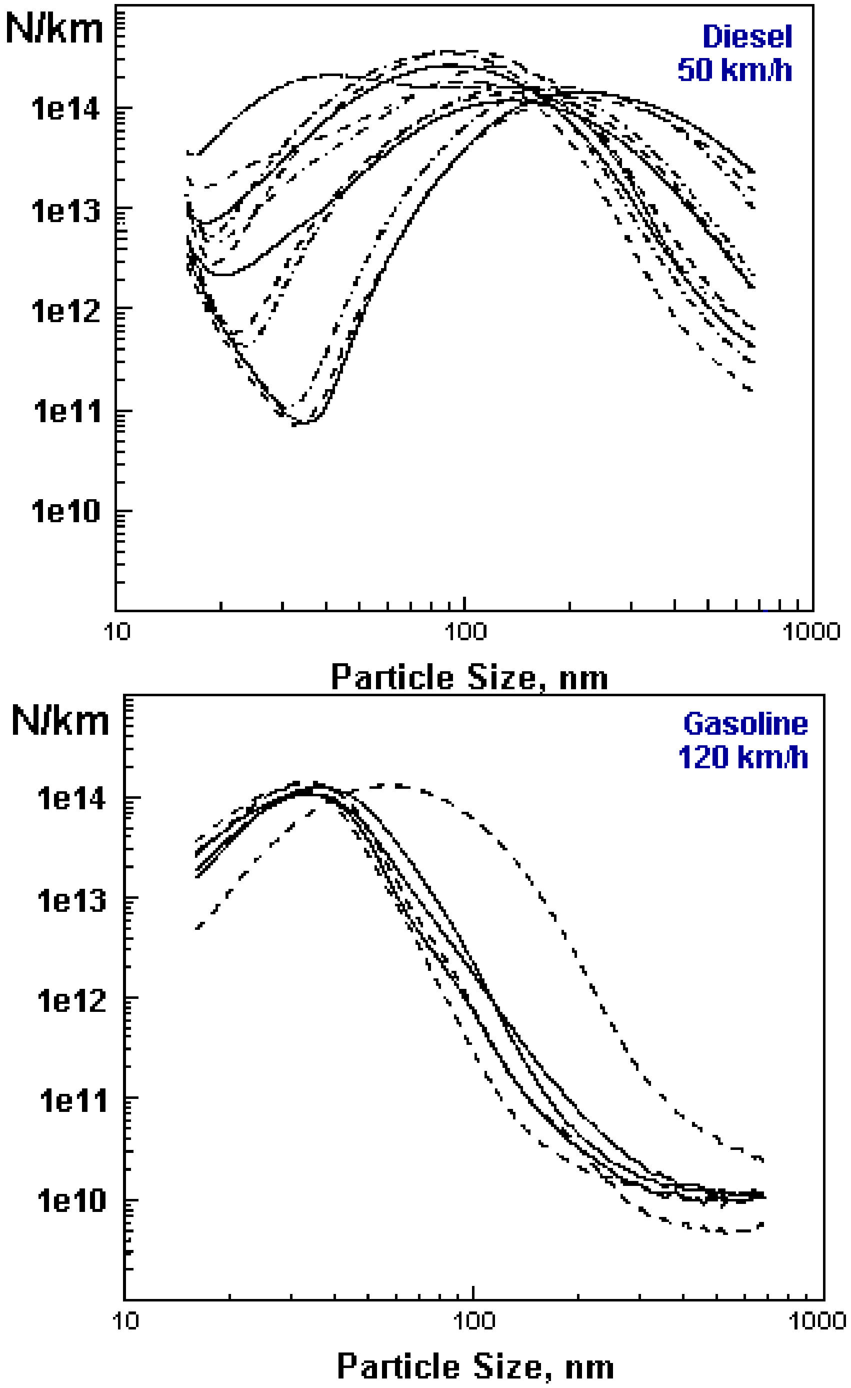


Figure 5. Particle Size Distributions from Diesel and Gasoline Cars

Gasoline fueled cars have been increasingly adopting the direct injection engine (GDI) technology. Cars with GDI engines are already commercially available in Japan and Europe. The fuel injection strategy adopted by those engines depends on the engine operating condition. Typically, under low load conditions fuel is injected during the compression stroke resulting in a stratified charge with an overall air-to-fuel ratio of 30:1 - 40:1. Under moderate and high load conditions fuel is injected during the intake stroke, resulting in a homogeneous charge. At moderate loads the A/F ratios in the range 20:1 - 24:1, while at high loads the engine enters into closed-loop stoichiometric feedback mode [Kazunari 1998].

The GDI injection strategy at low loads bears some similarity to the diesel injection process, while at high loads it is identical to the traditional PFI gasoline engine. GDI emission studies indicate that the complex injection strategy produces equally complex particle emission behavior. When tested at high engine loads, under stoichiometric control operation, GDI engine emissions are similar to those of PFI gasoline engines. At lower loads on the other hand, when the engine enters stratified combustion regime, its PM emissions may resemble those from the diesel engine. In one GDI vehicle study, when tested at high engine load (stoichiometric operation), particle numbers reached 9.3×10^7 particles/cm^3 with the characteristic spiking time-resolved pattern [Graskow 1999a]. At lower engine loads—in the stratified, lean burn mode—particle counts were much higher, reaching up to 2.8×10^8 particles/cm^3. They also exhibited a steady-state, diesel-like time distributions. Furthermore, the GDI engine produced agglomeration mode particles of a maximum concentration at about 100 nm at all but one operating modes. This is again similar to the diesel engine and unlike the PFI engine that generates particulates primarily in the nanoparticle size range (<50 nm). High particle number from GDI engines have been reported by numerous other studies [Hall 1999][Maricq 1999]. The latter investigation also compared the FTP-75 cycle PM mass emissions from equivalent PFI gasoline engine, GDI gasoline engine, and a 1995 diesel IDI vehicle, reporting about 2 mg/mile, 10 mg/mile, and 100 mg/mile, respectively. By taking a position between the PFI and diesel, the GDI engine becomes a potentially significant source for not only particle numbers, but also PM mass emission.

The chemical composition of the GDI particles still remains an open question. Considering the similarity of the stratified combustion to the diesel cycle, it is likely that GDI particulate contain significant proportion of elemental carbon.

High emissions of small size particles have been also reported from natural gas engines. In a comparison of a diesel and CNG bus engine emissions, the diesel bus was shown to have 1 to 2 orders of magnitude higher particle counts in the size range of above 0.09 µm. However, at 0.04 µm (nanoparticle size range) the CNG and diesel emitted comparable particle numbers [Eastlake 1999].

Influence of Particulate Sampling

Contrary to the gravimetric measurements of total diesel particulate emissions, which are a well established routine measurement of good repeatability, size distributions measured at different laboratories show considerable variability. Reported distributions, especially those weighted by particle numbers, frequently disagree by several orders of magnitude. That spread of experimental results is related to the following issues:

- different measuring equipment and measurement errors,
- the influence of exhaust gas sampling and dilution parameters on the properties and size distributions of diesel particulates.

The measurements of diesel particle size distributions is a relatively new analytical discipline. As increasingly more experience is being accumulated, the analytical methods and instruments are becoming more reliable and accurate. The precision, repeatability, measuring ranges, response to transient conditions, and, generally, the quality of measurement has been improving and will continue to improve.

The exhaust gas sampling issues and their influence on the particles are a more serious consideration. There is a wide agreement that sampling parameters, such as dilution ratio, dilution rate and residence time have a critical impact on the properties and sizes of the particulates [Ahlvik 1998][Andersson 2000][Hall 2001], to the point that different set-ups of the same measurement system can produce conflicting data. That influence is especially strong in regards to the number concentrations and distributions, as opposed to the mass/volume particle concentrations. Another consideration is that exhaust gas dilution which takes place in the dilution tunnel(s) is not a good simulation of atmospheric dilution. In effect, conditions in the dilution tunnel may easily produce artifacts, or artificial particulates, which are not normally encountered when dilution takes place in the atmosphere.

Exhaust particulates in the tailpipe are very much different from those sampled in dilution tunnels or those present in the ambient atmosphere. At high exhaust temperatures the particles are composed primarily of solids, including elemental carbon and ash. When the gases are discharged to the atmosphere and mixed with ambient air, the particulate phase increases through nucleation, adsorption and condensation, which are driven by decreasing temperatures. Nucleation is a formation of new particles, solid or liquid, from gas phase components. The rate of nucleation rapidly increases when gas components approach their saturation. Although the nucleation is usually not very significant for mass concentrations, it can increase the number concentrations of particulates by an order of magnitude. The nuclei particles may grow due to coagulation, which occurs both in the hot exhaust gas and during the dilution. Other mechanisms of particle size growth include adsorption of gas molecules and condensation of vapors on the surface of particles.

Once finally released into the atmosphere, the particles are by no means stable. The processes that occur include atmospheric evaporation and desorption of the volatile particulate fractions, as well as changes in the particle sizes. It was found in several independent studies that the nanoparticles disappear with aging and their ambient concentrations quickly decrease with time. Particle lifetimes, τ_{90} and τ_{99}, are defined as the times necessary for the reduction of the total number concentrations from their initial plume values by 90% and 99%, respectively. An investigation of the lifetime of diesel aerosol found that for typical urban conditions τ_{90} is on the order of a few minutes and τ_{99} is on the order of 20-30 min (during these time periods, particulates can travel with the wind over the distance of 100-1000 m, and 0.5-10 km, respectively) [Capaldo 2001].

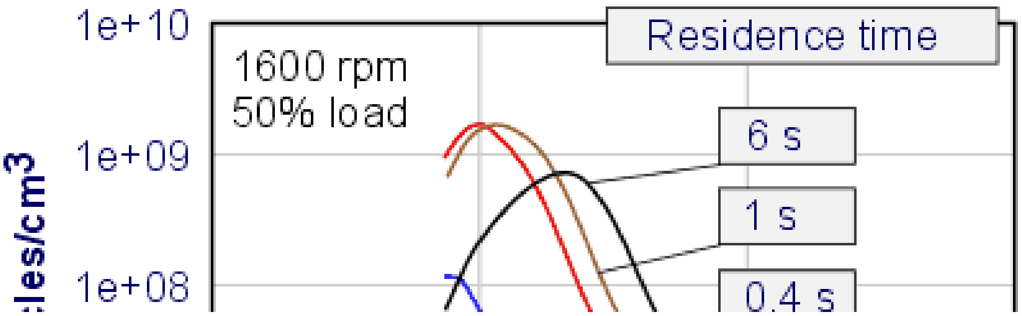
Important factors which influence gas to particle conversions, including nucleation and adsorption/

condensation, as well as coagulation, are:

- Dilution ratio,
- Cooling,
- Residence time,
- Temperature,
- Humidity,
- Ambient aerosols.

As a consequence, the gas to particle conversion processes are very sensitive to correct simulation of atmospheric dilution. The critical parameters include saturation ratios of volatile components, which influence the nucleation of new particles, and residence times, which influence particle coagulation. Typical atmospheric dilution ratios of vehicle exhaust gases are between 500 and 1000. Since dilution tunnels used for PM sampling operate at dilution ratios of about 10, the simulation is far from being perfect. The dilution tunnel saturation ratios are much higher than those in the atmospheric dilution, while the dilution rates are slower and the residence times are longer. As a result, particulate size distributions measured in a dilution tunnel may be very different from what would be seen in the atmosphere. Furthermore, different number concentrations and distributions may be measured whenever dilution ratios or residence times are changed.

Low dilution ratios lead to an increase in the total particulate mass due to increased SOF fraction. That effect has been known for quite a long time [Ahlvik 1998]. The influence of dilution ratio and dilution tunnel residence time on number weighted size distributions can be illustrated by the results of a study with a Perkins diesel engine [Abdul-Khalek 1999]. Diesel particulates were sampled from a Perkins T4.40, 4 cylinder, DI, turbocharged and aftercooled engine operated with low sulfur fuel (< 0.05% S). The particulate sampling system included a primary and secondary dilution tunnel of adjustable dilution ratio. The influence of dilution ratio on size distributions was measured by changing the primary dilution rate between 4 and 84 at a fixed secondary dilution rate. For dilution ratios above 60, both the number and volume concentrations were found to be essentially independent from dilution ratio. For smaller dilution ratios, number and volume concentrations increased with decreasing dilution ratio. Particles smaller than about 30 nm were more strongly influenced than the larger ones. For example, the number concentration of 8 nm particles increased 2.8 times when the dilution ratio was decreased from 59 to 4. The increased number concentrations of small particles can be explained by nucleation of hydrocarbons, sulfur compounds and water in the dilution tunnel. Particle nucleation is favored by higher saturation ratios which occur at lower dilution ratios.



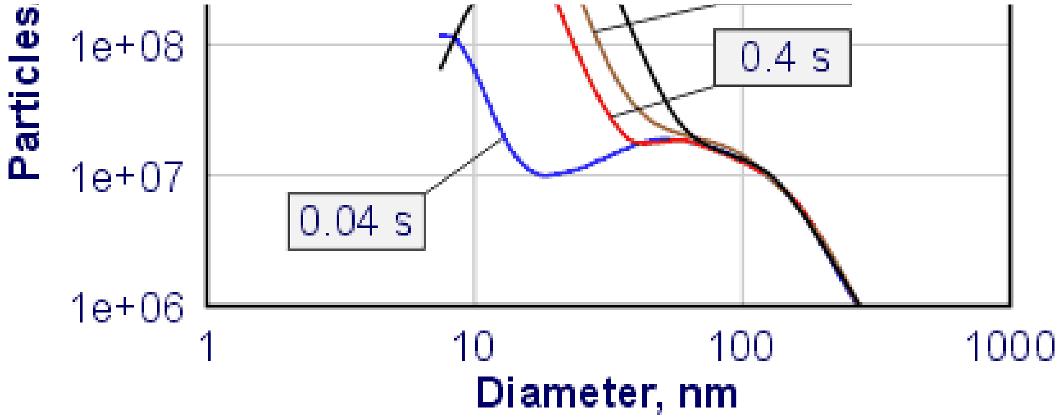


Figure 6. Effect of Residence Time on Particle Number and Size

The effect of residence time on particle number and size found in the same study is shown in Figure 6 [Kittelson 1998]. The residence times were measured as the time between primary and secondary dilution.The lowest particle numbers were recorded with the shortest residence time of 0.04 seconds. Since the residence time was probably too short to allow for condensation and particle nucleation, these particles may have been composed primarily of solids. The nuclei mode peak below 10 nm diameter might include oil-derived ash particles. As the dilution ratio was increased to 0.4 s, the number of small particles increased by one order of magnitude (note the logarithmic scale in Figure 6). This was the effect of formation of new particles through nucleation in the dilution tunnel. Further increase in the residence time leads to coagulation and size growth of small particles, as indicated by the decreasing number concentration and increasing particle diameter.

Clearly, in the sampling setup which was used in the above study, one could select the sampling parameters to obtain a wide range of number concentrations of small particles. For instance, for 10 nm particles, number concentrations spanning more than one order of magnitude could be realized by simply adjusting the dilution tunnel residence time.

Particle distributions measured from dilution tunnels are further influenced by sampling problems related to wall interactions. These problems include both (1) sample losses and (2) sample additions. Sample losses are due to deposition of particles on the walls of the sampling system by such mechanisms as:

- diffusion,
- inertial deposition, and
- thermophoresis.

Due to high diffusion coefficients, particles smaller than about 15 nm are subject to large losses in sampling systems and in instruments. Sample losses of more than 50% are not uncommon in diesel particle measurement systems, but are often not reported in the literature [Kittelson 2002].

Sample additions are caused by:

- re-entrainment, and/or

- outgassing of material deposited on the walls.

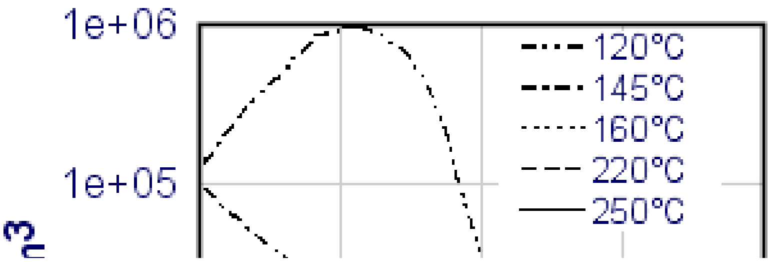
Outgassing may happen whenever the engine load is increased and hot gas enters sampling system of lower temperature. At such conditions condensation may occur at the walls. After some time the wall temperature will increase causing the condensates to evaporate and add to the sample material. In addition, certain materials or components used in sampling systems, such as silicone rubber hoses, were reported to produce ultrafine particle emissions under certain conditions and should be avoided [Maricq 1999a].

Measurement problems may be also caused by storage and release of particulates in exhaust systems. It was shown that diesel particulates can be stored in practically all components of the exhaust system, including pipe walls, mufflers, and catalytic converters [Andrews 2001]. Storage and release from the exhaust system did influence measured particle size distributions [Andrews 2000].

Nanoparticles: Composition and Formation

Generally, diesel nanoparticles include the same constituents which are found in the total particulate matter emissions including elemental carbon, ash, hydrocarbons, sulfuric acid, and water. Contrary to the total PM emission, diesel nanoparticles can not be chemically analyzed to precisely determine their composition. There is no sampling/analytical procedure which would allow to separate a sufficient mass of the nanoparticle material for such an analysis. As a result, the exact formulation of diesel nanoparticles has to be studied through indirect experiments. A consensus has been forming that diesel nanoparticles are mostly volatile. In most cases, they are composed primarily of hydrocarbon and sulfuric acid condensates, with small contribution of solid material, such as ash and carbon.

The nanoparticle composition can be dramatically changed by exhaust emission control measures, such as diesel particulate filters or fuel additives. Very high numbers of nanoparticles were measured downstream of particulate filters in the VERT study [Mayer 1997]. A special sampling technique was developed to distinguish between solid particles and volatile condensates. The diluted sample passed through a heated vapor trap (thermodenuder), filled with active carbon, before entering the particle size analyzer. Depending on the vapor trap temperature, different fractions of particle condensates were driven off the sample. An example of such condensate analysis is presented in Figure 7. The data was generated on a 100 kW DI diesel engine equipped with a particulate filter at full load with low sulfur fuel (< 0.04% S). The exhaust gas temperature in the particulate trap was 460°C. The temperature in the active carbon vapor trap were changed between 120 and 250°C, as shown in the graph.



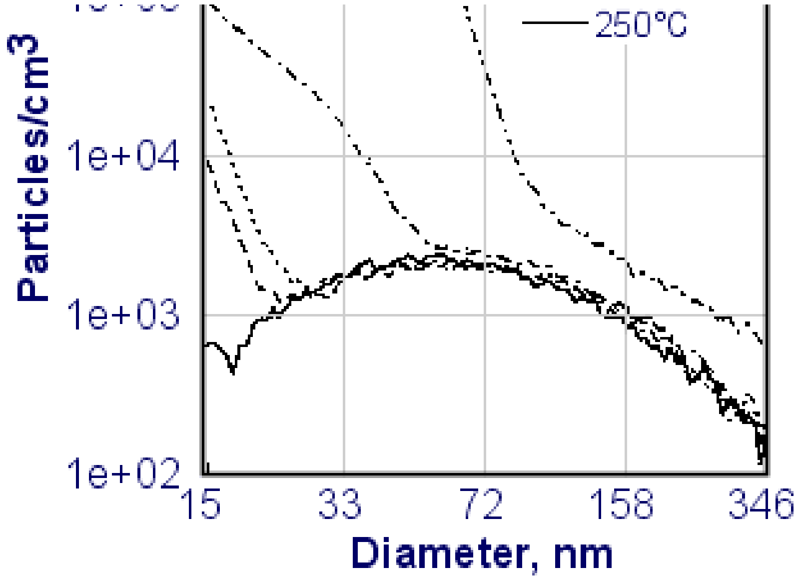


Figure 7. Solid Particles and Condensates in Diluted Diesel Exhaust

The high peak of 30 - 40 nm particles disappears from the graph when the sample is heated to 145° C. It is an indication that these particles included volatile materials, presumably hydrocarbons and hydrated sulfuric acid. As the temperature was increased to 250°C, the high nanoparticle emissions disappeared almost completely (note the logarithmic scale in the graph). It can be concluded that high nanoparticle emissions observed downstream of particulate filters were composed primarily of condensates (strictly speaking, this conclusion was valid only within the measuring system detection limit of 15 nm, below which solid particles still could be found).

In the same study, particle distributions with iron-based fuel additive were analyzed from an engine without a particulate filter. Distributions were found with two particle concentration peaks: (1) the additive ash particulate peak at about 20 nm and (2) the carbon particles peak at about 90 - 100 nm. As shown in Figure 8, the additive caused substantial increase of nanoparticle emissions. Analysis with the heated vapor trap did not significantly change these results, confirming the mostly solid character of nanoparticles in that case. These results indicate that metallic fuel additives, if used, may be a significant contribution to solid ash nanoparticle emissions.

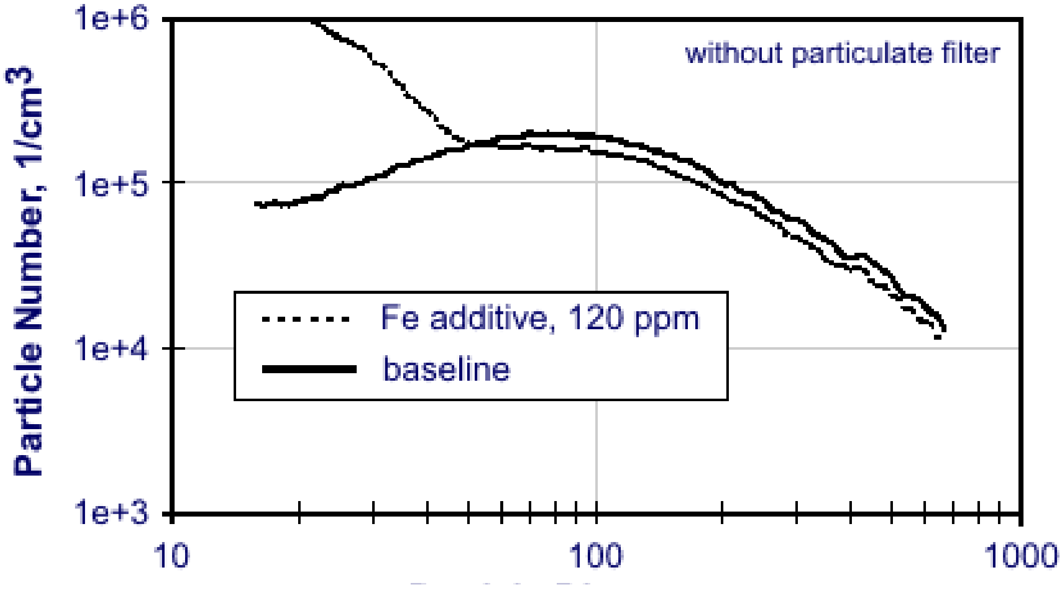


Figure 8. Nanoparticle Emissions with Fuel Additive

Nanoparticle volatility experiments were also conducted in the CRC E-34 study [Kittelson 2002]. The set-up involved a Cummins ISM engine and a nano-tandem differential mobility analyzer (nano TDMA). The instrument consisted of two differential mobility analyzers (DMA) with a heating section between the two DMAs. It allowed a single particle size to be selected with the first DMA, which was then heated, and the resulting size change determined with the second DMA.

Several particle sizes representing the bottom size end of the accumulation mode (50 nm) and the nuclei mode (down to 7 nm) were subjected to the experiment. It was expected that in this size range, representing the overlap between accumulation and nuclei modes, a mix of solid and liquid particles would be found. Upon heating, solid particles consisting primarily of carbon and volatile particles consisting primarily of hydrocarbons would be differentiated. Volatile particles would shrink until they totally disappear. Solid particles, on the other hand, would shrink only a little, as any volatile material on their surface would be removed, and then their sizes would stabilize. The results of the experiment, for initial sizes of 50, 30, 12 and 7 nm, are shown as a function of temperature in Figure 9. The 50 nm particles split into a mainly solid mode that shrinks to a diameter of 43 nm, and a volatile mode that rapidly shrinks to 15 nm. The 30 nm and 12 nm particles show a similar behavior, being differentiated into solid and volatile fractions. However, the 7 nm particles continue shrinking upon heating, not showing evidence of containing any solid material. (Volatile particles do not disappear due to a possible instrument artifacts around its detection limit.)

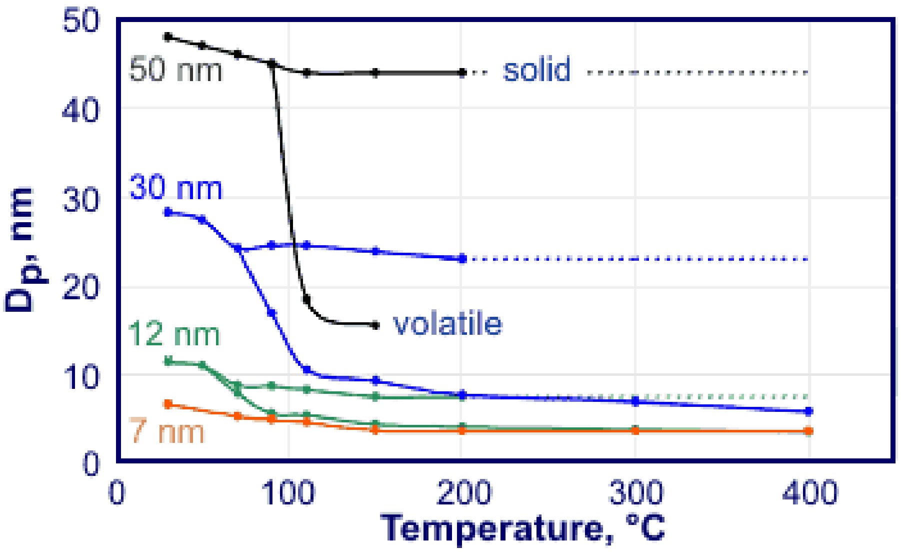


Figure 9. Volatility of Diesel Nanoparticles

The volume fraction that remained in the 12-30 nm particles after heating was also determined in the study. It was found that the volatile fraction amounted to 97-98% of the particle volume, leaving only 2-3% for possible non-volatile, solid cores in the tested particles. Similar heating experiments, as well as evaporation calculations, were conducted for particles made of pure alkanes of different carbon chain length. It was determined that the shrinkage of particles from diesel engines was in the same range as for C28-36 normal alkanes, thus corresponding to the hydrocarbons in the engine lube oil. These results suggest that hydrocarbons that make up diesel nanoparticles are derived mostly of the engine lube oil. It should be mentioned, however, that some fuel effect studies found increased nanoparticle numbers with more volatile fuels, indicating that fuel derived HCs may also present a noticeable contribution [Wedekind 2000].

Various hypothesis have been formulated to explain the increased particle numbers that were seen in certain studies with new diesel engines. It was once suspected that the high particulate numbers were related to high injection pressures, which are used by engine manufacturers as a strategy for meeting emission targets. That theory, however, has not been confirmed. On the contrary, a continuous decrease in mass and number emissions was shown when injection pressure increased from 400 to 1000 bar [Jing 1996]. In another study, the injection pressure had only small influence, and only under some engine operating conditions, on the particle size distribution [Pagan 1999].

It is believed that increased number emissions are a simple consequence of (1) high concentration of nanoparticle precursors (HC, SO4), combined with (2) decreased mass of accumulation mode particles. Normally, the accumulation particles act as a “sponge” for the condensation and/or adsorption of volatile materials. In the absence of that sponge, gas species which are to become liquid (or solid) will nucleate to form large numbers of small particles. The driving force for the gas to particle conversion is the saturation ratio, defined as the ratio of the partial pressure of a species to its saturated vapor pressure. For the constituents of the SOF or sulfuric acid, the maximum saturation ratios occur during dilution and cooling of the exhaust and are typically achieved at dilution ratios between 5 and 30 [Abdul-Khalek 1998]. The relative rates of condensation/adsorption and nucleation are a function of the saturation ratio, as shown in Figure 10 [Kittelson 1998].

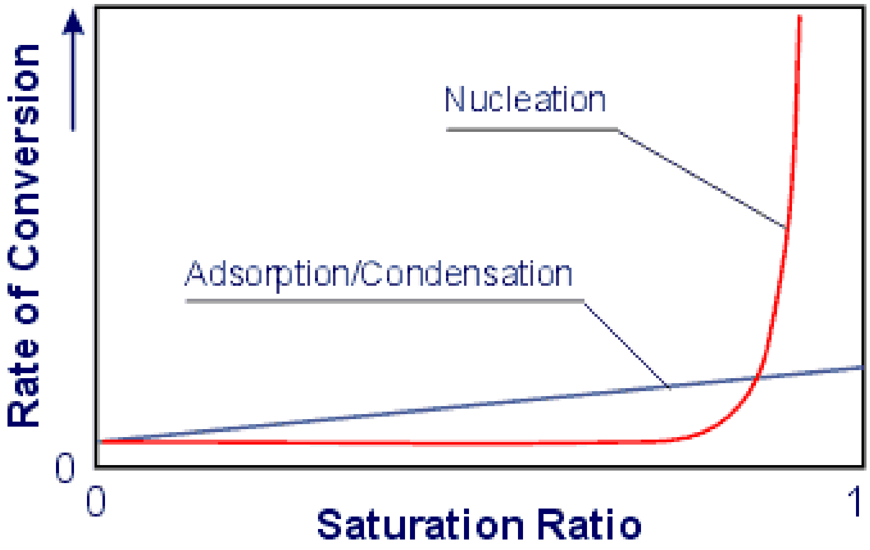


Figure 10. Relative Rates of Gas to Particle Conversion

The rate of adsorption/condensation is a linear function of the saturation ratio. The rate of nucleation, very low at low saturation ratios, becomes very high in the proximity of the saturation. Therefore, low saturation ratios favor adsorption/condensation, while high saturation ratios favor nucleation. The rate of adsorption/condensation is proportional to the surface area of available particulate matter. Since the large quantities of soot agglomerates present in the exhaust of old technology engines provide ample surface area, the vapors may be adsorbed and condensed. If such adsorption/condensation indeed occurs, the saturation ratio never rises high enough to produce nucleation. An opposite picture can be seen in systems with little accumulation mode particulates. Due to the low available soot surface area little condensation occurs and the nucleation becomes more likely. This is especially true if elemental carbon emissions are reduced more than the SOF and SO4 emissions.

The above nucleation theory explains the high number emissions seen downstream of particulate traps (which remove solid accumulation mode particulates, but not necessarily nanoparticle precursors), as well as high number emissions from engines of high SOF fraction, such as the ’91 Cummins engine in the HEI study (Figure 2). It is also consistent with the observation of high particle numbers from gasoline engines, which are believed to be composed primarily of liquid condensates [Graskow 1998]. In all of these cases, the low quantities of agglomerated particulates present in the gas cannot provide enough surface area for the condensation/adsorption of volatile material. As the species approach saturation, high numbers of small particulates are produced through nucleation.

A similar nucleation mechanism may also apply to the formation of ash particulate. In that case, the ash nucleation takes place inside the engine during the expansion stroke, rather than in the dilution tunnel. Once these ash nuclei are formed, they may serve as heterogeneous nucleation sites for SOF and other species during dilution and cooling in the exhaust. It was suggested that some particles in the high SOF nuclei mode may include ash cores [Abdul-Khalek 1998].

Engine Nanoparticles Issues

Findings of medical research indicate that small size particulates are more harmful to humans than the larger ones. Ambient concentrations of particulate matter below 10 µm (PM_{10}) have been regulated by law in the USA for many years. In 1997, the US EPA introduced new additional ambient air quality standard for particulates of aerodynamic diameter below 2.5 µm ($PM_{2.5}$). That standard was in part based on health studies that showed strong correlation between mortality and the concentration of fine particles below 2.5 µm.

It is clear that all diesel particulates fall under the $PM_{2.5}$ category. The increased interest in diesel nanoparticles has been sparked primarily by (1) their suspected deep penetration into human lungs, and (2) a belief that nanoparticles may be more harmful than larger particles—an extrapolation of the findings in the 10 - 2.5 µm size range. Much more medical research and diesel emission studies are needed to fully characterize the diesel nanoparticle emissions and their impact on human health. The following are some of the issues, related to the health effects, regulations, and measuring techniques, that will have to be addressed in the future:

1. If nanoparticles indeed present a higher health hazard than larger, agglomerated diesel particles, diesel PM emission regulations may have to include size distributions or number concentrations rather than be expressed only by the total particulate mass.
2. In the available medical research, the term “particles” refers to solids. There is probably no health study on the effects of volatile particulates. It is now known that diesel nanoparticles are normally composed mainly (>90%) of liquid condensates. The issue is: Are volatile particulates a health hazard? Their short lifespan (τ_{90} of a few minutes) makes 90% of ultrafine particle count to disappear within 100-1000 m from their source [Capaldo 2001]. This estimate indicates that the effect of diesel engines and other mobile ultrafine particle sources on ambient particle number concentrations will be limited to areas near roadways.
3. Under certain operating conditions, spark ignited engines emit comparable numbers of nanoparticles comparable to those from diesel engines. The SI engine particulates are believed to be mainly volatile. If volatile particulates are a health hazard, the way spark ignited engine emissions are regulated will have to be revisited.
4. If the health hazards are related to solids rather than to condensates, it would make sense to change the definition of particulate matter to include only solid materials. Such a change would seriously affect the regulations, the sampling and measuring techniques, as well as emission control technologies.
5. A similar approach has been suggested from pragmatic, rather than health, reasons. Sampling techniques that include volatiles cause measurements to be less repeatable. Considering that current laboratory dilution methods poorly simulate atmospheric conditions, artificial particulates may be produced which otherwise would not exist in the atmosphere. Therefore, diesel emission sampling and regulations should focus on the material found in the tailpipe, i.e. on solid particulates, rather than trying to simulate atmospheric dispersions of emissions. This philosophy is being adopted in the European Union, where future particle number/size measuring methods will likely be based on solid material only [Andersson 2002]. In the USA, on the other hand, research is conducted to develop laboratory dilution methods that would accurately reproduce atmospheric dilutions, involving both solid and volatile material [Kittelson 2002].
6. Whatever PM definition is adopted—including or excluding volatile fractions—standards must be developed that precisely specify sampling and analytical procedures for the measurement of particle numbers and sizes.

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