DIESEL AEROSOL SAMPLING METHODOLOGY - CRC E-43

TECHNICAL SUMMARY AND CONCLUSIONS

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TECHNICAL SUMMARY AND CONCLUSIONS

Introduction

Diesel engines are used extensively in transportation. In the U.S., Diesel engines are most commonly used in the over-the-road trucking industry due to their power, durability and efficiency. However, like other sources of combustion pollution, Diesels emit exhaust gases and particulates that are subject to regulation by State and Federal authorities. To meet these regulations, engine manufacturers have significantly lowered exhaust emissions, primarily by improving engine design and efficiency. Emission control technology and improved fuel and lube oil formulations have also led to a reduction in emissions. However, recent research suggests that there are still concerns related to health effects from exposure to fine particulate matter (< 2.5 micrometers in diameter, $PM_{2.5}$) in the atmosphere (Health Effects Institute 2001, 2002a). These concerns apply to Diesel exhaust and are discussed in depth elsewhere (Health Effects Institute 1995, 2002b).

Particulate emissions from internal combustion engines have traditionally been regulated solely on the basis of total particulate mass emissions; no reference is made either to the size or the number concentration of the emitted particles. Modern engines emit much lower particle mass concentrations than older engines. Another Health Effects Institute funded study reported, that for Diesel engines, the reduction in particle mass was accompanied by an increase in the number of nanoparticles < 50 nanometers (nm) in diameter (Bagley, *et al*., 1996 and Johnson and Baumgard, 1996). The low emission engine used in this study was a prototype engine with unusual emission characteristics characterized by a disproportionately high soluble organic fraction associated with the particulate matter. It is likely that excess volatile material in the exhaust contributed to the formation of the large number of nanoparticles. The Health Effects Institute and the investigators were careful to note that their results were preliminary and subject to confirmation by other investigations.

The University of Minnesota and partners under contract to the Coordinating Research Council undertook the study titled “Diesel Aerosol Sampling Methodology” to sample, characterize, and quantify nanoparticles in Diesel exhaust. The goal of CRC E-43 was to develop Diesel aerosol sampling methods for the laboratory that would produce results similar to those obtained under real-world roadway conditions. To accomplish this goal, a fundamental investigation was required to understand the physical processes that affect aerosol formation, transformation, measurement, and the resulting aerosol size distribution. These processes include dilution, nucleation, condensation, adsorption and coagulation. In addition to the physical processes, the nature of the particulate matter emitted in exhaust is affected by the engine condition, fuel, lube oil, exhaust system, sampling system, and other factors. The influence of these parameters on particulate matter emissions must be understood before real-world, on-road combustion aerosols can be duplicated in the laboratory. Results of this research have identified key parameters that must be controlled so that on-road Diesel aerosol size characteristics can be reproduced in the laboratory.

Diesel Aerosol

Diesel and other aerosols are often characterized by measuring particle diameters of the individual particles making up the aerosol. The aerodynamic diameter, defined as the diameter of a unit density (1 g/cm^3) spherical particle that has the same settling velocity as the measured particle, is frequently used to classify particles for determining their mass size distribution by gravimetric measurement. Typically, the electrical mobility diameter is used to classify aerosols for determining their number size distribution. The electrical mobility diameter is a close approximation of the Stokes diameter, which is defined as the diameter of a spherical particle having the same density and settling velocity as the measured particle. The Stokes diameter determines the particle diffusion coefficient and its diffusional deposition characteristics. The densities of Diesel particles are typically less than 1 g/cm^3 so that aerodynamic diameters are less than Stokes diameters. Other parameters, such as surface area and volume, are also useful in characterizing aerosols. In the E-43 project, multiple measures were used to characterize Diesel aerosols including particle number, volume, surface area and mass.

Figure 1 shows a typical Diesel particle size distribution weighted by number, surface area, and mass. Diesel particle size distributions typically fit a lognormal, trimodal form like those shown in Figure 1, with the concentration in any size range being proportional to the area under the corresponding curve in that range. The nuclei, accumulation, and coarse modes make up the trimodal size distribution. Nuclei mode particles range in diameter from ~ 0.003 to 0.03 micrometers (μm) or ~ 3 to 30 nm. In the past, the nuclei mode was defined as particles between 5 and 50 nm. However, in light of the E-43 investigations, it is appropriate to redefine the nuclei mode to encompass the range between 3 and 30 nm. These particles consist mainly of volatile organic and sulfur compounds in varying proportions as well a small amount of solid material likely to consist of carbon and metallic compounds. Most of the volatile particles form during exhaust dilution and cooling. The nuclei mode typically contains 0.1-10 % of the particle mass and up to 90 % or more of the particle number. The accumulation mode ranges in size from roughly 0.03 to 0.5 μm (30-500 nm). Most of the mass, composed primarily of carbonaceous agglomerates and adsorbed materials, is found in the accumulation mode. The coarse mode consists of particles larger than 1 μm (> 1,000 nm) and contains 5-20 % of the Diesel aerosol mass. These relatively large particles are formed by reentrainment of particulate matter, which was deposited on cylinder and exhaust system surfaces (Kittelson, 1998).

Figure 1 also shows some size definitions, notably, ultrafine and nanoparticles that have diameters less than 100 and 50 nm, respectively. There is some disagreement about the most appropriate boundary for the nanoparticle range, but 50 nm is widely used. Note that the nuclei mode falls nearly entirely within the nanoparticle range while the accumulation mode straddles the fine, ultrafine and nanoparticle ranges. The nuclei and accumulation modes of Diesel engine exhaust are formed at different times and have different compositions. It is more convenient and meaningful to describe Diesel exhaust size distributions in terms of the characteristics and sizes of the nuclei and accumulation modes rather than focusing on ultrafine and nanoparticle fractions; however, if there is a

significant nuclei mode, nearly all of the nanoparticles are found in this mode and the terms are nearly synonymous.

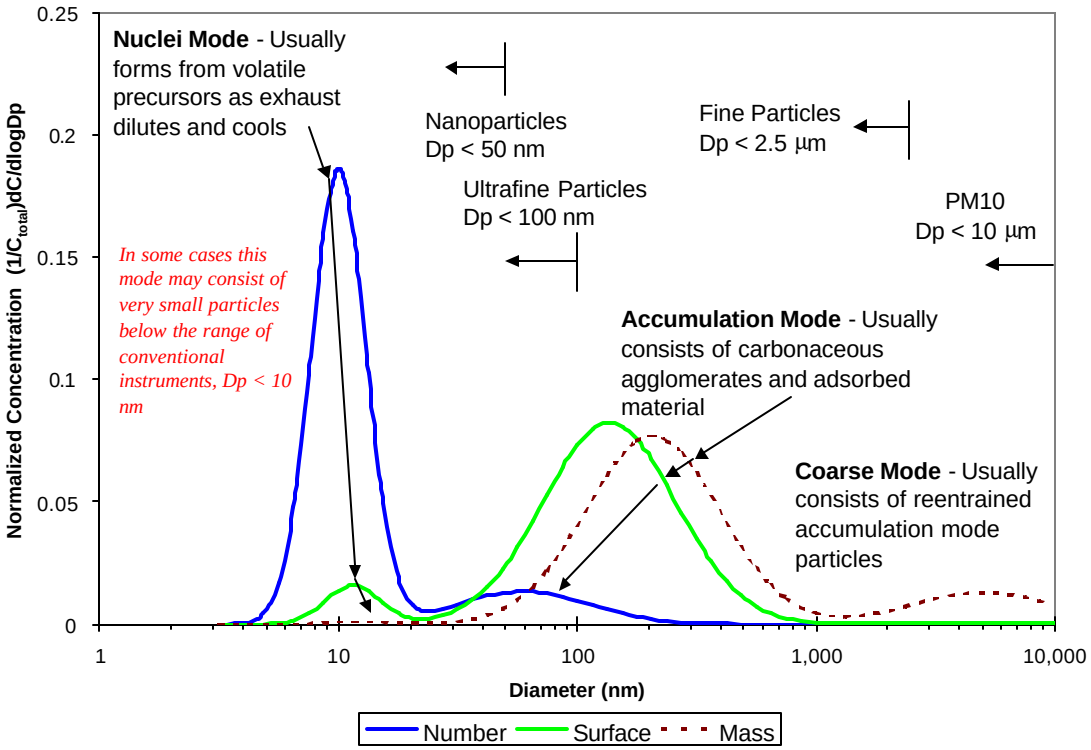

Figure 1. Diesel aerosol size distribution
D_p = particle diameter, C_{total} = total concentration

Approach

Field studies were carried out using four test trucks powered by Caterpillar and Cummins engines. Environmental Protection Agency certification (EPA fuel) and market basket blends of California fuels (CA fuel) were used for all tests. On-road, chase studies were carried out in Minnesota and a wind tunnel study was carried out at the Langley wind tunnel in Langley, Virginia. Both Caterpillar and Cummins engines were tested on-road, but only one Cummins engine was tested at the Langley wind tunnel. Engine and chassis dynamometer laboratory studies were carried out at Caterpillar and Cummins in Peoria, Illinois and Columbus, Indiana, respectively. Engine dynamometer studies were also done at the University of Minnesota.

Several mini-dilution systems were evaluated during the laboratory portions of the project. A 2-stage ejector system was used in multiple configurations throughout the project (Abdul-Khalek, *et al*., 1998a, 1998b and 1999). Another system was used at Caterpillar and Cummins laboratories to simulate the dilution system used in the Health Effects Institute studies conducted by Michigan Technological University (Bagley, *et al*., 1996 and Johnson and Baumgard, 1996). It consisted of a constant volume sampler (CVS) dilution tunnel and a secondary air ejector dilutor (CVS/ejector). Finally, a Sierra

Instruments BG-1 dilution system followed by an ejector dilutor (BG-1/ejector) was used at Caterpillar.

Quality Assurance

To ensure quality processes and products for the E-43 project, CRC appointed a separate quality assurance (QA) team. The primary goal of the QA team was to provide independent opinions and guidance for the research team in the development of QA protocols for the research and final evaluation of project data. The QA team patterned their activities according to the QA requirements and guidance recommend by the U.S. Environmental Protection Agency (Environmental Protection Agency, 1998). The QA team prepared a detailed final report describing their activities and findings (Ayala, *et al*., 2002). What follows is a brief summary of the findings from this report.

QA team activities were initiated after the start of the E-43 project; thus, all aspects of the project were not subjected to the same level of QA. Specifically, the Cummins on-road chase tests and the Langley wind tunnel tests were completed before implementation of the QA plan. Due to the late introduction of the QA team's plan, it became a working document rather than a planning document. Normally, a QA plan is in place before the beginning of the project to ensure the highest quality possible, but in this case changes or updates were made to the plan as new material became available.

The quality assurance level (level 3) attained for E-43 was consistent with "projects producing results used to evaluate and select basic options, or to perform feasibility studies or preliminary assessments of unexplored areas which might lead to further work" (Environmental Protection Agency, 1991). Level 3 is consistent with a research project investigating new methods for characterization and measurement of nanoparticles. Standard procedures were not, and are still not, available for many of the measurements made during the project.

It must be pointed out that there are no calibration standards for particle number or surface area. It is impossible to obtain the equivalent of a calibration grade span gas for such measurements. Instrument to instrument consistency checks were done as part of the E-43 program but these were relative rather than absolute checks. If any measure of particle concentration other than mass is to be used as a standard, reference calibration systems need to be developed.

QA team audits of project records indicate that data generated during the project are generally valid. QA team performance audits of the aerosol instruments revealed that the equipment was capable of generating consistent and valid measurements. The instruments were used in a manner consistent with standard operating and research procedures throughout the project. Surveillance visits by the QA team to the test sites documented that field activities were conducted in accordance with the agreed-upon protocol. Audits of the record archive revealed that the information collected by the research team was in conformance with the QA plan. The QA team concluded that the UMN research team demonstrated conformance with the QA plan for most of the

experimental tasks. The QA team also noted non-conformances and recommended corrective actions to the project investigators (Ayala, *et al*., 2002).

QA Report Recommendations

QA recommendations for project planning and execution were made in the QA final report (Ayala, *et al*., 2002) based on the E-43 project. These recommendations are summarized below. It should be emphasized that the points discussed below are meant to optimize the effectiveness and efficiency of a QA plan, and that not all of these points were integrated into the E-43 project.

- It is essential to determine QA goals and develop a QA plan before project activities are initiated.
- QA responsibility should be clearly assigned and the QA team should be involved in project planning.
- Quality control measures and procedures should be jointly developed and approved by the research team, the QA team and the sponsor.
- The QA plan should become an integral part of the execution plan.
- To ensure QA for field experiments, procedures should be developed and followed rigorously by project staff.
- Random audits of sampling systems and instruments should be conducted as frequently as required to meet QA goals.
- Instrument audits should be exhaustive and prescribed during project planning so as to establish the accuracy (precision and bias) of the sampling instruments.
- When attempting to measure the number and size of ultrafine emissions, transport losses by diffusion or other potentially relevant mechanisms such as turbulent deposition and thermophoresis should be quantified and reported. Losses may be considered a system bias or "persistent distortion of the measurement process" (Environmental Protection Agency, 1998). Thus, if instrument and sampling system precision and biases are established, the accuracy of the measurements may also be determined. [Particles smaller than about 15 nm have high diffusion coefficients and are subject to large losses in sampling and dilution systems and in instruments. Although particle losses in the sampling systems used in this program were determined as part of the QA effort, the loss studies were not comprehensive in scope, and the QA and research teams agree further work in this area is required. However, representative measurements with and without loss corrections are shown in the final report, but most data in the final report are uncorrected for particle losses. Particle losses of more than 50 % are not uncommon and are often not reported in the literature. By not correcting for particle losses, E-43 data can be compared to other published data.]
- The quantification of losses is likely to require additional experimentation due to the limitations of theoretical predictions. Therefore, if the performance of the sampling methods is ensured, including particle losses, and dilution conditions are known precisely, an accurate ultrafine particle number emission rate can be estimated.

- A record of all field activities should be submitted for custody, and a chain of custody mechanism should be implemented.
- Data post-processing procedures and software development should be decided upon during project planning and approved by the project staff, QA personnel, and the sponsor; and the final data format, data reduction, acceptance criteria, handling, and retrieval procedures should be delineated before activities are initiated.

When these measures are considered, it is feasible to design a quality integrated work plan for non-routine academic research that meets stringent quality assurance requirements.

Specific Objectives And Findings

The objectives of the E-43 project are listed below. Underneath each objective is a list of the pertinent findings relevant to that objective. Further details of the E-43 project are found in Cummins and Caterpillar data volumes and associated reports (Kittelson, *et al*., 2000, 2002a,b,c). Details on the wind tunnel study are available in two reports (Kittelson, *et al.*, 2002d and Clark, *et al.*, 2001). Detailed information on the findings from the surface area instruments used in the E-43 project is available in reports prepared by the Paul Scherrer Institute (Bukowiecki, N., *et al*., 2001 and 2002).

Objective 1. Conduct on-road chase and wind tunnel experiments to determine the actual particle size distribution and particle number concentration in the exhaust plume from heavy-duty Diesel vehicles operated on the road or in the wind tunnel.

The Diesel aerosol exhaust size distribution is influenced by many factors. These include engine condition, fuel and lube oil composition, exhaust system configuration, sampling system and sampling conditions. Engine and sampling system stabilization and previous engine operating history play important roles in determining the size distribution. Furthermore, ambient weather conditions, such as temperature, wind speed and direction also affect the on-road size distribution and the ability to capture a plume sample. These factors made the on-road sampling conditions less repeatable than what is normally encountered in an engine test laboratory. However, a consistent pattern of nuclei mode formation emerged supporting earlier roadside and on-road observations of nuclei mode particles (see for example Whitby *et al*., 1975, Kittelson, *et al.*, 1988). The findings below are based on on-road composite size distributions.

On-Road Findings:

- All of the test vehicles were found to have bimodal distributions under cruise and acceleration test conditions with both EPA and CA fuels.
- Nuclei mode geometric mean number diameter (DGN) ranged from 6-11 nm.
- Accumulation mode DGN ranged from 52-62 nm.
- The nuclei mode was highly variable. This variability was partly real and depended upon engine, fuel and environmental conditions, but it was also partly a

function of the difficulty in capturing a plume, distinguishing the plume from background and measuring the dilution ratio.
- Cold temperatures (5 to 11 ^{o}C) favored nuclei mode formation.
- California fuel produced fewer nanoparticles under most conditions, but the accumulation modes produced by EPA and CA fuels were similar.
- Both old and new technology engines produced nuclei modes of similar magnitude, but the newer technology engines produced smaller accumulation modes. This finding is consistent with new engine technology that has reduced mass emissions.
- When a thermal denuder was used to heat the sample to 300°C prior to passage to the instruments, the nuclei mode was found to shrink in size. This finding implies that the aerosol consisted largely of volatile compounds.
- On-road dilution is rapid, typically on the order of 1,000:1 in 2 s.
- On-road studies require fast response instruments with wide dynamic ranges.

Several ratios were used to describe the size of the nuclei mode relative to the accumulation mode to determine the relative contribution of nanoparticles. These ratios are the number fraction in the nuclei mode, the volume fraction in the nuclei mode, and the ratio of total particle number to total particle volume as determined by the Scanning Mobility Particle Sizer. We observed the following based on these ratios:

- The number fraction in the nuclei mode ranged from 37 to 87 %.
- The volume fraction in the nuclei mode ranged from 0.3 to 2.1 %.
- The number to volume ratio ranged from 2500 to 37000 particles/μm^3. Number to volume ratios greater than about 10^4 part/μm^3 generally indicated the presence of a distinct nuclei mode.

West Virginia University Wind Tunnel Findings:

- The plume was mapped and dilution ratios were determined. At steady-state conditions, dilution ratios of 75 and 125 were measured at distances of 5 and 8.5 m along the plume centerline. This range of dilution ratios was substantially lower than the typical on-road dilution ratio (1,000:1).
- In contrast to the on-road size distributions, the wind tunnel size distributions were predominantly unimodal throughout the plume and showed DGN values between 54 and 58 nm.
- Increased particulate matter production was evident during simulated accelerations. Near the stack, particle concentrations of 65 nm particles were dominant. This was also true on the plume edge and along the plume centerline, at 200 and 337 inches.
- Along the plume centerline, the concentration of 65 nm particles was one to two orders of magnitude greater than the concentration of 12 nm particles.
- Background particulate matter in the wind tunnel was dominated by accumulation mode particles that gradually increased in concentration throughout the day. This is consistent with recirculation of Diesel exhaust. A nuclei mode was observed

early in the test day (prior to starting the engine), but disappeared shortly after engine testing began.

- o A nuclei mode was observed under idle operation with a DGN ranging from 14 to 24 nm. It is likely that these particles were formed at the lower idle exhaust temperatures within the exhaust stack itself. These particles persisted and were detected in the background.
- o No appreciable count of nuclei mode particles was detected during cruise (steady-state) or transient operation.
- o Ambient sampling of particulate matter mass during the study showed a rise in particulate matter levels in the tunnel throughout the day. This was consistent with recirculation of Diesel exhaust.

The wind tunnel sampling conditions were quite different from those encountered on-road. On the highway, the closest point of plume capture was about 30 m under extremely turbulent mixing conditions. In the wind tunnel, samples were collected 2 to 10 m behind the vehicle stack under far less turbulent conditions. Wind tunnel background particle size distributions were characteristic of size distributions measured when running a Diesel engine in a confined space. Further, the range of dilution ratios achieved in the wind tunnel was not consistent with those achieved on the roadway; thus, the difference observed between the on-road and wind tunnel size distributions was a reasonable finding.

Objective 2. Conduct laboratory tests to compare on-road aerosol data with data generated in emissions test facilities to determine if current emission test facility sampling and analysis methods are adequate for characterizing particle size observed on the road.

Since transient engine dynamometer testing was not part of the E-43 program and only limited transient tests were performed, our results and recommendations are most appropriate for steady-state testing.

Duplication of on-road size distributions in the laboratory is made difficult because of unsteady conditions encountered during normal truck operation. Thus, those who attempt duplication of exhaust particle size distribution results need to be aware that current and past engine operating conditions, fuel, lubricating oil, dilution ratio, dilution rate, environmental conditions (temperature, humidity, background air quality), sampling system design features and other parameters are important influences on the size distribution. Tight control of these parameters is not possible during on-road chase tests, but can be achieved in the laboratory. Most nanoparticles are found in the nuclei mode. The nuclei mode is the most difficult part of the size distribution to reproduce because it consists mainly of volatile particles that are usually formed during dilution. The accumulation mode, which consists primarily of solid carbonaceous agglomerates, is much easier to reproduce.

While it was difficult to match on-road size distributions for individual test conditions with laboratory size distributions, much better agreement between on-road and laboratory

was achieved for composites of several test conditions. On-road measurements consistently showed the presence of a nuclei mode. Laboratory measurements also showed the presence of a nuclei mode under some conditions. The agreement between on-road and laboratory measurements improved as more experience was gained with sampling protocols. Consequently, more consistent results were obtained during the second year of the program (Caterpillar engines). Laboratory size distributions obtained using either the CVS/ejector or Sierra BG-1/ejector dilution systems were similar. It was found that any dilution system with a transfer line between the engine and the first stage of dilution that allowed significant heat and mass transfer underestimated the nuclei mode.

Figures 2 and 3 show comparisons between composite size distributions measured on-road and in the laboratory using the Sierra BG-1/ejector dilution system for the Caterpillar 3406E engine running on EPA and CA fuels, respectively. In both plots, the shapes of the accumulation modes on-road and in the laboratory are very similar. The differences in concentration between on-road and lab conditions are primarily due to difficulties in determining on-road dilution ratios. The size of the nuclei mode relative to the accumulation mode is not influenced by uncertainties in the dilution ratios. Comparisons of lab and on-road dilution shows, for EPA fuel, that the lab underestimates the relative size of the nuclei, N/V = 8800 vs. 12,600 part/μm^3. On the other hand, for the CA fuel, the lab slightly overestimates the small nuclei mode with N/V = 3700 vs. 2600 part/μm^3.

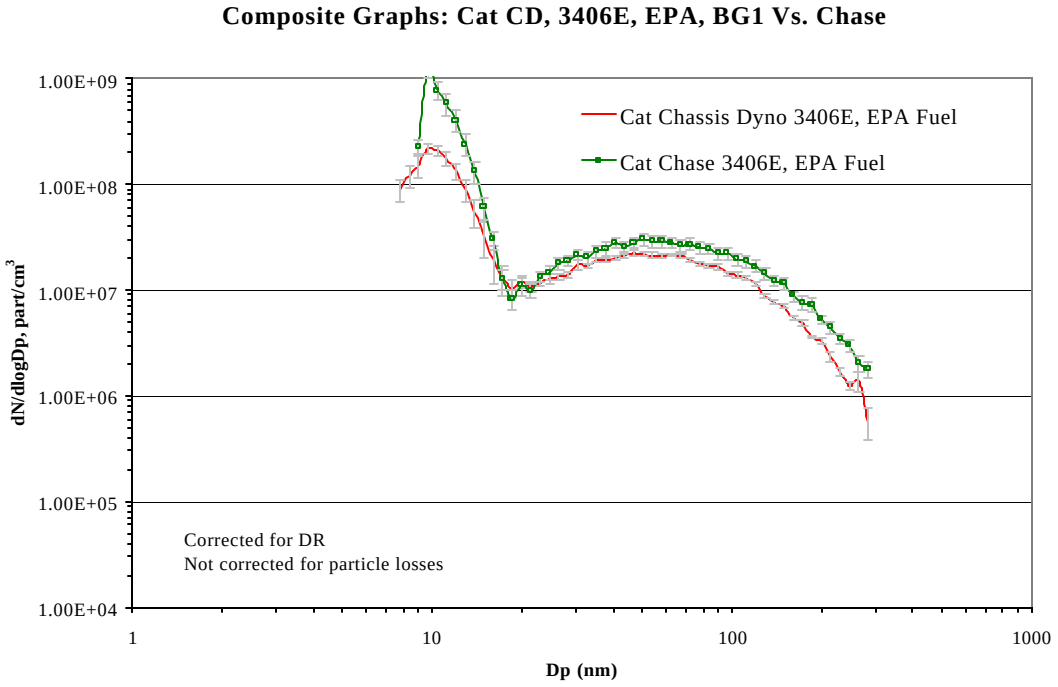

Figure 2. Composite particle number size distribution Caterpillar 3406E engines, EPA fuel, chassis dynamometer vs. on-road chase, BG-1/ejector dilution system

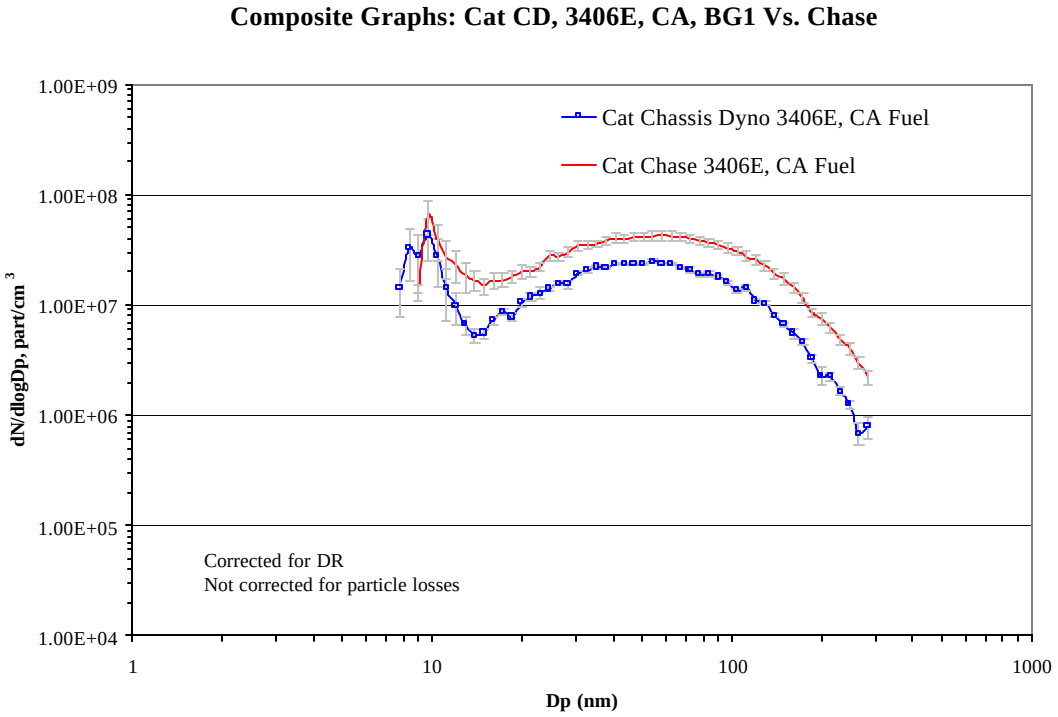

Figure 3. Composite particle number size distribution Caterpillar 3406E engines, CA fuel, chassis dynamometer vs. on-road chase, BG-1/ejector dilution system

Findings:

- Storage and release of semi-volatile material and particle precursors in the exhaust system play an important role in the formation of nanoparticles. Thus, the prior engine operating history is important when determining whether nanoparticles will be formed.
- Some engine conditions, such as idle, produce size distributions that are not appreciably influenced by the sampling conditions, while nuclei mode formation at other engine operating conditions is very sensitive to changing dilution conditions.
- It is difficult to simulate highway test conditions in the laboratory, because on-road conditions are not steady or repeatable. The on-road conditions never allow the engine to reach an equilibrium condition. In the laboratory, running at a single engine load and speed for a prolonged period can stabilize an engine. On-road conditions favor nuclei mode formation through constantly changing exhaust temperatures, traffic slow-downs that favor storage of material in the exhaust system, and release of this material at high load or under hard acceleration.
- The formation of nanoparticles from particle precursors is influenced by the residence time in the dilution tunnel or exhaust system. Short residence time in the exhaust and sampling system prior to dilution favor nanoparticle formation, while short residence time in the dilution system suppresses nanoparticle growth.
- The transfer line from the exhaust pipe to the dilution system is critical. Shorter heated lines minimize residence time, heat and mass transfer and loss of particle

precursors, while long transfer lines remove volatile material necessary for particle nucleation and growth.

- Nanoparticles are more easily formed when fuels with high sulfur content are used, but under some engine conditions, such as light load, nuclei mode formation is independent of fuel sulfur content and heavy hydrocarbons like those in lubricating oil play a major role.
- Catalyzed ceramic filters effectively remove accumulation mode (solid) particles from the exhaust, but can emit volatile precursors that lead to nanoparticle formation and a large nuclei mode under high load conditions.
- Engines of the same series tested with multiple dilution systems and in multiple locations showed engine-to-engine variability in absolute concentrations but the shapes of the size distributions were similar.
- Evaluation of nanoparticles, especially under transient conditions, requires multiple gaseous and particle instruments with synchronized data collection capabilities.

The CRC E-43 program included examination of particle size signatures from several dilution systems, including full flow tunnels and a variety of mini-dilution systems. The sampling and dilution system used in the E-43 that most closely met the goals of the program was the Sierra BG-1 / ejector combination. However, other systems that minimize transfer line losses and maintain constant dilution ratio, dilution air temperature and residence time might be appropriate.

Most full flow dilution systems run rather low primary dilution ratios under high speed and load conditions and high primary dilution ratios under low speed and load conditions. This will cause the laboratory sampling and dilution system to produce particle size distributions for different engine conditions that may be unlike those produced on-road. For example, in a full flow tunnel the exhaust plume dilutes more quickly at low engine speeds and loads than at high speeds and loads, while the opposite is likely to occur under atmospheric dilution conditions. Consequently, we recommend that with full flow dilution systems the dilution ratio be adjusted with engine condition to maintain a roughly constant dilution ratio. This would give a better simulation of what occurs in the atmosphere. However, this raises practical difficulties when doing transient cycles, and it may be difficult to measure size distributions during a transient cycle in a meaningful way using a full flow system for primary dilution. More intense study is needed in this area.

Particle losses in the instruments and sample lines were found to be significant and must be considered in the design of any laboratory dilution and sampling system. Losses in the instruments and sampling systems used in the E-43 program were significant. Correcting for losses decreased DGNs by about 10 % and increased N/V ratios and volume fractions in the nuclei mode by factors of 2 to 3, when a significant nuclei mode was present. However, correction for particle losses would not change any of the conclusions of the E-43 study.

Objective 3. Examine particle transformations as the plume disperses downwind of the roadway in a typical urban situation.

Findings:

Carnegie Mellon University (CMU) prepared a subcontract report titled "Lifetimes of Ultrafine Diesel Aerosol" as part of the E-43 program (Capaldo and Pandis, 2001). A computer model was used to determine the lifetime of ultrafine particles and evolution of particle size distributions measured during on-road testing. Their report addressed the following questions:

- What is the lifetime of particles emitted from on-road Diesels under typical conditions?
- How far are these particles going to be transported, and what is the range of influence of these mobile sources?
- Which are the most important factors influencing the lifetime of the ultrafine aerosols?

A one-dimensional Lagrangian trajectory model was used to simulate the evolution of the plume size distribution. This model simulated the dispersion, mixing with ambient particles, coagulation, and dry removal of the emitted particles. The effects of meteorology, topography, ambient aerosol and model assumptions were examined.

Particle lifetimes, τ_{90} and τ_{99}, were defined as the times necessary for the reduction of the *total number(nearly all in the ultrafine range) concentrations* from their initial plume values by 90 % and 99 %, respectively. Similarly, particle transport distances, s_{90} and s_{99}, were defined as the distance of transport of the emitted particles, measured along the prevailing wind direction, necessary to reduce the initial plume number concentrations by 90 % and 99 %, respectively.

Findings from the report are:

- For typical urban conditions, τ_{90} is on the order of a few minutes and τ_{99} is on the order of 20-30 min.
- s_{90} can vary from 100-1000 m, and s_{99} from 0.5-10 km. Typical values for these transport distances are 300 m for 90 % reduction and 2 km for 99 % reduction. These estimates indicate that Diesel trucks and other mobile ultrafine particle sources will have an effect on the aerosol particle number concentrations in areas near roadways.
- The degree of atmospheric mixing is the most important variable affecting characteristic times (τ_{90} and τ_{99}.) As wind speed increases from 1 to 10 m/s, τ_{90} and τ_{99} decrease by an order of magnitude.
- Characteristic transport distances (s_{90} and s_{99}) are rather insensitive to wind speed.
- For a given wind speed, ultrafine particles are expected to survive and travel a factor of ten greater distances in a rural flat area as compared to an urban downtown location. This is because of faster coagulation due to higher

background particle concentrations and faster mixing and deposition due to rougher terrain in urban areas.

- For the same meteorological conditions and topography, τ_{90} and τ_{99} are expected to be a factor of two and ten less, respectively, in a polluted area as compared to a rural area.
- Driving conditions have a minor effect on the τ_{90} and τ_{99} lifetimes.

Objective 4. Characterize the bulk Diesel particulate matter chemical composition and to determine surface properties and composition.

Findings:

Based upon the work done by Ziemann, Sakurai and McMurry (2002) in a project conducted simultaneously with the E-43 project, the following conclusions are made. These conclusions are based on tests done on a Deere 4045, a Caterpillar C12, and the same Cummins ISM engine used in the E-43 programs. The engines were tested at intermediate speed with light and medium loads.

- The organic component of total Diesel particles and nuclei mode particles appears to be comprised predominantly of unburned lubricating oil, whereas the fuel contribution to the total organic component appears to be relatively small, no more than 20 % and probably much less.
- Low volatility oxidation products (e.g., organic acids) and polycyclic aromatic hydrocarbons, which are compounds of interest and are known to be present (from previous analyses), do not appear to be a major portion of the organic mass.
- The major organic compound classes (alkanes, cycloalkanes, and aromatics) appear to be distributed fairly uniformly across the volatility spectrum.
- Sulfuric acid containing nanoparticles were formed using EPA pump fuel, which contains 410 ppm S. Fuel sulfur enhances nucleation. No sulfuric acid was detected in nanoparticles formed using CA (96 ppm S) or Fischer-Tropsch, (< 1 ppm S) fuel.
- Nuclei-mode particles and accumulation-mode particles are externally mixed across a wide size range, with the chemical components being distributed between two particle types: (a) “less volatile” particles, probably comprised of an elemental carbon core with a small organic component; and (b) “more volatile” particles.
- The volatility experiments showed that, except for the smallest particles, heating could differentiate volatile and solid particles. The fraction of solid particles decreased as particle size decreased, and only a volatile mode was detectable for the smallest particles tested (7 nm). It was found that more than 97% of the volume of the volatile constituents of 12 and 30 nm particles disappeared on heating to 400°C. The volatility of the Diesel nanoparticles was found to resemble that of C24-C32 normal alkanes, which implies a significant contribution of lubricating oil to these particles.
- Hygroscopicity experiments suggest the presence of sulfuric acid in Diesel nanoparticles when the engine was run with a normal 350-ppm sulfur fuel. The

hygroscopicity experiments could not detect sulfuric acid in particles produced by the engine when running on the 96-ppm sulfur CA fuel. When hygroscopic particles could be detected, it was found that the smallest particles were the most hygroscopic, suggesting that the smallest particles were relatively enriched with sulfuric acid.

Recommendations for Laboratory Dilution

The E-43 program has shown that highway dilution conditions lead to the formation of nanoparticles for both old and new technology engines. Dilution is very rapid, freezing the aerosol size distribution, and changing the time scale for further physical changes. The time scale is on the order of minutes, as described by Capaldo and Pandis, 2001, and results in nanoparticles being present near highways, with concentrations dropping over time and distance from the roadway. Nanoparticles are formed very quickly and then decay over a matter of minutes.

Supporting laboratory work and theory have shown that most nuclei mode formation and growth occurs in the low dilution ratio range between about 5 and 50:1. In this range, gas to particle conversion of volatile particle precursors, like heavy hydrocarbons and sulfuric acid, leads to simultaneous nucleation and growth of the nuclei mode and adsorption onto existing particles in the accumulation mode. Residence time and dilution air temperature are critical in this regime. In our tests, typical atmospheric dilution ratios and residence times ranged from 500 to 5000:1 and 1 to 3 s, respectively. Consequently, nuclei mode formation processes were essentially complete and on-road measurements did not significantly depend on these parameters. On the other hand, most laboratory dilution systems, at least in the first stage of dilution, operate in the critical dilution ratio regime where most nucleation and growth occur. The selection of suitable laboratory dilution ratio, temperature, and residence time will allow nucleation and growth to be varied over a wide range. Current laboratory dilution systems have a distribution of residence times at fairly low dilution ratios, but no consistent control of parameters influencing nuclei mode formation.

To best simulate atmospheric dilution processes, a dilution system must simulate the nucleation and growth conditions found in the atmosphere including the range of ambient temperatures and humidity that influence the formation and growth of the nanoparticle mode. On-road E-43 measurements showed the sensitivity of nanoparticle formation to ambient conditions and the variability of these measurements with engine and fuel combinations. The following three points should be made from the E-43 results:

- The Cummins ISM engine running on the CA fuel in cold climatic (5 to 11 ^{o}C) conditions produced a large nuclei mode that was not observed during the laboratory tests of the same engine with warm dilution air.
- On-road nanoparticle formation from Caterpillar engines did not appear to be influenced by temperature and humidity, but these tests were conducted with ambient temperatures ranging from 20°C to 30°C.

- Laboratory tests done at the University of Minnesota with Perkins and Caterpillar engines (Abdul-Khalek, *et al.*, 1998a, 1999 and 2000, Wei 2001a,b and 2002 thesis) show a nuclei mode formation increasing strongly with decreasing dilution air temperature but little or no dependence on humidity. Studies in Europe (Shi and Harrison, 2000 and Ristimaki, 2001) show similar temperature dependence, but a marked increase in nuclei mode formation at higher humidity. Further work on temperature and humidity effects is needed.

Other than ambient conditions, the main parameters influencing nanoparticle growth in the atmosphere are the composition of the growth species and the dilution rate. Evidence from E-43 and related projects suggest that these growth species are predominantly volatile or semi volatile materials such as heavy hydrocarbons (C24 and greater) and sulfuric acid. A dilution system should be designed that closely matches the concentration and time profile for these growth precursors. Wei (Wei, *et al.*, 2001a,b and 2002) built and tested a single stage dilution system that approximates the concentration time profile observed in the atmosphere, but the system is complex and needs refinement. At present, the only relatively easy method to approximate atmospheric dilution utilizes a two-stage dilution process. Two stage systems consist of an exhaust system, an exhaust transfer line that transfers exhaust from the exhaust system to the primary stage of dilution, a primary dilutor, an aerosol-aging chamber and a secondary dilutor. Design issues for these systems are described immediately below and numerical recommendations are made in the paragraphs that follow.

- Exhaust system design - Aging, storage and release processes take place in the exhaust system. It should be matched to that used in actual vehicles as closely as possible.
- Transfer line design - Samples must be taken in such a way that the growth precursors are not lost in sample lines from the tailpipe to the dilution system. The sample line should be designed for low heat and mass transfer rates. A combination of short residence times in the transfer line, achieved by high flow rates, and relatively small values of the ratio of the surface area to flow rate will allow this to be accomplished.
- First stage dilution system - The first stage dilutor should be designed to dilute quickly, with low particle losses. This is accomplished in a Sierra BG type dilutor through the use of porous walls that introduce dilution air. In a two-stage ejector dilutor, the dilution occurs very quickly in an ejector pump. Full and partial flow dilution tunnels used by industry for certification type testing combine aging and primary dilution in one stage.
- First stage residence chamber - An aging chamber is required after primary dilution in a 2-stage tunnel. Dilution and aging are combined in the full or partial flow systems. Whichever type of aging system is used, the combination of primary dilution ratio temperature and residence time must be sufficient to allow particles to grow into the size range encountered in the atmosphere.
- Conditions in primary dilution stage - The number and size of nanoparticles formed, are strongly dependent on the conditions in the first stage of dilution. Low temperatures, low dilution ratios, high humidity and long residence times

favor nanoparticle formation and growth. The BG1 system used in the Caterpillar experiments had a primary dilution ratio of 7.5 and diluted with dry, filtered air at 25° - 30°C. This system worked well under most test conditions.

- Second stage dilution - The secondary dilution system must quench further nanoparticle formation and changes caused by the physical processes of coagulation, nucleation and growth so that a stable aerosol is conveyed to the instruments. Dilution to an overall ratio of 200:1 or more is recommended, although lower ratios may be suitable for future low emission engines.

Even if all of these design factors are carefully considered, it may not be possible to exactly duplicate on-road size distributions due to the high variability of plumes, engine conditions, fuels, environmental conditions and other parameters. Based upon our experience, we believe that the best sampling strategy for measuring engine exhaust aerosol size distributions is to use representative and repeatable laboratory methods that incorporate accepted particle technology principles, rather than attempting to simulate the formation of these particles under ambient conditions that are highly variable. For a partial-flow dilution system, like the BG-1/2 or the 2-stage system, we recommend the following:

- Sampling should take place at the end of a realistic vehicle exhaust system,
- The exhaust transfer line should be designed for low heat and mass transfer,
- The primary dilution ratio should be 5-10:1,
- The residence time in the primary dilution system should be 1-2 s,
- Secondary dilution should be used to raise the overall dilution ratio to >200 to freeze coagulation and growth,
- The dilution air temperature should be 25°-30°C,
- Dilution air should be absolute filtered and charcoal scrubbed and
- Dilution air should be dry or precisely humidity controlled.

For a full flow tunnel, like those used in industry, sampling is more difficult, because it is more difficult to control the parameters that influence nanoparticle formation and growth. However, the goal should again be to measure an engine's nanoparticle emission characteristics. Thus, to the extent possible, the system should be designed to obtain the same dilution conditions recommended for the two-stage, partial flow systems.

Most full flow dilution systems run rather low primary dilution ratios under high load conditions and high primary dilution ratios under low load conditions. This will cause the growth rate of nanometer size particles to be different for different engine conditions, and the weighting of the formation of these particles will be different in a transient test cycle from what it is in the atmosphere. Consequently, we recommend that, with full flow dilution systems, the dilution ratio be adjusted with engine condition to maintain a roughly constant dilution ratio. This would likely give a better simulation of what occurs in the atmosphere. However, this raises practical difficulties when doing transient cycles, and it may be difficult to measure the nanoparticle emission characteristics in a transient cycle in a meaningful way. Recently Khalek, *et al* (2002) described possible scenarios for transient sampling, and although difficult, it may be possible to do this type of

sampling in the future. While it would be difficult to achieve a constant dilution ratio, stepping the total CVS flow in proportion to engine size would allow, at minimum, the average dilution ratio to be maintained constant for different size engines. Alternatively, average sampling zone temperature could be maintained constant. The new 2007 EPA Heavy-Duty test procedures specify an average filter face temperature of 47° ± 5°C. Following this protocol and sampling from the same zone might be an appropriate way of using a CVS system for nanoparticle measurement, but additional study and validation would be required.

Most constant dilution ratio partial flow sampling systems are not designed for proportional sampling and are not appropriate for traditional certification testing. However, meaningful transient tests may still be performed using fast response instruments like the CPC, SMPS in single channel mode, the diffusion charger, and the ELPI. New fast response SMPS-like instruments from Cambustion and TSI are expected to become commercially available in 2002.

Recommendations for Future Work

- **Calibration** - At present there are no convenient calibration standards for number concentration and surface area. A program should be established to evaluate the different types of standard particle generators available along with calibration systems based on primary measurements with the aim of developing a calibration system that could be used on routine basis in a manner analogous to span gases.

- **Chase experiments with low (mass) emission vehicles** - There are still important questions that can be resolved by doing chase experiments. Two additional types of vehicles should be characterized in chase experiments, natural gas powered trucks or buses and trucks or buses equipped with particle traps. Lubricating oil is a major contributor to nanoparticle emissions. Natural gas conversions of Diesel engines often consume as much or more oil as conventional Diesel engines. Lube oil that escapes the combustion system could be a significant source of nanoparticles. Similar arguments apply to Diesel engines equipped with particle traps. These traps are very efficient at removing solid particles but their effectiveness at removing volatile particle precursors has not been fully established.

- **On-road ambient monitoring** - When the mobile emissions laboratory is used to measure on-road aerosols in mixed traffic, the problems associated with trying to characterize a plume from a single source are eliminated. We have already demonstrated that it is possible to measure on-road mixed fleet fuel specific emission factors (Kittelson, *et al*, 2001). However, our study was only a pilot study, and a follow on study should include a variety of on-road locations and ambient conditions. Such sampling will identify areas with high concentrations of nanoparticles, $PM_{2.5}$, or gaseous pollutants, and could lead to recommendations for reducing these concentrations through traffic management. Additional sampling should also include the collection of size-fractionated samples for chemical analysis.

- **Mobile emission laboratory plume sampling** - The mobile emission laboratory is a convenient source of exhaust emissions that could be used as the platform for experiments. For instance, background measurements could be made continuously with additional instruments in the lab and stack emissions could be monitored simultaneously with onboard instruments. This would eliminate problems encountered during the E-43 program trying to capture a plume and differentiate the plume from the background. Tests could be run with different fuels, aftertreatment systems and operating conditions.

- **Single vehicle onboard plume sampling** – In our engine lab we have shown that sampling with a short heated transfer line using a two-stage dilution tunnel can simulate size distributions produced by roadway dilution conditions. This dilution system could be used in conjunction with a set of portable instruments to sample continuously from the exhaust of an individual vehicle, even a passenger car. Instruments like the condensation particle counter, photoelectric aerosol detector, and diffusion charger are available as portable units. All of these instruments could be carried onboard for real world characterization of size distributions

- **Validation of the E-43 recommended laboratory sampling methods** - One of the major limitations of the E-43 study was the difficultly in adapting our dilution and sampling procedures for use in laboratories not dedicated to research. Much of the time was spent moving and setting up equipment from one lab to another and learning about the special situations and limitations in each location. Consequently, there was insufficient time to systematically vary dilution and sampling conditions as we have done in the past in our lab. Our recommended test procedures for evaluating an engine's nanoparticle emission characteristics should be subjected to a series of validation experiments to confirm our recommendations.

- **Further research on the chemistry of nanoparticles** - It is necessary to develop a sampling system capable of generating size-fractionated samples that provides samples of sufficient mass for chemical speciation. This system should also allow for simultaneous physical aerosol characterization.

- **Fast response instruments for transient tests** - There is a need for relatively low cost instruments for near real time measurements in the nanoparticle range. Such instruments would allow size information to be obtained during transient cycles. The combination of the diffusion charger and condensation particle counter has shown promise during the E-43 program. Cambustion Ltd. has recently introduced a fast response, differential mobility particle sizer that yields SMPS like size distributions with 200 ms time response. Further testing is required to evaluate the effectiveness of these instruments, and other instruments that have recently become available, during transient engine tests conducted in the laboratory. If these instruments perform well, then they can be included in a suite of instruments used for on-board, real world, on-road tests.

Summary

The Diesel aerosol exhaust size distribution is influenced by many factors. These include engine condition, fuel and lube oil composition, exhaust system configuration, sampling system and sampling conditions. Engine and sampling system stabilization and previous engine operating history play important roles in determining the size distribution. Furthermore, ambient weather conditions, such as temperature, also affect on-road size distributions. All of these factors make precise definition and simulation of the on-road operating and dilution conditions very difficult. Measurement of the nanoparticle size range is the most difficult because it is dominated by nuclei mode particles, most of which are formed by nucleation of volatile precursors as the exhaust dilutes and cools. Nucleation is extremely dependent upon dilution conditions and these nuclei and their precursors may be strongly influenced by losses and sampling artifacts. While it was difficult to match on-road size distributions for individual test conditions, much better agreement between on-road and laboratory was achieved for composites of several test conditions. Size distributions generated in the laboratory under optimal engine, sampling, and dilution conditions can reproduce on-road size distributions. Based upon our experience, we believe that the best sampling strategy for measuring engine exhaust size distributions is to apply good particle technology principles in the laboratory using a standard set of sampling and dilution conditions that are reproducible, are sensitive to sampling the broad range of particle sizes known to exist in engine exhaust aerosols and minimize sampling artifacts. However, it is unlikely that dilution systems and methods currently used in the Diesel engine industry will be able to consistently reproduce on-road size distributions without substantial modification and strict adherence to test procedures and protocols.

REFERENCES

Abdul-Khalek, I. S., *et al*. 1998a. Diesel Exhaust Particle Size: Measurement Issues and Trends. SAE Tech. Pap. Ser. No. 980525, 13 pp.

Abdul-Khalek, I., D. Kittelson and F. Brear. 1998b. Diesel Trap Performance: Particle Size Measurements and Trends. SAE Tech. Pap. Ser. No. 982599, 14 pp.

Abdul-Khalek, I. S., D. B. Kittelson and F. Brear. 1999. The Influence of Dilution Conditions on Diesel Exhaust Particle Size Distribution Measurements. SAE Technical Paper Series. 1999-01-1142.

Abdul-Khalek, I. S., D. B. Kittelson and F. Brear. 2000. Nanoparticle Growth During Dilution and Cooling of Diesel Exhaust: Experimental Investigation and Theoretical Assessment. SAE Tech. Pap. No. 2000-01-0515.

Ayala , A., B. Olson, and B. Cantrell. 2002. Working Quality Assurance Project Plan for Diesel Aerosol Sampling Methodology (CRC Project E-43), 93 pp. Available from the Coordinating Research Council, Alpharetta, GA.

Bagley, S. T., *et al*. 1996. Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions. Health Effects Institute (HEI), Research Report No. 76.

Bukowiecki, N., *et al*. 2001. Subcontract Final Report CRC E-43: Surface Area Instruments Epiphaniometer. 20 pp.

Bukowiecki, N., *et al*. 2002. Real-time Characterization of Ultra Fine and Accumulation Mode Particles in Ambient Combustion Aerosols. J. Aerosol Sci. (In press).

Capaldo, K. and S. Pandis. 2001. Lifetimes of Ultrafine Diesel Aerosol. CRC E-43 Subcontract Final Report. Coordinating Research Council, Alpharetta, GA.

Clark, N., *et al*. 2001. Subcontract Final Report CRC E-43 Langley Wind Tunnel Research. Coordinating Research Council, Alpharetta, GA.

Environmental Protection Agency. 1991. Preparation Aids for the Development of Category III Quality Assurance Project Plans, EPA/600/8-91/005, February 1991.

Environmental Protection Agency, QA/G-5. 1998. Guidance on Quality Assurance Project Plans, EPA/600/R-98/018, February 1998.

Health Effects Institute. 1995. Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects. HEI Special Report. Health Effects Institute, Cambridge, MA.

Health Effects Institute. 2001. Airborne Particles and Health: HEI Epidemiologic Evidence, HEI Perspectives, Health Effects Institute, Cambridge, MA.

Health Effects Institute. 2002a. Understanding the Health Effects of Components of the Particulate Matter Mix: Progress and Next Steps, HEI Perspectives, Health Effects Institute, Cambridge, MA.

Health Effects Institute. 2002b. Research Directions to Improve Estimates of Human Exposure and Risk from Diesel Exhaust. HEI Special Report. Health Effects Institute, Cambridge, MA.

Johnson, J. H. and K. H. Baumgard. 1996. The Effect of Fuel and Engine Design on Diesel Exhaust Particle Size Distributions, SAE Tech. Pap. Ser. No. 960131.

Khalek, I., T. Ullman, and S. Shimpi., *et al*. 2002. Performance of Partial Flow Sampling Systems Relative to Full Flow CVS on Particulate Emissions for Steady-State and Transient Engine Operation. Presented at Spring Fuels & Lubricants Meeting & Exhibition, May 2002, Reno, NV, USA, Session: Diesel Emissions (Part C). SAE Tech. Paper Ser. 2002-01-1718 and SP-175.

Kittelson, D. B., *et al*. 1988. Characterization of Diesel Particles in the Atmosphere. AP-2 Project Group Final Report, Coordinating Research Council.

Kittelson, D. B. 1998. Engines and Nanoparticles: A Review. J. Aerosol Sci. 29(5/6):575-588.

Kittelson, D. B., J. Johnson, W. Watts, Q. Wei. M. Drayton, D. Paulsen and N. Bukowiecki. 2000. Diesel Aerosol Sampling in the Atmosphere. SAE Tech. Paper Ser. 2000-01-2212, 8 pp.

Kittelson, D. B., W. F. Watts and J. P. Johnson. 2001. Fine Particle (Nanoparticle) Emissions On Minnesota Highways. Mn/DOT Report No. 2001-12, 87 pp. Available at http://www.dot.state.mn.us/research/reports_online.html

Kittelson, D. B., W. F. Watts and J. P. Johnson. 2002a. Diesel Aerosol Sampling Methodology - CRC E-43 Final Report. Coordinating Research Council, Alpharetta, GA.

Kittelson, D. B., W. F. Watts and J. P. Johnson. 2002b. Diesel Aerosol Sampling Methodology - CRC E-43 Cummins Data Volume. Coordinating Research Council, Alpharetta, GA.

Kittelson, D. B., W. F. Watts and J. P. Johnson. 2002c. Diesel Aerosol Sampling Methodology - CRC E-43 Caterpillar Data Volume. Coordinating Research Council, Alpharetta, GA.

Kittelson, D. B., W. F. Watts and J. P. Johnson. 2002d. Diesel Aerosol Sampling Methodology - CRC E-43 Wind Tunnel Report. Coordinating Research Council, Alpharetta, GA.

Ristimaki, J. 2001. Nanoparticle Formation During Diesel Exhaust Dilution. Master's Thesis, Department of Electrical Engineering. Tampere, Finland, Tampere University of Technology. 62 pp.

Shi, J. P. and R. M. Harrison. 2000. Characterization of Particles from a Current Technology Heavy-Duty Diesel Engine. Env. Sci. Tech. 34: 748-755.

Wei, Q., D. B. Kittelson and W. F. Watts. 2001a. Single-Stage Dilution Tunnel Design. SAE Tech. Pap. Ser. 2001-01-0207, 14 pp. In In-Cylinder Diesel Particulate and NOx Control 2001, SAE SP-1592, p 119-131.

Wei, Q., D. B. Kittelson and W. F. Watts. 2001b. Single-Stage Dilution Tunnel Performance. SAE Tech. Pap. Ser. 2001-01-0201, 12 pp. In In-Cylinder Diesel Particulate and NOx Control 2001, SAE SP-1592, p 75-86.

Wei, Q. 2002. Systems to Simulate Engine Exhaust Dilution in the Atmosphere, Ph.D. Thesis, University of Minnesota, 2002.

Whitby, K. T., *et al*. 1975. Characterization of California Aerosols - 1. Size Distributions of Freeway Aerosol. Atmosph. Environ. 9:463-482.

Ziemann, P. J., H. Sakurai and P. H. McMurry. 2002. Chemical Analysis Of Diesel Nanoparticles Using A Nano-DMA/Thermal Desorption Particle Beam Mass Spectrometer. Final Report CRC Project No. E-43-4, 92 pp.