REVIEW OF DIESEL PARTICULATE MATTER SAMPLING METHODS

FINAL REPORT

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ABSTRACT

Federal government regulations limit emissions from heavy-duty, on-highway diesel engines. These regulations have reduced diesel particulate matter emissions (DPM) in the past few years. To meet these regulations diesel engine manufacturers have developed low-emission diesel engines. Recent laboratory tests conducted at Michigan Technological University by Bagley, et al. (1996) showed that a prototype, low-emission engine produced increased numbers of nanoparticles when measured under typical laboratory conditions, however it is unclear whether this increase was due to the engine or to the laboratory test conditions. Similar increases have been observed at the University of Minnesota and at other institutions but the test conditions were not the same.

Many factors influence the size distribution of DPM and the production of nanoparticles. However, comparing data from one laboratory to another is very difficult because there is no standard method for diluting, sampling and measuring the size distribution of diesel exhaust aerosol. Engine type is but one factor affecting the DPM size distribution, others include:

- the instrumentation used to measure the size distribution
- the method of dilution and the dilution ratio
- temperature and composition of dilution air
- particle residence time in the sampling system
- particle losses in the sampling system
- the chemical composition of DPM and exhaust gases
- adsorption and condensation characteristics of diluted exhaust constituents.

These factors must be considered when interpreting size distribution data gathered by different methods.

Understanding the fundamental science underlying particle formation and measurement is critical to research organizations such as universities, health and environmental organizations, and local, state and federal governments. Future low emission engines must be designed with an understanding of particle formation and measurement. Sound science dictates that future environmental decisions be based an understanding of the causes and effects of pollution. Further, it is important that data collected in the diesel test laboratory be representative of actual ambient exposure conditions. Environmental decisions should be based upon data that are not compromised by possible artifacts resulting from laboratory conditions.

With this in mind, the U.S. Environmental Protection Agency sponsored a one-year project at the University of Minnesota Center for Diesel Research to review DPM sampling methods. Project objectives were:

- to critically evaluate methods used in diesel test laboratories to determine diesel particulate matter size distributions under steady-state and transient operating conditions;
- to critically evaluate methods and data resulting from recent roadway studies to determine diesel particulate matter size distributions, and compare the results to determine how well laboratory size distributions mimic real-world conditions;
• to examine the relationship between methods used for laboratory dilution and the actual atmospheric dilution process;
• to recommend the best current method(s);
• to identify areas requiring further research;
• to publish the results in the refereed literature and make it available on the Internet.

Three reports were prepared under the EPA grant. The first report describes instruments used to characterize diesel aerosol, summarizes information obtained from engine laboratory visits and present results from a diesel aerosol sampling questionnaire circulated to major engine labs. The second report reviews fundamental aerosol dynamics and non-laboratory studies that have focused on determining the size distribution of diesel aerosol. This report summarizes the findings of the project including recently published information not included in the first two reports, presents general recommendations for diesel aerosol measurement and recommendations for future research.

The major findings from the literature review are:
• Because conditions vary so greatly in diesel exhaust testing, it is critical to understand how sampling and testing conditions may affect the nature of the diesel particulate matter being measured.
• The strongest driving force for gas to particle conversion occurs in the critical dilution ratio range (5 - 50:1), roughly the same range produced by the typical laboratory dilution tunnel system 3 - 20:1. These conditions are not representative of real-world conditions.
• The balance between carbonaceous agglomerates and volatiles (hydrocarbons and sulfuric acid) in diesel exhaust is critical to the understanding of particle dynamics.
• To correctly interpret diesel aerosol measurements and to correlate roadway and laboratory experiments, the relationships between exhaust aerosol and testing parameters must be well understood.
• Selection of aerosol instrumentation should be based on particle size and aerosol characteristics, the goals of the study, and the respective limitations of each instrument.

Laboratory techniques that result in diesel aerosol measurements similar to ones obtained under real-world conditions need to be developed and evaluated. This will allow future regulatory decisions to be based on laboratory data that differentiate solid and liquid (hydrocarbon and sulfate) aerosols and dilution conditions that are representative of actual tailpipe and on-highway conditions.
INTRODUCTION

Federal government regulations limiting emissions from heavy-duty, on-highway diesel engines have driven DPM emissions measured on the Federal Transient Cycle from 0.6 g/bhp-hr in 1988 to less than 0.1 g/bhp-hr in 1994 and 0.05 g/bhp-hr for urban buses in 1996. Diesel engine manufacturers have developed low-emission diesel engines to meet these regulations. Many of the engine modifications that reduce DPM emissions from on-highway engines are also applied to off-road engines.

Recently, Michigan Technological University (MTU) conducted a laboratory study to characterize the physical and chemical composition and the mutagenicity of emissions from two heavy-duty diesel engines operated with low-sulfur diesel fuel at a constant speed under two different steady-state load conditions, with and without an exhaust aftertreatment device. One interesting result reported by Bagley, et al. (1996) was that the newer engine, meeting 1991 emissions levels\(^1\), significantly reduced emissions, but dramatically increased the number and volume of very small nuclei mode particles\(^2\) when compared to a similar engine meeting 1988 emissions levels\(^3\). The research was conducted using a prototype 1991 Cummins LTA10 engine, with a high pressure, mechanically controlled, unit fuel injection system and other design features now commonly used in heavy-duty, high-speed, on-highway diesel engines. The particular engine configuration used for this research was a pre-production prototype developed to meet 1991 Federal on-highway emissions limits. Up to 40% of the volume of particles in the exhaust was found to be present within the nuclei-mode range of particle-size. It is important to note that the MTU data were generated under steady-state conditions. Outside of the laboratory, most DPM is generated under transient operating conditions. Dilution conditions used in the Federal Heavy Duty Test Procedure are quite different from on-highway dilution condition, thus transient particle size measurements based on this test procedure are also not entirely representative of real-world conditions. Therefore there is a need to gather field data representative of real-world conditions to confirm the MTU findings.

The large concentration of nuclei mode particles, accounting for a large percentage of the total volume of particles in the exhaust, differs from most past reported laboratory results. Previous research measuring the size distribution of DPM from diesel engines found distributions which were bimodal and lognormal (Abdul-Khalek, \textit{et al.}, 1995, Baumgard, \textit{et al.}, 1985, Kittelson \textit{et al.}, 1991). Typically, the majority of the mass or volume

---

\(^1\) 0.25 g/hp-hr particulate matter emissions and 5.0 g/hp-hr NOx emissions.

\(^2\) The nuclei mode particles present in diesel exhaust primarily consist of condensed organic compounds, condensed sulfuric acid, and primary soot particles. Nuclei mode particles typically have diameters of approximately 5 nm to 50 nm, with a volume mean diameter of approximately 20 nm.

\(^3\) 0.60 g/hp-hr particulate matter emissions and 6.0 g/hp-hr NOx emissions.
concentration\textsuperscript{4} of the DPM was found within the accumulation mode\textsuperscript{5} of the particle size distribution as opposed to the nuclei mode. However, the engines and sampling conditions used in these studies were not of the same type as used by MTU. On the other hand, roadway studies done in the late 1970s and early 1980s reported nearly as large fractions of aerosol in the nuclei mode as MTU (Whitby, \textit{et al.}, 1975 and Kittelson, \textit{et al.}, 1988).

Many factors influence the size distribution of DPM, and comparing data from one laboratory to another is very difficult because, as illustrated by the lab survey presented in EPA Supplemental Report No. 1 (Kittelson, \textit{et al.}, 1998a), there is no standard method for diluting, sampling and measuring the size distribution of diesel exhaust aerosol. Engine type is but one factor affecting the DPM size distribution, others include:

\begin{itemize}
  \item the instrumentation used to measure the size distribution
  \item the method of dilution and the dilution ratio
  \item temperature and composition of dilution air
  \item particle residence time in the sampling system
  \item particle losses in the sampling system
  \item the chemical composition of DPM and exhaust gases
  \item adsorption and condensation characteristics of diluted exhaust constituents.
\end{itemize}

These factors must be considered when interpreting size distribution data gathered by different methods.

Understanding the fundamental science underlying particle formation and measurement is critical to research organizations such as universities, health and environmental organizations, and local, state, and federal governments. Future low emission engines must be designed with an understanding of particle formation and measurement. Sound science dictates that future environmental decisions be based on understanding the causes and effects of pollution. Further, it is important that data collected in the diesel test laboratory be representative of actual ambient exposure conditions. Environmental decisions should be based upon data that are not compromised by possible artifacts resulting from laboratory conditions.

With this in mind, the U.S. Environmental Protection Agency sponsored a one-year project at the University of Minnesota Center for Diesel Research to review DPM sampling methods. Project objectives were:

\begin{itemize}
  \item to critically evaluate methods used in diesel test laboratories to determine DPM size distributions under steady-state and transient operating conditions;
\end{itemize}

\textsuperscript{4} For particles of a known density, particle mass concentrations can be determined from particle volume concentrations.

\textsuperscript{5} The accumulation mode particles typically have diameters ranging from approximately 50 nm to 1.0 \(\mu\text{m}\), with a volume mean diameter of approximately 100 to 300 nm. Accumulation mode particles in diesel exhaust are thought to primarily consist of agglomerated carbon soot particles with adsorbed volatile compounds.
to critically evaluate methods and data resulting from recent roadway studies to determine DPM size distributions, and compare the results to determine how well laboratory size distributions mimic real-world conditions;
• to examine the relationship between methods used for laboratory dilution and the actual atmospheric dilution process;
• to recommend the best current method(s);
• to identify areas requiring further research;
• to publish the results in the refereed literature and make it available on the Internet.

Under this program, the Center for Diesel Research reviewed the literature, conducted an engine laboratory survey, visited a number of engine labs and prepared three reports. The first report included:
• a description and characterization of the aerosol instruments used to measure diesel aerosol, and
• reported findings from the survey of engine laboratories.

The second report included:
• an overview of diesel aerosol chemical and physical characteristics,
• a discussion of the processes that affect measurement of diesel aerosol,
• illustrated how various parameters influence the size distribution of aerosol particles obtained under different experimental and real-world conditions.

This report summarizes the findings from the project, including recently published information not included in the other reports, presents general recommendations for diesel aerosol sampling and recommendations for future research. Major sections include:
• Diesel engine technology and regulations
• Physical and chemical nature of diesel aerosol
• Aerosol size distribution
• Diesel aerosol dynamics
• Instruments for measurement of diesel particulate matter
• Evaluation of roadway, tunnel and occupational test methods
• Evaluation of diesel test laboratory methods
• Recommendations
• Spark ignition measurements
• Future research.

DIESEL ENGINE TECHNOLOGY AND EMISSION REGULATIONS

Interpreting and comparing diesel aerosol studies conducted over the last 30 years is confounded by changes that have taken place in engine and aftertreatment technology and fuel quality. Many of these changes took place because of increasingly stringent State and Federal regulations limiting diesel emissions. Early diesel engines maximized fuel economy and performance, but Federal regulations required engine manufacturers to reduce emissions. In general manufacturers have met the standards by reducing emissions without decreasing
engine performance. Engine manufacturers improved engine design by modifying the fuel injection system, the combustion chamber and improving engine controls. These improvements enhanced combustion. Improved seals and rings reduced oil consumption, which reduced the organic component of diesel particulate emission. Electronic control systems were introduced to precisely control fuel injection. These changes resulted in reduced DPM emissions.

In 1993, the EPA established a fuel sulfur level of 0.05 wt % for fuel used on-highway. This represented a dramatic decrease in fuel sulfur content, which was typically at or above 0.3 wt % prior to the regulation. As a result of this regulation, the sulfur content of DPM was also reduced. As shown in the lab survey, all of the U.S. labs surveyed report using low sulfur fuel.

Table 1 lists changes in Federal heavy-duty diesel emission standards and table 2 summarizes changes in diesel engine technology and fuel over the last three decades. For the most part engine manufacturers have tried to avoid the use of expensive aftertreatment technology while focusing on improving engine technology. A review of aftertreatment devices and their impact on emissions can be found elsewhere (Johnson, et al., 1994).

<table>
<thead>
<tr>
<th>Engine Year</th>
<th>Oxides of Nitrogen, g/bhp-hr</th>
<th>Particulate Matter, g/bhp-hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Truck and Bus</td>
<td>Truck</td>
</tr>
<tr>
<td>1985</td>
<td>10.7</td>
<td>None</td>
</tr>
<tr>
<td>1988</td>
<td>10.7</td>
<td>0.6</td>
</tr>
<tr>
<td>1990</td>
<td>6.0</td>
<td>0.6</td>
</tr>
<tr>
<td>1991</td>
<td>5.0</td>
<td>0.25</td>
</tr>
<tr>
<td>1993</td>
<td>5.0</td>
<td>0.25</td>
</tr>
<tr>
<td>1994</td>
<td>5.0</td>
<td>0.10</td>
</tr>
<tr>
<td>1996</td>
<td>5.0</td>
<td>0.10</td>
</tr>
<tr>
<td>1998</td>
<td>4.0</td>
<td>0.10</td>
</tr>
</tbody>
</table>

### Table 2. Changes in diesel engine technology and fuel over time

<table>
<thead>
<tr>
<th>Technology</th>
<th>1970's</th>
<th>1980's</th>
<th>1990's</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy-duty diesel engine</td>
<td>Mostly naturally aspirated</td>
<td>Mostly turbo-charged / water to air aftercooling</td>
<td>Mostly turbo-charged / air to air aftercooling</td>
</tr>
<tr>
<td></td>
<td>Some turbo-charged / aftercooling</td>
<td>4 stroke cycle</td>
<td>4 stroke cycle Direct injection</td>
</tr>
<tr>
<td></td>
<td>Both 4 and 2 stroke cycles in use</td>
<td>Direct injection</td>
<td>Direct injection</td>
</tr>
<tr>
<td></td>
<td>Direct injection predominates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Light-duty diesel engine</td>
<td>Indirect injection</td>
<td>Indirect injection</td>
<td>Indirect injection, small direct injection introduced</td>
</tr>
<tr>
<td>Fuel sulfur content</td>
<td>&gt;= 0.3 wt %</td>
<td>&gt;= 0.3 wt %</td>
<td>&lt;= 0.05 wt % (1993)</td>
</tr>
</tbody>
</table>

Source: Sawyer and Johnson, (1995)

### PHYSICAL AND CHEMICAL NATURE OF DIESEL AEROSOL

Diesel aerosol consists 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 fuel rich regions. Much of the carbon is subsequently oxidized with the residue 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 (generally described as the soluble organic fraction, SOF) in the exhaust. The SOF contains polycyclic aromatic compounds containing oxygen, nitrogen, and sulfur. 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 sulfate aerosol. Metal compounds in the fuel and lube oil lead to a small amount of inorganic ash.

Figure 2 shows the 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 (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.
Figure 1. - Typical structure of engine exhaust particles (Kittelson, 1998a).

**Particle Composition For A Heavy-Duty Diesel Engine Tested in Heavy-Duty Transient Cycle**

- **Carbon** 41%
- **Unburnt Fuel** 7%
- **Unburnt Oil** 25%
- **Sulfate and Water** 14%
- **Ash and Other** 13%

Figure 2. - Particle composition for a heavy-duty diesel engine tested in a heavy-duty transient cycle (Kittelson, 1998a). [Composition varies widely with engine design.]
AEROSOL SIZE DISTRIBUTION

Figure 3 shows the idealized diesel aerosol number and mass weighted size distributions (Kittelson, 1998a). The distributions are trimodal and lognormal in form. 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 0.05 to 1.0 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 definitions used to define atmospheric particles: PM10, D (diameter) < 10 µm; fine particles, D < 2.5 µm; ultrafine particles, D < 0.10 µm; and nanoparticles D < 0.05 µm or 50 nm. Definitions of ultrafine and nanoparticles are not universally agreed upon. 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.

![Diagram of aerosol size distribution](image)

**Figure 3.** - Typical engine exhaust size distribution both mass and number weightings are shown (Kittelson, 1998a).

For comparison, figure 4 shows the idealized atmospheric aerosol size distribution, which is also generally trimodal and lognormal in form (Whitby and Cantrell, 1975). The figure shows the mechanisms such as condensation and coagulation that transfer aerosol mass from one size
range to another. The smallest of the three modes, 0.001 to 0.08 \( \mu m \), is the Aitken nuclei range, which consists of primary aerosol from combustion sources such as diesel engines and secondary aerosol formed from coagulation of primary aerosols to form chain agglomerates. The next size range, 0.08 to 1.0 \( \mu m \) is the accumulation range, that contains emissions in this size range plus aerosol accumulated by mass transfer through the coagulation and condensation processes from the nuclei range. The last range, 1.0 to approximately 40 \( \mu m \) is referred to as the coarse aerosol size range. Aerosols within this range generally originate from mechanical processes such as grinding, mechanical fracture and bulk material handling. There is very little exchange of mass from the nuclei and accumulation modes to the coarse particle mode under most conditions.

![Figure 4](image)

**Figure 4. - Idealization of an atmospheric surface area distribution showing the principal modes, sources of mass, and the processes involved in mass transfer and removal (Whitby and Cantrell, 1975).**

Figure 5 illustrates the fate of exhaust particles in the atmosphere and how the processes of nucleation, condensation and adsorption affect the formation, dispersion and deposition of exhaust aerosols.
Figure 5. - Schematic illustrating the fate of exhaust particles in the atmosphere and how the processes of nucleation, condensation, adsorption affect the formation, dispersion and deposition of exhaust aerosols.

DIESEL AEROSOL DYNAMICS

Diesel Particle Dynamics and Behavior

Measurement of diesel aerosol is affected by three main parameters: the environmental conditions experienced by the emissions, the sampling/measurement system used to characterize the emissions, and the chemical and physical composition of the engine emissions. An understanding of how exhaust conditions interact with exhaust constituents is critical if the aerosol size distribution and composition are to be determined.

Many mechanisms affect aerosol behavior during sampling and measurement. These are described in numerous textbooks such as Hinds, (1982). These mechanisms can be divided into two categories: (1) wall interactions with the aerosol and (2) particle dynamics and transformations during sampling. The various mechanisms in the two categories are listed below and a more in-depth description of each of these mechanisms is presented in EPA Supplemental Report No. 2 (Kittelison, et al., 1998b).

Particle-Wall Interactions - Losses of Particles to Sampling Surfaces

Table 3 summarizes the impact of the various particle-wall interactions that affect particle measurement and recommends techniques to minimize their impact.
Table 3. Particle – Wall Interactions

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Impact</th>
<th>Recommendations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inertial impaction</td>
<td>• Removes small number of the largest particles (represents a larger fraction of the total particulate mass)</td>
<td>• Avoid sharp changes in sample line diameter or direction</td>
</tr>
<tr>
<td></td>
<td>• Introduces variability through unpredictable reentrainment of deposited mass</td>
<td>• Isokinetic sampling not as important for submicron particles</td>
</tr>
<tr>
<td></td>
<td>• Inertial and gravitational losses are quite small for particles in 0.1-1.0 μm range</td>
<td></td>
</tr>
<tr>
<td>Electrostatic deposition</td>
<td>• Electric charge build-up on sample lines attracts charged diesel particulate matter, causing it to deposit on line walls</td>
<td>• Use metal sample lines to avoid electrostatic build-up</td>
</tr>
<tr>
<td></td>
<td>• Use metal sample lines to avoid electrostatic build-up</td>
<td>• Avoid Teflon sample lines, prone to large build-up of electrostatic charge</td>
</tr>
<tr>
<td></td>
<td>• Avoid Teflon sample lines, prone to large build-up of electrostatic charge</td>
<td></td>
</tr>
<tr>
<td>Thermophoretic deposition</td>
<td>• Large temperature differences between exhaust gas and sample lines causes thermal driving force depositing particles on line walls</td>
<td>• Insulate / heat sample lines to avoid large differences in temperature between lines and exhaust gas</td>
</tr>
<tr>
<td></td>
<td>• Most significant losses occur during transient duty cycles</td>
<td></td>
</tr>
<tr>
<td>Diffusional deposition</td>
<td>• Diffusion for particles in the size range that represents the majority of the mass is negligible (&gt; 0.1 μm)</td>
<td>• Difficult to eliminate diffusional deposition</td>
</tr>
<tr>
<td></td>
<td>• Diffusion for particles (&lt; 0.03 μm) in the size range that represents the majority of number is also small, but should be considered for the smallest size ranges measured</td>
<td>• Use short sampling lines</td>
</tr>
<tr>
<td>Gravitational deposition</td>
<td>• Minimal impact on diesel particulate losses</td>
<td>• Avoid unnecessarily long horizontal sections of sample lines where large particles may settle</td>
</tr>
<tr>
<td></td>
<td>• May introduce variability through unpredictable reentrainment of small deposited mass</td>
<td></td>
</tr>
</tbody>
</table>

Heat transfer during sampling and dilution cools the exhaust and helps in meeting maximum temperature requirements. However, it results in thermophoretic deposition of particles on sampling and dilution system surfaces. Eventually, these deposits are reentrained in the exhaust stream. Reentrainment is unpredictable and increases variability in mass measurements because of the increase in the number of coarse (> 1,000 nm) particles. These particles are not necessarily representative of diesel aerosol and make aerosol size distribution measurement more difficult. Another problem related to temperature is the condensation of volatile matter (hydrocarbons and sulfates) on cooler dilution tunnel walls. These volatiles are precursors of new nanoparticles that form when the walls are heated volatizing the material.

In their review of variability in particle emission measurements during heavy duty transient tests, Kittelson and Johnson (1991) discussed the impact of exhaust system temperatures on particle measurement and provided recommendations to minimize the effects on aerosol sampling. They calculated losses during the heavy-duty transient test for a typical test facility (Caterpillar). Calculated mechanical losses in the accumulation mode size range were less than 0.2%, but total losses of about 5% were predicted when thermophoretic deposition was included.

A recent study by Ahlvik, et al. (1998) calculated that sampling losses due to mechanical deposition (diffusive, gravitational, inertial, aspirational) were less than 5 % for tests conducted in a light-duty chassis dynamometer test facility and a heavy-duty test cell.

**Particle Dynamics and Transformations**

Particle dynamics and transformations also impact aerosol measurement and are well understood qualitatively. These processes include coagulation, nucleation, adsorption/desorption, and condensation/evaporation. However, the application of those theories to explain or predict diesel exhaust behavior during sampling and measurement is not easy. Table 4 summarizes these particle processes and their impact on particle measurement. Further discussion of how these particle processes can affect diesel exhaust aerosol characteristics is presented in subsequent sections. Included for each particle process is a brief statement of the impact of the mechanism on the aerosol being measured.
Table 4. Particle Dynamics and Transformations

<table>
<thead>
<tr>
<th>Process</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle coagulation</td>
<td>• Dependent on particle size and concentration</td>
</tr>
<tr>
<td></td>
<td>• Does not affect total particle mass</td>
</tr>
<tr>
<td></td>
<td>• Causes decrease in particle number concentration and increase in particle size</td>
</tr>
<tr>
<td></td>
<td>• Increase in particle size may affect loss mechanisms</td>
</tr>
<tr>
<td></td>
<td>• May affect diesel aerosols if dilution is delayed, not critical after typical diesel exhaust dilutions</td>
</tr>
<tr>
<td></td>
<td>• Typical time constant, $\tau = 1/kN_o \sim 10^9/N_o$ (s) for diesel size particles, $N_o = \text{initial particle concentration (1/cm}^3\text{)}$ (Fuchs, 1964)</td>
</tr>
<tr>
<td>Adsorption/desorption</td>
<td>• Adsorption / desorption of volatile components will affect size and mass of measured particulate matter</td>
</tr>
<tr>
<td></td>
<td>• Availability of particulate surface will affect degree of adsorption / desorption</td>
</tr>
<tr>
<td></td>
<td>• Driven by saturation ratio</td>
</tr>
<tr>
<td>Nucleation</td>
<td>• Homogeneous nucleation may create large numbers of new particles</td>
</tr>
<tr>
<td></td>
<td>• Nucleation rates are highly nonlinear functions of saturation ratio</td>
</tr>
<tr>
<td></td>
<td>• Heterogeneous nucleation leads to the growth of existing particles</td>
</tr>
<tr>
<td>Condensation/evaporation</td>
<td>• Condensation / evaporation of volatile constituents will affect size and mass of measured particulate matter</td>
</tr>
<tr>
<td></td>
<td>• Affected by saturation ratio, testing conditions such as: temperature, pressure, humidity</td>
</tr>
<tr>
<td></td>
<td>• Particles formed by nucleation may grow by condensation</td>
</tr>
</tbody>
</table>

Effects Of Test Conditions on Diesel Aerosol

The environmental conditions experienced by diesel exhaust after leaving the engine tailpipe coupled with the characteristics of the engine emissions will influence the nature of the measured aerosol. It is critical to understand this interaction if sampling conditions in the laboratory are going to produce results similar to those generated under real-world conditions.

*Because conditions vary so greatly in diesel exhaust testing, it is critical to understand how testing conditions may affect the nature of the diesel particulate matter being measured.*

The key environmental or test parameters that have been identified include:
• dilution ratio and the resulting saturation ratio
• dilution rate
• time the particles spend at varying dilution ratios or sampling conditions (residence time)
• humidity and temperature
• background particle and gas concentrations

Emission characteristics that have a role in affecting the measured aerosol include:
• size, number, and composition of particles emitted from the engine
• composition and quantity of volatile particle precursors in the exhaust

**Dilution and Saturation Ratios**

To interpret diesel aerosol measurements and to reproduce environmental aerosol conditions in the laboratory, it is necessary to understand how the dilution ratio affects the saturation ratio, the exhaust temperature and the volatile fraction of the exhaust. As shown in the laboratory survey, the type of dilution, dilution ratio and the environmental conditions vary between facilities. Further, these conditions can be vastly different from the dilution and environmental conditions experienced on-highway, resulting in an aerosol with markedly different chemical and physical characteristics. The parameters that affect the gas-to-particle processes of adsorption/desorption, condensation/evaporation, and nucleation are summarized in this report. EPA Supplemental Report No. 2 (Kittelson, *et al.*, 1998b) presents a more detailed discussion of these processes. This section will relate the dilution ratio to the resulting particle processes that may occur.

**Exhaust Sampling System Dilution**

Regulations for the Federal Test Procedure define DPM by specifying the maximum temperature in the primary mixing zone (190° C, 375° F), and the maximum temperature of collection at the filter face (52° C, 125° F) for DPM samples. The filter face temperature may be achieved by single or two-step dilution. Some test facilities use additional dilution for aerosol instruments that require lower particle concentrations. There are no set guidelines for the amount of dilution at each step or the residence times of exhaust at the various dilution ratio values. This wide latitude in achieving the desired conditions for an exhaust sample introduces a wide variance in DPM measurements especially those measurements to determine the aerosol size distribution.

**Volatile Particle Precursors in the Exhaust**

One of the important parameters to consider in characterizing diesel aerosol is the amount and fate of volatile organic matter. The fate of the hydrocarbons is affected by the dilution process, laboratory or atmospheric. The resulting dilution air/exhaust mixture temperatures and organic concentrations during dilution will affect the saturation ratios and aerosol behavior during sampling or during particle lifetimes in the atmosphere. Volatile organic matter is associated with the smallest diesel exhaust particles (nanoparticles) and understanding processes that affect the fate of these exhaust hydrocarbons is becoming increasingly important.
Volatile organic matter may remain gaseous (disregarding the use of a catalytic converter) or may undergo gas-to-particle conversion to form the SOF, the extractable fraction of DPM. As engine exhaust is diluted and cooled, SOF may move from the gas phase to the particle phase by two paths: adsorption on or absorption into existing particles or nucleation to form new particles. All of the hydrocarbons that are collected on a filter are called the SOF.

Adsorption of hydrocarbons from the gas phase to existing aerosol particles will increase the size and mass of nuclei and accumulation mode diesel aerosol while decreasing the gaseous hydrocarbon concentration. Nucleation of new particles formed mostly of hydrocarbons from the gas phase will leave the accumulation mode particles unaffected, but may cause a dramatic increase in the number nanoparticles in the nuclei mode.

**Adsorption or Nucleation of Volatile Particle Precursors**

Adsorption of hydrocarbons on the surface of the carbonaceous core of diesel particles may be modeled using the Langmuir, BET, or other theories of isothermal adsorption behavior. The saturation ratio, $S$, is the ratio of the partial pressure of a condensable species to its local vapor pressure. For both models, increasing $S$ (at low values of saturation ratio) causes a corresponding increase in organic adsorption to available surface area. For intermediate values of $S$, there is a slow increase in adsorption for increasing saturation ratio. As $S$ approaches 1.0 adsorption gives way to condensation. Supplemental Report No. 2 (Kittelson, 1998b) provides more information on the modeling of adsorption of hydrocarbons on soot particles and includes illustrations of the relation of adsorption to saturation ratio.

If saturation ratios are sufficiently high, new particles may form by homogeneous nucleation of gaseous species. High saturation ratios are more likely if there is insufficient particle surface available in the exhaust for extensive adsorption. Nucleation can be responsible for the formation of nuclei-mode particles in diesel aerosol. The nuclei mode is frequently observed when diesel exhaust is rapidly diluted under either atmospheric or dilution tunnel conditions (Dolan, et al., 1975; Kittelson et al., 1988). Nuclei-mode particles consist primarily of volatile materials and will be affected by changing saturation conditions that may cause continued condensation or evaporation back into gaseous form.

It has been observed in diesel exhaust that volatile organic matter can nucleate and grow to form nuclei mode particles at saturation values below supersaturation. There are heterogeneous nuclei present in diesel exhaust in the form of sulfuric acid and possibly metallic ash. It has been hypothesized that these heterogeneous nuclei are acting as the nucleation sites for the SOF and that the particles are growing by adsorption onto the metallic ash or absorption into the sulfuric acid. This would allow the growth of SOF nuclei mode particles at saturation values below 1.0. Calculations of saturation ratios associated with hydrocarbons comprising the SOF, suggest that they rarely approach 1.0, and never reach values of 3 - 4 necessary for homogeneous nucleation (Friedlander, 1977). Thus, sulfuric acid nuclei are likely precursors to the formation hydrocarbon containing nanoparticles.
Doyle (1961) predicted that homogenous nucleation between sulfuric acid (H$_2$SO$_4$) and H$_2$O may be triggered in the atmosphere with a minute partial pressure of H$_2$SO$_4$ of 10$^{-9}$ 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$_2$SO$_4$ 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. In the current work of Abdul-Khalek (1999), it is also shown that sulfuric acid may nucleate in mini-dilution systems at dilution ratios between 10-50.

Saturation ratios of both hydrocarbons and sulfuric acid behave in essentially the same manner during exhaust dilution. As the saturation ratios of a diesel exhaust increase, the favored process changes from adsorption to nucleation. While the rate of adsorption increases with increasing S, the rate of nucleation is extremely nonlinear in S. Nucleation can be described as nearly an “on - off” phenomenon. Once supersaturation is sufficiently high and the nuclei are present, large numbers of small particles form very quickly.

Figure 6 shows the relation of saturation ratio and the competing gas-to-particle processes of adsorption and nucleation with the onset of nucleation occurring at a critical value of saturation ratio above which the nucleation rate rapidly increases. Thus, engine and dilution conditions that lead to sufficiently high saturation ratios may cause nucleation to increase dramatically.

![Relative Rates of Gas to Particle Conversion](image)

**Figure 6.** - Figurative diagram showing the effect of saturation ratio on competing gas-to-particle conversion processes.
Figure 7 shows the relation of dilution ratio and the resulting saturation ratio for two representative condensable hydrocarbons of a diesel exhaust. The two hydrocarbons have different boiling points and are shown at exhaust temperatures of 480° K (207° C) and 600° K (327° C). The dilution air temperature is 300° K (27° C) and the dilution process is assumed adiabatic. Using these hydrocarbons as representatives of typical diesel exhaust volatiles, the saturation ratio has the highest values for dilution ratios of about 5 to 50 for both hydrocarbons.

Thus, the strongest driving force for condensation, adsorption and nucleation occurs in the critical dilution ratio range (5 - 50:1), roughly the same range produced by a dilution tunnel system (3 - 20:1).
**Engine Emission Characteristics**

Engines are characterized based upon the particulate matter emissions in g/bhp-hr and by the type of engine such as heavy-duty on or off-highway and light duty. Prior to 1988, EPA did not regulate emissions but from 1990 to 1994 EPA required engine manufacturers to reduce emission for heavy-duty on-highway emissions from 0.60 - 0.10 g/bhp-hr. As engine technology improved, some engine types experienced greater reductions in solid carbonaceous particles than in volatile materials. This was the case for the engine family tested in the HEI study (Bagley, *et al.*, 1996). The 1988 engine gave SOF values in the range 0.25 - .30 while the newer 1991 engine gave values in the 0.60 – 0.75 range.

While dilution ratio is a critical parameter of the atmosphere or laboratory conditions, the amount of particulate surface available on which volatile organic matter may adsorb is a critical parameter of the exhaust aerosol. The amount of material adsorbed onto the carbonaceous agglomerates is dependent on the particulate surface area available as well as the saturation ratio.

Older engine designs that emit higher concentrations of carbonaceous agglomerates have large surface areas available for adsorption of volatile materials. This will tend to prevent saturation ratios from going high enough to trigger nucleation. On the other hand, with newer designs in which the carbonaceous component has been removed more effectively than volatiles, there is little surface area available for the adsorption of these volatiles. This drives saturation ratios higher and makes nucleation more likely.

Figure 8 shows how the presence of carbonaceous agglomerates keeps the organic saturation ratio low by adsorbing the SOF. The depletion of organic vapor will prevent the saturation ratio from becoming high enough during dilution to promote nucleation.

Even for diesel engines emitting relatively low concentrations of carbonaceous agglomerates and high hydrocarbon fractions, saturation ratios high enough for homogeneous nucleation are not usually reached during exhaust dilution. Thus, other types of particles might serve as heterogeneous nucleation or absorption sites. It is possible that even the reduced sulfuric acid levels found in the exhaust of diesel engines fueled with low sulfur fuel may be sufficient to form nuclei that absorb hydrocarbons. It is also possible that other exhaust constituents such as metal contaminants from lubricating oil may be acting as heterogeneous nucleation sites for nanoparticle formation. At present details of these processes are not understood.

In summary, an engine producing a large amount of volatile material but a low amount of carbonaceous soot is likely to have more particle nucleation and growth than an engine producing an equal amount of volatile material with more carbonaceous agglomerates.
Influence of Exhaust Soot on Saturation Ratio
Adiabatic Dilution, Equilibrium Adsorption

High saturation ratios may lead to nucleation of new particles

Saturation Ratio vs. Dilution Ratio

Figure 8.- Saturation vs. dilution ratio for engines emitting different amounts of DPM.

Residence Time

The kinetics of adsorption become important when the exhaust is going through rapid changes in temperature or adsorbate concentration. For laboratory measurements, filters used to measure DPM are usually in the exhaust stream long enough that it is assumed that the SOF will reach equilibrium with the solids on the filter. For laboratory studies attempting to simulate on-highway dilution conditions using near real-time instruments, the rate at which adsorption and condensation occurs must be considered.

It is expected that the tendency to produce nuclei during dilution will be maximized at an intermediate rate of dilution. Higher saturation ratios will be produced and nucleation will be more likely if dilution takes place on a time scale faster than characteristic times for adsorption. Under these circumstances, there is little time for adsorption to take place and the exhaust behaves as if there is a much smaller surface area available for adsorption. On the other hand, if the rate of dilution is too high, the exhaust will spend little time in the intermediate dilution ratio range where saturation ratios and nucleation rates are highest and nucleation will be minimized.

Calculations were made for adsorption of a representative organic at dilution conditions that led to the highest saturation ratio. A typical SOF of 10% on DPM was assumed and an
accumulation mode particle diameter of 0.1 µm was used. These assumptions gave a time constant for adsorption/condensation mass transfer of 0.25 s. (Kittelson and Dolan, 1980) This value provides a time scale when considering the roadway and laboratory dilution values and residence times provided below.

**On-Road Exhaust Dilution**

Figure 9 shows measured roadway dilution ratios with respect to time from emission from the engine stack for a heavy-duty diesel engine. For this study, exhaust measurements were taken at varying distances behind a flatbed diesel truck traveling at about 55 mph. Figure 9 shows the dilution ratio as a function of atmospheric residence time. For this study, the exhaust passed through the range of critical dilution (5 and 50:1) in less than 0.25 s. The exhaust was diluted about 100:1 in approximately 0.45 s and above 1000:1 in approximately 1 s.

**Laboratory Exhaust Sampling Dilution**

Table 5 shows typical laboratory values at primary and secondary dilution stages and the typical residence times at each stage. The values in the table are taken from the survey of diesel engine test facilities performed and from the literature.

<table>
<thead>
<tr>
<th>Table 5. - Primary and secondary dilution values and typical residence times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Dilution Ratio Range</td>
</tr>
<tr>
<td>Residence Time at Primary Dilution</td>
</tr>
<tr>
<td>Total Dilution Ratio Range (including secondary dilution)</td>
</tr>
<tr>
<td>Residence Time at Secondary Dilution</td>
</tr>
</tbody>
</table>

Laboratory aerosol measurement conditions are within the critical range of dilution ratio and corresponding saturation ratios that will greatly affect the adsorption, nucleation and condensation processes of the particles.

*To correctly interpret diesel aerosol measurements and to correlate roadway and laboratory experiments, the relationships between exhaust aerosol and testing parameters must be well understood.*
Figure 9. - On-road diesel exhaust sampling time exhaust aerosol spent at critical dilution ratios for a heavy-duty diesel engine in a flatbed truck traveling at 55 mph (Kittelson, et al., 1988 adapted from figure 4.46).

INSTRUMENTS FOR MEASUREMENT OF DIESEL PARTICLE MATTER

This section summarizes real-time or near-real-time instruments used to measure DPM. Critical aerosol parameters are listed and discussed to provide context for the instrument discussion. The principle of operation of each instrument is listed and related to the corresponding particle property. Further detail is provided in Supplemental Report No. 1 (Kittelson, et al., 1998a).

Critical Aerosol Parameters

The U.S. has historically regulated DPM emissions based on a particulate mass standardized to engine output. Gravimetric analysis of DPM collected on filters placed in engine exhaust lines has given an indication of engine output of total mass of particulate matter.

However, there is a growing recognition that other particle characteristics may have a more significant impact on health than total particulate mass.

Historically, PM10 (particles smaller than 10 µm) has been used to define the respirable aerosol fraction. Now regulations include standards for PM2.5 for particles smaller than 2.5 µm. With the recognition that over 90% of the number of diesel particles reside in the range below 0.1 µm while only 1-20% of the mass typically resides in the same ultrafine particle range, the parameters used to characterize diesel particles need to reflect these new concerns.
Adverse health effects of respirable aerosol are a function of particle size, deposition rate, composition and other factors. The smaller the particle the greater the penetration. Particle toxicity is related to particle composition and physical characteristics. The smaller the particles, the greater the surface area for the same overall particle mass respired and the higher the potential activity of the particles in the lung. Figure 3 illustrated relationships between idealized DPM number and mass weighted size distributions and the alveolar deposition curve (Kittelson, 1998a, Morrow, et al., 1964, Raabe, 1982). On a number basis, nanoparticle deposition efficiency is much greater than accumulation mode deposition efficiency, although on a mass basis it is less. Nanoparticles are typically hydrocarbons or sulfate and form by nucleation during dilution and cooling of the exhaust, while accumulation mode particles are mainly carbonaceous soot agglomerates formed directly by combustion.

To determine the mass and number size distribution of diesel aerosol over the entire size range requires more than one instrument. Depending upon the principle of operation these instruments can determine the size distribution in a span of time ranging from seconds to hours.

Table 6. Critical Particle Measurement Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle mass</td>
<td>• total particle mass may not be the best indicator for possible health impact</td>
</tr>
<tr>
<td>Particle size</td>
<td>• instruments measure different properties that are translated to different particle diameters (i.e. aerodynamic diameter, electrical mobility diameter, etc.)</td>
</tr>
<tr>
<td>Particle number concentration</td>
<td>• majority of number of diesel particles resides in ultra-fine size range that penetrate deepest into the lung</td>
</tr>
<tr>
<td>Particle surface area</td>
<td>• may be a more accurate indication of degree of adverse impact on health</td>
</tr>
<tr>
<td>Particle composition</td>
<td>• compounds adsorbed to particle surfaces may play a more important role in interactions with lung tissue</td>
</tr>
</tbody>
</table>

Instruments Used to Measure Diesel Aerosol Size Distributions

Frequently used instruments to measure diesel aerosol size distributions are briefly described below and table 7 provides a summary. The listing of instrumentation is not an exhaustive list, however the instruments most commonly mentioned in the literature and those instruments that have unique capabilities for measuring the diesel aerosol size distribution or chemical composition below 100 nm are discussed.

**Micro-Orifice Uniform Deposit Impactor (MOUDI):** is a cascade impactor that provides a mass weighted size distribution of an aerosol. Particles are separated by aerodynamic diameter on aluminum foil stages or substrates for subsequent gravimetric analysis. Depending upon the amount of mass to be collected and the nature of the particles, the substrates may be used with or without grease. The MOUDI sizes particles from 0.56 to 10
µm using 4 stages per decade, although the number of stages can be altered depending upon experimental conditions. Measurements are susceptible to measurement artifacts and are not near to real-time. (Marple, et al. 1991)

**Nano-Micro-Orifice Uniform Deposit Impactor (Nano-MOUDI):** is a modified MOUDI. The final four stages of the nano-MOUDI use low-pressure operation to size particles down to 10 nm. The nano-MOUDI also provides mass-weighted size distributions. Measurements are susceptible to measurement artifacts and are not near to real-time. (Marple, et al. 1994)

**Electrostatic Low Pressure Impactor (ELPI):** is a cascade impactor used in Europe that collects particles separated by aerodynamic diameter for gravimetric analysis and provides real-time number-weighted size distributions. The particles are charged and each stage uses an electrometer to measure the charge of the particles deposited on the collection plate. Measurements are near real-time with a scan time as low as 2 s. (Keskinen, et al., 1992; Dickens, et al., 1997; Ahlvik, et al., 1998)

**Electrical Aerosol Analyzer (EAA):** has historically been the most common instrument used in the U.S. for diesel particulate measurement. The EAA provides a number-weighted particle size distribution based on electrical mobility. Diesel exhaust particles are electrically charged and then routed through an electric mobility analyzer that only allows particles of a specified electric mobility to pass through and be measured by a downstream electrometer. (Liu, et al., 1974; Liu and Pui, 1974a; Dolan, et al., 1980; Groblicki and Begeman, 1979; Fang and Kittelson, 1984; Baumgard and Kittelson, 1985; Baumgard and Johnson, 1992; Bagley, et al., 1996)

**Differential Mobility Particle Sizer (DMPS):** measures an electrically charged aerosol with an electric mobility analyzer that only allows particles of a specified electric mobility to pass through and be measured downstream. A DMPS uses a condensation nucleus counter to count the particles within an electric mobility range because of its increased sensitivity over an electrometer. This allows the size interval of particles passed by the mobility analyzer and counted to be smaller than for an EAA with an electrometer. (Pui and Swift, 1995)

**Scanning Mobility Particle Sizer (SMPS):** is similar to a DMPS except that while the electric mobility analyzer of the DMPS makes discrete changes in the voltage used to control what interval of electric mobility of particles passes through, the voltage of the SMPS is ramped exponentially. This allows a scan of exhaust size distribution in a time interval as short as 30 s. A SMPS also uses a condensation nucleus counter to count particles passing through the mobility analyzer. (Wang and Flagan, 1990; Keady, et al. 1983; Greenwood, et al. 1996)

**Photoelectric Aerosol Sensor (PAS):** provides a surface area-weighted particle concentration and is related to the quantity of particle-bound PAH in the exhaust. Particles are irradiated with an UV light with enough intensity to cause the particles to emit electrons and become positively charged. The positive particles are then collected and the charge measured by an electrometer. The intensity of the particle photoemission is directly related to the PAH
content of the particle. (Burtscher and Siegmann, 1993; Burtscher, et al., 1993; Hart, et al. 1993)

**Aerosol Time-of-Flight Mass Spectrometer (ATOFMS):** measures both aerodynamic size (~0.2 to <10 µm,) and chemical composition of individual particles up to about 600 particles per minute. A particle enters the ATOFMS and is accelerated to its terminal velocity. Smaller particles have greater aerodynamic mobility and reach higher terminal velocities. The particles are sized based on time of flight between two lasers. Each particle is then pulsed by a laser and the resultant desorbed and ionized material is characterized for chemical composition by a dual-polarity mass spectrometer. (Silva and Prather, 1997; Noble and Prather, 1996, 1998; Gard, et al. 1997)

**Epiphaniometer:** measures surface concentration of an aerosol by passing the particles through a chamber with radioactive lead isotopes that attach to the particles. The level of radioactivity of the particles is measured and is directly proportional to the particle surface area. (Gaggeler, et al., 1989a,b)

**Summary of Particle Measurement Instruments**

Table 7 summarizes current aerosol instrumentation used to measure diesel aerosol size distributions and lists some of the limitations associated with each instrument. The particle mass collected by the MOUDI can be analyzed for chemical composition and the ATOFMS can provide chemical composition by particle size over a limited range. However, as shown in the figure 10, selection of such instruments as the MOUDI and the ATOFMS will preclude measurement of the nuclei mode of a diesel exhaust aerosol. While the nano-MOUDI measures down into the nuclei mode particle sizes, it does not provide real or near real-time measurements. Although the ELPI measures only the larger nuclei particles, its fast response and ability to measure down to ambient particle concentrations account for its use in European DPM studies. The EAA covers both the nuclei and accumulation mode particle size ranges, but is susceptible to error introduced by changes in the aerosol during its relatively long sampling time. The DMPS and the SMPS both cover more of the nuclei mode size range than the ELPI but require at least 30s to obtain a size distribution, compared to about 2s for the ELPI. Figure 10 summarizes the typical dynamic particle size range covered by these instruments.

As illustrated in the instrument descriptions and the instrument summary table, instruments measure different particle characteristics based on different particle dynamics. This wide array of instruments can be used to measure different particle size ranges and parameters. Supplemental Report No. 1 provides a more in-depth discussion of these instruments.

*Which instrument is used is dependent on the particle sizes and characteristics of interest, the goals of the study, and the respective limitations of each instrument.*

---

6 As illustrated by the lab survey, many of the European labs are using both the ELPI and the SMPS.
Table 7. Instrument summary

<table>
<thead>
<tr>
<th>Instrument Parameter</th>
<th>Instrument</th>
<th>Range</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inertial mobility instruments (cascade impactors)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micro-orifice uniform deposit impactor (MOUDI)</td>
<td>Aerodynamic diameter</td>
<td>0.056 - 10 um</td>
<td>* Not real-time, gravimetric and chemical analysis performed after collection.</td>
</tr>
<tr>
<td>Nano-MOUDI</td>
<td>Aerodynamic diameter</td>
<td>0.010 - 18 um</td>
<td>* Same as MOUDI</td>
</tr>
<tr>
<td>Electrical low pressure impactor (ELPI)</td>
<td>Aerodynamic diameter</td>
<td>0.030 - 10 um</td>
<td>* Near realtime with time resolution from 2 - 15 s.</td>
</tr>
<tr>
<td><strong>Electrical mobility instruments</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical aerosol analyzer</td>
<td>Electrical Mobility Equivalent Diameter</td>
<td>0.003 - 1 um</td>
<td>* Time resolution between 2-3 min, 11 size intervals.</td>
</tr>
<tr>
<td>Differential mobility particle sizer (DMPS)</td>
<td>Electrical Mobility Equivalent Diameter</td>
<td>0.01 - 0.5 um</td>
<td>* Discrete changes in electric field of DMPS makes sampling for entire range slower than for SMPS.</td>
</tr>
<tr>
<td>Scanning mobility particle sizer (SMPS)</td>
<td>Electrical Mobility Equivalent Diameter</td>
<td>0.010 - 0.7 um</td>
<td>* 2 - 4 min scan time for 100 size intervals - can ramp DMA electric field to reduce scan time.</td>
</tr>
<tr>
<td>nano-Differential mobility analyzer (nano-DMA)</td>
<td>Electrical Mobility Equivalent Diameter</td>
<td>3 - 50 nm</td>
<td>* Time resolution of about 10 s required to scan all intervals.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* Not fully characterized and developed</td>
</tr>
</tbody>
</table>
Table 7. Instrument summary

<table>
<thead>
<tr>
<th>Miscellaneous instruments</th>
<th>Surface area - &lt; 1 um</th>
<th>Material condensing on particle surface can interfere with measurement.</th>
<th>Does not measure particle size</th>
<th>Response time &lt; 1 s</th>
<th>Particles &gt; 1 um are not charged efficiently.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoelectric aerosol sensor (PAS)</td>
<td>&lt; 1 um lower limit not reported</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol time-of-flight mass spectrometer (ATOFMS)</td>
<td>0.3 - 50 um</td>
<td>* Real-time measurement of up to 600 part./min.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epiphaniometer</td>
<td>&lt; 7.0 um</td>
<td>* Time resolution is between 5 - 30 min depending upon the analysis code used.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion battery</td>
<td>0.01 - 0.5 um</td>
<td>* Slow sampling time requires steady-state conditions.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 10. - Dynamic range of particle sizing instruments

EVALUATION OF ROADWAY, TUNNEL, AND OCCUPATIONAL TEST METHODS

A number of studies have determined the size distribution of diesel aerosol in different environments such as mines, tunnels, roadways and ambient atmosphere. In most cases these studies have evaluated a mixed combustion aerosol consisting of emissions from both gas and diesel fueled vehicles. In some cases the investigators determined the mass, number and
volume size distributions, and in a few cases the nanoparticle size distribution was determined. The methods and procedures used to determine these size distributions varied as did the conditions under which the aerosol was generated. However, despite these differences the characteristic multi-modal size distribution is frequently observed. The results from these studies are summarized in table 8.
Table 8. Studies Measuring Diesel Aerosol Size Distributions Outside of The Laboratory.

<table>
<thead>
<tr>
<th>Type of Study and Aerosol</th>
<th>Dilution Ratio(^1)</th>
<th>Measurement Method(s)</th>
<th>Results</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mining/Heavy Duty Diesel</td>
<td>100 - 150:1</td>
<td>MOUDI</td>
<td>Accumulation mode by mass: 0.15 - 0.2 (\mu m)</td>
<td>Bureau of Mines, 1992</td>
</tr>
</tbody>
</table>
| Mining/Heavy Duty Diesel  | < 100:1              | CNC                   | Aitken nuclei count:  
  - No diesels 78 - 175 \(x 10^3\) part./cm\(^3\)  
  - With diesels 3.1 - 17.0 \(x 10^5\) part./cm\(^3\) | Gillies and Schimmelpfennig, 1983 |
| Roadway/Mixed             | \(\geq 500 - 1,000:1\) | CNC, prototype EAA    | Nuclei V mode peak at 0.02 \(\mu m\)  
  Mean Aitken nuclei count:  
  - 1.75 \(x 10^6\) N/cm\(^3\)  
  N/V\(^a\) ratio: 2 \(x 10^7\) - 5 \(x 10^4\)  
  Smog chamber samples showed effects of coagulation on particle size. | Whitby, et al., 1975 |
| Roadway/Auto Spark ignition, Catalyst equipped | \(~500 - 1,000:1\) | EAA, OPC, CNC         | Background -Three distinct modes with mean size by V of 0.03, 0.24, 6.0 \(\mu m\)  
  Test - 0.02, 0.24, 6.0 \(\mu m\) (V)  
  Nuclei mode shift due to coagulation effects - longest aerosol aging times transferred about 1/3 nuclei mode V to accumulation mode. | Wilson, 1977, et al. |
| Roadway/Light Duty Diesel | 100 - 1,000:1        | Mobile lab - EAA primary instrument | DR of 100:1 within 20 m of exhaust pipe at 20 Km/hr in 0.4 s; DR of 1,000:1 after 1 s  
  N/V range 7.0\(x10^4\) - 2.1 \(x10^5\)  
  VMD 0.2 \(\mu m\) | Dolan and Kittelson, 1979 |
| Roadway                   | 1,000:1              | NA                    | Summary paper:  
  - Roadway dilution < 1 s dilution ratio > 1,0000:1  
  - Lab dilution 1 - 5 s dilution ratio 5 - 20 :1  
  - Results from roadway and lab differ due to coagulation, condensation, adsorption and DR effects. | Kittelson and Dolan, 1980 |
| Tunnel/Mixed              | \(~500 - 1,000:1\)   | Impactor              | Principal exhaust components EC and OC  
  - MMD 0.15 \(\mu m\) | Pierson and Brachaczek, 1983 |
| Tunnel/Mixed              | ~ 500:1              | Hering low pressure impactor | After correction for background a unimodal distribution was observed with 85 % of the mass < 0.12 \(\mu m\). | Venkataraman, et al. 1994 |
| Tunnel/Mixed | ~100-500:1 | TEOM, LAS-X, DMA, CNC, Epiphanometer, Aethalometer, Photoemission sensor | Tunnel entrance:  
- Nuclei count between 1.4 - 5.1 x 10⁴  
- Nuclei mode peak between 0.02 - 0.03 μm  
Tunnel exit:  
- Accumulation mode peak N and V between 0.12 - 0.20 μm  
- Mass shift between nuclei and accumulation mode occurring during 6-20 min residence time. | Weingartner, *et al.*, 1997 |
| Atmospheric/Mixed | ~ > 1,000:1 | DMA clone | Influence of heterogeneous reactions on particle growth observed:  
- Nuclei mode peak 0.02 - 0.04 μm  
- Accumulation mode peak 0.05 - 0.3 μm | Ulevicius, *et al.*, 1994 |
| Atmospheric/Mixed | ~ > 1,000:1 | 10 stage impactor | Size distribution and composition analysis:  
- Accumulation mode peak 0.5 μm in urban samples  
- Coarse mode peak 3.0 μm  
- Accumulation mode peak for black carbon 0.25 μm  
- For particles < 0.06 μm elemental carbon from combustion is the main contributor. | Horvath, *et al.*, 1996 |
| Atmospheric/Mixed | ~ > 1,000:1 | SMPS, CNC, LAS-X | Particle number concentration determined primarily by particles < 0.1 μm, N/Mμ mean 1.6 x 10⁴  
Mass concentration was determined by particles 0.1 - 0.5 μm, N/M mean 8.4 x 10⁴ | Tuch, *et al.*, 1997 |
| Atmospheric/Mixed | ~ > 1,000:1 | HE-NE laser spectrometer | Observed particle concentrations in the 65 - 900 nm range were 2 - 16 x 10³ part./cm³; did not detect < 50 nm particles  
GMD 0.10 - 0.16 μm  
Nuclei mode peak 0.084 μm  
Accumulation mode peak 0.181 μm | Trier, 1997 |

¹In some cases the dilution ratio was not given in the paper and is estimated. In these cases a ~ is shown.
²N/V = number of particles/volume [units]
³N/M = number of particles/mass [units]

*Kittelson, *et al.* (1988)*, conducted a very comprehensive study for the Coordinating Research Council. Five field studies were conducted: three studies of particles in the exhaust plumes of diesel highway tractors operating on roadways, a study of particles upwind and downwind of
slowly moving diesel trucks, and a study of particles upwind and downwind of a diesel engine test center. These field studies provide the most comprehensive diesel aerosol information and are discussed in detail.

The objectives were to examine the physical, chemical and biological characteristics of diesel aerosol as a function of atmospheric dilution and aging. Atmospheric dilution ratios of the samples ranged from 2 to 24,000. Atmospheric residence times ranged from about 0.01 to 120 s, however, the effective aging times associated with some of the measurements were longer due to long residence times in the sampling bags and longer filtration times.

The principal findings of this study are summarized below.

- Typically about 85% of the mass of particles emitted by diesel engines was in the submicron diameter range. The submicron size distribution was typically bimodal with "nuclei" and "accumulation" modes at about 0.025 and 0.25 μm volume geometric mean diameters, respectively.

  Figure 11 illustrates an average size distribution based on a series of measurements made over a roadway in the plume of a large heavy-duty highway tractor. For comparison figure 12 illustrates a laboratory size distribution obtained from a Volkswagen rabbit operating at simulated 50-mph road load conditions. The measurements were made with an EAA and rapid dilution system providing 1000:1 dilution to prevent coagulation effects. The size distribution is quite different as the nuclei mode is totally absent. The absence of the nuclei mode is attributed to the fact that the Rabbit engine produced little volatile material, which would normally nucleate during the dilution process. The heavy-duty engine on the other hand produced a substantial amount of HC, which was available for nucleation.

- The volume fraction in the nuclei mode was highly source dependent. It was found to range from 0 to 35% in these experiments. Consequently, the number-to-volume (or number-to-mass) ratio was highly variable, ranging from 2,300 to 62,000 part/μm³. Number concentration was not a good indicator of DPM volume or mass concentration. [Note: the similarity to the Whitby, et al. (1975) roadway data]

- For most of the cases studied, the volume fraction in the nuclei mode was nearly equal to the solvent extractable fraction. This suggests that much of the material in the nuclei mode was extractable. This is illustrated in figure 13.
Figure 11. - Average size distribution obtained from chase experiments, heavy-duty diesel (From Kittelson, et al. 1988)

Figure 12. - Average size distribution obtained from laboratory experiments using a Volkswagen Rabbit light-duty engine (From Kittelson, et al. 1988)
Coagulation increases the mean diameter of the nuclei mode and transfers mass from the nuclei mode into the accumulation mode, thus moving the two modes closer together and reducing the mass in the nuclei mode. It also increases the mean diameter of the accumulation mode, but much more slowly. The decrease in the mass and number of nuclei mode particles takes place on a time scale ranging from minutes for highly polluted urban conditions to hours for clean rural conditions. Thus, coagulation may significantly alter the size distributions of diesel particles as they exist in the atmosphere.

For the highway cruise conditions the dilution ratio increased nearly linearly with time and typically took only 1-2 s to reach 1,000. Under these dilution conditions little coagulation occurs. The time scale of dilution for particles emitted from the engine test cell stacks was much longer than that of roadway dilution. In the worst cases over 100 s were required to reach a dilution ratio of 1,000. With this relatively slow dilution, coagulation during dilution was significant and reductions in the number of nuclei mode particles and the number to volume ratio by as much as a factor of 3 were observed. Although the dilution conditions of the test cell study may appear to be somewhat non-representative, the time scale of dilution is not very different from that associated with slow moving congested urban traffic, where coagulation during dilution will probably also be important.
• Light absorption cross sections for diesel particles observed in this study ranged from 5.7 to 6.1 $m^2/g$ and did not seem related to particle size. Light scattering cross sections ranged from 1.5 to 3.9 $m^2/g$ and increased with particle size. Thus, coagulation growth should not have a strong influence on light absorption cross sections but may increase the light scattering cross sections of diesel particles as they age in the atmosphere.

Table 9 summarizes the properties of the aerosol size distributions measured in this study. The range of N/VT (number of particles divided by EAA volume concentration) ratio (2,300 to 62,000) is similar to the one reported by Whitby, et al. (1975). Kittelson (1998a) summarizes the data from the Kittelson, et al. (1988) study and additional data from the University of Minnesota and others in table 10. It is clear from these tables that N/VT ratio and thus the number of particles emitted per unit mass of particulate matter are highly variable. The results suggest that N/VT ratios in the range of 50,000 to 60,000 part./$\mu m^3$ (or, assuming spherical, unit density particles, 5 to 6 x $10^{16}$ 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/VT ratio of 26,000 (Kittelson, et al., 1988) observed over a rural freeway under mixed traffic conditions. This ratio is lower than source levels because of dilution with aged ambient aerosol and coagulation. The values of 120,000 to 360,000 observed by Bagley, et al. (1996) are significantly higher than reported for other engine types. The only way such a high N/VT ratio was produced at the University of Minnesota was when a diesel engine equipped with a catalyst in an off-design was operated in the laboratory under high load condition that led to significant sulfate formation. This led to an N/VT ratio of 400,000.

<table>
<thead>
<tr>
<th>Property</th>
<th>$C_{cp}/C_t$</th>
<th>$m/VT$ g/cm$^3$</th>
<th>N/VT part/$\mu m^3$</th>
<th>VN/VT</th>
<th>$E_c$ $\mu m$</th>
<th>DGV$_{n}$ $\mu m$</th>
<th>DGV$_{a}$ $\mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>0.12 - 0.2</td>
<td>1.2 - 2.2</td>
<td>2,300 - 62,000</td>
<td>0 - 0.35</td>
<td>0 - 0.38</td>
<td>0.022 - 0.032</td>
<td>0.19 - 0.34</td>
</tr>
<tr>
<td>Typical value</td>
<td>0.15</td>
<td>1.2</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.025</td>
<td>0.25</td>
</tr>
</tbody>
</table>

$C_{cp}/C_t$ Mass fraction of particles with aerodynamic diameters greater than 0.9 $\mu m$.
$m/VT$ Submicron filter mass concentration divided by EAA volume concentration.
N/VT Number of particles divided by EAA volume concentration.
VN/VT Volume fraction in the nuclei mode.
$E_c$ Solvent extractable fraction.
DGV$_{n}$ Geometric volume mean diameter of nuclei mode.
DGV$_{a}$ Geometric volume mean diameter of accumulation mode.
NA Highly variable so that defining a typical value was not appropriate.
Table 10. N/VT Ratios (Number of particles divided by EAA volume concentration)
Calculated from Various Sources (1 part/µm$^3$ corresponds to 10$^{12}$ particles/g for spherical particles with a density of 1 g/cm$^3$) (Kittelson, 1998a)

<table>
<thead>
<tr>
<th>Condition</th>
<th>SOF</th>
<th>N/VT part/µm$^3$</th>
<th>Source</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roadway dilution</td>
<td>0.13</td>
<td>62,000</td>
<td>1979 DI diesel, Cummins</td>
<td>Kittelson et al., 1988</td>
</tr>
<tr>
<td>Roadway dilution</td>
<td>0.38</td>
<td>57,000</td>
<td>1979 DI diesel, Detroit Diesel</td>
<td>Kittelson et al., 1988</td>
</tr>
<tr>
<td>Atmospheric dilution</td>
<td>~0</td>
<td>3,700</td>
<td>1979 DI diesel, Caterpillar endurance test stand</td>
<td>Kittelson et al., 1988</td>
</tr>
<tr>
<td>Rural freeway</td>
<td>0.24</td>
<td>26,000</td>
<td>Mixed traffic</td>
<td>Kittelson et al., 1988</td>
</tr>
<tr>
<td>Rural background</td>
<td>0.14</td>
<td>4,300</td>
<td>Background</td>
<td>Kittelson et al., 1988</td>
</tr>
<tr>
<td>Chassis dynamometer - lab dilution</td>
<td>NA</td>
<td>56,000</td>
<td>SI non-catalyst - In use vehicles</td>
<td>Hildemann et al., 1991 N/V calculated from their data.</td>
</tr>
<tr>
<td>Chassis dynamometer - lab dilution</td>
<td>NA</td>
<td>46,000</td>
<td>SI catalyst - In use vehicles</td>
<td>Hildemann et al., 1991 N/V calculated from their data.</td>
</tr>
<tr>
<td>Engine dynamometer</td>
<td>NA</td>
<td>400,000</td>
<td>1995 DI diesel, ox. catalyst in sulfate forming mode</td>
<td>Work in progress, University of Minnesota</td>
</tr>
<tr>
<td>Engine dynamometer</td>
<td>NA</td>
<td>25,000</td>
<td>4-stroke DI diesel, iron additive</td>
<td>Work in progress, University of Minnesota</td>
</tr>
<tr>
<td>Engine dynamometer</td>
<td>NA</td>
<td>2,900</td>
<td>4-stroke DI diesel, baseline</td>
<td>Work in progress, University of Minnesota</td>
</tr>
</tbody>
</table>

One of the objectives of the Kittelson, et al., (1988) roadway study was to determine the relationship between dilution ratio and sampling distance and the impact these variables have on particles. Figure 14 illustrates dilution of diesel aerosol as it exits the tailpipe and figure 15 summarizes the atmospheric dilution ratios measured during the roadway experiments.
Data shown in figure 15 came from two different field studies (Kittelson, et al., 1988). In field study 2 the sampling distance was determined by towing a mobile laboratory on a flatbed trailer behind the tractor at speeds of 50 to 55 mi/hr (22-25 m/s). Atmospheric residence times were very short, ranging from 0.01 to 0.4 s. Dilution ratios ranged from 3 to 90:1. In field study 5 the mobile laboratory followed the tractor down the roadway at the same speeds. Dilution ratios of 1,000:1 were obtained in approximately 1 s at a distance of about 25 m.

The relationship between the saturation ratio and dilution ratio and impact on the extractable fraction is complex. The saturation ratio and extractable fraction peak at intermediate dilution ratios (approximately 5 to 50:1). The opportunity for homogeneous and heterogeneous nucleation is greatest when the saturation ratio is highest. However, the amount of time spent at high saturation ratio is very short for on-highway conditions, typically less than 1 sec. The importance of the extractable fraction to the nuclei mode was suggested in the discussion of figures 11 and 12 where size distributions for engines with high and low extractable fractions are shown. The VN/VT ratio (volume fraction in the nuclei mode) for the engine with high extractable fraction is 53,000 part/µm³ compared to 5,100 part/µm³ for the engine with low extractable fraction.
In most respects the diesel aerosol observed in this study were similar to those observed by others in dilution tunnel and roadway studies. The findings confirmed the existence of the nuclei mode reported by Whitby, *et al.* (1975) although the size of the mode was unexpectedly large.
These results demonstrate the subtle but important changes in the nature of diesel aerosol occur as the aerosol dilutes and ages in the atmosphere. All the roadway studies, regardless of engine, exhibited strong nuclei modes. In studies where it was measured, the volume fraction in the nuclei mode was almost the same as the solvent extractable fraction, suggesting that much of the extractable material resides in the nuclei mode. Apparently, engines which produce a nuclei mode emit two distinct populations of particles. The nuclei mode consists of particles composed of primarily extractable or volatile materials with a number mean diameter falling between 0.02 - 0.04 \( \mu m \). These nuclei presumably form during dilution in the atmosphere. The accumulation mode consists of particles composed of primarily solid carbonaceous agglomerates having a mass median diameter between 0.1 - 0.25 \( \mu m \).

**EVALUATION OF DIESEL TEST LABORATORY METHODS**

The conditions a diesel exhaust sample stream experiences during the measurement process may greatly affect the particle size, number and mass concentration and chemical composition of the particulate matter. This section will evaluate current test laboratory procedures for the sampling and measurement of diesel exhaust aerosols. Specific examples taken from the lab survey performed for this study and recent literature are provided below to illustrate how diesel exhaust aerosols are affected by laboratory parameters.

In summary, the behavior and characteristics of a diesel exhaust aerosol are dependent on:
- sampling conditions of the exhaust
- chemical and physical properties of the exhaust aerosol

Issues to be considered when evaluating a diesel exhaust measurement strategy include:
- Does the competition of the processes of adsorption and nucleation achieve the same balance as seen in an on-road environment?
- Does the coagulation in the exhaust and sampling lines of the testing environment adequately match the real situation of the engine exhaust during on-road operation?

In addition to the two main issues of adsorption versus nucleation competition and coagulation behavior, the following issues that affect these particle processes should also be considered:
- Is the final dilution ratio of the exhaust above the critical range (about 5 to 50) that favors nucleation?
- Does the exhaust spend sufficient time (~0.25 s) in the critical range of dilution ratio to allow the volatile hydrocarbons to adsorb to nuclei and accumulation mode carbonaceous particles? Is there sufficient time to form or grow nuclei to a detectable size?
- Is the ratio of particle surface area to volatile hydrocarbon and sulfate sufficient to adsorb enough volatile matter to suppress nucleation?
- Are there sampling conditions, such as dilution air relative humidity, that may affect the characteristics of the measured exhaust aerosol?

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7 The laboratory survey is not a comprehensive survey, but the results indicate that there are few if any standard protocols for diesel aerosol measurement.
Exhaust Constituents

The nature of the exhaust leaving the tailpipe of a diesel engine is dependent on the load and speed of the engine, the fuel, lubricating oil composition and consumption, and the amount of carbonaceous solid particles and volatiles (mainly hydrocarbons and sulfuric acid) emitted by the engine. To evaluate sampling methods and interpret results it is necessary to understand how the exhaust interacts with the environment from the point of generation to the point of measurement.

Emission of Carbonaceous Agglomerates and Volatile Material

The current trend in diesel emissions has been a decrease of the mass of emitted DPM. This reduction was achieved by reducing accumulation mode mass. However, recent studies have demonstrated that there may be a sharp increase in the number of nuclei mode particles under certain conditions. When mass concentrations are low and volatile concentrations are high the number of nanoparticles may increase. These particles may include hydrocarbons (SOF), carbon fragments, sulfates, and metallic ash. Hydrocarbons are probably the main source of nuclei mode particle mass for engines running under normal conditions with low sulfur fuels (< 0.05 %), but even in this case sulfuric acid may play a role in initial nuclei formation.

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 carbonaceous material mass.

As an engine exhaust dilutes and cools, the sulfuric acid and SOF may pass from the gas phase to the particle phase by two paths: nucleation to form new particles or adsorption onto or absorption into existing particles. The exhaust of an engine with high carbonaceous particle mass emissions may have sufficient particle surface area to adsorb volatiles. This will prevent the saturation ratios from rising high enough to favor nucleation and most of the volatiles will be adsorbed by the carbonaceous particles which reside mainly in the accumulation mode diameter range. An engine with low carbonaceous particle mass emissions may not have sufficient particle surface area to adsorb volatiles. An exhaust with low carbonaceous material emissions may also be achieved by the addition of aftertreatment devices, such as particle traps, that remove solid particles. If an engine with low emission of carbonaceous material also emits high values of volatile matter, the saturation ratios may rise high enough during exhaust dilution and cooling for nucleation to be favored. Nucleation of volatile matter may generate large numbers of nuclei mode particles.

If this interpretation is correct, the formation of nuclei mode particles by future engines will depend upon the relative amounts of condensable species and solid surface on which to condense or adsorb.

Bagley, et al. (1996):  The new engine technology represented by the engine used in this study, while markedly reducing particle mass emissions, led to sharp increases in number

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8 The engine lab survey indicates that a variety of engine oils are used including synthetic oils.
emissions of nuclei mode particles. The 1991 diesel engine tested showed exceptionally high number concentrations, more than an order of magnitude higher than the 1988 engine and two orders of magnitude higher than the 1995 engine tested by the University of Minnesota described below. The engine studied is of very modern design with a very high-pressure (150 MPa peak injection 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, 1997). 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, tested at the University of Minnesota, which uses a moderately high pressure (90 MPa peak injection pressure) fuel injection system. The mass of particles in the accumulation mode that could adsorb SOF has been significantly reduced for the 1991 engine when compared to older engines.

Kittelson (1998a): The results of this study further illustrate the impact of the nature of the diesel exhaust on the measured particles. The 1995 engine tested in this study has a similarly low concentration of particles in the accumulation mode to the HEI engine discussed above. However, only a small nuclei mode was formed. This engine has significantly lower SOF values (around 30-40 %) than the engine used by Bagley, et al. Nucleation is a highly non-linear process (Friedlander, 1977) and the concentration of condensable species in the exhaust of this engine may not be high enough during the dilution process to cause significant nucleation. Most of the work done at Minnesota used a two-stage dilution system that has a very short residence time (< 100 ms) in the critical 5 to 50 dilution ratio range. The dilution system was designed to simulate the rapid dilution that occurs in the atmosphere. This is in contrast to the dilution system used by Bagley, et al. that had a primary dilution ratio in the main dilution tunnel of about 10 and a residence time at this dilution ratio greater than 1 second. The test conditions used by Kittelson will tend to minimize nucleation while those used by Bagley, et al. will favor nucleation.

More recent work at Minnesota (Abdul-Khalek, et al. 1998a) has shown that by using a residence time in the primary dilution system on the order of a few hundred milliseconds and varying the dilution ratios the nucleation mechanism could be “turned on or off”. This work was done using a two-stage dilution system with residence times ranging from 40 - 6,000 ms and a primary dilution ratio of about 18:1 and a secondary dilution ratio of about 25:1. The study measured particle size distributions upstream and downstream of a particle filter both with and without a catalytic stripper (Abdul-Khalek and Kittelson, 1995). The catalytic stripper consists of a small oxidizing catalyst mounted in an oven followed by a cooling coil. The system is used to differentiate between volatile and non-volatile particles in a diluted sample stream. Major conclusions from this study were:

- Emission of nanoparticles downstream of the filter was dramatically affected by residence time in the primary dilution tunnel. Changing the residence time from 40 to 6,000 ms...
increased number concentrations of nanoparticles by up to four orders of magnitude. Volume concentration was not strongly influenced by residence time.

- Nearly all particles in the nuclei mode were volatile and < 20 nm diameter.
- The filter performed much better on a volume (or mass) than on a number basis because nanoparticles formed by nucleation downstream of the filter influence the number emissions appreciably but usually constitute little volume because of their very small size.

Further work by Kittelson and Abdul-Khalek (1998) examined the influence of primary dilution temperature and residence time at a fixed dew point of 10 °C on particle size and concentration. All tests were done with a 1995, medium-duty, direct injection engine running on 0.03% S diesel fuel at 1600 rpm, 50% load. The concentration of particles in the nanometer range increased with decreasing temperature and increasing residence time. An increase in nanoparticle concentration of more than two orders of magnitude was observed as the dilution temperature decreased from 65 to 32 °C and the residence time was increased from 100 ms to 1 s. There was little influence on larger, accumulation mode size particles. This illustrates the extreme sensitivity of nanoparticle concentration to dilution conditions.\(^9\)

Ahlvik, et al. (1998): The effects of dilution ratio and residence time were compared over a series of tests using a light-duty chassis dynamometer and ELPI to measure the size distribution. The dilution ratio varied on average from 2.0 to 5.5 with a residence time of about 2 s. In this regime it was observed that number concentration increased slightly with higher dilution. The authors attribute this to coagulation, nucleation and condensation occurring in the dilution tunnel. However, a strong dependence on dilution ratio was not observed. This is probably because of the inability of the ELPI to measure particles < 30 nm, the long residence time, and the low dilution ratios.

Kauffeldt and Schmidt-Ott (1998): The study demonstrated the effects of a particle trap on a passenger car diesel engine exhaust. Figure 16 is the particle number concentration measured with and without the trap for an exhaust sample dilution of 1:12. Without the trap, the particle number count peaks in the accumulation mode size range at about 100 nm. The same engine operated under the same conditions with a filter shows the number concentration peak shifting to the nuclei mode size range between 10 and 30 nm. While operating with the particulate trap, the exhaust was heated and it was found that the nuclei mode number count decreased with increasing temperature until it disappeared at 175 °C, indicating the nuclei mode particles are composed of volatile materials.

These findings support the theory that an engine that emits low amounts of carbonaceous material with sufficient quantities of volatile hydrocarbons will form large numbers of volatile nuclei mode particles under the appropriate dilution and sampling conditions.

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\(^9\) The dilution air temperature varies between laboratories, generally lying between 20 and 30 °C as illustrated by the engine lab survey. It is desirable to use filtered dilution air and to record air temperatures before and after mixing with the exhaust. Humidity control also varies between laboratories, but it is desirable to record the humidity after primary and secondary dilution.
Kruger, Lüders, Luers, Kaufmann, Koch and Kauffeldt (1997) and Lüders (1997): This study also investigated the influence of exhaust gas aftertreatment and measurement conditions on particle size characteristics of exhaust from diesel engines. (This research is described in more detail in Supplemental Report No. 2.)

Number weighted size distributions were obtained using a differential mobility particle spectrometer (DMPS). Sampling was done from a dilution tunnel followed by secondary dilution. The authors suggest that their results are largely independent of secondary dilution process, although they said it had some influence. The secondary dilution ratio was usually about 10:1 and was obtained using an ejector diluter.

The engines tested were 3 l, indirect injection (IDI), naturally aspirated and 1.9 l DI, turbocharged and intercooled passenger car diesels and a 6.9 l, DI, turbocharged and intercooled truck engine.

- When a trap was used, the passenger car with the DI engine showed a significant decrease in particle number for particles > 50 nm, but a significant increase in particle number for particles < 50 nm.
- For the truck engine the particle trap again showed an increase in the number of particles < 50 nm, but a decrease in larger particles. The use of an oxidation catalyst also showed an increase in the number of particles < 50 nm, but this effect was time dependent.

To determine the nature of the < 50 nm particles the DMPS was modified so the < 50 nm particles could be analyzed separately. A heating element was integrated into the measurement system so the aerosol could be heated before passage into the DMPS. With this

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10 Not reported in the published literature. Based on personal communication with the authors. (Kittelson, 1997)

**Figure 16.** - Measured size distributions with and without particle filter (v = 120 km/h) at a dilution ratio of 1:12 for a passenger car (from Kauffeldt and Schmidt-Ott, 1998)
system, volatile particles evaporate and lose their charge, while solid or solid core particles retain their charge. Volatiles that nucleate upon cooling have no charge and are not detected. One potential problem is that some particles may pyrolyze in the heater.

This system was used to examine particles emitted from the different control devices. As temperature was increased the number of 6-12 nm particles decreased, when the truck engine and fiber coil were used at 2400 rpm, full load. A similar observation was made with the truck engine and oxidation catalyst. As the temperature was increased up to a approximately 175 °C, a decrease in the < 50 nm particles was observed. The authors conclude that the nuclei mode particles observed after the particle filter or oxidation catalyst consist entirely of volatile material that evaporates at 180 °C. The authors suggest that the material primarily consists of sulfuric acid droplets. The condensation effect is strongly dependent on the temperature and the partial pressures of the single components, which are affected by the dilution of the exhaust gas.

The effect of the dilution ratio was further characterized. For the truck engine running at rated power without a control device while the dilution ratio was varied from 12 to 32, no effect on the size distribution was observed. However, when the particle filter was installed an increase in the number of < 50 nm was observed at a 12:1 dilution ratio. However, when the ratio was increased to 19 and 32:1 the increase disappeared, as illustrated in figure 17. The dependence of nanoparticle formation on dilution conditions is consistent with findings from Abdul-Khalek, et al., 1998a.

The < 50 nm particles appear after the particle trap below a critical dilution ratio. The trap drastically reduces the mass and the number of particles available as condensation adsorption sites. This leads to the process of homogeneous nucleation of the exhaust gases and the creation of a large number of new particles not previously observed in the exhaust stream. The oxidation catalyst does not reduce the quantity of particulate material but can lead to an increase in the concentration of sulfuric acid in the exhaust gas, which leads to the same effect because of the change in the ratio of adsorption sites to condensing matter.

Compared to tunnel dilution, ambient dilution ratios may be much higher, therefore the authors question whether the < 50 nm particle increase would be observed under ambient driving conditions. However, it should be noted that dilution conditions found in a city are probably quite different from those encountered on-highway (at high speed) in that combustion particle concentrations are higher and are generated under different driving conditions. A number of measurements on and near roadways show a nuclei mode is present under real atmospheric conditions (Kittelson, et al., 1988, Weingartner, et al., 1997a, Harrison, et al., 1996).
Ash Constituents in Exhaust

Recent studies suggest that ash constituents in diesel exhaust may contribute to the nuclei mode. Ash constituents may come from contamination from lubricating oil or additives to the fuel and typically may account for more than 10% of exhaust particle mass (Cadle, et al., 1997; Williams, et al., 1987, 1989a and 1989b; Abbass, et al. 1987; Andrews, et al. 1993)

Abdul-Khalek, et al. (1998a) studied a 1995 DI diesel engine that exhibited both a nuclei and an accumulation mode in the number distribution of exhaust particles. They used a catalytic stripper to determine concentrations of solid and volatile particles in the nanometer size range. Although the results were somewhat uncertain they suggested that although most particles in this size range were volatile, solid particle were also present (this was later confirmed by Abdul-Khalek, et al., 1998b). The authors attributed the formation of the nuclei mode to the relative reduction of solid carbonaceous particle emissions compared to volatiles and the presence of ash constituents such as calcium, zinc, and magnesium. The ash components contribute to the nuclei mode either directly as nanoparticles themselves or by acting as heterogeneous nuclei for condensation of volatile hydrocarbons. They performed chemical equilibrium calculations and demonstrated that calcium compounds are gaseous at diesel combustion temperatures but should form solid compounds within the engine as the products expand and cool during the exhaust stroke.
With low carbon emission engines, the solid carbonaceous particles will not provide enough surface area to adsorb the ash constituents and relieve the metal supersaturation. The metals will nucleate to form solid nanoparticles that may serve as sites for heterogeneous nucleation of hydrocarbons and sulfuric acid.

*Mayer, et al. (1998)* studied metals as fuel additives to reduce particulate matter emissions from diesel engines. The metallic fuel additives included iron, copper, and cerium and were used as catalysts to oxidize carbon during combustion and on a passive particulate trap. When added without a particulate trap, the metallic additives reduced the total particulate matter mass emissions by about 10-15%. When used with a particle trap, the additives reduced total mass emissions of particulate matter by up to 90%.

However, the investigators also found that the engine out number emissions of nanoparticles increased, depending on the amount of metals added. Figure 18 shows the effects of metallic fuel additives on the number of nuclei mode particles emitted from a diesel engine. *There is a dramatic increase in nanoparticle emissions with the addition of the metallic fuel additives.* Because of this effect, the authors concluded that metallic fuel additives for soot emission reductions should not be used without a particulate trap that has the correct filtration characteristics to remove the fine particles.

![Graph showing nanoparticle emissions from a diesel engine using iron (satacen) as a fuel additive with and without a particle trap. (Mayer, 1998)](image_url)
Exhaust Sampling Conditions

Relative Humidity and Temperature of Dilution Air

Recent studies have investigated the impact of the relative humidity and temperature of the air used to dilute diesel exhaust during sampling for particle measurement or in the environment for on-highway studies.

Weingartner, Burtscher, and Baltensperger (1997b) performed a fundamental study on the hygroscopic properties of diesel particles. The study included generating diesel particles under different engine conditions, conditioning the particles to change their hygroscopicity, and then varying the relative humidity and measuring the effects on particle size and number. Results included:

- When particles were dried, exposed to higher humidity and then re-dried, they shrank with subsequent exposure to higher humidity levels.
- When particles were not dried, they grew with increasing relative humidity.
- When particles were not dried and the fuel sulfur concentration was increased, more growth of the exhaust particles with increasing relative humidity was seen.
- Particles generated under idle conditions shrank with increasing relative humidity even with high sulfur fuel. Investigators attributed this to increased organic fraction of particles generated at idle acting as a barrier to water.
- Particles generated under load that were treated with ozone and ultraviolet light formed a bimodal number distribution with the new peak in the nuclei mode at about 30 to 40 nm.
- When a filter was used to remove the diesel particles and the remaining gas phases were treated with ozone and ultraviolet light, a nuclei mode of particles appeared with the peak also at about 30 to 40 nm. The investigators believed gaseous constituents were nucleating to form nuclei particles.
- When the exhaust was not treated and no filter was used, the exhaust had a single peak at about 90 nm in the accumulation mode size range.

These results demonstrate that particle composition including organic fraction and sulfur, particle hygroscopic properties, and the relative humidity of the aerosol in the environment or laboratory dilution conditions may change the measured exhaust aerosol properties. Testing conditions for this study were not representative of dilution conditions of diesel exhaust in an on-highway setting. However, changes in particle number and size measured with changing relative humidity and particle hygroscopic properties indicate humidity in the environment or dilution air in a laboratory setting could play a role in affecting diesel exhaust particle formation and transformation.

Shi and Harrison (1997) also reported finding effects of relative humidity of dilution air on particle number concentration and size. Increasing dilution air humidity increased the peak diameter of the particle number concentration and total particle number and volume concentrations. (These results are currently unpublished and were presented at a nanoparticle measurement workshop. No further details were provided.)
Kreso, et al. (1998a,b) looked at the effect of relative humidity of the dilution air on the nucleation of condensable sulfur species in two low sulfur (0.031% wt. sulfur) fuel diesel engines. The relative humidity in the sampling dilution tunnel of these tests was varied from 10 to 30%. No significant effect was observed on the particle number and volume concentrations with the varying humidity levels. The authors concluded that the nuclei mode particles from the low sulfur diesel engines tested did not consist primarily of condensable sulfur species (H$_2$O-H$_2$SO$_4$ particles) that would respond to changes in relative humidity.

Although there is evidence that the relative humidity of a diesel exhaust aerosol may affect the particle characteristics, these effects have not been conclusively demonstrated. Further work to determine the impact should be performed.

Dilution Ratio and Residence Time

Other issues should be considered if nanoparticle emissions are a concern. If these particles are primarily composed of volatile materials they are formed as the exhaust dilutes and cools. For most of the engines and fuels tested at the University of Minnesota, nuclei mode particles appear to be mainly volatile. The only exception to this was observed when the use of metallic fuel additives caused the formation of a large, solid nuclei mode. (Du, et al. 1998; Kittelson, et al., 1978) The number formed depends primarily upon the dilution ratio and residence time. Atmospheric dilution should be simulated to obtain measurements representative of real-world conditions. Furthermore, volatile particles may have different health impacts than solid carbonaceous particles.

Formation of nanoparticles during the dilution process has been seen to be a highly non-linear function of dilution ratio, temperature and residence time. From figure 9 it can be seen that the time spent in the critical dilution ratio range of 5 - 50:1 is about 0.25 s.$^{11}$ This is near the lower end of residence times used in laboratory dilution systems, so that one might expect that laboratory conditions might often tend to overestimate nanoparticle formation. However, many measurements made in the atmosphere over roadways show large concentrations of nanoparticles. This suggests that roadway dilution conditions may lead to nanoparticle formation.

Concentrations of nanoparticles over roadways are high enough that coagulation is likely to cause nanoparticles to grow quickly into the accumulation mode size range (Harrison, et al., 1996). The character of these agglomerates will depend upon whether the nanoparticles are solid or volatile. Because of coagulation, the highest number concentrations and exposures to nanoparticles will occur on or near roadways where particles are fresh.

$^{11}$From the engine lab survey it can be seen that the residence time from the tailpipe to the primary dilution tunnel varies considerably based upon the engine and duty cycle. Times range from 0.015 - 4 s with longer rather than shorter times being more common. Reported primary dilution ratios are within the critical range of 5 - 50:1. Long residence times within the critical dilution range favor the formation of nanoparticles.
Current emission standards are mass based. Particulate matter mass tends to be conserved during the dilution and sampling process. Some gas-to-particle mass transfer occurs during dilution so that the mass of SOF collected depends upon dilution ratio (Kittelson and Johnson, 1991). However, for the range of dilution ratios typically used, this effect does not change the total collected mass significantly. Temperature also changes and this affects adsorption. On the other hand, even a small amount of mass transfer by homogeneous nucleation can have an enormous effect on the number concentration and number-weighted size distribution. Furthermore, coagulation, which conserves mass, may significantly change the number concentration and size distribution. Homogeneous nucleation and coagulation are highly nonlinear and sensitive to small changes in the dilution process. Thus, any changes in, or additions to, current mass based emission standards to include size or number concentration measurements will lead to significant sampling and measurement challenges.

Conclusions

It can be seen from the preceding discussion that test laboratory procedures including the conditions of the dilution air and the amount and rate of dilution can greatly affect the nature of the sampled exhaust. In addition, the availability of particle surface area for adsorption and the quantity of volatile material in the emitted exhaust may also change the number and size of the sampled particle emissions. **In summary:**

- dilution ratios in the critical range of 5 to 50 may promote the formation of a nanoparticle mode as particles nucleate as the exhaust is cooled
- the role of relative humidity in dilution air is not fully understood
- the lack of carbonaceous material surface area in modern diesel engines for adsorption of volatile compounds may allow saturation ratios to become high enough to favor nucleation and the creation of a large nanoparticle number mode
- non-carbonaceous material in the exhaust such as metals or sulfuric acid may act as nucleation sites for heterogeneous nucleation of volatiles, even in the presence of carbonaceous material
- temperature residence time in the critical dilution ratio range can markedly affect the production of nanoparticles.

RECOMMENDATIONS

Understanding diesel aerosol emissions and behavior is critical if meaningful regulations are to be set. General recommendations for laboratory diesel aerosol measurement are made below. These recommendations are intended to promote measurement repeatability between testing facilities and to assist laboratories in defining critical measurement system parameters. Future research may be required to implement these recommendations effectively. Each of these recommendations is discussed in more detail elsewhere in the Supplemental Reports.

- **Treatment of emissions sample**
  - carefully temperature and residence time in critical dilution ratio range (5 – 50)
  - minimize residence time after final dilution
  - engine to tunnel lines should be similar in temperature to exhaust pipe
• **Treatment of sample dilution air**
  - filter to remove ambient particulate matter
  - control temperature
  - control humidity

• **Emission sampling lines**
  - minimize heat transfer in sampling lines
  - use conducting lines to minimize electrostatic losses
  - minimize sampling line length

• **Aerosol measurement instruments**
  - avoid using instruments outside reliable measurement range (i.e. below a certain particle size or above a particle concentration)
  - be aware that instruments may have different capabilities when operated in different modes
  - errors associated with incorrect dilution and sampling may be much larger than those associated with misapplication of an instrument

• **Meticulous reporting of testing conditions**
  - fuel properties including sulfur content
  - lubricating oil properties including metal content
  - history of engine and sampling system conditioning
  - dilution air treatment
  - dilution ratios (including any final dilution for instrument concentration requirements)
  - sampling line residence time at each dilution ratio
  - order of testing at different operation modes

Specific guidelines on dilution ratios, dilution rates, residence times, temperatures, humidity, aerosol measurement instrumentation and other details related to sampling protocol are more difficult to provide at this time. Research is ongoing to clearly define the impact these factors have on the diesel aerosol size distribution. However, before specific sampling protocols are recommended sampling priorities must be established. Sampling protocols which produce aerosol size distributions similar to those found in the ambient atmosphere may not be the same as those needed to simply compare emissions between engines or to establish mass emission rates. Sampling should allow characterization of the parameters of greatest importance. These parameters include particulate matter mass, number, surface area, chemical composition of particles and exhaust gases. Unfortunately, their relative importance is not known. Sampling to determine one parameter may bias result for another. Clearly, sampling priorities must be established and it is likely that as a result, multiple test protocols will be required.

**SPARK IGNITION (SI) MEASUREMENTS**

Uncertainty exists regarding the relative contribution of atmospheric aerosol from SI and diesel exhaust in real-world conditions. Diesels emit more particulate matter on a fleet average, gram-per-vehicle mile mass basis, but because SI vehicles, at least in the U.S.,
account for most of the vehicles operating on-road, the direct PM emissions from SI engines may be more important. The Northern Front Range Air Quality Study (NFRAWQS) recently addressed this issue.

In addition, several recent studies have determined the number size distribution from SI exhaust. These studies are briefly described primarily to provide a comparison between gasoline and diesel fueled engines.

_Cadle, et al., (1998) and Watson et al., (1998):_ The goals of the NRRAWQS study were to:

- Attribute the existing air pollution in the Denver urban region to a source or source category;
- Collect data necessary to support informed decisions leading to attainment of Federal air quality standards.

Specific objectives included:

- Apportion carbonaceous material in airborne particles to sources;
- Determine the extent to which the Denver area is ammonia-rich (or anion-deficient) with regard to the formation of secondary ammonium nitrate and ammonium sulfate;
- Apportion sources leading to the formation of non-carbonaceous portion of PM$_{2.5}$ with emphasis on nitrate and sulfate.

The NRRAWQS found that vehicle exhaust was the largest PM$_{2.5}$ total carbon (TC) contributor, constituting about 85 % of PM$_{2.5}$ carbon at sites in the Denver metropolitan area. Sources with emissions similar to light duty gasoline vehicles contributed about 60 % of PM$_{2.5}$ TC at urban Denver sites, and these contributions were 2.5 -3 times the diesel exhaust contributions. Emissions were particularly high during cold, cold starts and from vehicles identified as “smokers”. However, diesels contributed the largest share of the elemental carbon at these locations.

_Maricq, Podsiadlik and Chase, (1998):_ This study, conducted at the Ford laboratory, compared emissions from a variety of recent model gasoline engines and one European diesel engine. The SMPS and ELPI were used to obtain size distribution data. Distributions were built from repeated cycles using the ELPI or SMPS and CNC over a fixed size range. This was necessitated due to the relatively slow response time of the SMPS when used in the scanning mode. Size distributions derived from the two methods were consistent.

Exhaust flow rates ranged from 0.1 m$^3$/min at idle to 2.5 m$^3$/min during heavy acceleration and transfer residence times ranged from 7 s to 0.4 s. The tunnel operated at constant total flow and the instantaneous dilution ratio varied from 120:1 at idle to 2.5:1 at heavy acceleration. For about 25 s during the FTP the dilution ratio fell below 5. The residence time in the dilution tunnel was about 3 s. The exhaust of the diesel engine was further diluted by a factor of 9 using an ejection pump.

Measurements were reported over the 3 phases of the FTP cycle. Mass emission rates were low for all engines (<2 mg/mi particulate matter). The number weighted mean diameter ranged from 35 - 65 nm with the range for mass mean diameter shifting to 100 - 300 nm. For the diesel and direct injection spark ignition (DISI) engines the number mean diameter was
somewhat larger, 60 - 70 nm. The mass and number of particles are much lower for the spark ignition engines compared to the diesel and DISI engines. DISI emissions are about 20 mg/mi. and $10^{14}$ particles per phase compared to 1 mg/mi and $10^{12}$ particles per phase for conventional gasoline engines. The diesel engine emissions were higher, about 80 mg/mi and $10^{15}$ particles per phase.

**Greenwood, Coxon, Biddulph and Bennett (1996):** Emissions from two diesel (IDI no catalyst and turbocharged with catalyst), three gasoline and two compressed natural gas (CNG) vehicles were evaluated using an SMPS to determine aerosol size distributions with the focus on the number distribution. Exhaust was diluted about 20:1 in a 0.20 m diameter tunnel with a total flow rate of 9.2 m$^3$/min. Engines were operated on a chassis dynamometer at constant speeds representative of the European emissions drive cycle. Speeds ranged from idling to 120 km/h with loads ranging from 0.0 to 16.0 kW.

The aerosol size distributions from all three engine types appeared to have a lognormal form; thus the peak maximum number concentration was lower in diameter than the mean diameter. The measured peak number concentration for the diesel vehicles under load ranged from 70 - 90 nm for the IDI engine and 50 - 60 nm for the turbocharged engine. At idle these were 32 and 46 nm, respectively. The gasoline fueled vehicles produced lower particle concentrations at low and medium power. At higher loads a range of peak number concentration was observed between 20 and 30 nm. At the highest load condition the total number concentration for the IDI engine was $2.4x10^7$ and for the turbo it was $5.3x10^6$. The three gasoline fueled vehicles had total number concentrations of $2.58x10^4$, $4.23x10^6$ and $1.61x10^7$ at the high load condition. Much lower number concentrations were produced at the medium and low power test conditions.

**FUTURE RESEARCH**

Research is recommended in the following areas:

- The diesel aerosol size distribution (mass, volume, number and surface area) must be determined under real-world (roadway dilution) conditions using a variety of heavy and light-duty engines operated under varying load and speed conditions in the city and on the highway using state-of-the-art instrumentation.
- Diesel aerosol generated under conditions representative of real-world dilution must be chemically characterized based on particle size.
- A variety of fuels must be evaluated, including low sulfur and zero sulfur fuel.
- The sensitivity of particle generation in diluting exhaust plumes to dilution ratio, dilution rate, temperature, and humidity should be evaluated.
- Particle transformations that occur as the plume disperses downwind of the roadway under typical urban and highway situations must be measured.
- The species and mechanisms involved in nucleation during dilution should be identified.

Appropriate engine and chassis dynamometer laboratory techniques that result in diesel aerosol measurements similar to ones obtained under real-world dilution conditions need to be
developed and evaluated so that future regulatory decisions are based upon data that are not biased by artifacts created in the laboratory.

The fundamental goal should be to develop laboratory methods to measure diesel aerosol size distributions and chemical characteristics in the laboratory that result in data that are similar to those measured under roadway conditions. These methods must yield results, which are repeatable within labs and enable inter-laboratory comparison. This entails a fundamental understanding of aerosol formation, transformation and measurement, and the processes that have a major effect on the aerosol size distribution such as dilution, nucleation, condensation adsorption and coagulation.

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12 Combined bibliography from Supplemental Reports 1 and 2


