REVIEW OF DIESEL PARTICULATE MATTER SAMPLING METHODS

Supplemental Report # 2

AEROSOL DYNAMICS, LABORATORY AND ON-ROAD STUDIES

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ABSTRACT

This report reviews fundamental aerosol dynamics as well as on-highway and laboratory studies that have focused on determining the size distribution of diesel aerosol. It is the second supplemental report to the final project report prepared for the Environmental Protection Agency (EPA) grant titled “Review of Diesel Particulate Matter Sampling Methods”. This report is a revised version of a previous project report and is an accompaniment to Supplemental Report No. 1, titled “Diesel Exhaust Particle Measurement Instruments” (Kittelson, et al., 1998a) and the final project report (Kittelson, et al., 1998b).

INTRODUCTION

Measurements of diesel aerosol are 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 emissions.

The first quarterly report for this project (EPA Supplemental Report No. 1) described and characterized instruments used to measure diesel aerosol. This report focuses on the fundamental chemical and physical processes that affect diesel aerosol size distribution measurements and presents data from laboratory, occupational, and ambient studies that reflect the types of size distributions obtained under different conditions.

Part I provides an overview of diesel aerosol chemical and physical characteristics. Part II provides the theoretical background of aerosol behavior and a description of processes that affect measurement of diesel aerosol. Part III illustrates how various parameters influence the size distribution of aerosol particles obtained under different experimental and real-world conditions.

PART - 1

Diesel Aerosol Composition and Structure

To understand the impact of aerosol processes, the chemical and physical nature of diesel exhaust must be understood. The composition, size, and concentrations of diesel aerosol and the amount of volatile organics, sulfur compounds, and ash material will affect both the measurement of the exhaust and the impact of aerosol processes on the exhaust during sampling and measurement.


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 1. - Typical structure of engine exhaust particles (Kittelson, 1998)

Figure 2 shows typical composition of the particulate matter for a current technology diesel engine tested using the U.S. Heavy Duty Transient Test. The sulfuric acid/sulfate fraction is roughly proportional to the fuel sulfur content. The fraction associated with unburned fuel and lube oil (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.
Aerosol Size Distribution

Figure 3 shows the idealized diesel aerosol number and mass weighted size distributions (Kittelson, 1998). 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 consists of volatile organic and sulfur compounds that form during exhaust dilution and cooling, along with solid carbon and metal compounds from the combustion process. The nuclei mode typically contains 1 - 20% of the particle mass and more than 90% of the particle number. The accumulation mode ranges in size from 50 - 1,000 nm and contains the majority of particle mass. 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 nano-particles D < 0.05 µm or 50 nm. Definitions of ultrafine and nano-particles 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 nano-particles.
Figure 3. - Typical engine exhaust size distribution both mass and number weightings are shown (Kittelsson, 1998).

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 μm, 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 μm 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 μm 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 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 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. - Schematic illustrating 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.
PART - 2

Diesel Particle Dynamics And Behavior

It is critical to understand the nature and relative influence of processes affecting diesel exhaust components to understand why important differences may exist between diesel aerosol measured in the atmosphere and in the laboratory. The following is a discussion of processes controlling diesel aerosol behavior with an emphasis on nano-particle formation and dynamics and the link between atmospheric diesel aerosols and what is seen in a test cell environment.

Many of the processes affecting the formation, behavior, and measurement of diesel aerosols are discussed in the literature and are fundamental topics in numerous aerosol physics text books. They are briefly summarized here. These processes include: condensation / adsorption, evaporation / desorption, coagulation, particle losses in sampling systems, and chemical reactions. The relative importance of each process for atmospheric and laboratory diesel aerosol behavior is described. In addition to these more fully understood mechanisms, a developing view of nucleation and the effects of dilution ratio and residence time on particulate behavior is presented. The role of nucleation, dilution ratio and residence time have come to the forefront due to recent findings of nano-particle formation from current diesel engines.

The underlying principles of aerosol behavior are presented in this section. They will provide a background for the more in-depth discussion in the following sections on measured diesel aerosols with applications of the theories to observed behavior.

A. Particle Size Regimes

The processes affecting particles described in the following sections are controlled by aerosol and system characteristics. The aerosol particle diameter and its size relative to the gas molecular free path is one of the critical parameters in determining the significance of the various particle processes affecting aerosol behavior. Diesel aerosols have historically been measured into the micron and sub-micron ranges where the particle size is large compared with the gas molecular free path. As diesel particle measurements extend down into the nanometer range particle, the interaction of individual gas molecules with the particles becomes increasingly important.

Particle size affects how particles interact with the surrounding medium as well as the role of different particle processes. As the particle size decreases, the air can no longer be treated as a continuous fluid and is considered as individual molecules colliding with the particles. The mean free path is defined as the average distance traveled by a gas molecule between successive collisions.

\[ \lambda = \frac{c}{n_z} \]

where:
\[ c = \text{mean molecular speed} \]
\[ n_z = \text{rate of molecular collisions} \]

for air at 1 atm, 20 °C \( \lambda = 0.066 \mu m \)
Aerosol behavior is categorized by the particle size relative to the molecular free path. Three different regimes have been defined for when the particle size is much smaller than, on the order of, and larger than the molecular free path.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Condition</th>
<th>Description</th>
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<tr>
<td>Free Molecule Regime</td>
<td>$D_p \ll \lambda$</td>
<td>Gas acts as a series of discrete collisions with particle</td>
</tr>
<tr>
<td>Continuum Regime</td>
<td>$D_p &gt; \lambda$</td>
<td>Gas acts as a continuous fluid</td>
</tr>
<tr>
<td>Transition Regime</td>
<td>$D_p \approx \lambda$</td>
<td>Behavior has components of both free molecule and continuum regimes</td>
</tr>
</tbody>
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The relation between particle diameter and the fluid surrounding the particles will be illustrated in the particle process described below.

### B. Particle Dynamics and Particle-to-Particle Processes

Particles may be lost traveling through a sampling system due to inertial impaction, thermophoresis, diffusion, and deposition on electrically charged sampling system surfaces. These processes have been presented extensively elsewhere in the literature and will only be described briefly here. The particle-to-particle process of coagulation will also be presented in this section.

Particle-to-particle processes that lead to losses in an exhaust and sampling system include:

- Thermophoresis
- Diffusion
- Coagulation
- Inertial Impaction
- Electrostatic Deposition
- Chemical Reactions

#### B.1. Thermophoresis

Thermophoresis is the motion of a particle from asymmetrical forces that arise from a temperature gradient. The asymmetry of the force arising from a temperature gradient is very weak, but the mobility of the diesel particles is high enough to make this process important. Although the importance of thermophoresis increases as particle diameter decreases with the greatest impact on particles in the free molecule regime, it plays a role with all but the largest diesel particulates. (Hinds, 1982) Where most of diesel aerosol resides it is mostly size independent.

The thermophoretic motion of particles down a temperature gradient is a result of more vigorous gas collisions with the particle on the high temperature side. The importance of thermophoresis increases for systems with exhaust and sampling lines with cool walls that promote thermophoretic deposition. Deposition of soot particles to cylinder and exhaust walls and sampling lines has been attributed to a thermophoretic process. Thermophoretic forces cause soot to form a layer on the cool cylinder walls. High velocities during blowdown cause high shear forces that strip the soot off the walls. Reentrainment of deposited soot into the exhaust is unpredictable and may account for as much as 20-45% of the measured soot mass. (Kittelson, et al. 1990)
For small particles in the free molecule regime (nano-particles), the thermal force from a temperature gradient results from more energetic gas molecules colliding with the hotter side of the particle thus imparting a greater momentum force to that side compared to the colder side. The thermal force and resulting particle motion follow the decreasing temperature gradient. Figure 6 illustrates the thermal force acting on the particle arising from a temperature gradient in the aerosol.

![Diagram of thermal force on a particle](image)

**Figure 6. - Thermophoresis from a temperature gradient**

For larger particles in the continuum regime, thermal forces still act on the particle, but the temperature gradient in the gas around the particle is influenced by a temperature gradient in the particle itself. The temperature gradient set up in the particle is a function of the particle conductivity.

The thermal velocity induced by the thermal forces can be determined for both continuum and free molecule regime particles. For the small free molecule regime particles, the thermal velocity \( V_{th} \) is a function of the gas viscosity and density, the temperature gradient and the particle temperature.

For particles in the continuum regime where resistance from the continuous fluid counteracts the movement from the thermal forces, the thermophoretic velocity can be calculated based on equating the thermal force to the drag force also acting on the particle.

Table 1 shows the relative effect of thermophoresis for different size particles from 10 nanometers to 10 µm.
Table 1. Terminal settling and thermophoretic velocity in a unit temperature gradient at 20 °C (Hinds, 1982 table 8.2, p. 157)

<table>
<thead>
<tr>
<th>Particle diameter, µm</th>
<th>Terminal settling velocity, cm/s</th>
<th>Thermophoretic velocity(a), cm/s</th>
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<tr>
<td>0.01</td>
<td>6.7 x 10^{-6}</td>
<td>2.8 x 10^{-4}</td>
</tr>
<tr>
<td>0.1</td>
<td>8.6 x 10^{-5}</td>
<td>2.0 x 10^{-4}</td>
</tr>
<tr>
<td>1.0</td>
<td>3.5 x 10^{-3}</td>
<td>1.3 x 10^{-4}</td>
</tr>
<tr>
<td>10.0</td>
<td>3.1 x 10^{-1}</td>
<td>7.8 x 10^{-5}</td>
</tr>
</tbody>
</table>

\(a_k_p = 10kp_a\)

B.2. **Diffusion** of particles can occur from both Brownian motion and the movement of particles down a particle concentration gradient. Particles may be lost by diffusion through the boundary layer to the walls of the sampling system. The diffusion coefficient of a particle varies inversely with particle size with smaller particles diffusing more quickly than larger particles. Loss of particles by diffusion to the walls is much faster in highly turbulent flows which have thin boundary layers, and consequently, high mass transfer coefficients. (Kittelson, 1990)

Diffusion is most important for particles smaller than about 0.05 µm in diameter. Diffusional losses for a representative diesel exhaust aerosol were calculated (Kittelson, 1990) based on turbulent mass transfer to a pipe. Diffusional losses for 0.03 µm and 0.30 µm were found to be less than 0.2%.

B.3. **Coagulation** is the process of agglomeration from particle to particle collisions. Small particles may grow by collision with larger particles or with one another. Coagulation changes the size of particles, but does not change the total particle mass concentration. (Kittelson and Dolan, 1980). Thus it will not directly influence the results of certification tests that measure the particulate mass output from diesel engines. However, it is important to take coagulation into account when attempting to understand particle formation mechanisms. Furthermore, since coagulation changes particle size, it will indirectly influence size dependant loss mechanisms. The amount of coagulation which takes place will depend on the ratio of the residence time to the characteristic time for coagulation. The latter is inversely proportional to particle concentration, and thus dilution ratio.

B.4. **Inertial Impaction** arises from the inability of particles to follow fluid streamlines as a result of their inertia. Particles may be preferentially excluded or included from a sampling stream or lost to the walls by inertial impaction. Non-isokinetic sampling errors and particle deposition in bends and contractions will affect the indicated particle measurements. Particles that are deposited through inertial impaction may also be reentrained into the exhaust stream in an unpredictable manner.

The importance of these effects depends upon the particle diameter and is generally small for particles in the submicrometer diameter range characteristic of diesel particles. However, about 10% of the mass of particles emitted by diesel engines consists of particles larger than 1 µm in diameter. (Vuk, 1976) For these larger particles, even a small loss from inertial impaction can represent a relatively large loss in particulate mass. In addition to mass loss, the accumulation of
particles on sampling line walls can be reentrained in an intermittent and unpredictable manner and lead to significant mass measurement variability. Reentrainment is much more important than mass loss because of its unpredictable nature and the variability it introduces into size distributions.

**B.5. Electrostatic Deposition** can occur in sampling systems where sample transfer lines are made of a material that can be electrically charged. Diesel particles are naturally charged as a result of the combustion process. If a sample line carrying the diesel particles is charged, the resulting electric field will drive a portion of the charged diesel particles to the walls where they will be removed from the gas stream.

Approximately 85% of diesel particles are charged with larger soot particles more likely to be charged than smaller nuclei mode particles. (Kittelson, et al, 1986 and Johnson, 1993) The electrical mobility of charged particles increases with increasing particle diameter, thus larger particles are more likely to experience electrostatic loss in a transport line. On the other hand, small nuclei mode particles in diesel exhaust have the highest velocities and are less likely to carry charge, thus they are less likely to experience electrostatic loss in an aerosol transport line.

**B.6. Chemical Reactions**

Diesel exhaust aerosol may undergo a complex variety of atmospheric photochemical reactions. These are beyond the scope of this report but a summary of these reactions was prepared by Winer and Busby, in 1995, for the Health Effects Institute.

**C. Gas-to-Particle Conversion**

One of the important parameters to consider in characterizing diesel aerosol is the amount and fate of volatile organics. Volatile organics are associated with the smallest diesel exhaust particles (nano-particles) and recent research has focused on understanding processes that affect the fate of exhaust hydrocarbons.

Volatile organics may remain as gaseous organics (disregarding the use of a catalytic converter) or may undergo gas-to-particle conversion to form the soluble organic fraction (SOF - the extractable fraction of diesel particulate matter). As engine exhaust is diluted and cooled, SOF may move from the gas phase to the particle phase by two paths: adsorption on existing particles or nucleation to form new particles. [Alternatively, in the presence of sunlight and other atmospheric chemical processes or physical processes such as dilution, some particulate material may return to the gaseous state.]

Adsorption of SOF 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 almost entirely of SOF will leave the accumulation mode particles unaffected, but may cause a dramatic increase in the number nano-particles in the nuclei mode.
The theory behind these two competing processes will be presented in this section. Exhaust sampling conditions that will affect these gas-to-particle conversion mechanisms will be discussed in Section D.

C.1. Adsorption / Desorption

Adsorption is the process of the adherence of molecules onto an adsorbent. In diesel exhaust, volatile organics will adsorb onto diesel particles. While condensation requires a supersaturated state to occur, adsorption can occur with the adsorbate at pressures well below saturation.

The amount of organics adsorbed or condensed on diesel particles depends on:
1) the saturation ratios for the various organic species
2) the amount of diesel aerosol surface area available for adsorption
3) adsorption energy
4) time for adsorption to occur

The saturation ratio is defined as the partial pressure of the gaseous organic species divided by the saturation pressure of the same organic species. When a vapor is at the saturation pressure, it is in equilibrium with the condensed phase and the amount of organic condensing and evaporating will be equal. (Hinds, 1982) If a vapor is supersaturated, \( S > 1.0 \), then it will condense. Condensation may take place at \( S < 1 \) for multi-component droplets. The saturation ratio also controls the extent a vapor will adsorb on an adsorbate material. The adsorption of diesel exhaust organics onto particles can be modeled using the conventional adsorption models described by the Langmuir and by Brunauer, Emmet, Teller isotherm (BET) isotherms. The models are referred to as isotherms because temperature is held constant for the adsorption process model.

There must be surface area available from existing particles for adsorption. As adsorption of hydrocarbon (HC) in diesel exhaust begins, vapor molecules form a single molecular layer by physically binding to surface sites available for attachment. If adsorption continues after the initial layer is formed, more layers of HC will adhere to the particle in a process which increasingly resembles condensation.

The Langmuir isotherm model of adsorption is based on single-layer adsorption and uniform energies of adsorption. The Langmuir isotherm adsorption pattern is illustrated in figure 7. Adsorption of organic material on diesel particles is increased by increasing \( S \) until a complete monolayer of adsorbate is formed on the adsorbent surface. Once the sites available on the surface are filled, no further increase in adsorption occurs with increasing \( S \) and the curve in figure 7 flattens out.

The BET isotherm is illustrated in figure 8. The BET model allows multiple layers to be formed, and also assumes uniform energies of adsorption for each layer of molecules. The figure shows generalized regions for the adsorption pattern: Region I \( S = 0 - 0.1 \) promotes monolayer adsorption; Region II \( S 
\approx 0.1 - 0.8 \) increasing \( S \) has little effect on additional adsorption; Region III \( S 
\approx 0.8 - 0.9 \) promotes multi-layer adsorption. For values of \( S \) greater than about 0.9
adsorption resembles condensation and as $S$ approaches and exceeds 1.0 supersaturation leads to condensation.

Figure 7. - Langmuir isotherm - Effect of saturation ratio on adsorption and condensation single layer adsorption

Figure 8. - BET Isotherm - Effect of saturation ratio on adsorption and condensation multiple layer adsorption
Both models have been applied to the adsorption of diesel exhaust organics onto diesel particulate matter. Because the behavior of HC adsorption on diesel particles has not been rigorously investigated, it has historically been modeled using representative HC and activated carbon. (Clerc, et al., 1986, Johnson, 1993 and Barris, 1981)

Adsorption of SOF onto diesel aerosol is a physical process, not a chemical binding of the HC to the particle surface. If saturation ratio values were to decrease, as during continued dilution of the exhaust, the SOF may desorb from the particle surfaces and return to gaseous form.

C.2. Nucleation / Condensation

If saturation ratios are sufficiently high, new particles may form by nucleation of gaseous organic species. This is even more likely if there is insufficient particle surface available in the exhaust for extensive adsorption. During nucleation, a forming particle must reach a critical diameter before stable growth will begin. Once the particle has reached sufficient size, the particle will continue to grow by condensation as long as the species is not below saturation.

Nucleation is responsible for the formation of the nuclei-mode particles measured in diesel aerosol. The nuclei mode is frequently observed when diesel exhaust is rapidly diluted under either atmospheric or dilution tunnel conditions. (Dolan, 1975) 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.

Nucleation of SOF in diesel exhaust may occur by two paths: homogeneous nucleation and heterogeneous nucleation. In homogeneous nucleation or self-nucleation, vapor molecules form molecular clusters that form and disintegrate even for unsaturated species. If the vapor is sufficiently supersaturated, the clusters will be sufficiently large to allow condensation. The cluster will grow into a particle and will continue to increase in size as long as supersaturation continues.

Heterogeneous nucleation is also called nucleated condensation and occurs when there are nuclei already available in the exhaust. Heterogeneous nucleation can occur at supersaturation values of just a few percent. Heterogeneous nucleation can occur at much lower saturation values than homogeneous nucleation because of the high supersaturation values required for the formation of the homogeneous nuclei from vapor molecules.

It has been observed in diesel exhaust that volatile organics are nucleating and growing 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.

Heterogeneous nucleation of H$_2$SO$_4$ plays an important role and will be discussed in the final report.
C.3. Condensation / Evaporation

Condensation can be viewed as an extension of nucleation and adsorption. In the case of adsorption, as saturation ratios approach and exceed saturation, continued addition of the organics to the particles comes by condensation. For nucleation, the initial formation of a droplet or particle is through nucleation of molecules or ions, but once the critical diameter is reached, growth continues by condensation and requires a supersaturated state of the condensing species. If the saturation ratio falls below saturation as may occur with high levels of exhaust dilution, condensed species will evaporate and the particles will decrease in size or disappear.

D. Effects Of Testing Conditions on Measured Particulates

The conditions diesel aerosol experiences after leaving the engine tailpipe coupled with the characteristics of the engine emissions will influence the nature of the measured aerosol.

The theory behind the important processes affecting the behavior of diesel emissions was presented in the preceding sections. Specific processes affecting diesel aerosol formation and transition depend on the nature of the exhaust and the conditions during measurement. This section will discuss how an exhaust measurement system and strategy will affect the aerosol being measured. Because conditions vary so greatly in diesel exhaust testing, it is critical to understand how sampling and test conditions may affect the nature of the diesel aerosol being measured.

The key environmental or test parameters that have been identified include:
- dilution ratio and the resulting saturation ratio
- the time the particles spend at varying dilution ratios
- humidity

The characteristics of the engine emissions that will also have a role in affecting the measured aerosol include:
- size, number, and composition of particles emitted from the engine
- composition and quantity of exhaust volatile constituents

D.1 Dilution Ratio

To interpret diesel aerosol measurements and to reproduce environmental aerosol conditions in the laboratory, it is necessary to understand how dilution ratio affects the critical parameter of saturation ratio and the resultant processes that may occur. The dilution and conditions of a diesel exhaust aerosol in the laboratory can vary between facilities, from test to test and can be vastly different than the dilution observed under atmospheric on-highway conditions. The size, mass, and composition of particulate matter generated from the same engine may markedly differ when evaluated under on-highway as opposed to laboratory conditions.

Section C introduced the parameters that affect the gas-to-particle processes of adsorption/desorption, condensation/evaporation, and nucleation. In a diesel exhaust measurement system, dilution ratio will be extremely important in determining the aerosol
temperature and saturation ratios for the volatile organic species. This section will relate the dilution ratio to the resulting particle processes that may occur.

D.1.1. Exhaust Sampling System Dilution

U. S. Environmental Protection Agency guidelines for diesel exhaust sampling systems are given in the Code of Federal Regulations, Number 40, Part 86. Rules for measuring exhaust particulate mass by collection on a filter and continuous monitoring of exhaust hydrocarbons are specified. The temperature of the exhaust sample immediately upstream of the primary particulate filter is specified to be 125°F (51.7°C) or less. Temperature of the diluted exhaust gas sample for hydrocarbon measurement is specified at 375°F +/- 10°F (191°C +/- 10°C).

Only the temperatures of the exhaust samples are specified. The temperatures may be achieved by a single dilution or by a two-step dilution and some test facilities may use additional dilution before particle measurement instruments that require lower particle concentrations. There are no established guidelines for the amount of dilution at each step or the residence times of exhaust at the various dilution ratio values. A minimum residence time after dilution is specified for equilibrium purposes although no dilution ratio is specified in the regulation.

Appendix 1 in the first supplemental report (Kittelson, et al., 1998a) presents results from a questionnaire completed by different diesel research laboratories and visits to several diesel labs in the U.S. by Drs. Kittelson and Johnson. As can be seen in the table, the amount of dilution and the duration of sample transfer time varies greatly among the laboratories. As the importance of dilution ratio on the aerosol behavior becomes more evident, it also becomes more important to be able to account for the variance in sampling conditions and the resulting measured particles.

Figure 9 illustrates a typical exhaust sampling set-up based on the federal requirements.
D.1.2. Effects Of Dilution Ratio

Most of the material that becomes SOF is in the vapor phase in the exhaust and substantial gas-to-particle conversion takes place during dilution and sampling. When volatile HC in the exhaust nucleates, a significant increase in nuclei mode aerosol particles is observed and/or an increase in adsorbed SOF on accumulation mode aerosol particles causes their size and mass to increase. The fate of the hydrocarbons is affected by roadway atmospheric dilution or laboratory dilution strategy. 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.

In the preceding discussion of adsorption in Section C, figures 7 and 8 show the saturation ratio as a driving force for adsorption. This model has been applied to the adsorption of volatile HC on the carbonaceous material of accumulation mode diesel aerosol. In the section on nucleation, the effects of saturation ratio on homogeneous and heterogeneous nucleation of volatile exhaust components were discussed. These two regimes of behavior are linked in figure 10.

As the saturation ratio increases, the favored process changes from adsorption to nucleation. While the rate of adsorption increases with increasing S, the onset of nucleation is rapid once the correct conditions are in place. Nucleation is an "all or nothing" phenomenon. Once supersaturation is sufficiently high and the nuclei are present, high numbers of small particles will form quickly. (Friedlander, 1977)

**Relative Rates of Gas to Particle Conversion**

*Figure 10. - Figurative diagram showing the effect of saturation ratio on competing gas-to-particle conversion*
Figure 10 shows nucleation occurring at a critical value of saturation ratio. In the case of measured diesel exhausts with a wide range of gaseous organic species, concentrations and exhaust temperatures, there is a range of critical values of saturation ratio where volatile organics in the exhaust may nucleate to form nuclei mode particles rather than adsorb to exhaust soot particles.

Figure 11 shows the relation of dilution ratio and the resulting saturation ratio for two representative condensable hydrocarbons of a diesel exhaust. The two hydrocarbons have boiling points of 610 and 720° K and are shown at exhaust temperatures of 480° K and 600° K. The dilution air temperature is 27° C. The saturation ratio has the highest values for dilution ratios of about 5 to 50 for both hydrocarbons. Thus, the strongest driving force gas to particle conversion occurs in the critical dilution ratio range (5 - 50:1), which is roughly the same range produced by a dilution tunnel system (3 - 20:1).

Figure 11. - Effect of saturation ratio for two condensable species at two exhaust temperatures (Kittelson and Dolan, 1980)
D.2. Engine Emission Characteristics

While dilution ratio is a critical parameter of the atmosphere or laboratory conditions, the amount of surface available for volatile organics to adsorb to is a critical parameter of the exhaust aerosol. As mentioned above, the amount of material adsorbed onto exhaust soot particles is dependent on the particle surface area available as well as the saturation ratio.

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 1998 EPA has required engine manufacturers to reduce emission for heavy-duty on-highway emissions from 0.60 - 0.10 g/bhp-hr. As engine technology has improved some engine types have experienced greater reductions in solid carbonaceous particles than in volatile materials. This was the case for the engine family tested in the HEI study. 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.

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, 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 12 shows how the presence of carbonaceous agglomerates can keep the organic saturation

![Graph showing Saturation Ratio vs. Dilution Ratio for different engines](image_url)
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.

A recent report published by the Health Effects Institute (Bagley, et al. 1996) reported exhaust particulate measurements for a 1988 diesel engine and a 1991 diesel engine. The results indicated a large number of particles in the nuclei mode for a 1991 diesel engine. The engine had a high extractable organic fraction but low soot emissions typical of newer diesel engines. They measured 30 to 60 times the number of particles in the nuclei mode for a low sulfur fuel than they found in similar tests of the 1988 diesel engine.

In summary, a post-1990 diesel engine emitting less elemental carbon as carbonaceous agglomerates and more volatile organic material, may under certain dilution rate and ratio conditions, result in the nucleation process described above, to a greater degree than an engine emitting more carbonaceous agglomerates and volatile organic material.

D.3. Residence Time

The Langmuir and BET isotherms describe the equilibrium state of adsorption for a system. They are limiting cases if sufficient time exists for the adsorption/condensation to go to completion. For laboratory measurements, filters used to measure diesel particulate matter mass are usually in the exhaust stream long enough that it is assumed that the SOF will reach equilibrium with the solids on the filter. The kinetics of adsorption become important when the exhaust is going through rapid changes in temperature or adsorbate concentration. Kinetics must also be considered for laboratory measurement strategies that approach real-time measurement more closely and roadway conditions where dilution to higher levels may be more rapid. In these cases, the equilibrium partitioning of volatile organics between particles and gaseous forms may not be reached and departures from equilibrium 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 system behaves is a much smaller surface area is available for adsorption. On the other hand, if the rate of dilution is too high, the system will spend little time in the intermediate dilution ratio range where saturation ratios and nucleation rates are highest and little time available will be available for nucleation.

Calculations have been made for adsorption of a representative organic at dilution conditions that led to the highest saturation ratio. A typical SOF of 10% on diesel particulate matter was assumed and an accumulation mode particle diameter of 0.1 µm was used. These assumptions
gave a time required for adsorption/condensation mass transfer of 0.27 s. (Kittelson, 1980) This value provides a time scale when considering the roadway and laboratory dilution values and residence times provided below.

D.3.1 On-Road Exhaust Dilution

Figure 13 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 14 shows the dilution after the amount of time the exhaust has been in the atmosphere (converted from the distance behind the truck of the sample). For this study, the exhaust passed through the critical dilution ratio values between 5 and 50 in less than 0.4 s. The exhaust was diluted above 1000 :1 in approximately 1 s.

D.3.2 Laboratory Exhaust Sampling Dilution

Table 2 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 diesel engine test facilities surveyed for this project and the literature.

Table 2. Primary and secondary dilution values and typical residence times

<table>
<thead>
<tr>
<th>Primary Dilution Ratio Range</th>
<th>2 - 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residence at Primary Dilution</td>
<td>0.5 - 2 (s)</td>
</tr>
<tr>
<td>Total Dilution Ratio Range</td>
<td>5 - 1000</td>
</tr>
<tr>
<td>(including secondary dilution)</td>
<td></td>
</tr>
<tr>
<td>Residence at Secondary Dilution</td>
<td>0.5 - 3 (s)</td>
</tr>
</tbody>
</table>

![Figure 13. - 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, 1988 adapted from figure 4.46)](image-url)
Laboratory particle 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 make correlations between roadway and laboratory experiments, the relationships between exhaust aerosol and testing parameters must be well understood.**

Part 3

**Illustration of Factors Influencing Diesel Aerosol Size Distribution Obtained from Different Environments**

The objective of this section is to illustrate, with examples from the literature, how diesel aerosol size distributions are affected by various parameters and to provide real-world size distribution data obtained from various environments. The section focuses on studies which provide data on diesel aerosol nano-particles.

A. Laboratory Studies

*Weingartner, Burtscher and Baltensperger (1997b)* conducted laboratory experiments using a tandem differential mobility analyzer (DMA) to study the hygroscopic properties of freshly produced carbon and diesel soot particles at relative humidity < 100%. This was a fundamental study of the properties of diesel aerosol particles and how they might behave in the atmosphere. Although this study is not representative of exhaust dilution conditions in an on-highway setting, it shows the dynamics of particle formation and transformation.

Diesel aerosol was generated with a small, 4 kW, direct injection (DI) generator set. The exhaust was diluted about 50:1 and then treated with combinations of O$_3$, ultraviolet radiation, and water vapor. The tandem DMA approach uses the first DMA to select a narrow band (cut size) of aerosol which is treated with varying levels of relative humidity and passed to the second DMA where the change in particle size is measured.

Wetted carbon aggregates collapsed to a more compact structure, while diesel exhaust particles exhibited a much smaller restructuring combined with condensational growth. The hygroscopicity of the diesel particles was enhanced when the sulfur content of the fuel was increased or when particles were subject to an ozone and ultraviolet light pretreatment. The authors conclude that freshly emitted combustion particles are unlikely to act as cloud condensation nuclei, but aging of the particles will enhance their nucleation ability.

Different patterns of hygroscopic growth were observed for diesel particles generated under different engine conditions with and without fuel sulfur enhancement and different pretreatment conditions.

- When monodispersed diesel particles, generated under load, were dried, exposed to higher relative humidity and dried again the particles began to shrink at a relative humidity of about 40% and reached a growth factor of 0.9925 at 65%.
• When the same particles were not pretreated (dried), the particles began to grow at a relative humidity of 80% and reach a growth factor of 1.025 at 95%.

• When the same particles were not pretreated but fuel sulfur content was enriched (0.2 % S by mass), the hygroscopic properties were more pronounced.

• In contrast, when the particles were generated at idle conditions no hygroscopic growth was observed at higher relative humidity. The particles shrunk with increasing relative humidity to a growth factor of 0.99 at 90%. Shrinkage was even produced with sulfur enhanced fuel. The authors suggest this behavior is due to an increase in the organic fraction which impedes the transfer of water across the surfactant layer of the particle.

• Pretreatment of the aerosol generated under load, without fuel sulfur enhancement, with ozone increased hygroscopicity. Hygroscopicity was further enhanced by ultraviolet treatment. After pretreatment with ozone and ultraviolet light a bimodal number distribution was measured with peaks at about 40 and 90 nm (figure 14). The authors observed that new particles were produced by homogeneous nucleation and concluded that ultraviolet radiation initiated a chain of gas-phase reactions in the exhaust gas leading to condensation of condensable vapors. If the diesel particles were removed by filtration and only the gas phase of the exhaust gas was subjected to the ultraviolet and ozone treatment, only nucleated particles appeared at a mode diameter of about 40 nm. Diesel aerosol generated under load without pretreatment, showed a single mode with a peak at about 90 nm.

The authors calculated the critical supersaturations $S_c$ of the diesel particles using a Kohler model. Diesel particles had an $S_c$ that was considerably higher than pure NaCl or $(\text{NH}_4)_2\text{SO}_4$ particles. Thus, fresh diesel aerosol particles are poor cloud condensation nuclei in the atmosphere, however, further aging in the atmosphere may lead to a higher hygroscopicity and to more efficient nucleation.

![Figure 14. - Size spectra of diesel engine particles (1kW load, no fuel additives) without pretreatment (O) and after an exposure to 37 ppm $O_3$ (●). If the particles are removed with a filter and only the gas phase is subjected to the same pre-treatment, then particles produced by homogeneous nucleation appear at a mode diameter of about 40 nm (□). Due to variations in the dilution ratio an absolute comparison of total number concentration is difficult. (Weingartner, Burtscher and Baltensperger, 1997b)](image-url)
**Rickard, Bateman, Kwon, McAughey and Dickens (1996)** investigated the impact of fuels (Swedish diesel, light and heavy diesel, and gasoline) on the size distribution from gasoline and diesel light duty vehicles operated on a chassis dynamometer. Two instruments (quartz crystal microbalance - QCM and scanning mobility particle sizer - SMPS) were used to measure particle size from dilute exhaust in the constant volume sample (CVS) tunnel. The dilution ratio is not clearly defined but probably varied from 2:1 to 12:1, and was obtained in a conventional dilution tunnel. The residence time of particles is also not defined. The QCM does not work well with diesel exhaust so only results from the SMPS are discussed. The SMPS was operated so that single size measurements were obtained at a variety of points over repeated transient duty cycles until a picture of the size distribution was built. The European legislated emissions test, ECE+EUDC (European Commission Emissions + European Union Driving Cycle) along with steady-state conditions were used. Major findings from the SMPS data in this study were:

- A log-normal distribution was used to fit the diesel particle count data and a peak was typically observed at about 110 nm (60 nm for gasoline vehicles). For some test conditions a peak was observed at 40 nm and few particles < 20 nm were observed. From this distribution the volume distribution was estimated and the peak occurred between 100 and 200 nm. Similar distributions were estimated from data collected during transient tests.

- Particle concentrations were highest during acceleration and high speed conditions.

- Diesel fuel effects on particle number emissions correlated with equivalent effects on regulated mass particulate emissions.

The particle number counts observed in this study were generated under conditions that would not necessarily make it possible to observe the fuel effects on the nuclei mode, that is, conditions for particle growth were such that coagulation would tend to remove the nuclei.

- The size distribution for all vehicles, both gasoline and diesel, were similar, with most particles in the 50 to 100 nm range.

- At 50 km/h gasoline emissions (particles/km) were lower than diesel emissions but at 120 km/h gasoline emissions were similar to diesel emissions (~10^{14} particles/km).

This is an interesting finding because normally diesel engines emit far more particulate matter on a mass basis than gasoline engines, but under high speed conditions the numbers of particles emitted from gasoline engines and diesel engines is about the same.

**Kruger, Luders, Luers, Kaufmann, Koch and Kauffeldt (1997) and Luders (1997)** investigated the influence of exhaust gas aftertreatment and measurement conditions on particle size characteristics of exhaust from diesel engines. [This research was described in both the MTZ magazine and at the First International ETH-Workshop.] The authors address the issue of how particulate mass-reducing measures influence the non-mass-related particulate characteristics.
such as particle number and surface area, and point out the importance of dilution ratio and dilution rate to the process of particle formation. Oxidation catalysts and diesel particulate filters were evaluated.

Number weighted size distributions were obtained using either an EAA or a differential mobility particle spectrometer (DMPS). Only the DMPS data are reported. A low pressure cascade impactor was used to obtain mass size distributions. The authors do not describe the sampling system in detail, but based upon discussions with Prof. Kittelson at the 1997 Nano-Particle Workshop held in Switzerland it is known that 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. The test configuration is shown in table 3.

Key findings of the paper are discussed below.

• The passenger car with the IDI engine showed no significant effects of the oxidation catalyst on the size distribution.
• 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 oxidation catalysts also showed an increase in < 50 nm particles 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 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.

Table 3. Test configuration

<table>
<thead>
<tr>
<th>Engine/Vehicle</th>
<th>Configuration</th>
<th>Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 l - IDI passenger car engine, naturally aspirated</td>
<td>• Production exhaust system with oxidation catalyst&lt;br&gt;• Without catalyst&lt;br&gt;• Sinter metal plate trap³</td>
<td>Chassis dynamometer testing:&lt;br&gt;• ECE-part of NEDC¹&lt;br&gt;• EUDC²-part of NEDC&lt;br&gt;• Constant speed of 120 km/h</td>
</tr>
<tr>
<td>1.9 l DI passenger car engine, turbocharged and intercooled</td>
<td>• Production exhaust system with oxidation catalyst&lt;br&gt;• Without catalyst&lt;br&gt;• Ceramic filter³</td>
<td>Chassis dynamometer testing:&lt;br&gt;• ECE-part of NEDC&lt;br&gt;• EUDC-part of NEDC&lt;br&gt;Constant speed of 120</td>
</tr>
</tbody>
</table>
This system was used to examine particles emitted from the 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 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 is primarily sulfuric acid droplets. The condensation effect is strongly dependant 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.

![Effect of Dilution Ratio on Particle Size Distribution from a HD Diesel Engine (Raw Exhaust)](image)

*Figure 15. - Effect of dilution ratio on the particle size distribution. (Luders, 1997)*

When the truck engine was operated at rated power without a control device and the dilution ratio was varied from 12 to 32 no effect on the size distribution was observed as illustrated in
However, when the particle filter was installed an increase in the number of < 50 nm was observed at a 12:1 dilution ratio (figure 16). However, when the ratio was increased to 19 and 32:1 the increase disappeared.

![Effect of Dilution Ratio on Particle Size Distribution from a HD Diesel Engine with Exh. Gas Aftertreatment](image)

*Figure 16. - Effect of dilution ratio on the particle size distribution from a heavy duty diesel engine with a particle filter. (Luders, 1997)*

The < 50 nm particles only appear after the particle trap below a critical dilution ratio. The trap drastically reduces the mass of particulate 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.
Figure 17. - Effect of dilution air temperature on the particle size distribution from a heavy duty diesel engine with a particle filter. (Luders, 1997)

A system was set up to independently vary the dilution air temperature and the dilution ratio. Figure 17 illustrates the effect of dilution air temperature on particle size. At a dilution ratio of 12:1 and a temperature of 20 °C ultrafine particles are present, but numbers decrease when the dilution ratio is raised to 32:1. They increase again at a dilution ratio of 4:1 and temperature of 35 °C.

Figure 18 illustrates the effect of heat treatment on particle size following a diesel oxidation catalyst. From this graph it can be concluded that the ultrafine particles do not have a carbon core because carbon oxidizes at a temperature significantly higher than 175 °C. Presumably these particles are composed mainly of H$_2$SO$_4$. The authors did not provide details on fuel sulfur content.
Figure 18. - Effect of heat treatment on the ultrafine particle size downstream of a diesel oxidation catalyst. (Luders, 1997)

*Mayer, Czerwinski, and Scheidegger (1996)* measured the diesel particulate trapping efficiency of eight different filter media and noticed differences in filtration efficiency for particles < 50 nm. The particle size distributions were measured using a DMA. No details are given on the dilution system used to obtain the samples. Four diesel engines were evaluated under steady-state conditions. The engines included a 1.6 l Volkswagen, 2.5 l Audi, 6.11 l Liebher and a 6.6 l Caterpillar. The paper is discussed in detail due to the information provided on nano-particle formation.

Diesel aerosol consists of elemental and organic carbon, adsorbed or condensed hydrocarbons and sulfates. The authors pay close attention to the adsorbed or condensed hydrocarbons, because in the absence of solid particles, as is the case in very clean exhaust exiting a filter, these hydrocarbons nucleate to form new, very small particles. These particles, in their opinion, should not be considered in diesel particle measurements because they lack solid cores. To determine the presence of these particles, size distributions were determined with and without an active carbon denuder in place in front of the DMA. The denuder consisted of a heater followed by an activated charcoal trap. It removed volatile material such as water, sulfuric acid and hydrocarbons.

The 1.6 l engine (vortex chamber, turbocharged, no inter-cooling) was tested at four steady-state conditions and very consistent size distributions were obtained with number distribution peaks
between 80-100 nm. No dependence upon load was observed. Based upon these results, the other three engines were tested at only a single steady-state condition.

The 2.5 l engine (DI, no inter-cooling) was tested at 2,000 rpm and 4 bar both with and without the denuder and no catalytic converter. The peak number concentration again occurred between 80-100 nm, but when the denuder was not used there were twice as many total particles and there were far more particles ≤ 30 nm. This demonstrates the impact of the condensation nuclei on particle count.

The 6.11 l construction engine (DI, no inter-cooling) was tested at 1400 rpm and full load, but engine emissions were artificially deteriorated by installing an exhaust baffle and changing the injection timing in combination with suction throttling. This was necessary because the particulate emissions were quite low. The magnitude of the particulate emissions was increased but the number size distribution peak remained at about 90 nm. The distribution was somewhat flatter with a large number of < 30 nm particles.

The 6.6 l engine (DI, turbocharged, no inter-cooling) was also tested at 1400 rpm and full load and the particulate emissions were sufficiently high to conduct the filtration tests so no degradation was needed. The engine produced slightly larger particles with a peak around 100 nm, but the concentration count at 50 nm was about 50 % of the maximum value.

Filtration tests showed that all but one of the filters provided acceptable gravimetric filtration rates, and the knitted fiber trap had the best particulate count filtration rate.

Mayer, Czerwinski, et al. (1998) expand upon the findings from the previous paper. The authors report on nano-particle emissions and reduction strategies as part of a larger program to reduce diesel emissions in tunneling operations. The authors do not elaborate on the dilution system(s) used in these tests although the AVL mini-diluter was used during some tests. The major findings are listed below and some are similar to findings described above (Kruger, et al., 1997 and Luders, 1997)

- The SMPS measured very high concentrations of nano-particles and a bi-modal distribution at engine conditions close to full load (above 450 °C). Upon reheating of the exhaust gas after the dilution tunnel some of these particles disappeared as a function of temperature, and essentially disappeared when the temperature was above 250 °C.. This suggests that these ultrafine nano-particles probably consisted of sulfuric acid and hydrocarbons.
- For the diesel engines evaluated the median particle count diameter was around 100 nm. There was evidence, that due to saturation the value of 10^8 particles/cm^3 is generally not exceeded: the particulates agglomerate and the distribution shifts slightly to larger diameters.
- A 1996 low-emission, EPA certified Liebher 6.64 l engine (DI, turbocharged, inter-cooled) emitted more fine particles at all operating conditions when compared to an older version of the same engine.
- Nano-particle emissions were not reduced by the use of a special fuel which contained < 1.0 ppm S and < 0.1 % aromatics. This is a very interesting finding, which will be discussed further in the final report.
- The use of an oxidation catalysts increased the number concentration of nano-particles with the production of sulfuric acid aerosol.
• Deep bed fiber filters were more effective reducing the concentration of solid nano-particles.
• Use of Ce, Fe, or Cu fuel additives causes the formation of metal oxide ultrafine nano-particles particulate which are smaller than carbon particulate, hence fuel additives should not be used without a particle filter. Copper fuel additives were not recommended due to the formation of dioxin and furanes.

*Matter, Czerwinski, Mosimann and Mayer (1997)* investigated penetration of particle filters by various measurement techniques including SMPS, total particulate matter by gravimetric analysis, elemental carbon by coulometric analysis, black carbon by aethalometer and photoemission of submicrometer particles by a photoelectric sensor. All methods except the gravimetric method showed particulate matter reductions by two orders of magnitude. The gravimetric method showed only a single order of magnitude reduction. This difference is due to material that passes the particle filter (trap) at temperatures above 300 °C in the gas phase and nucleates when cooled, before passage through the particle measuring filter. These new particles account for the majority of the mass passing through the filter and the difference in filter efficiency between the gravimetric and other methods. This phenomenon was confirmed using the denuder discussed above. Measurements were made using either the AVL smart sampler II or a rotating valve method for dilution, which is described elsewhere (Hueglin, et al, 1997). It dilutes by introducing a short pulse of sample into a diluting stream, and appears to work well for solid particles.

Comparisons of the SMPS size distributions measured with and without the denuder showed that most of the volatile particles emitted were in the nano-particle range. Downstream of a trap, nearly all of the particles were in the nano-particle diameter range. As the temperature of the denuder is gradually increased, the nano-particles disappear. It is likely that these particles consist of sulfuric acid hydrocarbons. As shown in previously described Swiss work the solid particle number size distributions peak in the 90-100 nm range.

Two nearly real time methods for characterizing soot particles, photoemission (measures particle bound PAHs) and the aethalometer (measures light absorption) are described. A good correlation between elemental carbon, photoemission, aethalometer, and SMPS measurements is shown downstream of the denuder.


• The gasoline engines emitted 40 – 85 times less particle mass compared with the diesel engines for all test conditions.
• However, the number of particles emitted by the gasoline engines was 2000 times lower than the diesel engines at urban speeds, but only about 3 times lower at the higher highway speed tested. This trend has been reported in other studies (Rickeard, 1996).

The four diesel engines used in this study were tested using three different fuels.
• No differences in the number of particle emissions from the diesel engines using the different fuels were observed.
• A modest decrease in particle mass emitted was seen for a Swedish Class I fuel with substantially lower sulfur levels than the other two fuels tested.

Number weighted size distributions were obtained using several approaches including: EAA, DMA, DMPS, SMPS (version number of the software not provided), and ELPI instruments. The best repeatability was found with the DMPS/SMPS and the ELPI instruments.

This study also looked at the effects of post-tailpipe conditions on particle emissions to determine if mixing with ambient air would affect the contribution to ambient air quality of diesel particulate matter. Diesel exhaust was collected in a sealed container for up to 1000 seconds at a dilution ratio of 4.8. It was found that the number of particles decreased over time (approximately by a factor of two) and this was attributed to agglomeration processes.

It should be noted that while on-highway studies have indicated that dilution ratios are typically > 500 and may be as high as 2000 (Kittelson, 1988), dilution ratios at a busy urban intersection are typically much, on the order of 50:1 (Dolan and Kittelson, 1979).

**Moon and Donald (AEA - ETSU 1997):** conducted a test of four light duty and three heavy duty diesel engines and two light duty gasoline engines. Particle number-weighted size measurements were taken with a SMPS and mass-weighted size distributions were taken with a Quartz Crystal Microbalance (QCM) and an Anderson MkIII impactor, while total mass was measured with filters and a TEOM. An ELPI was also used to investigate its usefulness as an instrument for real-time number- and mass-based particle size distribution of diesel aerosols.

• A comparison of two sampling lines provided evidence of the effects of the aerosol sampling line on particle measurements. A sampling line with additional lengths of flexible tubing, sharp bends, and a “Chinese-hat” impactor cut-off plate showed significantly reduced sampling efficiency for particles larger than 3 µm.
• The SMPS (version number of the software not provided) gave consistent, repeatable number-weighted size distributions. In a direct comparison between the SMPS and the ELPI, the ELPI indicated about 25% of the number of particles measured by the SMPS and indicated the mean diameter to be consistently larger than what the SMPS measured. The authors hypothesized that the particle number concentrations were too high for the ELPI charger to operate efficiently. Recent tests by Ford (Maricq, 1998) comparing the ELPI to the SMPS show good correlation and do not support the findings by AEA-ETSU in this report.
• The ELPI gave conflicting results between the mass-mode and number-mode. The authors felt further development of the algorithms used to convert instrument output to number data is needed.
• The QCM was found to be unreliable and the mass-based particle measurement data was significantly low compared with other mass data. Data from the QCM instrument was not considered to be valid.
• The ELPI, TEOM and Anderson impactor gave similar mass particle flux measurements for the different engines and loads tested.
**Kreso, et. al. (1998a):** tested the effects of exhaust gas recirculation (EGR) on heavy-duty diesel engine emissions. A 1995 Cummins M11 heavy-duty diesel engine was used, which is a newer model of the 1988 and 1991 engines tested in the Bagley, et. al. (1996) study. Only work on the 1995 engine was performed for the Kreso, et. al. study, but results from the previous study on the older engines were presented in this paper side-by-side with the 1995 engine results for comparison.

The work from the Bagley study is discussed in the final report for this project and reported evidence of a shift from accumulation mode particles to a large number of nuclei mode particles in the 1991 engine. This same trend was seen by Kelso, et. al. for the 1995 engine.

The primary dilution ratio for the 1995 engine was in the range of 7 to 13 with a residence time from the exit of the turbocharger to the point of secondary dilution at 3.27 seconds. Secondary dilution was in the range to bring the total dilution to a range of 540 to 1777. The engine was tested in EPA Modes 9 (75 % load) and 11 (25 % load) with EGR rates of 10.5 % and 16.5 %.

Results of baseline (no EGR) testing:

- Both the 1991 and 1995 engines had overall reduced total particulate matter (TPM) than the 1988 engine.
- There was a significant increase in the number of particles in the nuclei mode for the 1991 and 1995 engines over the 1988 engine.
- There was a significant decrease in the accumulation mode for the 1991 and 1995 engines over the 1988 engine.

The investigators believed the shift of particulate matter from the accumulation mode to a significantly larger number of nuclei mode particles was due to the increased injection pressure of the newer engines. The higher injection pressure improves atomization and evaporation of the fuel and results in a lower size of primary carbonaceous particles or fewer of the primary particles bind together.

Effects of EGR on particles:

- EGR increased accumulation mode (number and volume) in 1995 engine.
- EGR decreased nuclei mode (number and volume) in 1995 engine.

As the EGR was increased, solid primary particles residing in the accumulation mode also increased. The authors hypothesized that *the exhaust SOF would adsorb or condense on the additional carbonaceous surface area available in the accumulation mode and never reach conditions favoring nucleation of nano-particles.* Although not suggested by the authors, the baseline results (no EGR) showing increased nuclei particle number concentration for the newer engines is likely the reverse of this situation. *For the 1991 and 1995 engines, accumulation mode carbonaceous particles were decreased over the 1988 engine and there was insufficient surface area to soak up the volatile hydrocarbons. This allowed nucleation to occur as the exhaust is cooled and large numbers of nano-particles to be formed.*
The study included an investigation of the effects of varying sample dilution ratio on the particles measured. The primary dilution ratio was held constant at around 10 while the secondary dilution ratio was varied for a total dilution ratio from 540 to 1770. The engine was run in EPA Mode 11 and with 10.6% EGR. The reported number and volume particle size distributions showed no effects of varying the secondary dilution. However, the conditions of this test do not explore the critical parameters of dilution ratio discussed in Part 2 of this report. In this test with EGR, there were two reasons why the variance of the secondary dilution did not affect the exhaust aerosol dynamics.

1. There was sufficient accumulation mode carbonaceous particles to adsorb the volatile hydrocarbons.
2. There was sufficient residence time at the primary dilution for the accumulation particles to grow as condensing/adsorbing hydrocarbons attached to the surface of the particles.

*Changing the secondary dilution in these conditions would not be expected to have a significant impact on the measured particles because, as illustrated in figure 13, the critical range is (typically 5 to 50:1) of dilution is already surpassed.*

**B. Studies Conducted In Underground Mines Using Diesel Equipment**

*The U.S. Bureau of Mines and the University of Minnesota Particle Technology Laboratory* conducted numerous studies in underground mines using diesel equipment. The objective of these studies were to: 1) reduce miner exposure to diesel exhaust pollutants; 2) characterize diesel aerosol; and 3) develop a size selective sampling technique suitable for discriminating diesel aerosol from mine dusts (Bureau of Mines, 1992). The studies were carried out in coal and noncoal mines and included mines which used only electric equipment.

Diesel equipment in underground mines is similar to equipment used off-highway for construction and ranges in size from small bobcat front-end loaders, light-duty diesel Isuzu trucks to 50 t or more haul trucks and large front-end loaders. Horsepower typically ranges from 50 - 700 hp and some mines use 100 or more pieces of diesel equipment. Production vehicles typically have a very heavy-duty cycle and frequently are left idling for long periods.

The studies evaluated different types of control devices including catalyzed ceramic filters, disposable diesel exhaust filters, catalyzed ceramic filters + diesel oxidation catalysts, and blended biodiesel fuel under in-use conditions. Although the collection of size distribution data was never the primary objective of these studies, mass size distribution data were collected using micro-orifice uniform deposit impactors (MOUDI). A number of these distributions are shown and the conditions under which they were obtained are briefly described. They represent average size distributions obtained during the course of the studies which typically lasted between 1-3 weeks. The general rule-of-thumb for ventilation in underground mines is 100 - 200 cfm/br-hp.
In the distribution shown in figure 19, coal haulage vehicles were equipped with and without a low temperature disposable diesel exhaust filter, that was placed on the vehicle following a water scrubber. Details of the control device are found elsewhere (Ambs, Hillman, 1992). The magnitude of the accumulation mode peak, occurring between 0.1 - 0.2 µm was substantially reduced when the filters were in place. The magnitude of the coarse mode is primarily related to the generation of coal dust by continuous mining machines and is not significantly affected by the operation of the diesel vehicles. The water scrubber removes about 30 % of the mass of diesel particulate matter. Essentially all particles > 1.0 µm are removed by the water scrubber. In mines where water scrubbers are not used a small diesel peak occurs between 1-2 µm. In mines using only electric equipment the accumulation mode peak is essentially non-existent. During the studies conducted by the Bureau and the University, MOUDIs were located in numerous places at the mines; including the portal or mine entrance and in the haulageways where diesel vehicles operated. Figure 20 a and b illustrates distributions collected at the portals and haulageways of three coal mines. The portal of these mines is representative of rural mountain air with windblown fugitive dusts from coal storage piles, belt conveyors, and vehicular traffic. Note that the accumulation mode peak is quite small compared to the distribution from the haulageways where diesel coal haulage vehicles are in use.

During studies conducted by the Bureau and the University of Minnesota in Missouri lead/zinc mines it was observed that the aerosol size distribution was drastically affected by mine fog. Nearly an order of magnitude increase in accumulation mode particle size distribution was

\[ \text{Figure 19. - Underground coal mine size distributions obtained using MOUDIs with coal haulage vehicles equipped with and without a disposable diesel exhaust filter (Adapted from Bureau of Mines data, 1992).} \]
observed. However, accurate MOUDI data were difficult to obtain due to the accumulation of water on the greased substrates.

Figure 20a. - Size distributions obtained at the portal of three underground coal mines using diesel equipment. Mass size distributions obtained using MOUDIs ( Adapted from Bureau of Mines data, 1992).

Figure 20b. - Size distributions obtained at the in the haulageways of three underground coal mines using diesel equipment. Mass size distributions obtained using MOUDIs (Adapted from Bureau of Mines data, 1992).
Gillies and Schimmelpfennig (1983) investigated fogging in an underground lead mine in Missouri. Aerosol size data were obtained using a Gardner small particle detector (condensation nuclei counter) and a Royco aerosol monitor. The Gardner small particle detector counted Aitken nuclei (<100 nm) while the Royco monitor was used to provide a number size distribution for particles from 0.5 - 15 µm. The number of Aitken nuclei present when no diesel vehicles were operating ranged from 78,000 - 175,000 particles/cm³. The number of Aitken nuclei increased from 260 - 970 % in the presence of diesel equipment (310,000 - 1,700,000 particles/cm³). Measurements made on the surface averaged about 4,200 particles/cm³.

Fog formation occurs when the air-water vapor mixture becomes supersaturated in the presence of condensation nuclei. In the mine atmosphere the presence of diesel aerosol, blasting fumes and mine dusts serve as condensation points. The authors observed that as the fog formed and the visibility decreased the number of Aitken nuclei decreased. Typical findings are summarized in table 4. These data provide evidence of diesel aerosol growth by coagulation. As the density of the fog increased, as measured by a decrease in visibility, the Aitken nuclei concentration decreased, thus Aitken nuclei were attaching to the fog droplets.

Table 4. Visibility during fog formation in a lead mine related to particle count

<table>
<thead>
<tr>
<th>Test date</th>
<th>Visibility (m)</th>
<th>Aitken nuclei (particles/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22Sept81</td>
<td>15</td>
<td>155,000</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>995,000</td>
</tr>
<tr>
<td>29Sept81</td>
<td>21</td>
<td>80,000</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>210,000</td>
</tr>
</tbody>
</table>

C. Roadway and Tunnel Studies

A number of investigators have gathered aerosol size data along freeways or in tunnels. Comparing studies is frequently difficult because seldom are the same aerosol parameters reported and frequently different instruments are used to collect size distribution data. However, the studies do provide ambient aerosol size distribution information, which in some cases, is diesel specific. The most comprehensive of these studies are summarized below.

Whitby et al. (1975) characterized aerosols from a California freeway. The aerosol size distribution was measured with four continuous instruments over the particle size range of 0.003 to 40 µm. The contribution of the freeway traffic was determined by subtracting the background aerosol from the aerosol measured directly from the freeway. Morning rush hour traffic contributed about 17.1 µm³/cm³ to the aerosol volume, predominantly in the particle size range < 0.15 µm. The freeway aerosol exhibited a strong nuclei mode at about 0.02 µm, and a typical trimodal distribution was observed. The measurements are not diesel specific, and are representative of older engines operated on leaded fuel without catalysts.

The relative emissions of tiny particles are well represented by total aerosol number count to total aerosol volume ratio (N/V) calculated from the Whitby data. Table 5 shows the N/V calculated from the California freeway study.
Number concentrations were obtained from a condensation nuclei counter (CNC) and volumes were calculated from a Whitby aerosol analyzer (a prototype electrical aerosol analyzer). The table clearly shows how the nuclei mode increased throughout the day as a result of increasing traffic and smog formation. N/V ratios fluctuated widely from about 2,000 to > 50,000 showing that the number of particles per unit mass of particulate matter is highly variable and is dependent upon traffic and smog conditions. Whitby, et al. do not provide an estimate of the freeway dilution ratio, but it is estimated (based on NO data provided in the report and known NO emission rates) that the dilution ratio was between 500 - 1,000:1 or more.

The study compared the surface area size distribution obtained on the highway to the size distribution obtained in a dilution tunnel using a sample drawn from the tailpipe of an automobile operated at speeds of idle, 35 and 50 mph. The effective dilution ratios in the tunnel at these speeds were 56, 17 and 10. The shape, spread and mode size of the distributions was similar suggesting that the rate and magnitude of dilution in the tunnel approximated that occurring on the freeway. However, comparison to samples drawn from the smog chamber at the end of the tunnel showed the effects of coagulation, as the mode size was 0.12 µm compared to 0.03 µm mode size of fresh freeway aerosol. Tests using unleaded fuel produced far fewer particles, with smaller mode diameters. It is likely that lead, emitted as submicron particulate matter, provided sites for condensation of hydrocarbons and rapid particle growth. Removal of lead from the fuel, reduced overall particulate mass and reduced the opportunity for coagulation and particle growth.

**Table 5. N/V ratios for the California freeway study (Whitby, et al., 1975).**

<table>
<thead>
<tr>
<th>Run</th>
<th>Hour</th>
<th>Type</th>
<th>CNC N/cm³</th>
<th>V V&lt;0.1 um³/cm³</th>
<th>N/V N&lt;0.1 um³/cm³</th>
<th>V&lt;0.1 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>49</td>
<td>21:00-</td>
<td>Background</td>
<td>150000</td>
<td>55 2727</td>
<td>3.3</td>
<td>6.1</td>
</tr>
<tr>
<td>50,5123:00-</td>
<td>Background</td>
<td>170000</td>
<td>82 2073</td>
<td>4.5</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>01:00-</td>
<td>Mixed</td>
<td>680000</td>
<td>86 7899</td>
<td>7.6</td>
<td>8.8</td>
</tr>
<tr>
<td>53</td>
<td>03:00-</td>
<td>Mixed</td>
<td>1310000</td>
<td>86 15268</td>
<td>13.8</td>
<td>16.1</td>
</tr>
<tr>
<td>54</td>
<td>05:00-</td>
<td>Peak Rush</td>
<td>2560000</td>
<td>125 20480</td>
<td>25.7</td>
<td>20.6</td>
</tr>
<tr>
<td>55</td>
<td>07:00-</td>
<td>Background</td>
<td>250000</td>
<td>133 1880</td>
<td>9.4</td>
<td>7.1</td>
</tr>
<tr>
<td>56</td>
<td>09:00-</td>
<td>Traffic</td>
<td>2420000</td>
<td>114 21228</td>
<td>11.7</td>
<td>10.3</td>
</tr>
<tr>
<td>57</td>
<td>11:00-</td>
<td>Traffic</td>
<td>2520000</td>
<td>134 18806</td>
<td>12.8</td>
<td>9.6</td>
</tr>
<tr>
<td>58</td>
<td>13:00-</td>
<td>Traffic</td>
<td>3560000</td>
<td>109 32661</td>
<td>15.4</td>
<td>14.1</td>
</tr>
<tr>
<td>59</td>
<td>15:00-</td>
<td>Traffic</td>
<td>3030000</td>
<td>67 45427</td>
<td>12.1</td>
<td>18.1</td>
</tr>
<tr>
<td>60</td>
<td>17:00-</td>
<td>Traffic</td>
<td>4040000</td>
<td>76 52880</td>
<td>20.6</td>
<td>27.0</td>
</tr>
<tr>
<td>61</td>
<td>19:00-</td>
<td>Background</td>
<td>340000</td>
<td>72 4716</td>
<td>7.9</td>
<td>11.0</td>
</tr>
<tr>
<td>Avg</td>
<td></td>
<td></td>
<td>1750000</td>
<td>95 18440</td>
<td>12.1</td>
<td>12.8</td>
</tr>
</tbody>
</table>

**CNC** Condensation nuclei counter

**N** Number of particles/cm³

**V** Total volume of particles/cm³

**N/V** Number of particles/µm³

Wilson, Spiller, Ellestad, et al. (1977) summarized measurements collected during the General Motors sulfate dispersion experiment conducted at the GM Milford Proving Grounds. The objective was to characterize potential sulfate exposures using a fleet of catalyst equipped
automobiles in controlled, simulated highway driving conditions under different meteorological conditions. GM operated 352 vehicles at 80 km/h for 2 hr, which was equivalent to a traffic density of 5,500 vehicles/hr. Unleaded gasoline containing 0.03 % sulfur by weight was used.

Size distribution measurements were collected along the roadway using an instrumented mobile laboratory and from an instrumented auto. Data were collected using an EAA, optical particle counter (OPC) and Aitken nuclei counter. Sampling chambers were used to accommodate the scan times of the EAA and OPC. These instruments provided overlapping ranges to measure aerosol size from 10 nm to 7.5 µm. Approximately 900 distributions were measured by the car and trailer.

Background aerosol volume size distributions exhibited three distinct modes with mean sizes of 0.03, 0.24 and 6.0 µm. Aerosol sized distributions measured during test runs also exhibited three modes with the accumulation and coarse modes remaining essentially unchanged. The nuclei mode volume increased significantly with the amount of increase related to meteorological parameters. The mean size of the nuclei mode decreased to about 0.02 µm. The authors concluded that the primary aerosol volume emission of the catalytic converter equipped cars is of a mean size of 0.02 µm, and that the increase in volume in the size 0.1 to 1.0 µm is primarily caused by coagulation of nuclei mode particles, which occurs in the atmosphere after emission and dilution at the tail pipe. The shift in size is supported by the observation that when aerosol aging time was shortest (wind direction across the roadway), most of the aerosol contributed by the cars was < 0.1 µm, but when the aerosol aging time was longest (wind direction parallel to the roadway), coagulation transferred about one third of the aerosol from the nuclei mode to the accumulation mode.

Dolan and Kittelson (1979) conducted a series of tests using two light duty diesel vehicles either operating in a stationary mode or on-highway at 16, 48, or 80 Km/hr. In both cases a mobile laboratory was used to collect aerosol and gas samples. The dilution ratio was estimated to be more than 100:1 within 2 m of the tailpipe at idle with a wind speed of 20 Km/hr. Dilution occurred in less than 0.4 s. During the chase experiments the dilution ratio was estimated to be 1000:1 after 1 s. The percentage contribution of the nuclei mode particles to the total volume of particles decreased from 7.5 to 3 % for the Volkswagen Rabbit engine as it went from idle to 80 Km/hr but increased slightly (from 2 to 3 %) for the Oldsmobile engine. The nuclei mode was determined by fitting a curve to data and is not directly comparable to the Whitby et al., data.

Kittelson and Dolan (1980) summarize diesel aerosol dynamics. Typical roadway dilution has a time scale of < 1 s and a dilution ratio of >1,000:1 while laboratory tunnels, exposure chambers or mixing chambers have a time scale of 1 - 5 s and a typical dilution ratio of 5 - 20:1. As a result of processes taking place in these relatively concentrated air streams, the particle size distribution, chemical composition and biological activity may be different from roadway aerosol. Factors affecting the aerosol include: coagulation, condensation and adsorption and dilution ratio. These factors are discussed elsewhere.

Pierson and Brachaczek, 1983 conducted experiments to describe aerosols associated with highway traffic in the Allegheny and Tuscarora Mountain Tunnels of the Pennsylvania Turnpike. Emission rates were determined for gasoline and diesel-powered vehicles. The principal
components of exhaust were elemental and organic carbon (EC and OC) from diesel-powered vehicles which comprised 10-15 % of the traffic. The mass median diameter determined by Andersen cascade impactor samples was 0.15 µm, which is consistent with diesel exhaust aerosol. (Note: the similarity to in-mine data presented earlier]. Thirty-four elements were identified, which accounted for all of the vehicle related aerosol. Other aerosol components included; oxidation of sulfur to H₂SO₄ (5 % of the aerosol mass), inorganic additives and adventitious components of fuels and motor oils (10 % with over half being Pb), tire wear debris (1 %), soil dust (10 %), and other materials (~ 3.5 %).

Kittelson, Kadue, Scherrer and Loverien, 1988 conducted five field studies: 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. The objective of these studies was 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 long filtration times. These field studies provide the most comprehensive diesel aerosol information and are discussed in detail.

The principal findings of this study are listed.

- 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 21 illustrates an average size distribution obtained from the field study. Note the presence of both a nuclei and accumulation mode. For comparison figure 22 illustrates a laboratory size distribution obtained from a Volkswagen rabbit operating at simulated 50 mph roadway 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 from the one shown in figure 21 as the nuclei mode is totally absent. The absence of the nuclei mode is attributed to the fact that the Rabbit engine produced very little volatile material, which would normally nucleate during the dilution process. The heavy-duty engine on the other hand, produced a substantial amount of volatile material, which nucleates for form many nano-particles. Earlier laboratory work (Dolan, Kittelson, Pui, 1980) compared the Rabbit engine to a Deere engine and showed that only the Deere engine produced the nuclei mode. The Deere engine produced a large quantity of volatile material.
Figure 21. - Average size distribution obtained from chase experiments, heavy-duty diesel (Kittelson, et al. 1988)

Figure 22. - Average size distribution obtained from laboratory experiments using a Volkswagen Rabbit light-duty engine (Kittelson, et al. 1988)
• 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 2300 to 62,000 part/µm^3. Number concentration was not a good indicator of diesel particle volume or mass concentration. [Note: the similarity to the Whitby, 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 23.

![Figure 23. - Volume fraction versus extractable fraction in the nuclei mode (Kittelison, et al. 1988)](image)

• 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.

- The atmospheric residence times in these experiments were very short compared to filter collection times, thus most of the particle aging took place on the surface of the filter, in the dark, in flowing ambient air. Photochemical reactions promoted by light are precluded under these conditions, but gas to particle mass transfer will continue.

- Adsorption/desorption and/or condensation/evaporation processes caused the amount of extractable material associated with the particles to change with dilution ratio. This showed up most clearly in Field Study V where stack samples collected in a mini-dilution tunnel at a dilution ratio of 25 had an extractable fraction of 0.26 compared to 0.13 for plume samples collected at an average dilution ratio of 1200.

- As a result of different residence times and adsorption/desorption and/or condensation/evaporation processes, low dilution ratio dilution tube experiments and high dilution ratio roadway studies may give significantly different emission factors for particle bound organic materials.

- Ames responses without metabolic activation for extracts from diesel particles collected under atmospheric dilution conditions ranged from 0.4 to 5.3, and from 0.1 to 1.8 rev/\( \mu g \) for tester strains TA98 and TA1537, respectively.

- HPLC and Ames responses for diesel particle extracts showed little or no correlation with dilution ratio or sample collection time. This suggests that the composition of particle bound materials aging in the dark is not significantly changed by dilution for the range of conditions evaluated. However, significantly less extractable material, and thus HPLC and Ames activity, was present in plume samples than in mini-dilution tunnel stack samples.

- Total HPLC response for extracts from background particles increased significantly with collection time. It was not clear why these particles are more subject to change than diesel particles.

Table 6 summarizes the properties of the aerosol size distributions measured in this study. The range of N/VT ratio (2,300 to 62,000) is similar to the one reported by Whitby, et al. 1975.
One of the objectives of the Kittelson, Kadue, Scherrer and Loverien, 1988 roadway study was to determine the relationship between dilution ratio and sampling distance and the impact these variables have on particles. Figure 24 illustrates dilution of diesel aerosol as it exits the tailpipe and figure 25 summarizes the atmospheric dilution ratios measured during the roadway experiments.

Table 6. Properties of Diesel Exhaust Size Distributions (Kittelson, Kadue, Scherrer and Loverien, 1988)

<table>
<thead>
<tr>
<th>Property</th>
<th>C_{cp}/C_{t}</th>
<th>m/VT</th>
<th>N/VT</th>
<th>VN/VT</th>
<th>E_c</th>
<th>DGV_n</th>
<th>DGV_a</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 µm.
m/VT Submicron filter mass concentration divided by EAA volume concentration.
N/VT Number of particles per unit submicron volume.
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.

Figure 24. - Illustration of factors affecting diesel aerosol dilution at the tailpipe
The data shown came from two different field studies. 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 illustrated in figures 23 and 24 where size distributions for engines with high and low extractable fractions are shown. The VN/VT ratio 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.

The results demonstrated that subtle but important changes in the nature of diesel particles occur as they dilute and age in the atmosphere. All three roadway studies, done with three different contemporary engines of two different types exhibited strong nuclei modes. The volume fraction in the nuclei mode was almost the same as the solvent extractable fraction, suggesting that much of the extractable material resided in the nuclei mode. Apparently, engines which produce a nuclei mode emit two distinct populations of particles; a nuclei mode consisting of tiny particles composed of mainly extractable or volatile materials with diameters of 0.025 µm, and an accumulation mode consisting of larger particles with diameters of 0.25 µm composed of mainly solid carbon.

Venkataraman, Lyons, and Friedlander, 1994 measured PAH and elemental carbon (EC) at two traffic tunnels to characterize the vehicular source. A Hering low-pressure impactor aerosol sampler (0.05 - 4 µm range) was used to collect samples gravimetric and high-resolution PAH analysis using HPLC and fluorescence detection. PAH and EC mass size distributions measured in the Caldecott Tunnel were unimodal (after correction for ambient air intrusions) with over 85 % of the mass in particles smaller than 0.12 µm. The study provides interesting data on the chemical composition and size distribution of particles between 0.05 and 4 µm but does not provide information on particles < 50 nm, nor particle number distributions.

Weingartner, Keller, Stahel, Burtscher, and Baltensperger, 1997 performed continuous measurements of aerosol emissions in the Gubrist tunnel, a 3,250 m long freeway tunnel near Zurich, Switzerland. The objectives of the study were to determine emission factors and to study changes of the characteristics of combustion aerosols during their residence time in the tunnel. The tunnel has a 1.3 % upgrade and is 3.2 km long giving 6 to 20 minute residence times with fans off. Measurements were made 100 m downstream of inlet and upstream of outlet, 50 cm below ceiling.

Respirable particles (< 3.0 µm) were found to be mainly tailpipe emissions with very small amount of tire wear and road dust. The calculated PM₃ emission factor for diesel engines was 310 mg/kg, where the main part (63 %) of the diesel vehicles were heavy-duty vehicles. Thirty-one percent of the PM₃ emissions from diesel vehicles were black carbon with 0.86 % particle
bound PAH. During their residence time in the tunnel the particles became more compact in structure.

The aerosol measurements in this study were comprehensive in nature. At the tunnel entrance an impactor to remove particles > 3.0 µm was followed by a tapered-element oscillating microbalance (TEOM), photoemission sensor to determine surface area bound PAH, differential mobility analyzer/condensation nuclei counter (DMA), additional 1:6 dilution, epiphaniometer to determine surface area and aethalometer to determine black carbon mass. At the tunnel exit a LAS-X determined particle size from 0.1 to 7.5 µm and an impactor to remove particles > 3.0 µm was followed by a TEOM, additional 1:11 dilution, photoemission sensor, epiphaniometer and aethalometer.

At the tunnel entrance the particles were mainly in the 20-30 nm range as measured by the DMA with total number counts ranging between 14,000 at 20:00 and 51,000 at 13:00. At the tunnel exit the size distribution shows a peak number count at 150 nm, which suggests transfer of material from the nuclei to accumulation mode, but the LAS-X is limited to particles with diameters of > 100 nm and the DMA was not used at the tunnel exit so it is not clear what the number counts are below 100 nm. The calculated volume size distribution shows a peak at about 180 nm. The calculated average mass concentration at the exit was 220 µg/cm³, which agrees quite well with TEOM PM$_3$ concentration of 272 µg/cm³.

The authors make a strong case for the adsorption of semi-volatile compounds onto particulate matter during residence time in the tunnel. From the tunnel entrance to exit the total mass concentration increased by a factor of 9 while the total black carbon concentration increased only by a factor of 4. Further, the black carbon to PM$_3$ ratio shifted from 0.5 at the entrance to 0.3 at the exit. This means that about twice as much material is adsorbed on the particle surface at the exit compared to the entrance. During weekends the ratios were lower which means the fraction of adsorbed material was higher. This is consistent with what is known about emissions from gasoline powered autos (more volatile material, which also may produce nuclei) versus diesels (more black carbon) and the different traffic mix observed on weekends versus weekdays.

The adsorption and restructuring behavior is also illustrated by the epiphaniometer and TEOM signals for both stations as the surface area to volume ratio of particles decreases during the residence time of the particles in the tunnel. The particles become more compact. They report a rather low contribution of tire wear to PM$_3$. Perhaps this fits with inability to pick out emission factors for gasoline vehicles.

This is one of the best recent studies of exhaust particles under near ambient (dilution ratios over an unconfined roadway would be higher) dilution conditions. Although they did not measure size by same method or number upstream and downstream, many of instruments that they use would be useful in future studies of roadway aerosols. The surface area and particle bound PAH measurements give size and, probably, health related information.
D. Atmospheric Studies

Many studies have characterized the size distribution of atmospheric aerosols, but relatively few have provided detailed information on nano-particles. Several of the more recent studies are summarized. These studies are generally not diesel specific.

_Ulevicius, Trakumas and Girgzdys (1994)_ investigated the influence of heterogeneous reactions on aerosol particle growth in polluted winter fog by analyzing aerosol size distribution data collected in Vilnius, Lithuania. The sampling site was located on the western edge of the city center near thermoelectric power plants, homes, and industrial plants. During Winter the plants burned oil and coal and the homes used mostly coal for heating.

An electrostatic aerosol spectrometer was developed to measure atmospheric size distributions. The classifier is similar to a TSI 3071 differential mobility analyzer. Size distributions were plotted for a six hour winter fog period from 5 to 10 AM. Distributions are bimodal with a nuclei mode peak between 20 - 40 nm and an accumulation mode peak between 0.05 - 0.3 µm. During the course of the sampling period the nuclei mode number concentration increased by a factor of 12 and the accumulation mode number concentration by a factor of 1.5. The volume concentration of the accumulation mode increased by a factor of 1.15.

The functional dependence of growth on particle diameter was determined by calculating growth rates for particles of different sizes. These rates were compared with theoretical expressions relating particle diameter growth rates to particle diameter. By matching data with the growth laws, chemical reactions were identified that were consistent with the observed data. Experimental results for particle diameter growth rates in winter fog show that for accumulation mode particles > 0.1 µm the growth rates tend to increase with particle diameter, while for nuclei mode particles the growth rate decreases with increasing diameter. This suggests as discussed by McMurry and Wilson, 1982, that for nuclei mode particles aerosol formation was dominated by growth resulting from condensation of low vapor pressure species formed by gas phase reactions. Growth for particles > 0.1 µm was consistent with growth by heterogeneous chemical reactions.

The authors observe that for black carbon in Winter, growth occurs by formation of H₂SO₄ in the gas phase by free radical oxidation of SO₂ and the condensation vapor of H₂SO₄ on black carbon particles. Some of these particles reach the accumulation mode. Larger particles begin to grow by heterogeneous chemical reactions.

_Horvath, Kasahara and Pesava, 1996_ determined the size distribution and composition of atmospheric aerosol at a rural and urban location near Vienna. A rotating 10 stage impactor was used to classify aerosols from 15 nm to 16 µm. Gravimetric, light absorption and PIXE analysis were conducted to determine the size distribution, concentration of black carbon, and concentration of 15 elements. The accumulation mode peak occurred at 0.5µm in the urban samples with the suburban samples being slightly larger. The coarse mode peak was generally around 3.0 µm. Fifty-seven percent of the total average mass concentration (30 µg/m³) was submicron in size at the urban location and 48 % of the total average mass concentration (23 µg/m³) was submicron in size at the more rural location.
The accumulation mode peak for the black carbon size distribution, most of which is elemental carbon, occurred at 0.25 µm at both locations. Light absorption was nearly twice as high in the city as in the rural location. No other element showed such a large difference between the two locations.

Light absorption was used to estimate elemental carbon concentrations. Black carbon amounted to 5.5% (1.2 µg/m³) of the total mass in the rural area and 7.4% (2.2 µg/m³) of the total mass in town. Thus, the town contributed 1.0 µg/m³ of soot. The mass absorption coefficient is very high for particles below 60 nm, indicating that elemental carbon from combustion sources is the main contributor in this size range. Occasionally, indications of a black carbon peak below 30 nm were observed in town. The authors note that particles of this size are primarily produced by diesel engines, prior to coagulation and agglomeration.

The authors refer to an earlier paper by Horvath, et al. 1988 which estimated diesel particulate matter concentration to be 7.2 µg/m³ of which half was estimated to be elemental carbon. Based upon emission factor changes for diesel vehicles the authors suggest that over a 10 year period diesel emissions have decreased by a factor of 2.4. This factor would result in a diesel soot concentration of 1.5 µg/m³, which is in agreement with the observed levels.

Tuch, Brand, Wichmann and Heyder, 1997 determined the variation of particle number and mass concentration in various size ranges of ambient aerosols in Erfurt, a city in Eastern Germany. Particles in the size range from 0.01 - 0.3 µm were classified using an SMPS with CNC. Particles in the range of 0.1 - 2.5 µm were classified by a LAS-X optical particle counter. The particle number concentration was determined primarily by particles < 0.1 µm (72 %) the mass concentration was governed by particles in the range of 0.1 - 0.5 µm (83 %). The contribution of particles larger than 0.5 µm to the overall number concentration was negligible (0.3 %) and so was the contribution of particles smaller than 0.1 µm to the overall mass concentration (1.1 %).

The authors conclude the following.

- Particles > 2.5 µm are rare in the European urban environment so it is debatable whether inhalation of these particles is relevant to human health. This is probably also true for particles > 0.5 µm as well.
- Since particle number and mass concentrations were found to be poorly correlated variables, more insight into health related aspects of particulate air pollution could be obtained by correlating respiratory responses with mass and number concentrations of ambient particles.
- Particle mass and number distributions should be measured in at least two size ranges; 10-100 nm and 100 - 500 nm.

Trier (1997) determined the atmospheric particle size distribution, including number concentrations in the 0.065 - 0.900 µm range in the city of Santiago, Chile. Trier characterizes Santiago as an extended emission source of over 800 km² located in a poorly ventilated valley.
Industrial density is low, with a prevalence of hydroelectric power, circulation of thousands of diesel-powered buses and trucks, low annual rainfall and generally low relative humidity. The submicron size distributions were obtained using an active scattering multichannel He-Ni laser spectrometer.

Observed concentrations ranged from 2,000 - 16,000 particles/cm$^3$. Geometric mean diameters ranged from 0.100 - 0.160$\mu$m. The particle number distributions in many cases were fitted by single log-normal functions, but in some cases the fit was improved by fitting a second log-normal function, in most cases, to the accumulation mode peak. This secondary peak tended to be $< 10\%$ of the area of the principle peak. Typically when this was done the nuclei mode had a mean diameter of 0.084 $\mu$m and the secondary peak had a mean diameter of 0.181 $\mu$m.

E. Atmospheric Source Allocation for Engine Particulates

Recent studies using real-time particle measurement instruments have studied source allocation of atmospheric particles to vehicle engines. These studies may not look exclusively for diesel exhaust particles but for both diesel and gasoline particle emissions.

Silva and Prather (1997) and Noble and Prather (1996) have used a newly developed aerosol time-of-flight mass spectrometer instrument package (Kittelson, et al., 1998a) to perform real time analyses of size and chemical composition of individual atmospheric particles. One goal of their work is to identify diesel and gasoline engine particle signatures to differentiate vehicle engine atmospheric particle loading.

Silva and Prather tested a wide variety of gasoline engines with different aftertreatment devices while Noble and Prather sampled particles directly from the atmosphere in an urban setting. While neither study targeted diesel particulates directly, the approach should prove valid for diesel engines as well. These studies have shown that not only chemical composition, but composition and size of particle used together can indicate particle source. The ATOFMS gives the aerodynamic size of the particle before it performs the mass spectrometry to determine particle constituents. Preliminary findings from these studies have shown that the presence of calcium and organics together in fine particles appears to be an indicator of a vehicle engine source. This should prove to be much more informative than traditional methods of particles by collection on a substrate and subsequent chemical analyses.

In addition to source allocation of diesel particles, the ATOFMS may be used in the future to quantify chemical transformations of particles as they age in real-world conditions, a key to understanding the fate of diesel particles in the atmosphere.

Siegmann, Scherrer, and Siegmann (1998) reported the use of an instrument that integrated photoelectric charging, diffusion charging, and light scattering into a portable three way sensor. They used the sensor to analyze particles from the following different combustion sources: a diesel bus, a paper fire, a candle, and a cigarette. Particles from each combustion process gave different responses by the three methods. By comparing the output of the photoelectric charging and diffusion charging of particles, they found it possible to differentiate between various combustion sources. A plot of photoelectric charging against diffusion charging demonstrated a
linear relation with a different slope for each type of combustion particle. (When comparing light scattering and diffusion charging, the diesel bus, candle and paper fire exhibited similar trends that prevented distinguishing between the different combustion sources.) This approach of comparing diffusion charging with photoelectric charging shows potential for source allocation of particles from different combustion sources.

*Matter, Paul, Scherrer, and Siegmann (1998)* also reported on the use of diffusion charging and photoelectric charging together for measurement of diesel exhaust particles. Both diffusion and photoelectric charging are related to the particle surface. However, diffusion charging is affected by volatiles condensed on particles (surface chemistry) while photoelectric charging is not. Additionally, photoelectric charging does not measure ash particles which can be formed from additives or impurities in the fuel. The study used a SMPS as a baseline measurement for a monodisperse soot aerosol. Good agreement was found between the SMPS and the photoelectric charger for measuring soot particles. Using these a photoelectric charger in conjunction with a diffusion charger with and without a thermal desorber to remove condensed volatiles, the investigators were able to distinguish between the different types of particles which can be emitted from diesel engines. (This study did not focus on atmospheric sourcing but is included here because of the similar study by Siegmann, et. al. with the integrated photoelectric and diffusion charging integrated sensor described above.)

*Burtscher and Siegmann (1993)* used a photoelectric aerosol sensor (PAS) to monitor solid particulate loading in a tunnel near Basel, Switzerland. Ventilation in the tunnel is normally controlled by visibility and CO concentration. Figure 26 shows results from measurements of CO, visibility, and photoemission levels from soot particles. During the week days visibility at the tunnel is reduced by a high number of diesel trucks, while over the weekends, CO concentration is high from the presence of gasoline engines. A PAS was used to measure particle photoemission simultaneously with measurements for CO and light extinction and was found to track these measurements very well. The PAS gives an in-situ measurement of the “Fuch’s surface” of particles below 1 µm. The photoemission of an aerosol is directly related to the surface area of soot particles generated by diesel engine combustion.

In this application, the PAS gives total surface area particle emissions rather than a size distribution. However, since both diesel and gasoline engines emit particles, the generation of particles falls between CO and visibility and gives a more even method of controlling ventilation.
Burtscher, Matter, and Steiner (1993) reported the use of a photoelectric aerosol sensor to examine the photoemission characteristics of particles from different combustion sources. They compared the photoemission response to different photon energies of gasoline engines, diesel engines, and cigarette smoke. Each class of combustion particle showed a unique photoemission

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response to different light sources with different wavelengths and photon energies. Although the results stated here are not comprehensive, this method may be useful for determining sourcing for combustion particles in atmospheric studies.

Hart, McDow, Giger, Steiner, and Burtscher (1993) used a photoelectric aerosol sensor to study ambient particulates in an atmospheric study near Zürich, Switzerland. The PAS was found to given good correlation between total solid particulates and the particle-bound polycyclic aromatic hydrocarbons associated with the measured particulates. The urban setting of the study included combustion sources in the industrial centers of Zürich and nearby Dübendorf as well as major freeways, preventing discernment of loading from vehicle engines specifically. The study did clearly find a diurnal pattern of combustion particle loading but also found that the PAS was susceptible to aerosol aging. The authors believed that as the particles aged in the atmosphere, condensation of water and volatile hydrocarbons may interfere with the PAS reading. In spite of this limitation and a long sampling period of over three weeks, correlation’s between the PAS response and PPAH content were at 0.87. (PPAH content was measured by extraction from particulate matter collected on filters simultaneous to PAS measurements during the study.)

SUMMARY

Nearly all the mass emitted by engines is in the submicron diameter range. Figure 3 shows the mass and number weighted exhaust particle size distributions typical of a diesel engine. Most of the particle number emitted is in the nano-particle (or nuclei mode) range, $D_p < 50$ nm, while most of the particle mass (and surface area) is in the accumulation mode range, $50$ nm $< D_p < 1000$ nm. Nuclei mode particles are typically hydrocarbons or sulfate, while accumulation mode particles are mainly carbonaceous soot agglomerates.

Ever tightening emission standards for new diesel engines have led to dramatic reductions in particle mass emitted by these engines. However, a recent HEI study (Bagley et al., 1996) shows that some new, low emission, diesel engines emit much higher concentrations of tiny particles than older designs and some current designs. Engines meeting the same mass emission standards may differ by a factor of 100 in number emissions.

Some of the differences in size distribution and number concentration measurements may be due to differences in dilution and sampling systems used. The influence of dilution and sampling on these measurements is poorly understood. So is the relationship between laboratory and atmospheric processes. However, it is clear that a significant amount of particulate matter may be formed during exhaust dilution from material present in the vapor phase in the tailpipe (e.g., sulfuric acid, fuel and oil residues). Particulate matter is present in the diluted exhaust that is not present in the tailpipe. These particles are most likely formed by heterogeneous and homogeneous nucleation and are generally less than 50 nm in size. These particles grow by adsorption or condensation. Adsorption is likely to occur on the agglomerates found in the accumulation mode.

Nucleation and adsorption are competing gas-to-particle conversion processes. Carbonaceous agglomerates provide a large surface area for adsorption that suppresses nucleation. Thus, diesel engines with reduced elemental carbon mass emissions, may have enhanced nucleation and
higher nano-particle emissions, by number concentration. These processes occur very rapidly (and somewhat irreversibly) as the plume dilutes. The particle number concentration near roadways (and in some dilution systems) may be formed by nucleation during the dilution process.

Thus, the high particle number concentrations observed on and near roadways are likely to have been formed by nucleation during dilution. Coagulation will cause these nuclei to grow quickly into the accumulation mode diameter range during atmospheric aging, especially if a large accumulation mode is present. Consequently the highest number weighted exposures will occur on or near roadways where particles are young before significant coagulation has occurred.

While many of these nano-particles may be formed by nucleation of semi-volatiles, some may be solid primary particles.

If nano-particles are a problem, spark ignition engines may have to be considered. Recent studies have shown similar number emission rates for spark ignition and diesel vehicles under high speed cruise conditions ($10^{14}$ particle/km SI, $2x10^{14}$ diesel) although SI engines have much lower number emissions in the FTP cycle (Rickeard, et al. 1996).

If standards are imposed on particle number or size, sampling and measurement issues will be nontrivial. Nucleation and coagulation are highly non-linear processes that may dramatically change the size distribution and number concentration. Unless these processes are managed carefully during sampling, accurate measurement of number concentration and size will be difficult. **To correctly interpret diesel aerosol measurements and to make correlations between roadway and laboratory experiments, the relationships between exhaust aerosol and testing parameters must be well understood.**

REFERENCES


