

Particulate Matter Mass Measurement and Physical Characterization – Techniques and Instrumentation for Laboratory Source Testing

Final Report

**Prepared for:
Hector Maldonado
Research Division
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812**

July 2004

Thomas D. Durbin, Co-Principal Investigator
Joseph M. Norbeck, Co-Principal Investigator
David R. Cocker III, Co-Principal Investigator
Theodore Younglove
Bourns College of Engineering-Center for Environmental Research and Technology
University of California
Riverside, CA 92521
(909) 781-5781
(909) 781-5790 fax

Table of Contents

Executive Summary	iii
1. Introduction.....	1
2. PM Formation Mechanisms and the Fate of PM in the Ambient Atmosphere	4
2.1 PM Size Ranges	4
2.2 PM Formation Mechanisms	4
2.3 Fate of Mobile Source PM in the Ambient Atmosphere	7
3. Techniques for Measuring of Real-Time PM Emissions and PM Size Distributions.....	10
3.1 Real-Time PM Measurement Techniques	10
3.2 Technologies for Measuring PM Size Distributions	13
3.3 Other Instruments	19
4. Laboratory Studies and Methods for PM Measurement	21
4.1 Laboratory Measurements of PM	21
4.2 The Implementation of Aftertreatment for Diesel Vehicles and Its Influence on PM Mass and Chemistry	34
4.3 Factors that can Influence PM Measurements	40
4.4 Improved Methods for Sampling PM	43
5. Portable Instruments for PM Measurements Under In-Use Conditions.....	49
5.1 Mobile Emissions Laboratories	49
5.2 Portable/In-use PM Measurement Systems	51
5.3 Remote Sensing of PM Emissions from Mobile Sources.....	55
6. Summary and Conclusions	57
7. Bibliography	60

Appendix A. Certification Standards for Heavy-Duty Diesel Engines

List of Figures

Figure 2-1	Particulate Size Distributions based on Mass and Number.....	4
Figure 2-2	Schematic Representation of Processes Influencing Exhaust Particles in the Air and When Sampling.....	5
Figure 3-1	Condensation Particle Counter Schematic.....	11
Figure 3-2	Tailpipe Setup of Laser Induced Incandescence Particle Measurement System	12
Figure 3-3	Cascade Impactor Schematic.....	16
Figure 3-4	Photoelectric Aerosol Sensor Schematic.....	18
Figure 3-5	Epiphaniometer Schematic	18
Figure 5-1	Schematic of UCR’s Heavy-Duty Mobile Emission Laboratory	50
Figure 5-2	Schematic of the US EPA’s On-Road Diesel Emissions Characterization Facility.....	51

List of Tables

Table 4-1	DETR/SMMT/CONCAWE 1998-2001 Particle Research Programme Engine and Vehicle Test Matrix	26
Table 4-2	CARB Verification Classifications for Diesel Emission Control Strategies...	36

Executive Summary

One of the most important issues in the control of emissions from mobile sources is the reduction in particulate matter (PM) emissions from diesel engines/vehicles. Over the past three decades, diesel PM emissions have been studied extensively, including emissions measurement and characterization studies and health studies. As regulations become increasingly more stringent, more advanced diesel technologies and diesel particulate filters (DPFs) are being implemented on a wider basis. As diesel technology evolves, it is important to understand how the PM component of vehicle exhaust has changed over the years in order to gauge the expected improvement in air quality. One of the most critical aspects of evaluating these changes is the application of the most robust, comprehensive and accurate measurement tools available. This includes instruments for the measurement of PM mass in real-time, PM size distributions, and portable instruments that can be used to measure PM under in-use conditions. The objective of this project is to evaluate and assess the international and domestic literature on PM measurements and measurement technology from vehicles. This work included a comprehensive literature review that identified over 250 references.

The fate of vehicle exhaust PM in the ambient atmosphere is an important issue in evaluating the real-world characteristics of PM. These studies have included roadside studies and chase studies. These studies have shown that atmospheric dilution is on the order of 1000:1 after 1 second, considerably higher than that obtained in the dilution tunnel measurements. Ambient measurements also typically show a strong nuclei mode, although this is source dependent. Comparisons of particles in chase studies have also shown considerably higher number of particles measured by a condensation particle counter (CPC) in comparison with a scanning mobility particle sizer (SMPS), which is attributed to a large number of particles <10 nm that can be detected by the CPC but not the SMPS. In the recent CRC E-43 program, extensive roadside tests were conducted along with experiments in a wind tunnel. The results showed the nuclei mode was quite variable depending on engine operation, thermal history and other parameters, while the accumulation mode was a repeatable function of engine and operating conditions. A model was also developed and it was found that after leaving the tailpipe total particle numbers are reduced by 90% on the order of a few minutes and after traveling 100-1000m.

The regulation of PM has typically been based on measurements of integrated mass over the Federal Test Procedure Transient Heavy-Duty Engine Test protocol. With the lower of regulatory levels from 0.1 g/bhp-hr to 0.01 g/bhp-hr, essentially mandating the use of DPFs, there has been an effort to develop more advanced PM sampling methodologies capable of measuring at levels considerably below those of older technologies. In response to the issues associated with measurement of PM at low levels, the United States Environmental Protection Agency (EPA) has an ongoing program to examine methods to tighten the procedures for PM measurement. This program has resulted in considerable changes to 40 CFR Part 86, Subpart N as part of the 2007 heavy-duty diesel engine regulation. Specific changes to the regulation are as follows:

- Requirements for balance precision were increased from 20 to 2.5 μg .
- A preclassifier was added to eliminate large particle not associated with the exhaust

- A temperature range of $47\pm 5^{\circ}\text{C}$ was implemented, in contrast to previously only an upper limit of 52°C .
- 47 mm single filter assemblies are now required as opposed to the 70 mm dual filter holders.
- Primary dilution air filtration is specified as 98%.
- Filter room specifications were tightened to $22\pm 3^{\circ}\text{C}$ ($\pm 1^{\circ}\text{C}$ at microbalance) and a dew point of $9.5\pm 1^{\circ}\text{C}$.
- Reference filter drift limits were tightened from $40\ \mu\text{g}$ to $10\ \mu\text{g}$.
- Recommendations were made that class 1000 clean room specifications be met.
- A 20 minute steady-state, high-temperature cycle was added for preconditioning.

With the changes implemented above, as well as others included in the CFR regulations, EPA has achieved significant improvements in reducing the variability associated with PM mass measurement. For a 10 mg/mi light-duty diesel vehicle, coefficients of variation (COVs) of ~5% can be achieved using these techniques, based on $\sim 100\ \mu\text{g}$ filter loading. For a 0.004 g/bhp-hr engine over the heavy-duty transient engine dynamometer test, COVs of ~10% can be achieved.

Other techniques are also now being investigated more extensively, since parameters such as particle number and size are thought to also have potentially important health consequences and since there is interest in real-time PM emissions measurements. Instruments that can be used for measuring PM in real-time include the Tapered Element Oscillating Microbalance (TEOM), Quartz Crystal Microbalance (QCM), Nephelometer, Aethalometer, Photoacoustic Instrument, and Fast FID. There are a number of instruments available that can provide measurements of PM size distributions either over a fixed duration such as a cycle or in real-time. Two of the more common methods of measuring PM size distributions are using electrical mobility and inertial impaction. Instruments that utilize the principle of electrical mobility for sizing include the Electrical Aerosol Analyzer, the Differential Mobility Particle Sizer, the Scanning Mobility Particle Sizer, and the Nanometer Differential Mobility Analyzer. Instruments using inertia sizing methods include the Microorifice Uniform Deposit Impactor (MOUDI), Electrostatic Low-Pressure Impactor, and Nano-MOUDI. Other available sizing techniques include the Aerosol Time-of-Flight Mass Spectrometer, Photoelectric Aerosol Sensor (PAS) which can be used to quantify polycyclic aromatic hydrocarbons (PAHs) in diesel PM, the ephiphaniometer, which measures surface area using a radioactive isotope, diffusion batteries, and time resolved laser induced incandescence.

The Europeans have been extensively investigating and further developing techniques for PM measurement. This includes programs by Ricardo and AEA Technology in the United Kingdom, EMPA in Switzerland, CONCAWE, the Association of European Automobile Manufacturers (ACEA), the Abgaszentrum Der Automobilindustrie, the International Organization of Motor Vehicle Manufacturers and others. Some of the methodologies that have shown the most promise are as follows:

- Modified 2007 PM (filter-based method).
- Raw exhaust + thermodenuder + electrical diffusion battery
- Constant volume sampler + laser induced incandescence
- Raw exhaust + laser induced incandescence

- Constant volume sampler + thermodenuder + condensation particle counter
- Constant volume sampler + photo acoustic soot sensor
- Constant volume sampler + secondary dilution + MEXA (a filter-based method for determining PM mass with chemical analysis)

Of these systems, the modified 2007PM method and the constant volume sampler + thermodenuder + condensation particle counter were recommended most strongly for further study. Since the repeatability of number based systems is dependent on volatile/nucleation mode particles, sample treatment systems are suggested that can remove these particles and provide for a more repeatable sample.

Automobile manufacturers in Europe and elsewhere have expressed concerns about the reliability of the non-standard measurement techniques suggested by the European Particle Measurement Programme for use in regulatory applications. The International Organization of Motor Vehicle Manufacturers critically examined each of the proposed new methods and included measurements from the automobile manufacturers and found that the gravimetric method was the only one sufficient for regulatory application. This report pointed out that nucleation is susceptible to large measurement artifacts and thus methods that are sensitive to nucleation would not be reliable. This commentary also indicated that the combination of a thermodenuder with size-unresolved total particle counts would not give valid data due to size dependent particle losses and dependence of the chemical nature of the particle. Additionally, test results were presented showing the variation between an ELPI, DMA + CPC, and diffusion charger was very high, even when they were simultaneously measuring from the same particle source. Their results indicated that PM measurement down to a level of 0.01 g/kWh with a 10% measurement were achievable, with further refinements possible using a sulfur-free fuel. Overall, it was concluded that the current gravimetric regulatory measurements should be retained into the future.

The importance of sampling conditions has also been investigated in the United States by Kittelson et al. and others. Among the factors considered important in laboratory sampling is the dilution ratio. In particular, the dilution ratio affects the saturation ratio that in turn influences the formation of soluble organic particles via gas to particle conversion and the nucleation of volatile hydrocarbons to form nuclei mode particles. It was found that the saturation ratio has the highest values for dilution ratios of about 5 to 50, thus, the strongest driving force for gas to particle conversion occurs in approximately the same range produced by conventional dilution tunnel systems. Nucleation can take place if high saturation ratios are produced and dilution takes place on a time scale faster than the characteristic time for adsorption.

To provide more representative sampling conditions, some recommendations on sampling of exhaust particles were made at the conclusion of the E-43 program. It was suggested that the most feasible solution to designing a system to approximate atmospheric dilution is using a two-stage dilution system. This system would incorporate a primary dilutor, an aerosol-aging chamber, and a secondary dilutor. A Sierra BG-type dilutor, with porous walls to introduce dilution air and low particle losses, was suggested for the first stage of dilution. The secondary dilution system would be designed to quench nanoparticle formation and changes caused by coagulation, nucleation and growth to provide a stable particle for measurement by the instrumentation. From a practical standpoint, it was suggested that a more important

consideration is probably the use of representative and repeatable laboratory procedures, rather than to try to simulate the formation of particles under conditions that are highly variable. Partial flow dilution systems where the dilution ratios and residence time can be more readily controlled are one option. With a more standard full flow dilution tunnel, to offset the fact that dilution values can vary considerably, the dilution ratio can be adjusted to maintain a constant dilution ratio to provide a better simulation of what occurs in the atmosphere.

The importance of understanding PM emissions for a range of different vehicle types and operating conditions has led to considerable progress in different methodologies for measuring PM under in-use conditions. These techniques include mobile emissions test facilities, on-board instruments, mini-dilution systems, and systems for measuring the plumes of vehicles under in-use conditions. Mobile emissions test facilities reviewed include units developed by University of California at Riverside CE-CERT, West Virginia University (WVU) and the University of Minnesota. Portable systems reviewed include systems developed by WVU, Analytical Engineering, Inc., Sensors, Clean Air Technologies International, Inc. (CATI), and the RAVEM system. The BG-1 through 3 mini-dilution system by Sierra Instruments, Inc./Caterpillar is also reviewed.

As sampling methods become more advanced, it is also important to understand the change that advances in technology will have on the nature of particles and their composition. DPFs are expected to expand considerably in the near future, as these devices will essentially be required to meet regulatory standards for 2007. CARB and Switzerland, and EPA have also put programs in place to promote the extended use of DPFs in retrofit applications. The Swiss VERT program in the mid- to late-1990s included an extensive technology survey that identified DPFs as the best available technology. DPFs can typically achieve >90% reduction of both particulate mass and number. The VERT program requirements for certification include efficiencies of >95% for particle counts and >90% for elemental carbon mass for the new traps and efficiencies of >90% for particle counts and >85% for elemental carbon mass after 2000 hours of operation.

1. Introduction

Since the mid-1990s, there has been increasing concern over the potential health effects of particulate matter (PM) from internal combustion engines. Airborne PM is composed of liquid and solid particles small enough to be suspended in the atmosphere. PM is a complex mixture of organic and inorganic compounds from dust, soot, smoke, and gaseous emissions from a wide variety of sources, with major contributions from mobile sources. Airborne PM is characterized by mass concentration as well as by particle size. PM greater than 2.5 microns is generally defined as coarse particulates, while the fraction smaller than 2.5 microns is defined as fine particulates (PM_{2.5}). Fine particulates comprise about 24% of the larger PM₁₀ mass emitted by all sources in the United States (US EPA, 2000). The fine particulate fraction contains a significant portion of the acid component and most of the mutagenic activity of PM (World Bank Group, 1998). As regulatory standards have gotten increasingly stringent, it is important to understand how the PM component of vehicle exhaust has changed over the years in order to gauge the expected improvement in air quality. The adoption of new regulations for heavy-duty 2007 engines has also created measurement challenges for both PM and NO_x. To provide the most technically sound basis for the development of regulations, it is important to have as complete an understanding as possible of previous as well as current studies related to PM emissions rates and measurement methodologies.

The potential health hazards of diesel PM have been known for several decades already. As early as the 1950s, diesel exhaust extracts were found to cause skin tumors in mice. Since then, diesel exhaust has been the subject of numerous epidemiological, animal and other studies. The emphasis on the health effects of PM can be traced to the studies in the 1970s that indicated that extracts from diesel soot were mutagenic to bacteria. In the late 1970s and early 1980s researchers conducted more detailed characterization of the PM and were able to identify polycyclic aromatic hydrocarbons (PAHs) known to be potential mutagens and carcinogens (Schuetzle 1983, Schuetzle et al., 1985). In the mid-1990s, interest in the potential health effects intensified as a number of health studies suggested that ambient PM could have more dramatic effects than originally thought and effects at levels below the current air quality standards. Some of the major findings included studies showing increased morbidity and hospitalization during episodes of high PM (Dockery et al, 1993, and Dockery and Pope, 1994). More detailed discussions and reviews of the potential health risks have been conducted by a number of groups and can be found elsewhere (IRAC, 1989, HEI, 1995). Two recent reviews of interest are assessments by the California Environment Protection Agency which identified diesel exhaust as a toxic air contaminant (Cal. EPA, 1998) and by the United States Environment Protection Agency (US EPA, 2002) which found that long-term (i.e., chronic) inhalation exposure to PM is likely to pose a lung cancer hazard to humans, as well as damage the lung in other ways depending on exposure (EPA, 2002). An extensive review of health effects of PM with a focus on developing countries has recently been reported as well (Panyacosit, 2000).

Ambient PM health effects studies have shown varied, sometimes contradictory effects that likely stem from methodological differences in PM measurement, physical and chemical differences in PM composition, and differences in the specific health measures used in the studies. Some of the major findings include studies showing increased morbidity and hospitalization during episodes of high PM (Dockery et al, 1993, and Dockery and Pope, 1994).

Other studies have identified sub-populations that are susceptible to health effects of PM. The sensitivity of individuals with heart disease and lung disease are documented in a number of studies (Schwarz, 1994; Ostro et al., 2000). The discovery of PM health effects at low levels of exposure presents a regulatory problem for the EPA because of the requirement that economics not be taken into account in the standard setting process. This has the potential to produce unattainable standards in many areas of the county if sensitive populations are to be protected with the required margin of safety (Reichardt, 1995). Modification of PM standards has the potential to affect industry in the United States in an adverse fashion. One proposed solution to protecting health while avoiding economic disadvantages to US business interests would be to develop standards jointly with other nations to equalize the economic effects (Friedlander and Lippman, 1994).

Up until 1987 ambient air standards for PM were based on total suspended particulates (TSP) but shifted to regulations including particle size with the EPA's PM₁₀ regulations. In 1999 the state of California called for a review of all of the existing health-based air quality standards by the California Air Resources Board (ARB) in consultation with the Office of Environmental Health Hazard Assessment (OEHHA) in the "Children's Environmental Health Protection Act", (California Senate Bill 25, Senator Martha Escutia; Stats. 1999, Ch. 731, Sec. 3). The review concluded that the existing standards for PM should be given a full review because of the statewide exposure and potential for significant health effects. The PM review concluded that the ambient air quality standard (AAQS) for PM needed to be revised to include separate standards for PM 2.5 and revised PM 10 standards (ARB 2002). Although there is some uncertainty in the exposure risk, the health benefits of attaining the revised standards were estimated to include a reduction of 6,500 premature deaths, 350,000 asthma attacks, and 2,800,000 lost workdays.

In response to these potential health risks from diesel exhaust, regulators at both the state and national level have developed a series of regulations for diesel exhaust and diesel PM over the years. Initial regulations of diesel exhaust began with the regulation of diesel smoke in the early 1970s with regulations of gaseous diesel exhaust species added by the late 1970s. Standards for PM emissions were first put in place for light-duty diesel cars and trucks in 1982. Standards for heavy-duty engines were implemented shortly thereafter in the mid-1980s and were harmonized between California and the US in 1988. Since 1987, the heavy-duty emission standard has been reduced from 0.60 grams per brake horsepower-hour (g/bhp-hr) to 0.10 g/bhp-hr today. With the introduction of the newest set of regulations an additional reduction to levels of 0.01 g/bhp-hr will be required starting in 2007. The US, the European Union, and Japan all use different test procedures which makes exact comparison problematic, however on a g/kWh basis the US 2007 regulations for heavy-duty vehicles fall midway between Japan on the high end and the European Union on the most restrictive end, see Appendix A (European Conference of Ministers of Transport, 2000). It is expected that achieving these low emission levels will require the use of diesel particle filters.

Although reduction of PM mass has been the emphasis of regulatory efforts, there is an increasing body of evidence that PM size distributions may be as important if not more important in determining the potential health effects of PM. Some health studies indicated that the concentration of fine PM rather than the concentration PM₁₀ may be more directly linked to health effects. Although PM size distributions from internal combustion engines have been studied since the 1970s (Kittelson et al. 1978; Wilson et al. 1977; Miller et al. 1974), the recent information on potential health effects has provided renewed interest in this area of study.

With the continuing reduction in and importance of diesel PM emissions, it has become increasingly more important to obtain accurate and representative measurements of PM emissions. The implementation of diesel aftertreatment control systems and other advanced strategies for diesel emissions control is anticipated to reduce PM emissions to levels near the detection limits of more traditional measurement techniques. The need to better understand PM size distributions will also likely present new measurement challenges. Clearly, an understanding of the accuracy and availability of different measurement techniques for exhaust PM is critical in the scientific and regulatory areas. To reach such an understanding, it is important to have a comprehensive understanding of on-going projects, current peer-review journal articles and reports in the field. The object of the present project is to provide a broad literature review of recent and classical publications and on-going projects related to the measurement of PM from vehicle exhaust, including international sources. This review will cover instruments suitable for measurement of PM mass, real-time PM mass, and PM size distributions. This will include portable instruments that can be utilized for the measurement of PM under in-use conditions. Important considerations in the formation of PM and the sampling PM will also reviewed.

2. PM Formation Mechanisms and the Fate of PM in the Ambient Atmosphere

2.1 PM Size Ranges

PM from internal combustion diesel engines typically have size distributions that range over several modes and orders of magnitude. PM size distributions are trimodal and composed of nuclei, accumulation and coarse modes, as shown in Figure 2-1. The smallest particles comprise the nuclei mode that ranges in size from 3 to 30 nanometers (nm), although the nuclei mode in earlier studies had a broader range from 5 to 50 nm. Another term associated with the smallest PM size is nanoparticles, which is typically used to describe PM below 50 nm in size. The accumulation mode PM ranges in size from 30 to 500 nm. The accumulation mode includes PM in the ultra-fine range that is defined as particles less than 100 nm. The largest particles are those in the coarse mode which is defined as particles >1 μm or 1,000 nm. The particles in the accumulation mode make up a majority of the mass, but particles in the nuclei mode make up to 90% of the particle number. Particles in the coarse mode can generally be attributed to reentrainment and represent 5-20% of the total mass.

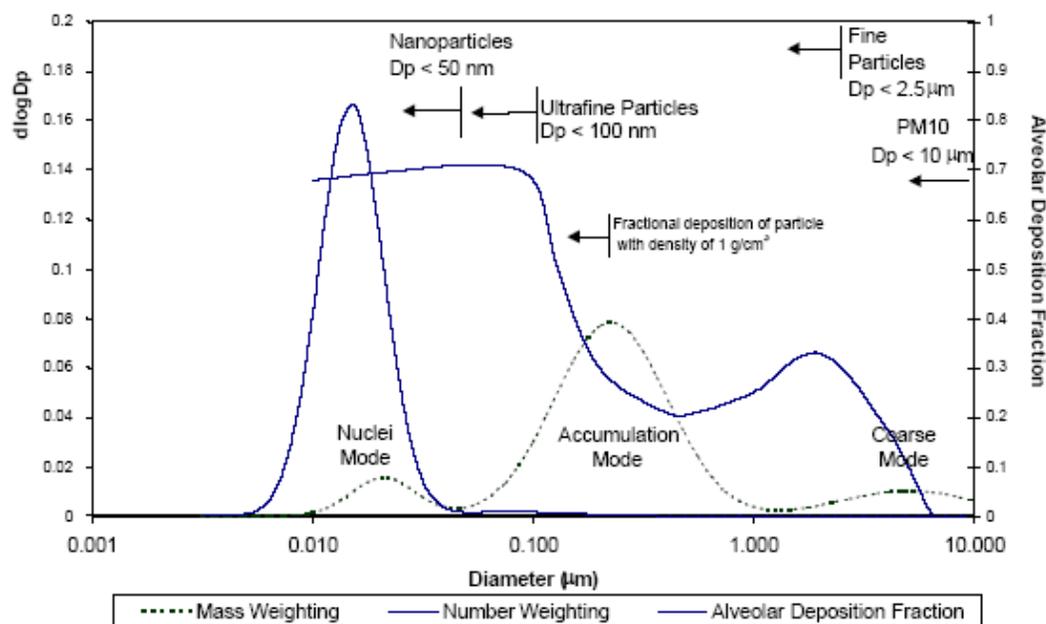


Figure 2-1. Particle Size Distributions based on Mass and Number (Kittelson, 1998a)

2.2 PM Formation Mechanisms

To understand the range and strengths and weaknesses of instruments applicable to the measurement of PM and evaluate PM sampling conditions, it is important to understand some of the fundamental processes that influence PM formation and behavior. These processes include: condensation/adsorption, evaporation/desorption, coagulation, particle losses in sampling systems, and chemical reaction. A schematic of the various processes influencing exhaust particles as they exit the tailpipe is provided in Figure 2-2. The mechanisms of PM formation have been described extensively in the peer-review literature, aerosol textbooks, and review

papers by researchers such as Kittelson and Johnson. A brief overview of these mechanisms is provided below. Several papers are available in the literature that describe and model the combustion processes involved in diesel engines (Woshni et al., 1995, Kazakov and Foster, 1998, Mueller and Zillmer, 1998, Taskinen et al, 1998, SAE 1999, Zhang and Reader, 1999).

One of the most critical parameters in aerosol behavior is how the aerosol particle diameter compares with the mean free path, or average distance between successive collisions, for a gas molecule. Particle size affects how particles interact with the surrounding medium as well as the role of different particle processes. Diesel aerosols have historically been measured in the micron and sub-micron size ranges where the particle diameter is large compared to the gas molecular free path. 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. At particle diameters comparable to those of the gas molecule free path, the particles have characteristics of both free molecule and continuum regimes.

The processes attributable to particle to particle interaction may lead to the loss of particles in the sampling system, including thermophoresis, diffusion, coagulation, inertial impaction, electrostatic deposition, and chemical reaction.

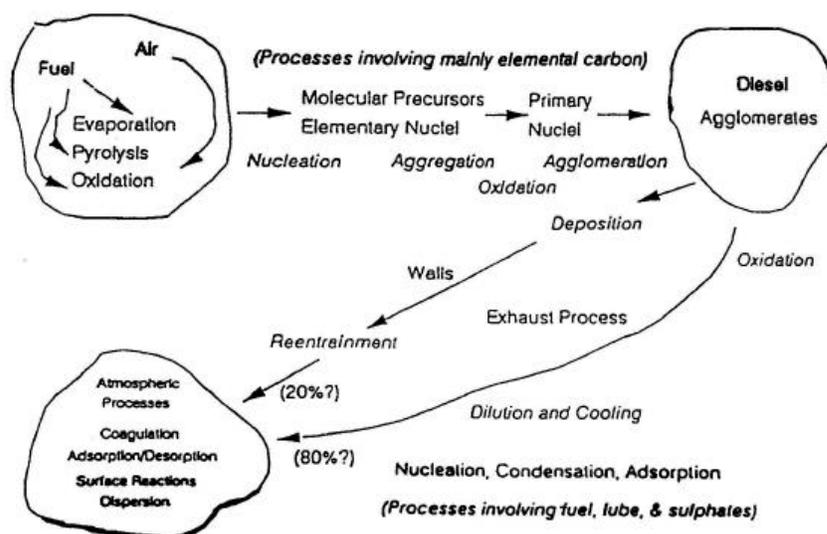


Figure 2-2. Schematic Representation of Processes Influencing Exhaust Particles in the Air and when Sampling (Kittelson et al., 1998a).

Thermophoresis is the motion of a particle from asymmetrical forces that arise from a temperature gradient. Essentially, particles are subject to more vigorous gas collisions and greater momentum force on the higher temperature side compared to the colder side. The thermal force and resulting particle motion follow the decreasing temperature gradient. The importance of the thermophoresis increases for systems with exhaust and sampling lines with cool walls that promote thermophoretic deposition

Diffusion of particles can occur from both the movement of particles through a particle concentration gradient and through Brownian motion. The diffusion coefficient of a particle varies as the inverse of particle size, with smaller particles diffusing more quickly than larger particles. Calculations of diffusional losses for typical diesel exhaust particles indicate that for particles with diameters between 0.03 and 0.30 μm , less than 0.2% losses are observed (Kittelson, 1990).

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 the particle, but does not change the total particle mass concentration. This means it does not influence the results of certification tests that measure the particle mass output from diesel engines. However, it is important to take coagulation into account when attempting to understand particle formation mechanisms. Also, since coagulation changes particle size, it will indirectly influence size dependent loss mechanisms. The amount of coagulation that takes place depends on the ratio of the residence time to the characteristic time for coagulation. The latter is inversely proportional to particle concentration, and thus the dilution ratio.

Inertial impact arises from the inability of particles to follow fluid streamlines as a result of their inertia. Particles may preferentially be excluded or included from a sampling stream or lost to the walls by inertial impaction resulting from non-isokinetic sampling errors and particle deposition in bends. The accumulation of lost mass on the sampling walls can result in subsequent reentrainment in an intermittent and unpredictable manner that can lead to mass measurement uncertainty. The importance of these effects depends on the particle diameter and is generally small for particles in the submicrometer range characteristic of diesel particles.

Electrostatic deposition can occur in sampling systems where sample transfer lines are made of materials that can be electrically charged. Approximately 85% of diesel particles are charged as a result of the combustion process, with larger particles more likely to be charged than smaller nuclei particles. Thus larger particles are more likely to experience electrostatic loss in a transport line than smaller nuclei particles.

Adsorption and desorption of volatile organics from the gas to the particle phase and back is an important mechanism of particle formation. Adsorption of volatile organics onto the particle surface to form the soluble organic fraction is one of the more important processes, which results in an increase in the size and mass of nuclei and accumulation mode diesel particles while decreasing the gaseous hydrocarbon concentration.

The amount of organics adsorbed on the particle surface depends on the saturation ratios of the various organic species, the amount of surface area available for adsorption, the adsorption energy and the time for adsorption to occur. The dependence of the adsorption of gaseous species on the saturation ratio can be modeled by conventional adsorption models such as the Langmuir or Brunauer, Emmet, Teller models (Haywood and Trapnell, 1964). The adsorption of gaseous species also depends on the surface availability, with vapor molecules forming single molecular layers by binding to the surface, and the adherence of molecules in subsequent layers, increasingly resembling condensation. Under the Langmuir model, adsorption increases with saturation ratio until the first molecular layer is formed and subsequently flattens out as all the sites in the initial monolayer are filled. The BET model has provisions for both monolayer

deposition as well as multi-layer adsorption. It should be noted that adsorption of soluble organic fraction (SOF) onto diesel particles is a physical process, not a chemical binding of the hydrocarbons (HC) to the particle surface. If the saturation value were to decrease, as during dilution of the exhaust, or through chemical processes such as sunlight or other atmospheric process, the SOF may desorb from the particle surfaces and return to gaseous form.

New particles may form by nucleation of gaseous organic species if saturation ratios are sufficiently high. 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. Nucleation of SOF in diesel exhaust may occur by two paths: homogeneous nucleation and heterogeneous nucleation. 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 is more likely if the particle surface area available for adsorption is limited.

Condensation can be considered an extension of nucleation and adsorption. In the case of adsorption, as saturation ratios approach and exceed saturation, continued addition of 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 species, condensing species will evaporate and the particles will decrease in size or disappear.

2.3 Fate of Mobile Source PM in the Ambient Atmosphere

Studies to understand the fate of PM from mobile sources in the atmosphere have been conducted since the 1970s. Some of the methods used include chase studies and roadside measurements. The focus of these studies is on understanding how particles behave and evolve in the time period immediately after formation in the engine as they dilute out of the tailpipe. This type of information is important in comparing with laboratory measurements where there is interest in obtaining realistic sampling conditions.

In the 1970s and beginning of the 1980s, early studies were conducted by General Motors, Whitby, Kittelson, Pierson and others. Whitby et al. (1975) made measurements for a California freeway and found particles largely < 150 nm in size. They also found that particle counts ranged from 2,000 to 50,000 in number per cm³ with the highest levels found during increasing traffic. General Motors did a more focused study to evaluate the potential exposure of the catalyst to sulfate (Wilson et al., 1997). These researchers suggested that the increase in particles in the size range between 100 and 1000 nm could be related to coagulation of nuclei particles. Dolan and Kittelson (1979) examined particle emissions from two light-duty diesel vehicles traveling at 16, 48, and 80 km/hr. They estimated the dilution was approximately 100 to 1 within 2 m of the tailpipe after 0.4 sec, and that the overall chase experiments showed a dilution ratio of 1000:1 after 1 sec. Pierson and coworkers did some early measurements in the Allegheny and Tuscarora Mountain Tunnels in Pennsylvania (Pierson and Brachaczek, 1976, 1983). Their studies were more focused on particle composition than detailed size measurements.

Kittelson et al. (1988) conducted an extensive series of field studies for the Coordinating Research Council in the late 1970s and early 1980s to examine the characteristics of diesel PM as a function of atmospheric dilution and aging. This included 3 tests with diesel trucks on roadways, a study of particles from upwind and downwind diesel trucks, and a study of particles upwind and downwind of a diesel engine test center. Over the range of the studies, with several different engines, a strong nuclei mode was observed, although the nuclei mode volume was very source dependent ranging from 0 to 35%. The volume fraction of the nuclei mode was found to nearly equal to the solvent extractable fraction, suggesting that most of the nuclei material was extractable. For experiments where a laboratory trailer was towed, atmospheric residence times were 0.01 to 0.4 seconds with dilution ratios of 3 to 90:1. In experiments where the laboratory was used in a follow/chase mode at a distance of 25 m, dilution ratios after 1 second were found to be 1000:1. In some cases, however, over 100 seconds were required to reach a dilution ratio of 1000. Under these slower dilution conditions, coagulation became significant, resulting in reductions in the number of nuclei particles and the number concentration by as much as a factor of 3.

More recently, the Kittelson et al (2001) conducted a study of on-road particles for the Minnesota Department of Transportation, with a focus on characterizing nanoparticles. Data were collected on Minnesota roadways during November of 2000 (temperatures of 1 to 13°C). The results showed that for measurements made at higher speeds, nanoparticles concentrations were found to be higher and the particles were smaller in size. Comparisons were also made between a CPC and an SMPS, with the best agreement found at slower speeds and less agreement at higher speeds. At high speeds, the CPC concentrations were found to be at least 3 times higher than those for the SPMS, which the researchers suggested was due to the ability of the CPC to measure particles in the 3-8 nm region that is below the range of the SMPS. An ELPI with a lower counting limit of 20 nm was found to nearly always have lower concentrations than either the CPC or the SMPS, although the up and down trends in the particle concentrations were found to be consistent among the three instruments. Siotas (2002) also investigated the transformation of vehicle exhaust particulate matter in the atmosphere.

Kittelson et al (2002a) also conducted a study for the Health Effects Institute (HEI) where exposure to PM in occupational settings was measured. Personal samplers were used to measure exposure for bus drivers, parking garage attendants, and mechanics in garage maintenance and repair facilities. Exposure was monitored in terms of a number of different metrics, including elemental carbon, black carbon, surface area, number concentration, and size distribution. They found that the CPC particle number measurements tracked the traffic pattern in the parking garage. In the parking area, the size distributions consisted of a nuclei mode at 20 nm and a smaller accumulation mode at about 50 nm. The CPC, with the lower size limit detection, consistently had number concentrations 3 to 4 times higher than the SMPS, indicating a large percentage of the number concentration < 10 nm. In earlier studies, the U.S. Bureau of Mines (1992) also examined particle number in underground mining situations. These studies showed the accumulation was more prominent relative to the coarse mode in tunnels where diesel vehicles were used for hauling, while the accumulation mode was essentially non-existent in mines where electrical equipment was used or reduced significantly when a disposable diesel exhaust filter was used.

The most comprehensive recent program examining atmospheric transformation is the Coordinating Research Council's E-43 "Diesel Aerosol Sampling Methodology" Program,

conducted by the University of Minnesota along with a number of other research organizations. The test program included roadway and engine dynamometer tests on Caterpillar and Cummins engines, wind tunnel experiments at the Langley Wind Tunnel in Langley, Virginia.

One of the main objectives of the program was to 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. These measurements showed that all test vehicles displayed a distinct nuclei and accumulation mode, with old and new technology engines producing nuclei modes of similar magnitude. The nuclei mode showed considerable variability depending on engine operation, engine thermal history, roadway grade, interaction with other traffic, background aerosol, and ambient temperature. The formation of the nuclei mode was more favorable under cold temperatures, for example. The fraction of particles found in the nuclei mode ranged from 37 to 87% by number and 0.3 to 2.1% by volume. The accumulation mode, on the other hand, was a repeatable function of engine and operating conditions. Samples collected in the wind tunnels differed from those collected on-road, with low dilution ratios, high background concentrations, and no significant nuclei mode.

Another important objective of the program was to examine particle transformations as the plume disperses downwind of the roadway in a typical urban situation. A computer model was used to evaluate characteristic times and transit distances for particles under typical urban conditions. A reduction of 90% in the total particle number was found to take on the order of a few minutes and 100-1000 m. Particles are expected to survive and travel a factor of ten greater distance in rural flat areas compared to an urban downtown location. This can be attributed to faster coagulation in urban areas due to higher background particle concentrations and more rapid mixing and deposition due to rougher terrain.

In Japan, Hirofumi and Yoshiharu reviewed the potential impact of 2005 PM regulations on roadside PM levels. They concluded that while the 2005 regulations would provide significant reductions in PM from automobiles, this will be partially offset by increases in emissions of PM from other sources. They recommended localized measures such as traffic flow controls and denitrification controls in some specific areas having high roadside concentrations of NO₂ and PM. In addition, they recommended PM 2.5 regulations be introduced to focus efforts on combustion sources that contribute fine particulates rather than the PM 10 regulations that are influenced by coarse mode particulates associated with natural sources. In other work, Hirabayashi et al. (2002) characterized sulfur in airborne particulate matter by the x-ray absorption near edge spectroscopy (XANES) method. The authors examined PM collected on arterial roadways and found that the contribution of tire wear to PM was low.

3. Techniques for Measuring Real-Time PM Emissions and PM Size Distributions

It is important to understand the state of the art techniques for measurement of PM mass and size in order to assess the state of laboratory measurements of PM. The implementation of Not-to Exceed (NTE) and in-use measurement requirements is, in part, driving the development of real-time PM instrumentation. Reviews of PM instrumentation have been conducted previously by Kittelson et al. (1998a) and others. A summary of instrument characteristics is provided in Table 3-1. A number of studies have also been conducted to evaluate the effectiveness of various instruments in making repeatable PM measurements under laboratory conditions, including extensive studies conducted in Europe and studies conducted by Moosmüller et al. (2001a, b) and others. The focus of this section is on a review of the instrumentation that can be used for measurement of exhaust PM emissions. Studies of more detailed comparisons among instruments will be discussed in the following section.

3.1. Real-Time PM Measurement Techniques

One of the most important aspects of PM is understanding the conditions under which PM is formed in real-time. There are a number of instruments available that can provide some measure of PM emissions in real-time. A brief description of available instruments and some of their strengths and weaknesses is provided below.

3.1.1 Tapered Element Oscillating Microbalance (TEOM)

The tapered element oscillating microbalance (TEOM) is capable of producing real-time mass measurements of PM within diesel exhaust. The TEOM uses a filter on the narrow end of a tapered tube. The tube is oscillating on a microbalance so that changes in the inertial weight of the filter can be measured by changes in the frequency of the oscillation. Measurements must be collected with a stable temperature (50°C) because changes in temperature induce changes in oscillation frequency. Commercially available units can report measurements with time resolutions down to 0.5 seconds (Moosmüller et al, 2001a). Currently, Rupprecht & Patashnick Co, Inc. (R&P) have also developed a TEOM Series 1105 that can be used for diesel PM measurements. The system provides mass concentrations, mass rates, and total mass on a second by second basis. The R&P instrument has been incorporated into an on-board measurement systems developed by the Flemish Institute for Technological Research (Lenaers et al., 2002). R&P was also recently awarded a contract by the US EPA for the design and construction of PM mass measurement modules to be used in the EPA's on-board measurement program (Anderson 2004).

3.1.2 Quartz Crystal Microbalance

Quartz crystal microbalances (QCMs) utilize the same operating principals as a TEOM, but the particles are deposited onto the quartz crystal via electrostatic precipitation. The oscillation frequencies of the QCMs are also much higher than those of the TEOM. QCMs were introduced in the 1970s, but suffered initially from problems with overloading, calibration problems, and vibration. More advanced QCMs are currently being used in conjunction with several on-board analyzers, including those from Sensors and an instrument developed by WVU (Booker 2001; Gautam et al. 2003c).

3.1.3 Nephelometer

Another PM mass measurement device is the nephelometer which measures light scatter within a sample chamber. Nephelometer units can be made simple and have good sensitivity and sampling resolution. The PM mass measurements from a nephelometer are influenced by the refractiveness of the particles that can lead to bias in results under some conditions. The low cost and compact size of the instrument provides significant advantages over many of the other methods. Nephelometers typically report measurements in mass density (i.e., mg/m^3).

3.1.4. Condensation Particle Counter (CPC)

The CPC is a particle counter based on the use of an alcohol saturation chamber (Hinds, 1999). Particles entering a CPC are initially saturated with a butanol mixture. These particles flow into a condenser that has a reduced pressure and is typically controlled to $\sim 10^\circ\text{C}$. The butanol droplets condense onto the already alcohol soaked particles causing them to grow to spheres with diameters $>10\ \mu\text{m}$. These larger and more uniform particles are then counted by an optical light scattering method. A CPC is typically used as the counting element for an SMPS. (Figure 3-1).

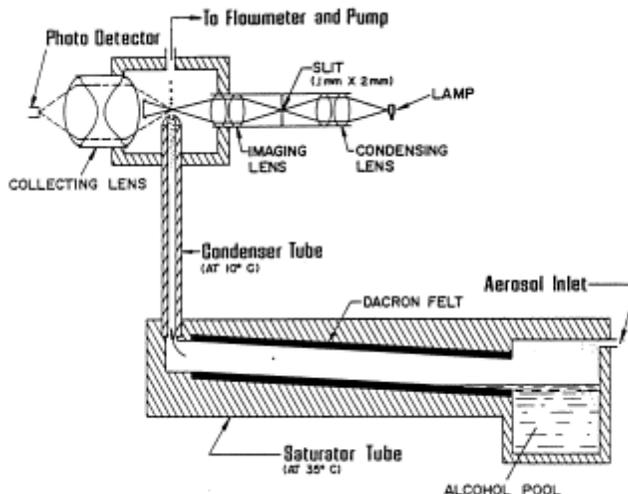


Figure 3-1. Condensation Particle Counter schematic. (Burtscher, 2001)

3.1.5 Aethalometer

The aethalometer provides a real time measurement of the mass using optical aerosol absorption methods. This instrument is primarily used for the measurement of elemental carbon (EC). The aethalometer uses a filter tape for sample collection. This allows for automated changes in the sample media that make the aethalometer good for ambient air measurements. Time resolution for aethalometers is on the order of several seconds. Output for the aethalometer is reported as black carbon concentration.

3.1.6 Photoacoustic Instrument

Photoacoustic instruments are another type of instrument utilized for the measurement of black or elemental carbon. Photoacoustic instruments have been used in automotive research for over 20 years for measurement of PM emissions (Japar and Sckarlat, 1981, Japar et al, 1984). Photoacoustic instruments use measurements of laser beam absorption in an acoustic resonator to determine EC particle mass. The laser beam is modulated at the acoustic resonance frequency

that corresponds to where aerosol compounds change energy into an acoustic signal when they cool. The photoacoustic signal is then measured by a microphone. The amplitude of the sound wave is then used to estimate PM mass through a linear relationship. While the methodology can give an accurate measurement of the EC component, the OC component of diesel PM is “transparent” to the technique. A detailed description of photoacoustic instruments is provided in Arnott et al (1999). Recently, AVL has developed and is commercializing a photoacoustic instrument for use on engine test stands and chassis dynamometers (Schindler et al., 2004). This unit has a range of 4 orders of magnitude in PM concentration and a detection limit around $5 \mu\text{g}/\text{m}^3$.

3.1.7 Time Resolved Laser Induced Incandescence

In time-resolved laser induced incandescence, particles are heated by a short laser pulse and the resulting radiation from the particles is measured (Figure 3-2). The intensity of the produced radiation can be used to determine the particle size based on the time dependence of the cooling of the particles, elemental carbon mass (Mewes and Seitzman, 1997; Schraml et al., 2000a,b; Bryce, 2000). The resulting measurements are thus representative of the elemental carbon mass in the exhaust PM. An advantage of this type of system is that it is relatively fast and sensitive, allowing measurements over transient tests and for modern low emission engines. Since the data evaluation is based on a radiation model, knowledge of a number of parameters such as volatile material is required to obtain accurate estimates.

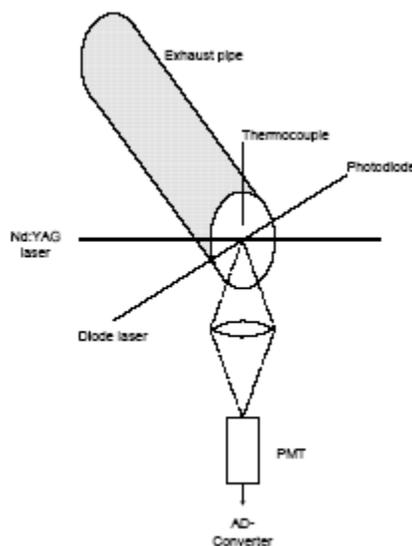


Figure 3-2. Tailpipe setup of laser induced incandescence particle measurement system. (Schraum et al., 2000b)

3.1.8 Fast FID

The Fast-response Flame-Ionization Detector (Fast FID) (Kawai et al, 1998) has recently been adapted for use in measurement of soluble organic fraction and soot (Fukushima et al, 2000). The fast FID instrument is based on measurement of an ionized gas mixture consisting of hydrogen-helium and the gas to be measured. The current produced by the ionization of the gas mixture is measured by electrodes, amplified and then converted into parts-per-million

concentrations. Fukushima et al used the pulse signature that the ionization current produces in the signal from the FID when PM is included in the sample gas to develop a differential signal processing methodology that is capable of measuring the SOF and soot components. The Fast FID was validated against the filter-weight methodology and a good correlation was found.

3.1.9 The Importance of Second-by-Second PM Emissions Measurements in Development of Emissions Models

Modeling of mobile source PM emissions has become an increasingly important use of the PM measurement data collected with the various PM measurement instruments described in this report. PM emissions estimates have been included in the main emissions inventory models for use nationwide in estimation of SIP's. Both the US EPA's Mobile 6 model and the California Air Resource Boards EMFAC model use average grams/mile PM emissions based on driving cycle and mostly certification data. These models do not require time resolution of the PM emissions and suitable data can be collected with a variety of instruments, although in most cases filter mass is used. In the last decade, there has been a good deal of activity in developing instantaneous or modal emission models to better predict mobile-source emission inventories, primarily at the microscale level. In the past, the conventional mobile-source emission models MOBILE and EMFAC were developed for calculating regional inventories using aggregated vehicle emissions data and estimates of vehicle activity in the form of VMT and average speed (i.e., at the macroscale level). To better capture emissions effects associated with a wide range of driving dynamics, instantaneous (i.e., second-by-second) models are better suited for evaluating traffic operational strategies that improve traffic flow (e.g., ramp metering, signal coordination, additional lanes, etc.). These instantaneous emission models can be used in conjunction with detailed vehicle activity data or with microscale traffic simulation tools to better predict the emissions impact of different traffic scenarios. The newer generation of mobile source models (MOVES, MEASURE, CMEM) will be modeling PM on a second-by-second basis and thus require second-by-second PM emissions measurements. In addition to requiring greater time resolution on PM, the next generation of mobile source models will require PM data collection on the road.

3.2. Techniques for Measuring PM Size Distributions

Unlike gaseous emissions, PM emissions have a second dimension beyond mass in particle size that affects dispersion and environmental and health effects on plant and animal living systems. Understanding PM sizing is necessary for a full understanding of the conditions under which PM is formed and transported as well. There a number of instruments available that can provide some measure of PM size distributions in real-time. A brief description of available instruments is provided below.

3.2.1 Electrical Mobility methods

Techniques in this subsection determine PM size distributions based on electrical mobility.

3.2.1.1 Electrical Aerosol Analyzer

The electric aerosol analyzer (EAA) is one of the most basic instruments for particle sizing (Dolan et al., 1980; Liu and Pui, 1974). Particles entering the EAA are initially charged by

exposure to unipolar positive ions. The particles then enter the section of the analyzer that separates based on mobility. To separate particles, the applied voltage within the mobility analyzer is varied, allowing the electrical mobility pass cut-point to be varied. In essence, the mobility analyzer acts as a low-pass filter. The concentration of particles for each particle size cut-point or corresponding voltage in the mobility analyzer is then determined by measuring the current of the detected charged particles.

3.2.1.2 Differential Mobility Particle Sizer

The differential mobility particle sizer (DMPS) is similar to the EAA in the use of electrical mobility. The DMPS only allows particles with a specific electric mobility range to pass through the electrical mobility analyzer for measurement. This is in contrast to the EAA that allows all particles with the low pass filter range to be measured. Again the size interval is ramped through in discrete stages by varying the applied voltage. The DMPS does provide improved resolution compared to the EAA. The sensitivity is reduced, however, since a smaller number of particles are measured. To counteract the decreased sensitivity, a condensation nuclei counter is typically used in place of an electrometer for measuring particle counts. The DMPS also uses a bipolar charger to charge the particles prior to entering the mobility analyzer, as opposed to the unipolar charger used by the EAA.

3.2.1.3 Scanning Mobility Particle Sizer

The SMPS is currently one of the most widely used instruments for measurement of particle sizing. This instrument also utilizes electrical mobility for size separation. In contrast to the EAA, the SMPS can be scanned continuous rather than in a stepwise manner. This allows for increased resolution and the ability to provide a complete size distribution in a single scan. One disadvantage of the SMPS is that a complete scan of 100 size intervals takes approximately 1 minute to provide relatively undistorted size distributions. This relatively slow scan time makes it difficult to obtain size distributions under more transient conditions.

The SMPS can also be used to measure a single particle size range continuously. Operating in this mode, measurements of particle size can be made over transient cycles, albeit one size range at a time. Unfortunately, since 3-5 size ranges are typically required to obtain an approximate size distribution of submicron particles, at least 3-5 tests are required to obtain a single size distribution in this mode of operation. The requirement of multiple tests can add considerably to the required time and the cost for a test program.

3.2.1.4 Nanometer Differential Mobility Analyzer

More recently, a nanometer differential mobility analyzer has been developed (Chen et al., 1996, 1998). This instrument scans a narrower range of voltages and particle sizes to allow optimization for the nanometer particle sizes, with a size range that corresponds approximately with the nuclei mode. This instrument is designed to provide a size distribution between 3-50 nm with a scan time of approximately 10 seconds.

3.2.1.5 Engine Exhaust Particle Sizer (EEPS)

TSI has recently introduced a new particle size instrument called the EEPS that is capable of providing sub-second response for PM size measurement during transient tests (Johnson et al. 2004). The instrument design is based on a method developed at the University of Tartu-Estonia over two decades ago. This instrument was found to compare favorably over engine dynamometer tests compared to an SMPS and a CPC.

3.2.1.6 Combustion DMS500

This instrument is a real-time differential mobility spectrometer for real-time PM measurement. This instrument combines the attributes of an electrostatic low-pressure impactor, which uses a corona charger, and a differential mobility analyzer (DMA), which uses electrical mobility for size classification. This instrument can provide size distributions in the 5 nm to 1000 nm size range, with a time resolution of 200 ms. It has been used for measurements of size distributions from light-duty vehicles and heavy-duty diesel engines (Reavell et al., 2002; Goto and Kawai, 2004).

3.2.2 Inertial methods

Another important method for characterizing particle size is by aerodynamic diameter using inertial methods. These measurements are typically made using a cascade impactor (Figure 3-3), in combination with different methods for measuring particle concentration. The cascade impactors operate by pulling a particle sample stream through a multi-stage impactor with impaction stages for each corresponding size distribution. Above each of the impaction substrates is a corresponding orifice plate with multiple holes of a specific diameter. The hole diameter of the orifice in turn helps determine the particle velocity through the orifice. The particle velocity in combination with the distance between the impaction substrate and the orifice plate determines if a particle will impact on the substrate and the corresponding size cut-point.

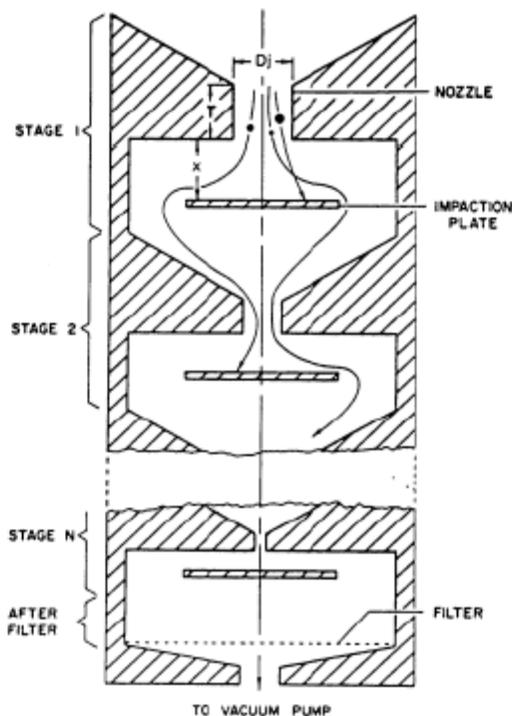


Figure 3-3 Cascade Impactor schematic. (Burtscher, 2001)

3.2.2.1 MOUDI

The Microorifice Uniform Deposit Impactor (MOUDI) is one of the earliest cascade impactors that has been applied to vehicle exhaust (Marple et al, 1991). The MOUDI is primarily used to determine the mass size distribution of exhaust. The MOUDI includes 10 impactor stages with 4 impaction stages below 1 micron. The MOUDI is utilized to collect mass samples on aluminum substrates that can subsequently be analyzed gravimetrically. Samples can also be subsequently used for chemical analysis. To provide a more uniform distribution on the filters for chemical analysis, a unit with rotatable stages is often used. The samples are collected over an integrated period corresponding to a specified cycle or time of operation, and hence the results are not provided in real-time. The MOUDI is also limited in that it does not provide size breakdowns < 50 nm.

3.2.2.2 Electrostatic Low-Pressure Impactor

The ELPI expands on the capabilities of the mass based impactors to provide the ability to measure size-distributed number distributions in near real-time (Keskinen et al., 1992). The ELPI works by charging the particles prior to entering the impaction stage. The particle concentration on each impaction stage is then measured with an electrometer that can be used to provide a number density. The ELPI provides size distributions between 30 nm and 10 μm with a time resolution of 2 seconds. It should be noted that some uncertainties were reported in ELPI measurements made in a study by researchers in the United Kingdom (Moon and Donald, 1997).

More recent measurements at the university of Birmingham, the University of Minnesota, and Ford Motor Company have shown better correlation, however (Maricq et al., 2000).

3.2.2.3 Nano-MOUDI

The nano-MOUDI operates similar to a more traditional MOUDI but includes a greater number of stages and stages at smaller particle diameters (Marple et al., 1994). In total, the nano-MOUDI incorporates 13 stages between 10 nm and 18 μm . Low-pressure operation is used for the stages with cut-points below 50 nm. Similar to the traditional MOUDI, the stages can be analyzed for either mass or chemical analysis.

3.2.3. Other PM Characterization Instruments

Other techniques that have been used for characterization of PM include methods utilizing mass spectrometry, photoemission sensors, and radioactive tracers. A summary of some of these techniques is provided in the following subsection.

3.2.3.1 Aerosol Time-of-Flight Mass Spectrometer

The aerosol time-of-flight mass spectrometer (ATOFMS) provides a measurement of the aerodynamic size and chemical composition of individual particles in an exhaust stream (Noble and Prather, 1996, 1998). As a particle enters the ATOFMS, it is accelerated to terminal velocity by a supersonic expansion of the carrier gas. This provides a size separation in that the smaller particles reach a higher velocity than the larger particles. The aerodynamic diameter can then be determined by the time-of-flight for the particle to travel between two lasers. After the time of flight is determined, the particle then passes the ionization region of the mass spectrometer where the particle is pulsed with another laser. The ions and molecules created by the laser are then measured by a mass spectrometer to determine the chemical components of the desorbed or ionized material.

3.2.3.2 Photoelectric Aerosol Sensor (PAS)

Photoelectric aerosol sensors are used to quantify the concentration of PAHs in diesel PM (Burtscher and Siegmann, 1994). The aerosol initially passes through an electrical condenser that removes any charged particles or ions. The neutral particles then pass through a photoemission chamber where they are irradiated with a UV laser or flash lamp (Figure 3-4). For particles with photoelectric work functions below the photon energy of the UV source, an electron is emitted and the particles become positive ions. In the photoemission chamber, the charged particles are subjected to an electric field that pushes the positive particles to a filter for collection and measurement using an electrometer. The resulting particle photoemission is linearly related to the particle surface area and the surface area concentration. The resulting photoemission can then be related to the PAH concentration determined by chemical analysis as discussed elsewhere (Hart et al., 1993).

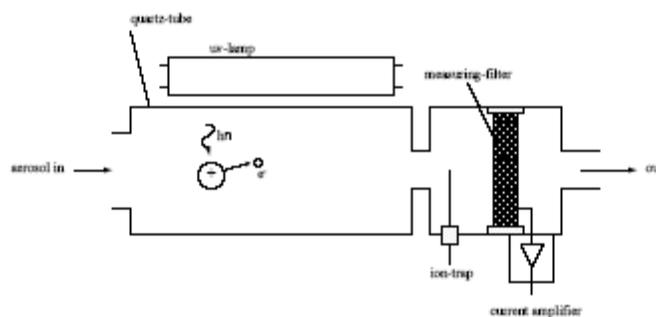


Figure 3-4 Photoelectric aerosol sensor schematic. (Burtscher, 2001)

3.2.3.3 Epiphaniometer

The epiphaniometer is an instrument that measures the surface concentration of particles using a radioactive isotope (Gäggeler et al., 1989a,b). Particles entering the epiphaniometer pass through a charging chamber where lead isotopes are created and attach to the particle surface (Figure 3-5). The lead isotopes are formed from a decaying actinium. The particles are then transported to a collection filter through a capillary. The level of radioactivity of the particles on the filter is measured using a surface barrier detector. The measured radioactivity is proportional to the surface area based on Fuchs theory of attachment of radioactive isotopes to surfaces.

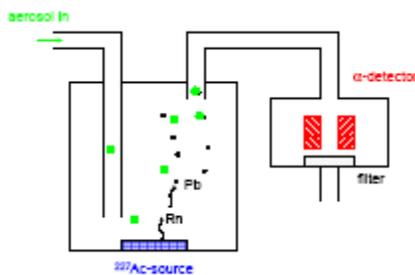


Figure 3-5 Epiphaniometer schematic. (Burtscher, 2001)

3.2.3.4 Diffusion Batteries

Diffusion batteries utilize the principle of diffusion mobility to size classify particles. Since diffusion is strong for very small particles, this method is generally useful for particles <300 nm. Diffusion batteries have been used for more than 50 years. Diffusion batteries can use different geometries, such as screens, tubes, and beads, to generate different flow profiles (Scheibl and Porstendörfer, 1984; Hinds, 1999). Usually values are applied to change the diffusion length (e.g., number of screens), although a parallel setup, using several CPCs, can also be used to allow fast measurement and real-time response. Electrical diffusion batteries have recently been introduced, where the particles are charged prior to entering the diffusion battery and the deposition related to each stage is measured using an electrical current (Burtscher et al., 2001). Mathematical expressions can be used to determine the particle size as a function of penetration for the different geometries in the diffusion batteries (Cheng 1993, Cheng et al., 1985, Cheng and Yeh, 1984, Kapadia, 1980, Maher and Laird, 1985). A CPC or Pollack counter, which

utilizes an expansion chamber but is very time intensive (Hoppel, 1978), is typically used to measure particle number.

Matter Engineering AG have developed a NanoMet modular system that combines microdiluter, a multi-stage diffusion battery, and two detectors (Kasper et al. 2001). The development of this system was sponsored by the Swiss EPA and European occupational health authorities for field use a certification. The sampling interface consists of two heated tubes that connect to the diluter that prevent the formation of condensates. The diluter provides a tunable dilution factor from 30 to 3000. The diluter can be heated to 150°C, which prevents the formation of nanoparticles from volatile organic compounds, sulfuric acid, and water. As the gas cools down after dilution, the volatiles do not condense because their vapor pressure is too low. A multi-stage diffusion battery is used to classify the particle sizes. The measurement size ranges from 10 nm to 1 µm with a time resolution of 1 second. This system is currently used for trap specification and field control in Switzerland and in Canadian mines. A modified version the NanoMet C was recently developed that can be used in a CVS dilution tunnel and combines a thermal diluter and a CPC (Kasper, 2004). This instrument is designed for evaluation as part of the round-robin testing planned for phase three of the European Particle Measurement Programme.

3.2.3.5 Aerosol Mass Spectrometer (AMS)

The Aerosol Mass Spectrometer (AMS) measures the size distribution and composition of volatile and semi-volatile organic aerosols for species such as NO_3^- and SO_4^- . The AMS uses an aerodynamic lens to sample particles between 0.03 and 1.5 µm in diameter. The particles are pulled into a vacuum where they are categorized based on aerodynamic size. The particles are then vaporized on a heated surface and chemically analyzed using electron impact ionization quadrupole mass spectrometry. The AMS system developed by Aerodyne has been described in detail in Drewnick, et al., 2003; Jayne, et al., 2000; Jiménez, et al., 2003.

3.3. Other Instrumentation Related to PM Sampling

The instruments discussed in this subsection include instruments used in the calibration of PM instrumentation or in addressing some of the artifacts associated with PM sampling.

3.3.1 CAST (Combustion Aerosol STandard)

The CAST is a stand-alone, soot-generating burner based on a co-flow diffusion flame that generates air suspended sub-micron combustion soot particles. The particles correspond to the PM emitted by diesel engines in many of the most important characteristics. The concentration and size distributions of the particles are reproducible and can be calibrated to an outside standard.

3.3.2 Thermal Denuders

Thermal denuders are used for the removal of volatile matter prior to sampling to reduce the impacts of any sampling artifacts. For the thermal denuders, the particles are initially draw through a heating zone that is typically a metal tube with the wall heated. This enables volatilization of the condensed hydrocarbons. The heated particle stream then passes through a channel lined with fibrous charcoal with a very large surface area that is the condensation zone.

Within the condensation zone, the coolant air is added causing the gaseous hydrocarbons to rapidly diffuse to the charcoal-lined walls where they are adsorbed. The solid particles with lower diffusivities then exit the instrument. The flow and operating characteristics of the instrument can be changed to provide different sampling characteristics.

4. Laboratory Studies and Methods for Particulate Matter Emissions from Vehicles

4.1 Laboratory Measurements of PM

Over the years, a number of studies throughout the world have investigated PM mass emission rates, size distributions and number from motor vehicles and internal combustion engines. The following section reviews studies primarily focused on the measurement of PM size distributions and number. Additional data on PM mass is available in a companion document (Zhu et al., 2004).

4.1.1 Measurements of Vehicle Exhaust PM in the US

Kittelson and coworkers made some of the earliest measurements of exhaust PM size distributions using instruments such as an electrical aerosol analyzer, a diffusion battery, and a micro-orifice impact (Kittelson et al., 1978; Dolan et al., 1980; Verrant and Kittelson, 1977). In the late 1970s and early 1980s, researchers at Ford Motor Company were already using techniques such as photacoustic spectroscopy and light extinction to measure vehicle PM (Truex and Anderson, 1979; Japar and Szkarlat, 1981), while researchers at General Motors were using an electrical aerosol analyzer to measure size distributions from diesel vehicles (Groblicki and Begeman, 1979). Researchers at the New York State Department of Environmental Conservation also conducted early vehicle experiments using a TEOM (Whitby et al., 1982). Work in measuring PM size distributions and number from vehicles continued sporadically throughout the 1980s and into the mid-1990s. This includes work by Kittelson et al. (Du et al., 1983; Piphon et al. 1986; Luo et al. 1989; Kittelson et al. 1991), the Coordinating Research Council through the E-24 project (Cadle et al., 1999), and others (Rogge et al. 1993). For the present section, however, the focus will be on more current literature by some of the groups with larger programs for PM size and number research.

Researchers at the University of Minnesota under Dr. David Kittelson continue to be among the most active in the area of PM size and number characterization. As discussed above, Kittelson et al. have conducted extensive studies to evaluate methods of accurately characterizing PM in comparison with distributions observed in the atmosphere, including the recent E-43 program. Previously, Kittelson et al. conducted a major review of diesel particulate matter sampling methods, including instrumentation (1998a) and comparisons of aerosol dynamics under laboratory and on-road studies (1998b). Schaberg of Sasol Oil in conjunction with the University of Minnesota studied size distributions produced by Fischer-Tropsch diesel fuels (Schberg et al. 2002). For both engines tested, the Fischer-Tropsch fuel showed a considerable reduction in the number of particles when compared to a conventional diesel fuel. Jung et al. (2003) looked at the influence of lubricating oil on nanoparticle emissions using a lube oil-dosed fuel. The particle size measurements showed that particle volume emissions decreased by about a factor of two while number emissions increased by an order of magnitude when the lube-oil dosed fuel was tested. Kittelson has also been involved in on-going collaborative work with the Professor Graskow of the University of Cambridge. Graskow et al. (2000) investigated the influence of fuel additives and dilution conditions on PM from a direct-injection, SI engine. Overall, the presence of additives did not have a strong effect of particle emissions, although a polyolefin

amine additive did produce increases in particles >100 nm at 15 and 30 km/hr. Graskow et al. (1999a) have investigated the size distributions from a gasoline direct injection vehicle at steady state speeds between 13 and 90 km/hr. The size distributions for this vehicle had a single peak for speeds from 32-90 km/hr with a slightly larger mean diameter for higher speeds. For the 13 km/hr operating condition, the size distribution was bimodal. In another study, Graskow et al. (1999b) tested also two port injected SI engines and examined the effects of catalysts and deposits.

West Virginia University also has an extensive program for the measurement of diesel PM emissions and factors that influence their size distribution, number, and mass. The WVU PM mass measurements are discussed further elsewhere (Zhu et al. 2004). For size distributions, some of the more recent work has investigated the effects of various fuels and lubricants on PM emissions. Gautam et al. (2003) measured the effects of Fischer-Tropsch diesel on PM size distributions. One of the findings of this study was that larger particles (>100 nm) had a significantly higher mutagenic response than smaller size particles (<100 nm). Gautam et al. (2002) also examined size distributions for DPFs on heavy-duty vehicles. They found that the DPFs provided dramatic reductions in particle concentrations across the nanoparticle size range. Gautam et al. (2000) also found in earlier work that CNG powered vehicles can emit an order of magnitude higher number of particles than comparable diesel vehicles even though the mass emission rates of the diesel vehicles can have an order of magnitude higher mass. Mostafa et al. (2001) studied the effect of sulfur content in lubricants and diesel fuel on size distributions. They found that lube oil sulfur levels and additive packages could have a significant influence on size distributions and concentrations of PM emissions. Researchers from WVU also were part of the CRC E-43 study and made measurements as part of the exhaust plume studies in the wind tunnel (Clark et al. 2003; Gautam et al. 2003b). They have also developed models for the effects of ambient dilution on the coagulation of PM in a turbulent dispersing plume (Kim et al. 2002).

Scientists at the Ford Motor Company Research Laboratory have extensively investigated the issue of PM emissions and size distributions. In some of their earlier work on size distributions, Maricq et al. (1999a) conducted FTP tests on twenty-one 1994-1998 gasoline vehicles. It was found that the FTP weighted emissions were all below 2 mg/mi for the gasoline vehicles. This is similar to other measurements of modern gasoline vehicles (Cadle et al., 1999; Durbin et al., 1999). The particles had diameters ranging between 10 and 300 nm, with geometric mean diameters of 45 to 80 nm. The PM emission peaks occurred as narrow peaks correlated with acceleration. Maricq et al. (1999b) also tested a set of 8 1996-1998 gasoline vehicles over the FTP and US06. These measurements showed that the US06 mass emission rates were similar in magnitude to the phase 1 FTP emission rates and ranged from 1.2 to 9.6 mg/mi. Size distributions were collected with both an SMPS and ELPI and showed mean particle diameters of 50-70 nm with a range from 10-300 nm. Harris and Maricq (2001) also studied the differences in size distributions between gasoline and diesel engines. This program included 3 diesel vehicles, 3 gasoline vehicles, one gasoline engine, and two diesel engines. The diesel engines exhibited a lognormal size distribution with a peak at approximately 60-100 nm depending on the test conditions. Increasing EGR from 0 to 37% for the diesel vehicle was found to shift the peak of the size distribution to slightly larger diameters and increase the total particle number. The direct injection spark ignition particle number emissions under stratified mode were slightly less than those of the diesel vehicle, but were about 2 orders of magnitude lower in homogeneous charge mode. The major difference between the diesel and the direct injection spark ignition was a slight but systematic asymmetry in the lognormal form. The port injection gasoline vehicles

were the lowest emitters, with particles numbers on the order of 10^4 - 10^5 lower than those for the diesel engines.

Maricq et al. (2000) have also compared PM measurements made with an ELPI compared to an SMPS. For this study, measurements were made with both gasoline and diesel vehicles and over both transient and steady state cycles. For the steady state cycles, the size distributions showed good agreement between the ELPI and the SMPS, although the ELPI did overestimate the particle number for the size range for the 37 nm impactor stage. For the transient tests, only the ELPI provided second-by-second size distributions. The SMPS was run at a single range per test, with multiple tests run to obtain the full size range. Using this methodology, the integrated size distributions were found to be in good agreement between the ELPI and SMPS. With the quicker response time, the ELPI was found to provide higher instantaneous PM emission rates.

Researchers at Ford in the US and in Europe have also investigated the effects of sampling conditions on PM formation. Maricq et al. (1999c) compared direct tailpipe sampling of PM for gasoline vehicles with dilution tunnel sampling and found the results to be basically the same. This was attributed to the relatively low particle number counts in the gasoline vehicle exhaust that made coagulation in the tunnel less probable and the removal of gaseous hydrocarbons by the catalyst, reducing condensation and nucleation rates. It was also observed that when an insulated hose or connection made of silicone rubber were used, an intense nanoparticle peak was observed at ~30 nm. In a follow-up to this study, Maricq et al. (2001) compared tailpipe, dilution tunnel and wind tunnel measurement of exhaust PM. They found that wind tunnel and direct tailpipe measurements showed good agreement. Conventional dilution tunnel measurements were subject to two main artifacts, however. This included artifacts attributed to hydrocarbon material stored in the transfer tube to the dilution tunnel and the effects of particle coagulation that occurs during transport. Vogt and Scheer (2002) of the Ford research laboratory in Aachen, Germany studied the PM size distribution for a diesel passenger car using a laboratory dilution tunnel, direct tailpipe sampling, and using a mobile laboratory chase experiment. Laboratory size distribution measurements showed a single mode around 50 to 70 nm that shifted to a larger particle diameter and lower total number for sampling conditions with longer residence times. Similar distributions were measured using a mobile laboratory on a high-speed test track. An additional nucleation mode at 10-20 nm was observed at 60 to 70 mph, however, when a higher sulfur fuel (360 ppm) was used in conjunction with an oxidation catalyst.

A number of other organizations have investigated the use of different instruments for the measurements of PM size and number. Researchers at Sandia National Laboratories and other collaborators have used a range of high-energy laser diagnostics (Witze, 2002). Some of the systems investigated include laser-induced incandescence (LII) for inorganic carbon, elastic light scattering (ELS) for total PM volume, a combination of these techniques for aggregate size, number, and structure, laser-induced desorption (LID) + ELS for the volatile volume, and laser induced breakdown spectroscopy (LIBS) for metallic ash. Comparisons of the LII, ELPI, and TEOM were also made over the FTP in collaboration with researchers from Ford (Witze et al. 2004). These tests indicated that the LII and the ELPI performed well, while the TEOM lacked the sensitivity for the low levels for one of the vehicles equipped with a DPF. In a collaboration between the Lund Institute of Technology and Sandia, the LII was used for measurements of

transient operation for a 1.9 L TDI diesel engine (Axelsson and Witze, 2001). Sandia has also demonstrated the LII for measuring PM from a vehicle under actual on-road driving conditions.

Moosmüller et al. (2001a,b) conducted a comparison study between several different real-time measurement techniques including a TEOM, a nephelometer, an aethelometer, a photoacoustic instrument, and a smoke meter. Of the instruments tested, the TEOM and nephelometer showed the most promise for total PM measurements in real-time. The TEOM showed good correlation with traditional filter mass measurements and a consistent calibration correlation that was independent of the test vehicle. The calibration for the nephelometer varied for different vehicles, but this instrument showed excellent signal-to-noise, no interferences, and good time resolution at a relatively low price. It was suggested that the two instruments could be used in combination to utilize the strengths of each instrument. In addition to total mass, it was also found that real-time organic carbon measurements could be made using a combination of a TEOM and a photoacoustic instrument.

Researchers at Argonne have also conducted several studies of vehicle PM. Zhu et al. investigated the morphology of PM from a 1.7 L CI engine. They used a thermophoretic system for sample collection and a high-resolution transmission electron microscope. Larger primary particles were found at higher EGR rates, lower air/fuel ratios, and lower exhaust temperatures. Gupta et al. examined a portable TG-1 instrument that uses an LII for transient PM emissions measurements. The TG-1 was found to have better time resolution than a TEOM and better performance for step changes in engine modes. The TG-1 also showed agreement within 0.1 mg in comparison with gravimetric methods.

Researchers at the National Research Council Canada have also investigated LII for the measurement of PM from the exhaust of a direct injection SI automobile. In comparing with gravimetric measurements, large differences were found and the LII also had relatively poor repeatability. This was attributed to differences in the levels of condensed PM, since the LII measures only elemental carbon. On the basis of the test work, these researchers suggested that the LII was a preferred method for the measurement of elemental soot carbon. Damm et al. of Sierra Nevada College in conjunction with University of California, Berkeley have also used laser fragmentation fluorescence spectroscopy for the measurement of exhaust PM.

Khalek (2000) of the Southwest Research Institute (SwRI) characterized the PM size distribution of a heavy-duty engine during an FTP transient using an ELPI. The size distributions showed a single mode between 0.14 μm and 0.084 μm , with no suggestion of nanoparticles below 0.032 μm . It was suggested that high temperatures in the primary tunnel, i.e., $>50^\circ\text{C}$, may have prevented the formation and growth of nanoparticles.

4.1.2 European Programs to Develop PM Measurement Techniques

The measurement of PM size distributions and numbers has been on-going in Europe since the 1980s, although the efforts were somewhat sporadic prior to the mid-1990s. In some early measurements, Krempl et al. (1985) of AVL in Gratz, Austria measured real time PM emissions from light-duty diesel engines. These researchers used an infrared extinction method that allowed for separate real-time measurements of graphitic carbon and hydrocarbons in the exhaust at a time resolution of < 0.1 seconds. The total PM mass difference between the

gravimetric mass and the mass obtained using the infrared system with a model was found to be within 16%. It was found that at certain defined speeds, PM emissions under acceleration could exceed those of steady state operation by factors of up to 6. They also suggested that engine temperature could be an important factor in influencing particle behavior and formation.

In the early 1990s, researchers at the Universität of Duisburg in Germany studied the size and fractal structure of diesel PM. In one study, tests were conducted on a 2-cylinder, 4 stroke DI-diesel engine at different steady state conditions with size distributions measured using a DMPS (Patschull and Roth, 1992). They found that at increasing load the mean particle diameter grew and more multiple-charged particles appeared. They also utilized scanning electron microscope measurements to determine the structure of the PM emitted from the engine (Klingen and Roth, 1989). Similar techniques using a scanning electron microscope have been used more recently by researchers at the University of Castilla-La Mancha, Spain (Lapuerta et al. 2003). In other research, Knobloch et al. (1992) investigated the contribution of platinum from a three-way catalyst using an inductively coupled plasma-mass spectrometer.

Other research in the early to mid-1990s included studies of the impacts of different fuels on size distributions from gasoline and diesel vehicles by researchers from the Esso Petroleum Company and AEA Technology (Rickeard et al., 1996). The fuels tested included a Swedish diesel, a light and heavy-duty diesel fuel, and a gasoline. Measurements were collected with an SMPS over repeated cycles to obtain a full size distribution. The diesel fuel effects on PM number were correlated with the corresponding effects on PM mass. The size distributions were similar for all vehicles, with a majority of the PM in the 50-100 nm range. The gasoline PM numbers were lower than those from the diesel vehicles at lower speeds (50 km/h), but at the higher 120 km/hr, the diesel and gasoline PM number levels were similar. In other studies, researchers at the Ford Motor Company and FEV Motorentechnik GmbH and Co. also performed some characterization of size distributions as part of a broader effort to characterize emissions from diesel, gasoline and CNG vehicles of the time (Hammerle et al., 1994; Lepperhoff et al., 1994; Greenwood et al., 1996). Panne et al. (1995) also measured size distribution from two diesel passenger cars over the FTP and at three constant velocities using a DMPS. Overall, the size distributions were similar to those reported in previous studies with a median diameter ranging from 47 to 71 nm. Kerminen et al. (1997) also made measurements of a VW Passat diesel passenger that meet EC 1996 standards.

Mayer et al. (1996) tested four diesel engines ranging in size from 1.6 to 6.6 liters over steady state conditions. Size distributions were measured using a DMA with and without a thermodenuder. These vehicles generally showed peaks in the 80-100 nm range. One vehicle was tested with and without the thermodenuder. Without the thermodenuder, the number of particles was found to nearly double and a much greater number of particles were observed <30 nm. Similar to other research, it was found that the nanoparticles essentially disappeared above 250°C, indicated a sulfuric acid or hydrocarbon composition (Mayer et al. 1998). The use of an oxidation catalyst was found to increase the nanoparticle concentration due to the production of sulfuric acid aerosols.

A more extensive effort for the development of methodologies for the measurements of particles from vehicles has been an on-going program for about 10 years. The UK government Department of the Environment, Transport and the Regions (DETR) in partnership with the society of Motor Manufacturers and Traders (SMMT) began an extensive particle measurement

programme in 1995. The oil companies European organization for environment, health, and safety (CONCAWE) also conducted several studies to evaluate different analytical techniques for measuring particle number and how particle number varied for different experimental conditions.

In one of CONCAWE's early studies of PM emissions, four light-duty diesel vehicles and three light-duty gasoline vehicles were tested, covering a range of vehicle technologies (CONCAWE, 1998; Hall et al., 1998a). Several literature reviews were also conducted related to measurement of PM size distributions and number and the impact of automotive PM on the environment (Hall et al., 1998b; CONCAWE, 1996). PM emissions for the diesel vehicles were found to be much higher than those for the gasoline vehicles, with greater differences observed for the MVEG compared to the steady state cycles. SMPS results showed that gasoline vehicles showed a higher proportion of PM <1 μm than the diesel vehicles. The differences in PM emissions for the gasoline and diesel vehicles decreased at higher speeds (120 km/hr). Comparisons between the two contract laboratories showed satisfactory performance for the SMPS/DMPS, gravimetric methods, and the impactor.

Moon and Donald (1997) conducted tests on a matrix of four light duty and three heavy-duty diesel engines and two light duty gasoline engines for DETR and SMMT. For this program, an SMPS, a QCM, an impactor, a TEOM, and an ELPI were compared. The SMPS gave the most consistent and repeatable size distributions. In comparing the SMPS with the ELPI, the ELPI was found to give particle number counts about 25% of those of the SMPS. The QCM was found to be unreliable and the mass based measurements were considerably lower than those of the other mass data. The ELPI, TEOM, and impactor gave similar mass particle flux measurements for the different engines and loads tested. In comparing sample lines, a longer sampling line with sharp bends was found to decrease particles > 3 μm .

In 1998, a partnership program between DETR, SMMT, and CONCAWE was established which lead to a large particle measurement program conducted by Ricardo (Andersson and Wedekind, 2001, Andersson et al., 2000, 2001, Wedekind et al., 2000). The engines and vehicles comprised a cross section of Euro I to Euro III certified vehicles and engines and included both heavy and light-duty applications. The engine and vehicle test matrix is presented in Table 4-1. This included some testing performed on a diesel particle filter (DPF). Vehicles and engines were tested over legislated European test cycles and additional steady state conditions. An SMPS and a MOUDI impactor were also used to collect information about size distributions.

Table 4-1. DETR/SMMT/CONCAWE 1998-2001 Particle Research Programme Engine and Vehicle Test Matrix

Emissions Stage	HD Diesel	HD Diesel w/ DPF	HD CNG	LD Gasoline	LD Gasoline/LPG	LD Diesel	LD Diesel w/ DPF
Euro I	1	1					
Euro II	1			1 (MPI)	1	1	
Euro III	1		1	1 (G-DI)		1	1

G-DI – gasoline direct injection, MPI – multi-point injection,
 Fuels used include EN590 – European Standard Diesel, LD – European Standard gasoline
 ULS – ultra low sulfur (<50 ppm), SWCL1 – Swedish class 1

The results of this study showed that particle number was a function of both vehicle technology and fuel. For light-duty vehicles, the particle numbers from diesel vehicles were an order of magnitude higher than those for the gasoline direct injection vehicles. A light-duty gasoline MPI vehicle, an LPG vehicle, and a diesel vehicle with a DPF had similar particle numbers, which were all several orders of magnitude less than those from the conventional diesel vehicle. All light-duty vehicle technologies (including gasoline and diesel) did have similar number of particles at higher exhaust temperatures, although differences in size distribution were still observed under those conditions.

The diesel particle filters provided the most significant impact on particle emissions, with particle mass and number being reduced several orders of magnitude for both light- and heavy-duty applications. Under high exhaust temperatures, however, the nuclei mode was still significant after the DPF. The heavy-duty CNG engine also emitted significantly lower particle mass and number emissions compared to the heavy-duty diesel engines. The Swedish Class I fuel also showed a significant reduction in particle mass and number compared to the other fuels for both light- and heavy-duty diesel engine types.

In the United Kingdom, AEA Technology conducted another investigation in 1999 to assess the performance of different instruments for the measurement of diesel PM (Bell et al., 1999). The initial phase of this experimental work focused on a diesel direct injection (DI) VW Golf. This vehicle was tested over hot and cold steady state cycles, a hot and cold New European Drive Cycle (NEDC) and Free Acceleration Smoke Tests. These researchers found that the sampling method did not have a significant effect on the particle measurements, somewhat in contrast to other researchers, and thus recommended the use of standard CVS conditions. In this study, a CPC, SMPS, and impactor were compared. Overall, the agreement between the CPC and the SMPS was found to be good, although the CPC gave more particles at higher speeds. The impactor had difficulty sampling sufficient volume to provide reliable mass data from the diluted samples but did give reproducible results when sampling from the raw exhaust. In the second phase of this experimental work, 8 diesel vehicles representing old and new technologies, covering DI and indirect ignition (IDI) technologies. Again the CPC and SMPS data showed good agreement for all vehicles except for the high-speed conditions, while the impactor gave poor results due to the small mass of sample collected. Interestingly, the older technology vehicles had higher smoke, CO, and THC emissions, but not higher PM mass over the NEDC. As part of another study, measurements of the number and size distributions of particles from a gasoline direct injection vehicle were also made (Hall and Dickens, 1999). Hall and Dickens (2000) also showed that particles can be formed during sampling due to elevated temperatures in the exhaust pipe and sampling system and subsequent release of deposited material. These reentrained particles can have important implications for dilution tunnel measurements for gasoline vehicles.

In a second CONCAWE study, the size distributions of heavy-duty engines representing Euro II and Euro III technologies were investigated (CONCAWE, 2001; Wedekind et al. 2000). This work included a Euro II and Euro III engine and additional testing with a continuously regenerating trap on the Euro III engine that provided emissions consistent with the Euro 4 level. This study showed that the size distributions from heavy-duty engines were bimodal, with peaks below 30 nm (nuclei mode) and a peak above 30 nm (accumulation mode). The accumulation mode measurements were found to be relatively repeatable and insensitive to changes in test conditions. The nuclei mode, on the other hand, was found to be very sensitive to changes in

sampling conditions and had the greatest influence on total particle number. A dual differential mobility particle spectrometer (DDMPS) was also found to provide measurement of particles as small as 3 nm.

Researchers in Finland and Sweden have performed some more focused studies on PM measurements with an ELPI. Researchers at the Motortestcenter (MTC), Sweden and the Tampere University of Technology in Finland evaluated the ELPI using a passenger car on a chassis dynamometer and a heavy-duty engine (Ahlvik et al. 1998). It was observed that the ELPI was able to determine transient effects in both PM number and size. The passenger car was tested over both the EDC and the FTP, with relatively similar size distributions found for both cycles. The heavy-duty engine, on the other hand, showed substantial differences in size distribution between the European ESC and US FTP cycles. Overall, comparable size distributions were obtained between a DMA and the ELPI. Marjamaki et al. (2002) of the Tampere University of Technology added an additional filter stage to an ELPI and evaluated this instrument over chassis and engine dynamometer tests. The additional filter along with changes in the charging unit allowed measurement of particles below 30 nm. Some differences in the size distributions were observed between the ELPI and SMPS over steady state cycles that would require the development of additional algorithms to correct for the final filter stage. Engine tests demonstrated, however, that the modified ELPI could be used to make real-time measurements of the nucleation mode, which was not possible without the modification. Researchers from this same group at the Tampere University of Technology have also used the ELPI and SMPS combined to provide estimates of PM particles densities, which varied between 1.1 and 1.2 g/cm³ (Virtanen et al. 2002). Other research of exhaust particles with an ELPI has been conducted by researchers at the University of Leeds in conjunction with the Ford Motor Company (Andrews et al. 2001).

The Swedish National Road Administration conducted an extensive test program where over 45 light-duty vehicles were tested with particle number samples on 18 of the vehicles (Färnlund et al., 2001). The technologies included DI, turbocharged diesel engines, spark ignited and natural aspirated [SI NA], spark ignited and turbocharged [SI turbo], and spark ignited and direct injected [SI DI] gasoline vehicles. The diesel engine PM emissions were found to vary by approximately a factor of 3 over the different models tested. For diesel engines, the number of particles and the size distributions were relatively unaffected by load, excess air and driving style. The emissions from the NA and turbo spark ignition engines were less than 1% of those from the diesel engines. The particle emissions from the NA and turbo SI engines were, however, significantly affected by load and air/fuel ratio, and in some cases approached those of the diesel engines. The particle emissions for the SI DI engines were found to behave like those of diesel engines when running lean and like more conventional gasoline engines when running rich. At low loads, the particle numbers were slightly less than those of the diesel vehicles and at moderate and high loads they are close to those from vehicles with SI NA engines.

MTC has also conducted a considerable number of studies through the years to evaluate the PM number and size distributions of a range of vehicles and vehicle technologies. In the late 1990s, the Swedish Environmental Protection Agency (SEPA) commissioned MTC to test 11 gasoline and 5 diesel-fueled cars over the NEDC (Ahlvik and de Serves, 1999). Overall, the gasoline cars were lower than those for the diesel cars, with the greatest difference observed during bag 2, or the UDC phase, of the NEDC. PM emissions for the gasoline cars did increase as the temperature was decreased from 22 to -7°C. MTC also studied a range of fuels including diesel,

rapeseed methyl ester (RME), gasoline, ethanol, methanol, and biogas, on three different vehicles (de Serves, 1999). The diesel vehicles were found to have 30 to 50 times more PM mass and number compared to the gasoline vehicles, with larger effects seen during portions of the cycle when the engine was fully warm. Lu (1999) examined the effects of 7 methanol, ethanol, and gasoline blends with a flexible-fuel SAAB using an EPPI and TEOM to measure size distributions. De Serves (2000, 2001) studied several different vehicle technologies over two programs including a diesel car, a diesel car with a DPF, a gasoline DI vehicle, and a gasoline MPI vehicle. In comparing the gasoline technologies, the results showed the DI engine had 30 times high PM number than the MPI vehicle. For the diesel vehicle, the DPF provided a reduction of 50 to 100 times compared to the standard diesel vehicle. More recently, a study of two diesel vehicles and one gasoline vehicle with modern combustion engines was conducted on the behalf of the Swedish National Road Administration (Sandström-Dahl, 2003).

A larger European Particle Measurement Programme (PMP) was inaugurated in March of 2001 as part of the Working Group on Pollution and Energy (GRPE) as part of the UNECE. The focus of this PMP was on the development of new approaches to measure particles in vehicle emissions that may be used to replace or to complement the existing regulation mass based systems. The PMP is large collaborative effort that includes government agencies, institutions, automobile makers, and oil companies in a number of European countries, including Germany, Switzerland, the Netherlands, Sweden, and the United Kingdom.

Richardo conducted a testing program on heavy-duty engines as part of phase one of the program for the UK (Andersson et al., 2001). They examined a number of candidate technologies for PM measurements including an SMPS, CPC, TEOM, QCM, and a differential mobility spectrometer. For tests conducted using a CVS, correlations were found between filter mass measurements and SMPS and CPC particle number measurements and QCM particle mass measurements under both steady state and transient conditions. At sub-Euro IV (post-DPF) emission levels, the CPC provided the most repeatable measurements. QCM measurements also proved to be more repeatable than gravimetric PM measurements at these levels. Two candidate systems were proposed (1) a CPC with a thermodenuder and secondary dilution and (2) a QCM with a secondary dilution system. With the proposed systems, it was suggested that coefficients of variation (COVs) of 5% or better could be achieved for Euro III levels and COVs of <20% could be achieved at levels approximately one quarter of those for the Euro IV standard.

AEA Technology studied particle measurement for light duty vehicles as part of the UK DTLR's phase one effort (Dickens et al., 2002). The methods surveyed included a CPC, QCM, DMS, diffusion charger (DC), and different sampling configurations. For mass measurements, it was concluded that the CPC with a high dilution sampling unit provided the best method for measuring total particle number, providing good repeatability and a minimum detection limit (MDL). The DMS also provided good repeatability and more complete information about the size distribution, but the higher MDL for the DMS made it unsuitable for low emission vehicles. For PM mass emission measurements, the QCM had the best MDL, while the MDL for the filter methods were not sufficient for measuring low emission vehicles. The QCM was found to be very sensitive to dilution ratio, however, and selection of the wrong dilution ratio could lead to misleading results. For sampling, a combination system with a CVS and a thermodenuder was considered to be promising for producing repeatable measurements while eliminating artifacts associated with volatile material. It was also suggested that a modification of the CVS to introduce the dilution air nearer to the tailpipe would help reduce artifacts associated with the

transport of the raw exhaust to the dilution tunnel. In conjunction with this effort, a literature review of different sampling techniques was also conducted with AEA Technology for the DTLR (McAughey, 2002).

The Association of European Automobile Manufacturers (ACEA) evaluated an SMPS, CPC and ELPI on a fleet of seven late model diesel and gasoline vehicles at the EMPA facility in Switzerland (ACEA, 2002). The size distributions from the modern diesel vehicles were found to be similar to those of older technology diesels studied in a previous ACEA programme (ACEA, 1999), while PM emissions from port-injected gasoline vehicles were near the detection limits of the analyzers. The DI vehicles did show a large variation in particle concentration depending on the type of vehicle and the operation mode. Under most conditions, the particles were found to be composed of largely insoluble matter. The effects of a high sulfur fuel were examined and it was found to increase both particle mass and number for both gasoline and diesel vehicles. In comparing instruments, the CPC measured higher particle numbers than the SMPS, which was attributed to the wider size range for the CPC. The agreement improved when a thermodenuder was used for the sampling. The diesel and gasoline PM emissions in the accumulation and nuclei modes were found to vary by 30-50% over transient tests depending on the dilution system used. The calibration of the particle number measurements was not found to be absolute, hence the measured particle numbers were only considered to be valid for comparison within the study.

Building on the results of Phase 1 of the GRPE PMP, additional test program were conducted to further evaluate PM measurement technologies. To provide a more uniform overview of the performance and quality of the PM measurement systems, Swiss authorities conducted an additional program where the comparisons between instruments were conducted at a single facility and at the same time (Mohr and Lehmann, 2003). The measurements were carried out at the EMPA facility in Deubendorf over a three-week period in June of 2002. A total of 21 particle measurement systems were investigated by making simultaneous measurements on a heavy-duty engine test bed and using an aerosol generator. The results of this study indicated that several measurement techniques provided performance equal to or better than the regulated filter method, and further investigation of these techniques was suggested for Phase 3 of the GRPE-PMP. Instruments with favorable comments included the Horiba MEXA 1370Pm, which is a filter evaporation/gas analysis method, the Dekati MasMo, which is an electrical mobility/impaction electrical detection, the LQ1-DC system by Matter Engineering, which is a diffusion charging with electrical detection technique, the EAD 3070A from TSI, which is a turbulent diffusion charging with electrical detection technique, the ELPI and the CPC. It was suggested that measurements methods based on solid particles, as opposed to volatile matter, can provide better repeatability and reproducibility. Number-based measurement methods can also provide greater sensitivity at lower PM levels.

As part of the UK PMP – Phase 2 effort, Ricardo expanded on the sampling system developed under the Phase 1 task to provide an exhaust system that could be operated with or without a DPF and allow for the collection of a number of identical samples using a number of different instruments (Andersson et al., 2003). This sampling system was used to evaluate a number of systems. The most promising mass based systems were the 2007 US PM standards and a system using a CVS and laser induced incandescence (LII). The results showed that the 2007 PM standards were reliable for measuring PM levels consistent with those found after a DPF, and the system was capable of COVs below 10% on both a daily and a day-to-day basis. The LII system is a real-time measure of elemental carbon. The instrument performed well with COVs of

<12.5% over transient cycles and <20% over the steady state cycles. The directional trends were comparable to the filter mass were found for engine out and post DPF measurements, although these trends were less consistent under certain steady state conditions where high volatile fractions were present. A QCM was also tested and showed good reproducibility within a single day, but day-to-day repeatability was poor due to instrument difficulties.

In this same study, the most promising systems for measurements based on particle number were a system using a CVS with a thermodenuder and a CPC and a system using raw exhaust, a hot diluter, and a diffusion charger. The system combining the thermodenuder and the CPC had some issues including the operation of the thermodenuder and a variation in the baseline measurements. The thermodenuder showed different characteristics depending on the changes in the chemistry of the particles sampled. This would have to be counteracted by standardized means of quantifying particulate losses and removal irrespective of composition. Although the CPC was very repeatable within a single day, differences in baseline/background levels between days led to larger variability from day to day. It was suggested that these two issues could be addressed by modifications to the CVS system for the background and potentially the use of different conditioning strategies with raw exhaust. The diffusion charger showed good comparison with the CPC and a COV of about 10% for integrated data, but showed much larger variability for individual stages and from day-to-day. The specific prototype diffusion charger used in the study was also not sufficiently sensitive for post-DPF measurements of individual sizes, although a more current version of the instrument was said to have greater sensitivity and the sensitivity could also be increased by sampling the raw exhaust.

The EU DG TREN “Particulate” project was developed is a multi-partner project to characterize exhaust PM from road vehicles (Samaras, 2002). The project includes universities (Aristotle, Tampere, Graz, Aachen), industrial partners (Volvo, CONCAWE, AVL, MTC, AEA Technology) and governmental agencies (EMPA). The goal of the program is to develop harmonized protocols for exhaust aerosol sampling, examine PM emissions from light-duty vehicles and heavy-duty engines, and to investigate engine technology, fuel and aftertreatment effects. This team developed a sampling procedure based on factors such as dilution ratio, residence time, humidity, and history effects. This sampling system is being tested on a range of different test vehicles and fuels.

Although a number of the European programs have indicated demonstrated potential for number based or other systems in making repeatable low-level exhaust PM measurements, several programs/commentaries have indicated that these systems still have insufficient reliability with respect to application to regulations. The Abgaszentrum Der Automobilindustrie (2002) conducted a comparison study using an ELPI, a LQ1-DC measurement method that uses the probability of deposition of ions on particles for measuring particle surface area, and a photoelectric aerosol analyzer (PAS). For the ELPI, it was found that the number size distributions were a function of the impact loading with a drop in the number of particles observed at higher loadings along with a corresponding increase in measured particle diameter. It was suggested that this could be due to an obstruction of charge transfer from the charged particle to the impactor plate that is already covered with particles. A similar effect could also be possible for the corona charger. The researchers also observed several issues with the LQ1-DC including a low stability of the measured signal requiring a zero adjustment, contamination and chemical influences on the corona charging, and questions about the surface area calculations below 50 nm. For the PAS system, it was observed that the measurements after the catalyst did

not correlate with the other instruments or the gravimetric measurements, the photoelectric charging was found to only function properly at low particle number. Overall, the researchers concluded that none of the measurements were suitable for reliable, quantitative measurement of PM emissions in exhaust gas from internal combustion engines.

The ACEA also has a program for the measurement of future PM emissions from heavy-duty vehicles (Stein, 2002). In this program, they examined a Euro I, II, and III engine and a Euro II engine with a PM trap and a deNO_x aftertreatment system over several different operating modes and over the ESC and ETC test cycles. This work was performed at the EMPA test laboratory. They found that increases in the ultrafine PM was not observed with the more advanced engine technology, and that lower PM mass emissions were generally related to lower particle numbers. In comparing sampling methodologies, they found that the use of a thermodenuder had a significant influence on the results of the PM measurements and that the operating characteristics of the thermodenuder had to be carefully controlled. They also found a poor correlation between the SMPS and the ELPI. They concluded in saying that significant research is still necessary for developing a type approval procedure for number measurement.

In providing commentary on the measurement techniques suggested as a result of the initial phases of the PMP, the International Organization of Motor Vehicle Manufacturers (www.oica.net/WWH/particulates/particulates.htm) also expressed concerns that the new particle measurement methods did not have sufficient reliability for use in regulatory application. This commentary critically examined each of the proposed new methods and included measurements from the automobile manufacturers and found that the gravimetric method was the only one sufficient for regulatory application. This report pointed out that nucleation is susceptible to large measurement artifacts and thus methods that are sensitive to nucleation would not be reliable. This commentary also indicated that the combination of a thermodenuder with size-unresolved total particle count would not give valid data due to the size dependent particle losses and dependence of the chemical nature of the particle. The effects of engine load, fuel and injection pressure on particle morphology and/or size distributions were also described and the potential effects on size. Additionally, test results were presented showing the variation between an ELPI, DMA + CPC, and diffusion charger was very high, even when they were simultaneously measuring from the same particle source. Results were also included indicating that PM measurement down to a level of 0.01 g/kWh with a 10% measurement were achievable, with further refinements possible using a sulfur-free fuel. Overall, it was concluded that the current gravimetric regulatory measurements should be retained into the future.

ACEA is currently expanding on their previous particulate measurement programs to focus primarily on gravimetric PM measurement methods (Hosier 2003). This program, known as PM-3, is designed to contribute more directly to the European PMP effort, and is being conducted at the AVL-MTC laboratory in Sweden. The preliminary conclusions from the program are that PM filter mass measurements can be effectively used at very low levels. In comparing different types of filters, it was found that the high efficiency TX40 or teflo filters provided the best performance and that secondary filter did not need to be used in conjunction with these higher efficiency filters. They also observed that a 1.0 µg balance performed better in a working environment than a 0.1 µg balance. Additional work for this study is still on-going.

4.1.3 Asian Particle Measurement Programs

Particle measurement programs have also been conducted in Japan by researchers at the Japan Clean Air Program (JCAP), the National Traffic Safety and Environmental Laboratory (NTSEL), Japanese Universities, instrument companies, and automobile manufacturers. A review of Japanese emissions regulations as well as identification of DPFs and low sulfur fuel as important technologies for future emission reduction is provided by Hirabayashi.

In Japan, several PM research efforts are also under way at the NTSEL. The laboratory is researching methods for measurement of PM size and surface area as well as weight. PM research is focused on size distribution measurements as well as nano-particle measurements in engine exhaust and the effects of engine exhaust temperature on nano-particle size distribution (www.ntsels.go.jp/e/main/imprv01.html). The NTSEL is also researching the effects of DPFs and other devices for the reduction of PM emissions (www.ntsels.go.jp/e/main/imprv02.html). The DPF's have been tested on a variety of test cycles from Japan, the United States, and the European Union. PM reductions ranging from 58.8% to 94.8% have been reported, depending on specific test cycle.

JCAP conducted an evaluation of PM measurement methods including establishment of statistical analysis methods, an inter-lab comparison study, and a survey of measurement methods (JCAP Test Methods Workgroup, 2002). In the first phase of this project, JCAP established test procedures and statistical analysis methods for PM measurements. This was followed by a laboratory cross-check for gasoline and diesel powered vehicles as well as diesel engines. Improvements to test facilities and test conditions were made based on the results of a cross-check study. In phase I, JCAP also evaluated PM size measurement methods being used in the US and Europe and performed trial comparisons with ELPI, SMPS, NanoMet, and LII. A summary of the results of JCAP I and an outline of JCAP II was provided by Uchiyama (2003) in a presentation "Future Challenge in Automobile and Fuel Technologies for Better Air Quality" at the JRC conference, as well as other sources (JCAP Test Methods Workgroup, 2002).

The Engine Measurement Division of Horiba Instruments Limited has been a major source of PM related research in Japan. In 1997, Sakamoto et al. (1997) described a particle characterization method using Helium Microwave-Induced Plasma Atomic Emission Spectrometry. Horiba researchers have also developed a real time analysis of PM using a fast FID (Kawai et al. 1998; Hirokazu et al. 2000). The focus of this research was on signal processing and consideration of instrument performance in practical situations.

Fukushima et al. (1999) presented a comparison of results of a real-time PM analyzer with the filter method over the Japanese Diesel 13-mode test cycle. He showed good correlations between the FID based system and the filter results as well as modal emissions measurement capability for soot, SOF, and total PM. The technical methods used to produce instruments capable of measuring modal PM emissions are described in greater detail by Yamagishi and Ohtsuki (2000).

For Horiba, Kihara (2002) reviewed the latest opacimeter for measurement of continuous smoke opacity including black, blue, and white. Fukushima and Uchihara (2002) explain the principals used on a new super-low-mass PM analyzer using vaporization, thermal decomposition, and oxidation reduction of the sample. Also in the same issue, Nakamura (2002) provided a brief overview of the development of PM measurement systems at Horiba. Nakamura's review gave

brief descriptions of the mini-tunnel, macro-tunnel, photo acoustic spectrometric, electron diffusion, filter combustion, CO₂ differential, and roll filter methods. Kihara and Tsukamoto (2001) from Horiba describe a PM mass measurement system that can be used to collect real time particulate matter, THC, and NO_x data on-road. The on-board device uses a fast FID and a smoke meter to evaluate the mass of the PM emissions.

4.1.4 Foreign Language Documents

Throughout the course of the literature review, references sources were examined to determine if any significant documents that were available in foreign languages but not in English. To address this question, we utilized direct contact with members of agencies and institutions in foreign countries, searches of websites for prominent institutions in other countries, and examination of reference lists for reports and review documents where references for literature in foreign languages might be found. Overall, it appears that a majority of the literature related to studies of PM and PM measurement techniques are available in English. Some relevant documents in foreign languages were identified and are briefly described here. The final report for the Swiss VERT program was one important document that is available only in German. The documentation for the VERT program in English is still considerable, however, including a number of Society of Automotive Engineers papers and other literature. This program is discussed in greater detail in the next section. A listing of other German documents related to diesel PM and emissions control devices has been compiled by the University of Biel in Switzerland (2003). Several documents from Ecotrafic of Sweden were available only in Swedish, including a document comparing emissions between a bus and car looking at health, energy and environmental use and a similar study comparing emissions of light-duty vehicles on different fuels (Ecotrafic 1999, 2001). A number of documents in German were also identified. Several of these papers were related to PM measurement methods, including studies by Schindler and Silvis (2000) comparing partial and flow dilution systems, by Thaller et al. (2000) for opacity measurements, by VDI (1996) on carbon analysis, and by Cartus et al. (1999) comparing different instrument methods. Volkswagen conducted an extensive study of 22 PM measurement techniques and determined methods for PM number and size distribution were too qualitative in nature for use in developing standards (Bechmann et al.). In another study by Siegmann and Siegmann (1999), vehicle measurements on a chassis dynamometer showed good correlation between the route-related values for total particle number (in number/km) and PM mass (in grams/km). Several German language reports have also been released on measurements of particle concentrations near roadways (Elbers and Techter, 1994; Ratenberg-Wulff et al., 1995).

4.2 The Implementation of Aftertreatment for Diesel Vehicles and Its Influence on PM Mass and Chemistry

Diesel particulate filters (DPFs) and other aftertreatment systems for diesel vehicles/engines are considered to be important elements in the attainment of current and future emission reduction requirements. Aftertreatment devices have been more widely implemented in Europe, where there is greater penetration of diesel vehicles into the light-duty fleet. In the United States, certain aftertreatment devices such as diesel oxidation catalysts (DOC) have also been widely applied.

DOCs are one of the first levels of aftertreatment applied for control in diesel emissions. Diesel oxidation catalysts can achieve reductions of 20-50% in PM, but also provide 60-90% reduction in hydrocarbons and CO. DOCs have been extensively applied throughout the world over the past 20 years. Over 250,000 off-road diesel engines have been retrofitted with DOC, particularly for engines used in mining applications. DOCs have also been employed on over 1.5 million trucks in the US and over 6 million diesel automobiles in Europe. Oxidation catalysts have been used along with engine modifications in medium-duty engines to meet the 1994 standards (Sawyer and Johnson, 1995). Since 1995, over 20,000 DOCs have been retrofitted on buses and highway trucks in the US and Europe, with another 3000 retrofits performed in Mexico.

DOCs are very effective in reducing organic particulate matter, with an efficiency of about 80% (Zelenka et al., 1990). They have less impact on carbonaceous particles. One potential drawback of using oxidation catalysts is that they can promote the formation of sulfates by oxidizing SO₂ to SO₃. In fact, high-sulfur fuel used in conjunction with an oxidation catalyst can actually lead to increases rather than decreases in particulate matter due to the formation of sulfates. The attractiveness of using oxidation catalysts increases as the sulfur levels in fuels are reduced. In particular, sulfate emissions can be reduced substantially using low sulfur content, reformulated diesel fuels in conjunction with selective catalysts having low SO₂ to SO₃ conversion rates (Farrauto and Mooney, 1992; Brear et al., 1992).

In the United States, the application of DPFs is expected to expand considerably over the next few years, and future regulations are designed to essentially require these devices for new heavy-duty highway vehicles beginning in 2007 (USEPA, 2000a). More stringent Federal standards to be implemented beginning in 2004 for light-duty vehicles will also require the use of DPFs on light-duty diesel vehicles to meet the PM standard (Code of Federal Regulations, 2000). DPFs are most effective at collecting the carbonaceous fraction of particulate matter, with collection efficiencies of up to 90% or more for this fraction (Zelenka et al., 1990). In many applications, an active catalytic coating is applied to the surface of the trap that provides additional reductions in the organic portion of the PM.

CARB has taken steps over the past several years to increase the implementation of aftertreatment devices for diesel engines. CARB (2000) developed a Risk Reduction Plan to reduce particulate matter emissions from diesel-fueled engines and vehicles. This plan includes procedures for implementing retrofits of existing diesel engines with aftertreatment systems and a Tiered strategy for verification status (Title 13, California Code of Regulations, Sections 2700-2710). Table 4-2 provides a listing of the verification levels. A listing of technologies that have been verified to different levels of emission reduction is provided at the CARB website (www.arb.ca.gov/diesel/verdev/verdev.htm). EPA also has a program for engine retrofitting, but their program is voluntary at this point.

Table 4-2. CARB Verification Classifications for Diesel Emission Control Strategies

Pollutant	Reduction	Classification
PM	<25%	Not Verified

	>25%	Level 1
	>50%	Level 2
	85% or <0.01 g/bhp-hr	Level 3
Optional Verification for NO _x Reductions		
NO _x	<15%	Not Verified
	>15%	Verified in 5% Increments

Early work in characterizing particle traps in the US was performed by researchers at the US Bureau of Mines, the University of Minnesota, and the Michigan Technological University. Baumgard and Kittelson (1985) found that traps were more efficient at removing particle <0.1 μm in diameter, but that a nuclei mode could form downstream of trap under certain conditions due to gaseous hydrocarbons making it through the trap or formed during regeneration. Baumgard and Johnson (1991) showed that a typical diesel fuel of the time (3,100 ppm) produced more than two orders of magnitude more nuclei particles with a DPF than a DPF with a 100 ppm sulfur fuel. For these measurements it was suggested that a large percentage of the nuclei mode particles could consist of sulfate particles or particles where sulfate acts as a nuclei. Bagley et al. (1991) also found that DPFs can reduce mutagenicity associated with particle PAHs by >98%.

Kruger et al. (1997) investigated the size distributions from three vehicles: a 3 liter, indirect injection (IDI) diesel passenger car, a 1.9 liter DI diesel passenger car, and a 6.9 liter, DI, turbocharged and intercooled truck engine. Oxidation catalyst and DPFs were used on each vehicle. Interestingly, the oxidation catalyst had no significant effects on the size distribution for the IDI passenger car. The DI passenger car showed a significant decrease in PM >50 nm but an increase in PM <50nm. For the truck, the DPF showed a decrease in larger particles, but both the DPF and the DOC showed increases in <50 nm PM. These researchers found that the increase in <50nm PM was primarily attributed to volatile matter that evaporated at 180°C. These researchers also observed that the increases in <50 nm PM was observed at dilution ratios of 12:1 but not at higher dilution ratios of 19:1 and 32:1. This is consistent with nucleation at the lower dilution ratio, but might not occur under conditions on the actual roadway. Mayer et al. (1998) also evaluated several different strategies for reduction of nano-particles over 5 engines and found an impressive reduction of PM over all size ranges for the DPFs, with engine modifications and fuel optimization providing minimal changes in nano-particle formation.

In Switzerland, there has also been an extensive effort to promote the retrofitting of existing diesel engines with DPFs (Mayer et al., 2004). In the early 1990s, this was a smaller effort, focused primarily on transport buses. In 1994, however, Switzerland classified “diesel particles” as carcinogenic, and in 1998, the Swiss Ordinance on Air Pollution Control (OAPC) legislated the reduction of diesel emissions at construction sites. The latest statistics indicate that about 6,500 engines have been retrofitted, with that number expected to increase to 15,000 by mid-2005. To identify the best available technology for reducing diesel particle emissions, the VERT project was conducted between 1993 and 1998. This was an international collaboration involving the occupational health agencies of Switzerland (Suva), Austria (AUVA), and Germany (TBG), along with the environmental agencies of Switzerland (BUWAL) and Germany (UBA) under management by Technik Thermische Maschinen of Switzerland.

The VERT program included both engine and field testing (Mayer et al., 1999). Engine tests were conducted on a total of 29 particle trap systems over steady state and transient conditions. Overall, the DPFs showed reductions of 78-86% for gravimetric mass, 86-92% for particulate counts, and 93-99% for particulate soot. For the particulate counts, a sintered metal trap had the lowest efficiency of 86%. By separating the solid particulates from the condensates in the size analysis, it was found that the reductions for solid ultrafine particles exceeded 99% despite the lower overall efficiency. Tests also showed that the total PAHs were found to decrease proportionately with decreasing total carbon mass. Fuel additives designed to lower the soot ignition temperature were also investigated, and it was suggested that fuel additives only be used in conjunction with traps that can effectively filter ultra-fine particles and also that copper additives should be excluded due to possible production of dioxins and furans (Mayer et al., 2003).

A total of 10 systems were tested over a 2-year field as part of the VERT program (Mayer et al., 1999; Czerwinski et al., 2000). The DPFs accumulated between 1,500 and 7,000 operating hours in the field over that time period. For these systems, losses in trap back pressure and exhaust gas temperature were acquired over the entire test period, with data sampled every 2-8 seconds. Comprehensive measurements of exhaust gases were also performed in the field, at intervals of 4-6 weeks. Finally, seven of the traps were retested on an engine test stand. Overall, the traps maintained their ability to dependably filter PM over the entire test period. Some of the fiber traps did become saturated with PM due to very low exhaust temperatures and corresponding insufficient regeneration, but these traps returned to their initial efficiencies after regeneration. The engine tests conducted after the field program show good reductions in particle number ranging from 87->99%. The mass reductions were lower, however, ranging from 55-87% for the five best performing traps. The other two traps, had extremely high sulfate emissions that contributed to poor overall efficiencies, and at full load actual increases in PM mass. For one of the traps this was attributed to clogging with additive ash, while copper oxide formation from the use of an additive was suggested for the high emissions for the other trap. In other field work, Mayer et al. (2001) measured and analyzed the exhaust temperature profiles of 11 pieces of equipment to determine the type of traps that would be appropriate for different applications. Mayer et al. (2000) have also investigated and evaluated the use to PM traps in city-buses in Switzerland.

As a result of the VERT program and associated work, a 4-stage procedure was developed for the approval of DPFs (Mayer et al., 2004). In step 1, a new trap is tested on an engine test stand to ensure filter efficiencies of >95% for particle counts and >90% for elemental carbon mass can be achieved. This step includes testing over the ISO8178 cycle as well as transient measurements during regeneration and free acceleration. In step 2, the new trap is tested on an engine dynamometer to ensure the trap does not produce any secondary emissions for over 150 toxic substances, including dioxins, furans, PAHs, and nitro-PAHs (Mayer et al., 2003). A controlled field test of the system is then conducted during step 3, with continuous monitoring of pressures and temperatures over 2000 operating hours. After the 2000 hours of operation, the device is reinstalled onto the engine test stand and filtration efficiencies of >90% for particle counts and >85% for elemental carbon mass must be verified. This is step 4 of the process. To date, 30 trap systems have been tested and 18 approved by the procedure. This included traps produced by Johnson Matthey and Engelhard which are being used in the US.

Researchers in Europe have also looked at the impacts of fuel additives designed to facilitate regeneration of DPFs on PM emissions. Burtscher of Fachhochschule Aargau and Matter of Laboratorium für Festkörperphysik (2000) found that exhaust particles incorporate a certain amount of the mass of the additives used, but if the level of additive exceeds a certain limit, additives can form new particles. This additive limit depended primarily on the level of PM emissions from the engine as opposed to the type of engine. These new ultrafine particles consisted almost entirely of additive material. Researchers at the Associated Octel Company Limited, measured the performance of a DPF using a fuel additive for regeneration on a VW Golf, a two Peugeot 306s, and a Renault truck (Richards et al. 2000). The program showed that the use of an iron and strontium fuel additive provided successful operation and regeneration for all of the test vehicles under a wide range of driving conditions without the need of other measures to assist regeneration. Recently, the Cummunauté Urbaine de La Rochelle in France has launched a program to retrofit their Euro 1 and Euro 2 buses, while replacing their older Euro 0 buses with new Euro III buses (Biancotto et al., 2004). For this retrofit program, a DPF with a ceria-based fuel-born catalyst is being used.

In other work in Europe, Hall of BP and Dickens of AEA Technology (2003) studied the effects of sulfur free fuel on diesel DPF PM number and size distributions. They found that the reduction of fuel sulfur level from 50 to 10 ppm had a significant effect on reducing nuclei particles. Using a combination of a 10 ppm sulfur diesel fuel and a low sulfur lubrication package, the formation of nucleation particles could be essentially eliminated, even for higher temperature operating conditions.

In the US, an extensive DPF retrofit demonstration program was carried out as part of the ECD program in the Southern California area (LeTavec et al., 2000). The DPFs include Johnson-Matthey's continuously regenerating technology filter (CRTTM) and Engelhard's catalytic soot filter (DPXTM). Tests of class 8 grocery trucks with DPFs showed PM reductions between 91 and 99% and also significant reductions in total hydrocarbons (THC) and carbon monoxide (CO) (Clark et al., 2000; Vertin et al., 2000). Similar results were also found in tests conducted on heavy-duty tanker trucks, school buses, and refuse trucks (LeTavec et al., 2000; Chatterjee et al., 2001). Lev-On et al. (2002) also reported on the PM composition noting very little to no elemental carbon, consistent with the DPFs elimination of elemental carbon.

Another aspect of the ARCO ECD program is the demonstration of ECD and DPFs on medium-duty diesel vehicles (Durbin and Norbeck, 2002; Durbin et al., 2003). This portion of the project was conducted in conjunction with the Hertz Equipment Rental Fleet in Carson, CA. Approximately 19 vehicles are included in this part of the demonstration program including 9 control vehicles and 10 DPF-equipped vehicles operating on ECD. As part of this program, emissions tests were conducted on one control vehicle and two vehicles equipped with Engelhard DPX filters. Tests on vehicles operating with DPFs showed reductions ranged from 89 ± 2.3 to $98 \pm 0.7\%$ for PM, 72 ± 2.5 to $80 \pm 0.6\%$ for THC, and 81 ± 1 to $90\% \pm 1.3$ for CO. For PM composition, carbonaceous material accounted a majority of the PM mass for runs with and without the DPF. For these tests, organic carbon represented 76 to 80%, with essentially the same fraction of organic carbon for the runs with and without the DPF. These results are consistent with a large reduction in both the elemental and organic carbon fractions of the PM.

In other work, Maricq and coworkers (Maricq et al., 2002a,b) studied the effects of catalytic converters and fuel sulfur levels on gasoline and diesel vehicles. For the gasoline measurements,

five 1994-1997 vehicles were tested. The results showed that neither the catalytic converter nor fuel sulfur level had a significant impact on gasoline vehicle PM emissions. Particle emissions for vehicles with a blank monolith were <2 times higher compared to vehicles with active catalyst, which was considered to be insignificant in view of the 90% removal of hydrocarbons and the 50-100% uncertainty in the experimental measurements. Gravimetric measurements did show a 3-10 fold PM mass increase when the active catalyst was removed, but this was attributed to adsorption of gaseous hydrocarbons onto the filter medium. For the diesel vehicle and a low sulfur fuel (4 ppm), particle number emissions were found to decrease 30-45% when using an active catalyst compared to a blank catalyst. The combination of an active catalyst with a higher sulfur fuel, however, produced a roughly 40% increase in soot emissions.

In Japan, several of the major automobile manufacturers have investigated aftertreatment strategies for reducing PM emissions from diesel vehicles. Hirota et al. (2001) of Toyota reported on the development and effectiveness of a diesel catalytic converter in reducing PM and NO_x simultaneously. The Toyota Diesel Particulate NO_x Reduction system was reported to reduce diesel emissions levels to less than half of the European STEP4 standard (Tahara et al. 2002). With a new DPF system, reductions of NO_x and PM in light-duty vehicles to meet new Japan ULEV regulations (75% reduced level) were found using a low sulfur diesel fuel (Kasai et al., 2004). A detailed description of the PM oxidation mechanism is provided by Nakatani et al. (2002).

At Mitsubishi, Kishi et al. (1992) reported on an analysis of the characteristics and combustibility of PM in relation to DPFs. A similar paper focusing on Direct Injection Gas Chromatography for PM sample analysis was reported in 1994 (Ara and Kishi, 1994). Mitsubishi Motors Corporation research on the durability of diesel oxidation catalysts reported good durability of the catalyst and its ability to reduce SOF in exhaust (Takahashi et al, 1995). In a pair of papers, Kumagai et al. (1996a, b) reported on development of a PM trap system for urban buses. Saito et al. (2003) reported on development of Urea-SCR catalysts systems for reduction of diesel NO_x and PM. They found that even in lower temperature urban driving that the Urea system worked well. Mitsubishi engineers reported on a DPF system for commercial vehicles that worked well in city operation (Hiranuma, 2003). They noted that additional development would be necessary for ash removal from the filter.

In other work, Kitahara et al. (1999) of Nissan described the effects of another new after-treatment system on reductions of diesel PM. Researchers at the Japan Automobile Research Institute (JARI) have also investigated the PM emissions of two-stroke scooters with and without oxidation catalysts (Sakai and Kashiwakura, 2002).

Aftertreatment systems are also being considered for emissions reduction in India. Das et al. (2003) of Bharat Heavy Electricals and the Karnataka State Road Transport Corp. developed a DPF system with a simple and variable regeneration strategy for suitable for Indian urban transport. This unit was tested over a 20,000 km with no observed degradation in performance. The developed DPF showed PM emissions on average of 0.4 g/km without any loss of power and no significant increase in fuel consumption. Baikerikar and Chaudhari (2003) of the Automotive Research Association of India also tested a diesel OC on a 3-wheeler vehicle, a utility vehicle, a heavy-duty engine, and a tractor engine to evaluate OC performance on fuels with 50, 150, 300, and 500 ppm.

4.3 Factors that can Influence PM Measurements

Given the characteristics presented above, it is important to understand how sampling conditions influence the particles that are measured. Some of the sampling factors that can influence particle formation are the dilution ratio and resulting saturation ratio, the time the particles spend at varying dilution ratios, humidity, and filter media. The engine emissions themselves also have an effect on the particles that are eventually measured, including the size, number, and composition of particles emitted by the engine, and the composition and concentration of exhaust volatile organics.

4.3.1 Dilution Ratio

One of the issues of great importance is the dilution ratio. The dilution conditions for laboratory measurement can vary considerably between facilities and from test to test, and can be vastly different than the dilution observed under on-highway conditions. The formation effects that occur upon dilution include the formation of SOF particles via gas to particle conversion and the nucleation of volatile hydrocarbons to form nuclei mode aerosols. The dilution air/exhaust temperatures and organic concentrations during dilution will affect the saturation ratios and aerosol behavior during sampling or during particle lifetimes at the atmosphere. As the saturation ratio increases, the favored processes change from adsorption to nucleation. Once supersaturation is sufficiently high and the nuclei are present, high numbers of small particles will form quickly. In examining the saturation ratio as a function of dilution ratio, it is found that the saturation has the highest values for dilution ratios of about 5 to 50. Thus, the strongest driving force for gas to particle conversion occurs in approximately the same range produced by conventional dilution tunnel systems, i.e., 3-20 (Kittelson et al., 1998b).

Although many of the processes of particle adsorption are discussed in the context of equilibrium conditions, the extent to which adsorption or other processes occur depends to a certain extent on the time available for the processes to occur. The kinetics of adsorption become important when the exhaust is going through rapid changes in temperature or adsorbate concentration as happens during dilution. Kinetics must also be considered for laboratory measurement strategies that approach real-time measurement more closely and roadway conditions where dilution to higher levels might 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.

Nucleation can become a more likely process if high saturation ratios are produced and dilution takes place on a time scale faster than the characteristic time for adsorption. Under these conditions, there is little time for adsorption to take place and the system behaves as if a much smaller surface area is available for adsorption. If the rate of dilution is too high, the systems will spend little time in the intermediate dilution ratio range where saturation ratios and nucleation rates are highest. For comparison, Kittelson and Dolan (1980) calculated a time required for adsorption/condensation mass transfer of 0.27 seconds. In studies of dilution ratios measured on a roadway, the exhaust passed through the critical dilution ratio values of 5-50 in less than 0.4 seconds. Laboratory dilution ratios, on the other hand, provide residence times of between 0.5 and 2 seconds with a dilution ratio range of 2-50 (Kittelson et al., 1998b).

4.3.2 Advances in Engine Technology

The engine out particle emissions can also impact particle sampling, since the amount of volatile organic material that can adsorb onto the particle surface depends on the surface area of the particles in the exhaust. Older engines with higher concentrations of carbonaceous agglomerates have large surface areas available for volatile materials. This will tend to prevent saturation ratios from going high enough to trigger nucleation. On the other hand, the carbonaceous component is significantly reduced for newer engines so there is little surface area available for the adsorption of volatiles. This drives saturation ratios higher and makes nucleation more likely. There is also some decrease in volatile components, however, that can 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.

Michigan Technological University conducted an experiment to evaluate the mass and number of particles from newer and older engines under an Health Effects Institute (HEI) (Bagley et al. 1996; Johnson et al., 1996). For this study a prototype Cummins L10 engine was tested. The engine had a high pressure, mechanically controlled fuel-injection system, designed to meet 1991 Federal on-highway limits. This engine had a reduction in PM mass compared to a 1988 engine, but a size distribution that was shifted towards nuclei mode particles. Under steady state conditions, the engine was found to produce up to 40% more particle volume in the nuclei mode range. In looking at the particle chemistry, it was found that the 1991 engine emitted low concentrations of particles in the accumulation mode, but had a relatively high organic PM fraction ranging from 60-75%. As additional data have become available, these observations have been better understood. As part of the recent CRC E-43 project, Kittelson et al. (2002b) suggested that these results can primarily be attributed to the reduction in mass in the accumulation mode with respect to the mass of volatile material for the new 1991 engine in this study. This correspondingly promotes nucleation as the combustion products expand and cool and during the dilution process.

Kreso et al. (1998) tested the effects of exhaust gas recirculation on size distributions from heavy-duty diesel engine emissions. A 1995 Cummins M11 was used as the test engine, although comparisons were also made with older 1991 and 1988 engines. The 1991 and 1995 engines both had lower mass, but higher number of particles compared to the 1988 engine. There was also a significant decrease in the nuclei mode for the newer engine compared to the 1988 engine. The authors suggested that the higher injection pressures for the newer engines improves atomization and evaporation that results in smaller primary carbon particles. For the 1995 engine, EGR was found to increase the accumulation mode while it decreased the nuclei mode.

Researchers in Japan have also put considerable development into engine strategies for reducing PM and other emissions. The influence of fuel spray, gas motion, and turbulent mixing on combustion and emissions in diesel engines was examined by Ikegami (1990). The paper described the effects of air utilization by macroscopic distribution of fuel. The paper also discussed the decrease over time of spatial heterogeneity with turbulent mixing. PM formation in fuel-rich mixtures in diesel engines was found to depend upon the equivalence ratio, with PM formation starting at an equivalence ratio of 2.2 (Ogawa et al, 1990). A more recent paper from

Tanzania described the analysis of NO_x and PM formation in diesel engines using a stochastic model (Mkilaha and John, 2001). In this paper, the authors examined the reduction of NO_x and soot in diesel engines by enhancing the turbulence of the air and fuel mixture. NO_x formation was modeled using thermal NO_x principles while soot formation was modeled using the global combustion model.

Researchers at Toyota Motor Corporation found that the unburned oil fraction in diesel PM could be attributed to oil consumed through the valve stem seal, piston rings, and exhaust side seal ring turbocharger (Mase, 1996). In a follow-up study they observed reductions in diesel PM after improving the valve stems and piston ring seals (Inoue, 1997). Toyota Motor Corporation focused their research for PM reduction in diesel engines on electronically controlled fuel injection, EGR, catalytic converters, and a high-efficiency turbocharger, allowing their 1998 Gaia to meet the 1997/1998 emissions regulations (Watanabe, 1999). In a 1998 paper, Toyota researchers describe reductions in PM in IDI diesel engines obtained through suppression of the initial injection rate at light load, obtaining sufficient soot-air mixing in the main chamber, and enlargement of the swirl chamber (Hotta et al., 1998). Ohki et al. (2002, 2003) describe a new Toyota exhaust port fuel injection system. Nakayama et al. (2003) also describes a dynamic combustion control system to reduce PM and NO_x fluctuations under turbo boost, with PM variability to 1/3.

The effects of an exhaust gas recirculation (EGR) system for diesel engines on NO_x and PM were reported by Nissan Motor Company engineers in 1997. They reported that excessive flow rate causes emissions of PM to increase, and investigated an EGR control algorithm capable of representing dynamic states of the intake and exhaust systems (Itoyama et al, 1997). Also in 1997, researchers at Nissan Motor Company described their work on low-temperature, pre-mixed combustion techniques for reducing NO_x and PM in small diesel engines (Kimura et al, 1997a, Kimura et al, 1997b). In a follow-up paper, they described the application of the Modulated Kinetics concept using various approaches (Kimura et al, 1998). Researchers at Nissan Motor Company investigated the effects of refined Modular Kinetics combustion methods on reducing PM in diesel engines (Aiyoshizawa et al, 1999). Nissan researchers also described the combustion and emission characteristics of MK combustion concepts applied to single-cylinder and multiple-cylinder test engines (Kimura et al, 1999). Kimura et al. (2001) described the optimization of combustion chamber specifications resulted in the avoidance of increased cold-start HC emissions and indicated that the MK engines could potentially meet ULEV emission standards.

Engineers at Mitsubishi also provided an overview of technology used for meeting the 1991 US PM standards on their heavy-duty diesel engines (Mori et al, 1990). In a follow up article they reported on Mitsubishi technology to be used in meeting the 1994 US PM standards, primarily combustion chamber shape and fuel injection timing (Kawatani et al, 1993). Researchers at Mitsubishi Motors Corporation in conjunction with Mitsubishi Heavy Industries reported on a water injection system for reducing emissions from diesel engines (Kohketsu et al, 1996). They reported reductions for PM in the Japanese 13 mode test cycle of 25% without a fuel consumption penalty. Also in 1996, Miyashita reported on noise reduction methods for diesel engines with a brief description of PM reductions associated with newer technology engines. A team of researchers from Mitsubishi Heavy Industries and Waseda University reported on theoretical studies conducted to investigate the effects of PAH's on PM emissions in diesel

exhaust (Yamamoto et al, 1999). Their results indicated that PAH's having a larger number of benzene rings tended to form higher particulate matter levels.

Researchers in India have incorporated engine improvements to meet the 2000 Indian standards. Suryanarayana Setty (1999) of Motor Industries Co. Ltd discussed the importance of high fuel injection pressures in meet the PM standards, apart from combustion bowl and swirl optimization. Trivedi et al. (1999) in a collaborative effort between Scooters India Ltd., Automotive Research Association of India, Emitec Emission Controls Pvt., Emitec GmbH developed a scooter with improved emissions using an enhanced air/fuel intake system and a catalytic converter. Lubrizol India Pvt. Ltd has also tested their emulsified fuel for PM emission reductions (Ravikumar et al. 2001).

4.4 Improved Methods for Sampling PM

4.4.1 New Regulatory Methods for 2007

The introduction of new PM standards for the 2007 model year will require the use of diesel exhaust aftertreatment and will correspondingly provide challenges to the current techniques of PM measurement. These standards are provided in Appendix A, showing that the PM requirements will require reductions to 10% of today's standards, or 0.01 g/bhp/hr. As a result of this lowering of the PM standards, EPA has implemented some significant regulatory changes to help improve the accuracy of the measurements.

Concerns over different sources of variability in the standard engine testing methods had been raised prior to the adoption of the 2007 standards. In the mid- to late 1980s round robin tests using an engine with a 0.48 g/bhp-hr PM levels gave an inter-laboratory variability of 0.09 g/bhp-hr, or approximately 20%. Given the implementation of the 1994 0.1 g/bhp/hr PM standards, a better understanding of the sources of variability in engine testing was required. In the early 1990s, Kittelson and Johnson (1991) conducted a comprehensive assessment of the different sources of variability in the heavy-duty transient test. This study examined a number of different possible sources of error including particle deposition and reentrainment, the influence of temperature and concentration gradients, electrostatic effects, gas-to-particle conversion, temperature and dilution ratio control, and filter weighing and handling. This study included visits to and comparisons of representative industrial and governmental test facilities and development of a model of the dilution and sampling systems used for the heavy-duty transient test. Some of the most significant sources of error identified in the study were thermophoretic deposition of PM onto the walls of the sampling system, the influence of dilution and cooling on the soluble organic fraction of the PM, inconsistent engine and dynamometer control strategies, and errors in the measurements of flows into and out of the secondary dilution tunnel. These researchers provided several recommendations based on their results. The principal recommendations included reduction of the heat transfer during sampling and dilution, standardized engine and tunnel conditioning procedures, more precise control of the dilution ratio by scaling the primary tunnel flow to the engine size, tighter specification of the test cycle, and more accurate measurement of the flows associated with the secondary dilution tunnel.

An interlaboratory crosscheck of heavy-duty chassis dynamometers was also conducted as part of the CRC E-55 program (Traver, 2002). The laboratories included in the program included the CARB facility in Los Angeles, CA, California Truck Testing Services in Richmond, CA, the Colorado School of Mines in Golden, CO, Environment Canada in Ottawa, Canada, SwRI in San Antonio, Texas, the West Virginia Transportable laboratory. Tests were conducted on a 1996 Ford L-9000 with a Cummins M11. The test matrix included cold and hot UDDS cycles and three steady state set points. Of the laboratories tested, 1 laboratory showed significantly different results than the others. The remaining laboratories were all within the critical thresholds for reproducibility and repeatability over the UDDS, although some of the critical thresholds were exceeded on the steady state cycles. Some potential causes for the variability between laboratories included testing conditions (engine cooling, atmospheric conditions, and altitude), road-load curve discrepancies, and the fact that most of the labs were not designed for steady state operation. An additional correlation exercise was also conducted between the CARB heavy-duty facility in Los Angeles and the CE-CERT Mobile Emissions Laboratory using protocols similar to those used in the main interlaboratory crosscheck (Cocker et al., 2004).

Clark (2002) examined the variability of PM measurements at the 2007 levels. He found that for a chassis dynamometer test on a truck without exhaust PM filtration, COVs of less than 5% can readily be obtained using standard procedures. In moving to a truck with a DPF, this variability increased to nearly 30%. Clark pointed out several sources of error, including the small proportion of the tunnel volume pulled by PM samplers, the potential 10% error induced by using a secondary filter, and problems with standard methods of calculating dilution factors and the fact that the dilution factors may be too low. Suggestions provided in this study included the tightening of controls on flow rates, temperature, and filter type for PM measurements, consideration of other methods of quantifying PM such as number, and hot filtration techniques to isolate the elemental carbon contribution supplemented with other methods to deal with organic carbon.

In response to the issues associated with measurement of PM at low levels, EPA examined methods to tighten the procedures for PM measurement and made considerable changes to 40 CFR Part 86, Subpart N as part of the 2007 heavy-duty diesel engine regulation. Specific changes to the regulation are as follows:

- Requirements for balance precision were increase from 20 to 2.5 μg .
- A preclassifier was added to eliminate large particles not associated with the exhaust
- A temperature range of $47\pm 5^\circ\text{C}$ was implemented, in contrast to previously only an upper limit of 52°C .
- 47 mm single filter assemblies are now required as opposed to the 70 mm dual filter holders.
- Dilution air filtration efficiency is specified as 98% for the primary with the HEPA filter.
- Filter room specifications were tightened to $22\pm 3^\circ\text{C}$ ($\pm 1^\circ\text{C}$ at microbalance) and a dew point of $9.5\pm 1^\circ\text{C}$.
- Reference filter drift limits were tightened from 40 μg to 10 μg .
- It was recommended that class 1000 clean room specifications be met.
- A 20 minute steady-state, high-temperature preconditioning cycle was added.

With the changes implemented above, as well as others included in the CFR regulations, EPA has achieved significant improvements in reducing the variability associated with PM mass measurement (Spears, 2002). For a 10 mg/mi light-duty diesel vehicle, COVs of ~5% can be achieved using these techniques, based on ~100 µg filter loading. For a 0.004 g/bhp-hr engine over the heavy-duty transient engine dynamometer test, COVs of ~10% can be achieved.

Researchers in Japan have also investigated methodologies suitable for PM measurements at 2007 levels. A team of Horiba engineers published a paper in March of 2001 describing an alternative methodology for measurement of low mass PM emissions expected under the 2007 US mandated HDD emission rate of 0.01 g/bhp-hr (Fukushima et al., 2001). The new methodology involves the use of quartz filters instead of the Teflon filters used in previous methods. After sample collection, the quartz filter is placed in a furnace and heated to 980 degrees Centigrade in a N₂ gas flow where the sulfate is vaporized and converted to SO₂ and measured using an SO₂ analyzer. The organic fraction of the particulates is oxidized by a constant flow rate of O₂ at a second quartz fiber and measured using a CO₂ gas analyzer. After evaporation of the SOF, O₂ is introduced into the furnace and the soot remaining on the filter is oxidized to CO₂. The mass of sulfate, SOF, and soot are calculated from the concentrations of the gases. Excellent correlations with gravimetric samples were found. This work is also summarized in "Controlled Measures" (Fukushima and Adachi, 2001). In a pair of technical reports, Horiba management (Readout No. 23, pgs 53-60) and system engineers (Readout No. 23, pgs 61-68) discussed the interaction of corporate globalization, increasingly stringent emissions regulations in developed countries, and the disparate trend towards diesel vehicles in Europe and the US. The needs of corporations to have uniform testing equipment across national boundaries was seen as a driving force in product standardization, while the divergent regulatory needs between the US, Japan, and EU were seen more as complicating factors. The sharp drop in emissions standards across the developed world was seen as one of the most important driving forces in changing instrumentation. The low PM measurement requirements necessitated by changes in regulations were a global factor, while the adoption of somewhat different standards and specific testing routines were considered a local need that could be met with local solutions. In 2004, Akard et al., (2004) presented a comparison of two particulate mass measurement methods including the advanced microbalance analysis. Researchers at the University of Castilla-La Mancha in Spain have also investigated guidelines for handling, weighing, and measuring diesel PM (Lapuerta et al. 1999).

4.4.2 Improved Sampling Methods

Although PM sampling using traditional methods can be improved, there is an emphasis on developing new sampling methods for a more realistic representation of PM under real-world sampling conditions. Based on their experimental work in the E-43 project, Kittelson et al. (2002b) and coworkers provided several recommendations on sampling of exhaust particles. Wei et al. (2001a,b) developed a single stage dilution tunnel that provided the capability of simulating many aspects of the atmospheric dilution process. This system provided the means to vary a number of parameters including the dilution rate and ratio, temperature, humidity, and residence time in the tunnel and transfer tube. In the design, numerical methods were used to simulate flow fields, velocity fields, and mixing profiles for gases and particles.

Although single stage dilution systems have been developed to match the concentration and growth profiles observed in the atmosphere, these systems are complex and still in need of refinement. Kittelson et al. (2002b) suggested that a more feasible solution to designing a system to approximate atmospheric dilution is using a two-stage dilution system. This system could incorporate a primary dilutor, an aerosol-aging chamber, and a secondary dilutor. The transfer line for such a system would be designed such that the growth precursors are not lost in the sample lines and that the residence time is minimized. A Sierra BG-type dilutor, with porous walls to introduce dilution air and low particle losses, was suggested for the first stage of dilution. The residence chamber after the primary dilution would be designed to provide the correct combination of primary dilution ratio temperature and residence time to allow particles to grow into the size range encountered in the atmosphere. The secondary dilution system is designed to quench nanoparticle formation and changes caused by coagulation, nucleation and growth to provide a stable particle for measurement by the instrumentation.

From a practical standpoint, Kittelson et al. (2002b) suggested a more important consideration is to use representative and repeatable laboratory procedures, than to try to simulate the formation of particles under conditions that are highly variable. These conditions can be met with a partial-flow dilution system since the dilution ratios and residence time can be more readily controlled. With a more standard full flow dilution tunnel, dilution values can vary more considerably from low values with the engine is operating under high load to higher values when the engine is operating under lower loads. To offset this factor, Kittelson et al. (2002b), recommended that the dilution ratio be adjusted to maintain a constant dilution ratio to provide a better simulation of what occurs in the atmosphere.

A number of researchers and companies have studied partial dilution flow systems for measurements of PM. Silvis et al. (2002) of AVL North America and AVL Graz Austria developed a partial flow system and compared results from the system to a full flow sampling system. They found that deposition losses from diffusion and thermophoresis were larger in the partial flow system due to the larger surface to volume ratio, lower flow rates and long samples tubes, but these losses could be minimized by using a short, insulated transfer tube and minimizing recirculation zones throughout the sampling path. They also found that the positioning, diameter, and probe size were important in minimizing sampling errors due to the need to sample directly from the exhaust stack. They also applied some straightforward equations to correct for any potential changes in the composition of the exhaust on the accuracy of the flow measurements. To proportion the sample to exhaust flow, they used a program with a look ahead algorithm, using pre-recorded flow control signals, and statistical regression checks. The incorporation of these measures provided good correlation between partial and full flow dilution for the insoluble fraction. For the soluble fraction, the measurements were found to vary with dilution ratio, temperature, and residence time, which had to be controlled to the same conditions for the two systems to match.

Ntziachristos et al. (2004) developed a partial flow sampling system as part of a collaborative effort between the Arisotel University in Thessaloniki Greece, the Swiss Federal Laboratories for Materials Testing and Research (EMPA), the Tampere University of Technology, Dekati Ltd., and Ford Forschungszentrum Aachen. It was found that the system allowed for characterization of particle properties over transient tests in real time, including number, surface area, and size distribution. Intralaboratory comparisons showed that the repeatability within a single laboratory was on the order of 10% for accumulation mode particles and 50% for

nucleation mode, while the overall reproducibility between laboratories was on the order of 20-30%.

Changes in diesel emissions testing from steady-state cycles to transient cycles led to several research efforts at Horiba to adapt measurement methods to the dynamic transient tests. Yamagishi (1999) describes the technical challenges encountered in the development of a partial-flow mini dilution tunnel in response to the measurement of PM in transient emissions test cycles. The MDLT-1302T was evaluated on the Euro Transient Cycle with the results showing a fast flow rate control with a response time of less than 0.5 seconds. Previous test systems used a full flow dilution tunnel to collect the entire exhaust sample. These systems were suitable for steady-state test cycles, but not well suited to the new transient test cycles and their greater flow control requirements. Sampling part of the exhaust stream allowed for a smaller tunnel and greater control under transient conditions. An updated evaluation of the mini-dilution sampling system for PM measurement was released as a technical report (Yamagishi and Otsuki, 2002). Their evaluation focused on the engineering issues and concluded that the micro-tunnel method will become the primary method of PM measurement in the near future. Researchers at Mitsubishi (Takeda et al. 1990) have also reported on a multi-tube mini-dilution tunnel for measurement of PM.

Researchers at SwRI have also made comparisons of several different partial flow sampling systems including the AVL SPC, Horiba MDLT, and Sierra BG-2 (Khalek and Ullman, 2002). The focus of the study was to evaluate the effectiveness of the different units in measuring PM emissions under steady state and transient engine operation in comparison with a full CVS. The results of these comparisons, however, showed the correlation between the partial flow units and the CVS was poor for both steady state and transient conditions. The agreement between the partial flow units and the CVS improved when a CO₂ based dilution ratio based on real-time exhaust CO₂ measurements was used instead of the flow-based measurements. For the transient cycles, operating the partial flow units in a look-ahead mode, where the sample probe response was advanced relatively to a pre-recorded exhaust flow trace of the same transient cycle, improved the PM emissions results. In this mode, agreement to within 5% was obtained for the AVL unit and to within 10% for the Horiba unit. This feature was not available for the BG-2. Overall, the study showed that additional improvements were needed to provide partial flow units comparable to CVS measurements.

Another factor considered as part of the E-43 program were diffusion losses when sampling diesel aerosol (Ayala et al., 2003). For sampling in the program, the determination of losses in the sampling system was an important aspect of the quality assurance (QA) plan. The magnitude of the losses in the sample train was determined using mono-dispersive particles in the sub-50 nm aerodynamic diameter size range. Theoretical calculations were also made for diffusion losses for 100 nm and less particles. Losses in the sampling system were found to be approximately 50% for 10 nm and 20% for 17 nm particles, with internal losses in the SMPS of about 70% for the 10 nm size range. To correct for these size distributions, the SMPS number concentrations at 10 and 20 nm were increased by a factor of 5 and 2, respectively.

5. Portable Instruments for PM Measurements Under In-Use Conditions

The importance of understanding PM emissions for a range of different vehicle types and operating conditions has led to considerable progress in different methodologies for measuring PM. Although conventional dilution tunnel PM measurements still represent the most common method for measuring PM, a number of researchers, government agencies, and equipment manufacturers have been developing technologies for the measuring PM under in-use or other conditions. These techniques include mobile emissions test facilities, on-board instruments, mini-dilution systems, and systems for measuring the plumes of vehicles under in-use conditions.

5.1 Mobile Emissions Laboratories

5.1.1 CE-CERT

In order to more realistically measure on-road, real-world emissions, UC Riverside has developed a unique Mobile Emissions Laboratory (MEL), see Figure 5-1. This unique laboratory contains all of the instrumentation normally found in a conventional vehicle emissions laboratory, but the equipment is mounted inside a 53-foot over-the-road truck trailer. A dilution tunnel inside the trailer mixes the truck's exhaust (sampled directly from the exhaust pipe) with dilution air, and the samples are measured just as they would be in a stationary laboratory using the procedures prescribed in the Code of Federal Regulations (CFR) Parts 86 and 89. Both gaseous and PM emissions are measured with the same levels of accuracy as measurements made in a stationary facility. The laboratory weighs approximately 45,000 pounds and serves as the truck's load. Thus, truck emissions under real-world operating conditions can be sampled with the accuracy and precision normally restricted to a stationary laboratory. Any class-8 tractor can be utilized with this laboratory on the road. The laboratory has also been used extensively for field measurements under steady state conditions such as for stationary source back-up generators. The laboratory has gone through extensive calibration, cross laboratory correlations, and testing to ensure accuracy and repeatability. MEL serves as an important tool for understanding how trucks pollute and for quantifying the effects of different fuels (reformulated diesel, etc.), alternative powertrains, different control strategies, and a variety of emission control equipment. Further details on MEL can be found elsewhere (Cocker et al., 2004).

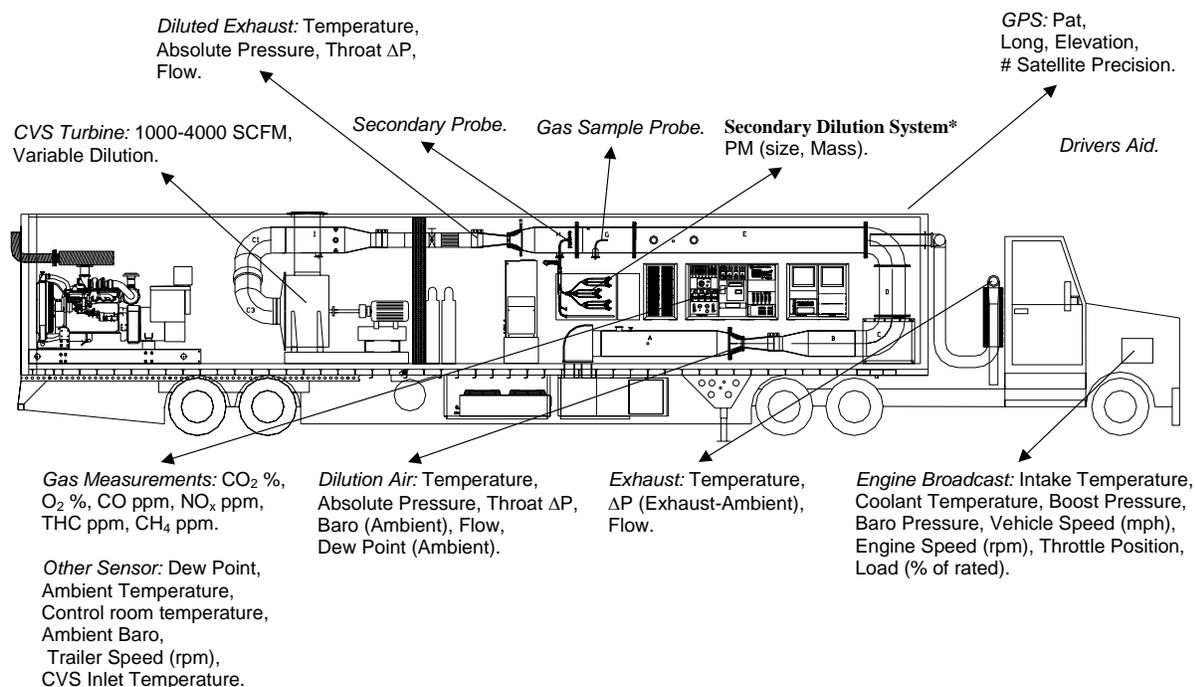


Figure 1 Schematic of UCR's heavy-duty diesel mobile emission laboratory (MEL)

5.1.2 West Virginia University

West Virginia University (WVU) has developed and extensively utilized a transportable laboratory for emissions testing of heavy-duty trucks and buses (Gautam et al., 1991; Lyons et al., 1992). This facility has been in operation for over a decade and has collected emissions data for hundreds of different trucks and buses (http://www.ctts.nrel.gov/heavy_duty/emissions.html/#truckemissions). The laboratory includes one semi-trailer that incorporates a chassis dynamometer and a second semi-trailer that contains the necessary emissions measurement and control technology. With the trailer, PM measurements are collected through a dilution tunnel similar to standard laboratory measurements.

5.1.3 University of Minnesota

The University of Minnesota mobile aerosol laboratory differs from the CE-CERT and WVU mobile laboratories in that it is primarily designed to better understand the atmospheric PM formation process associated with vehicle exhaust (Kittelson et al., 2002b). The U of M trailer is typically used in chase experiments, where it will closely follow a test vehicle and measures the PM in the exhaust plume as it dissipates into the atmosphere. This unit includes instruments for measuring regulated pollutants as well as PM measurement instruments including an SMPS, ELPI, CPC, diffusion charger, epiphaniometer, and PAS. This unit was used extensively in the CRC E-43 program to examine the formation of nanoparticles under in-use conditions.

5.1.4 US EPA

The US EPA's On-Road Diesel Emissions Characterization Facility has been in use for over 8 years. In 2001 it was extensively modified to improve PM measurement capability. The facility is equipped with multiple PM measurement instruments including an ELPI, TEOM, and a particle-bound Polycyclic Aromatic Hydrocarbon analyzer. All three instruments sample dilute exhaust drawn directly from the exhaust stream using a stack dilution system (Brown, 2001). A schematic of this unit is provided in Figure 5-2.

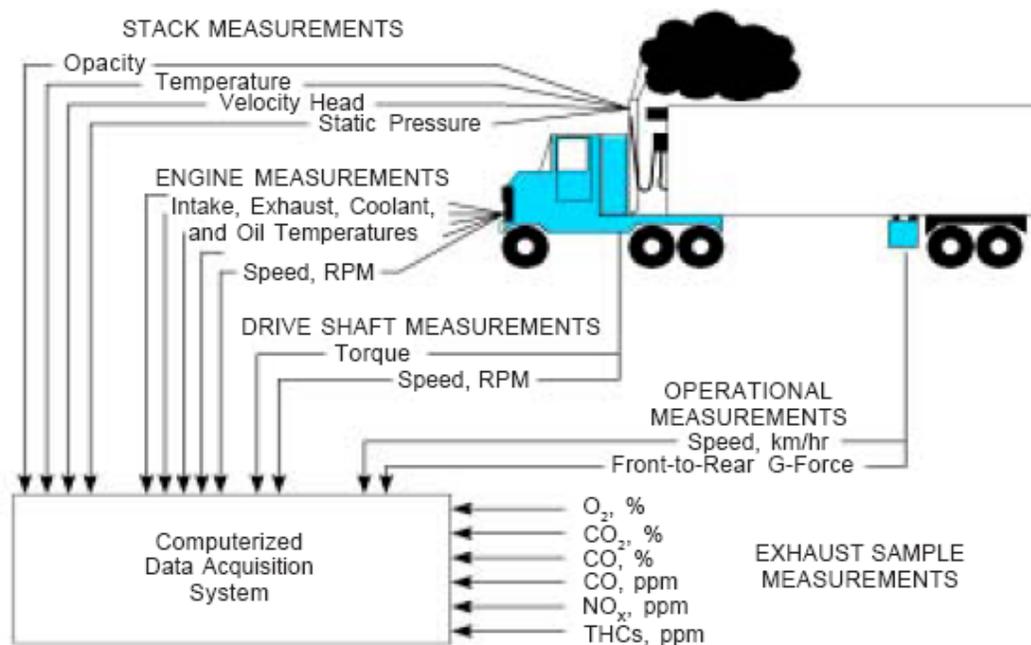


Figure 5-2. Schematic of the US EPA's On-road Diesel Emissions Characterization Facility

5.2 Portable/In-Use PM measurement Systems

A number of organizations have developed portable emissions measurement systems that can be used for either measurements in the field or actual on-board measurements of emissions. The scope of these instruments varies depending on the application and what specific emissions are measured. A review of various portable emissions systems are provided by Gautam et al. (2001) and Lenaers et al (2002) in Europe. In another article, Weaver (2001) discusses an instrument based on partial dilution for the measurement of gases and particles. Thompson (2002) reports that his review of portable and mobile emissions measurement systems over the past twenty years showed only limited success. Other reports include those of Reading (2001), Gazelle (2001), Spears (2002), and Ensfield (2003). Khalek (2002) evaluated to effects on particle sampling of using a partial flow sample system relative to a full flow CVS system. The situation is that portable or on-board instruments are in a state of flux and on a rather steep learning curve. The focus of the present review is on those systems with PM measurement capability.

5.2.1 Southwest Research Institute

The Southwest Research Institute developed a portable system to measure exhaust emissions from diesel buses in the early 1990s (Human and Ullman, 1992). The system utilized a mini-

dilution tunnel for PM measurement. The regulated gaseous emissions were measured with an Energy Efficiency Systems, Inc. Enerac 2000E. This system was designed for the collection of bag samples and was not used for any continuous exhaust measurements. The test sequence included idle, no-load, and loaded tests designed to be performed with the vehicle parked.

5.2.2 Environment Canada

As part of a study by the Northeast States for Coordinated Air Use Management (NESCAUM) to evaluate the impact of retrofit exhaust control on heavy-duty construction vehicles, Environment Canada developed an exhaust sampling system for the measurement of gaseous and PM emissions from heavy-duty construction vehicles under in-use operating conditions (Alnslie et al., 1999). The system incorporated a mini-dilution tunnel and could be mounted to each of the test vehicles while in use. At the outlet of the dilution tunnel, the diluted exhaust was passed through a filter for collection of PM. Tedlar bag samples were also collected upstream of the PM filter for measurement of the regulated emissions, so the primary measurements were for integrated samples. The unit was used for measurements on a backhoe, front-end loader, dump truck, and bulldozer. Measurements were collected over different cycles for the construction equipment, designed to represent typical operating conditions.

5.2.3 West Virginia University

WVU has developed a portable system called the Mobile Emissions Measurement System (MEMS) (Gautam et al., 2001). The focus of this instrument is on the measurement of NO_x and CO₂ since CO levels tend to be low for diesel vehicles and hydrocarbon emissions are difficult to measure accurately with an NDIR. The MEMS uses NDIR for measuring CO₂ and a zirconium oxide sensor for measuring NO_x with an electrochemical cell to further verify the NO_x levels. Flow measurements are made using an Annubar in the exhaust pipe. Comparisons between the MEMS and a full flow dilution tunnel system showed that the MEMS unit is capable of reporting integrated brake specific mass emissions for NO_x and CO₂ within 5% of the laboratory results.

WVU has also developed an instrument for the measurement of real-time PM from on-road and off-road vehicles (Gautam et al., 2003). The development of the instrument was through a collaboration between WVU, Booker Systems Ltd., and Mid-Atlantic Research Institute, LLC. This unit called the MARI RPM-100 utilizes a QCM for the real-time PM and has been used as a personal sampler, on dozers in off-road applications, and on class –8 trucks. Comparisons with a full flow dilution tunnel indicated that the PM emissions for the MARI RPM-100 were comparable to with –3.4 to 12.6%. The Booker Systems QCM is now being applied for the Sensors on-board systems.

5.2.4 Sensors

Sensors Inc. has developed an on-board emissions measurement system for emissions from gasoline and diesel vehicles, the SEMTECH-G and SEMTECH-D, respectively (Ensfield and Shah, 2002). For gaseous emissions, the SEMTECH instruments use an NDIR analyzer for CO and CO₂ and an NDUV analyzer for NO and NO_x. The SEMTECH-G uses NDIR for HC measurement. The SEMTECH-D differs from other on-board instruments in that a flame ionization detector is used instead of an NDIR and the HC line is maintained at a temperature of 200°C, similar to the conditions used in standard dilution tunnel measurements of diesel emissions. This should provide more accurate readings than could be obtained through more traditional on-board NDIR systems.

Sensors has also developed several systems for the measurement of on-road PM emissions. The initial version of the PM300 comprised a PM measurement system based on light scattering in conjunction with a micro-dilution tunnel (Eden, 2003). More recently, Sensors has unveiled the SEMTECH QCM and MPS (micro-proportional sampler) systems. These systems are based on an original design by Booker Systems Ltd. of Lancashire, England.

Sensors was awarded a contract by the US EPA to supply on-board emissions analyzers for both gasoline and diesel testing (Sensors, 2002). This contract was the culmination of over a year of testing by EPA. The initial contract called for the acquisition of two gasoline and two diesel SEMTECH units. The Sensors units were recently used by EPA as part of Michelin's 2003 Challenge Bibendum. As part of this Challenge, 32 vehicles were tested over two 1.5 hour sessions at the Infineon Raceway in Sonoma, CA (Spears, 2003). The Sensors units with a SEMTECH QCM and a MPS will also be used as part of a major study by the EPA in Kansas City (Buchholz, 2004). This study will be the largest to date for sampling using on-board emissions analyzers, and will comprise 220 cars and 260 light-duty trucks, with ages ranging from pre-1980 to 1996 and newer. The Sensors unit has also been tested by EMPA of Switzerland (Soltic and Rütter, 2003).

5.2.5 Clean Air Technologies International, Inc. (CATI)

CATI has developed a portable emissions measurement system called the OEM 2100 Montana System. This systems uses NDIR for HC, CO, and CO₂, an electrochemical cell for NO, and laser light scattering for PM measurement. The precision and accuracy of this unit was tested by the New York Department of Environmental Conservation and the US EPA's laboratory in Ann Arbor, MI. This instrument has been used by researchers at North Carolina State University for measurements of on-road emissions from various vehicles (Frey et al. 2001). This unit has also been used for monitoring emissions from diesel construction equipment at the World Trade Center Site (Lanni and Vojtisek-Lom, 2003). Other applications where the OEM system has been used include lawnmowers, trains, planes, and ferry boats (Vojtisek-Lom and Allsop, 2003).

5.2.6 RAVEM

Researchers at the Engine, Fuel, and Emissions Engineering, Incorporated developed a Ride-Along Vehicle Emission Measurement (RAVEM) system for on-board emissions measurements (Weaver and Balam-Almanza, 2001; Weaver et al., 2003). The system is based on a CVS principle and provides measurements of NO_x, CO₂, and PM. The RAVEM differs from the conventional CVS, however, in that it dilutes only a small fraction of the total exhaust stream. The RAVEM uses a feedback system to provide a sample flow rate that is proportional to the volumetric flow rate of the exhaust. PM measurements are collected on filters downstream of the dilution air and analyzed using gravimetric means. This instrument was tested for validation at the California Truck Testing Systems in Richmond, CA and has been used in field demonstrations for a refuse truck, a turbine powered locomotive, and a ferryboat.

5.2.7 Flemish Institute for Technological Research

The Flemish Institute for Technological Research, or VITO, has developed a system called Vito's On-the-road Emissions and Energy Measurement system (VOEM) (Lenaers et al., 2002; Lenaers, 2003). This system uses an NDIR for CO and CO₂, a FID for HCs, and a chemiluminescent analyzer for NO_x. For diesel applications at heated sampling line (190°C) is

also used to prevent the loss of heavy HCs. For PM, the system uses an R&P TEOM coupled with a Horiba MDT-905 microdilution tunnel. The accuracy of the instrument for CO is estimated to be within 10% while the accuracy for PM is estimated to be <25%.

5.2.8 Sierra Instruments, Inc./Caterpillar

The BG-1, BG-2, and BG-3 mini-dilution system was developed through a joint effort between by researchers at Sierra Instruments, Inc. and Caterpillar. Sierra Instruments is the exclusive licensee of this micro-microdilution technology originally patented by Caterpillar (www.sierraemissions.com; Graze, 1993). The BG systems are designed to provide a mini or fractional dilution tunnel for use in measuring engines such as non-road engines that can be difficult or expensive to measure on a dynamometer. The unit was initially designed to correlate to full dilution systems within ISO 8178 equivalency standards. The unit has been used extensively for field testing of locomotives, marine, mining and other off-road engines since the mid-1990s. Initial tests at SwRI by Khalek and Ullman (2002) did indicate poor correlations with a full dilution CVS system for several partial dilution systems, including the BG-2. More recently, of the six official transient runs made with transient dilution air controller at SwRI, however, only two exhibited a bias greater than 10% (12 and 14%). In these cases, both results were above CVS data. The other four runs yielded biases of less than +/-5%. Tests at Caterpillar with the more recent BG-3 unit have also shown correlations with the CVS of less than +/-5%.

5.2.9 ROVER

The US EPA has developed an on-board system called ROVER to measure real-time exhaust emissions. The system measures CO, CO₂, and HCs using an NDIR and O₂ and NO_x using an electrochemical cell. The system uses a Snap-On MT3505 multi-gas analyzer along with a Horiba Mexca-120 for quantification of NO_x. A version of this unit is also currently being developed and marketed by Horiba. At this point, the ROVER is not capable of making PM measurements.

5.2.10 Simple Portable On-vehicle Testing (SPOT)

Analytical Engineering, Inc. has developed an on-board measurement system called the Simple Portable On-vehicle Testing (SPOT) system, under funding from the US EPA. The initial goal of this instrument was to measure brake-specific NO_x, and it does not have the capability for PM measurements. The measurement capability for the instrument includes the following parameters: NO_x and O₂ concentration, exhaust mass flow, engine speed, exhaust temperature, ambient temperature, vehicle velocity and position. A ZrO₂ sensor was used for measurement of total NO_x and O₂. A total of at least 7 units were construction for a major program to measurement emissions from construction equipment throughout Indiana. A total of fifty 1-week tests were conducted for this program, including over 6000 hours of data (Spears, 2001, 2002, 2003). This unit is not used for PM measurements.

5.2.11 Horiba Instruments Inc.

Horiba Instruments and NGK collaborated to develop a system that can be used for on-board measurements of NO_x emissions from diesel vehicles (Kihara et al., 2000). The first generation of this system was equipped with two ZrO₂ sensors installed in the exhaust pipe between the pre-muffler and the main muffler, with one system used to measure NO_x concentration and the second used for lambda analysis. The system also included systems for measuring intake air-flow, air-to-fuel ratio, boost pressure, engine rpm, and other parameters. Overall, this system was

capable of NO_x measurements within 4% of laboratory measurements and fuel consumption measurements within 3% of the laboratory measurements. A second generation instrument, the OBS-1000, was introduced in 2002 (Nakamura et al., 2002). This instrument was based on a heated NDIR that measured CO and CO₂ under wet conditions using an algorithm to correct for the water interference. This NDIR was combined with an Annubar flow meter and an air/fuel sensor. The correlation between this combined system and laboratory measurements was within 7% for fuel consumption, within 5% for CO, and within 6% for CO₂ mass emission rates. In recent tests, a Horiba opacity-smoke meter was also used to measure fuel differences for a vehicle operating on biodiesel (Senda et al., 2004).

5.3 Remote Sensing of PM Emissions from Mobile Sources

Several research groups have developed remote sensing techniques for the measurement of exhaust PM on the open road. In the CRC E-56 Project, a field comparison was conducted in Denver, CO in early 2001 using remote sensing systems from the Desert Research Institute (DRI) and the University of Denver. For the DRI system, a LIDAR-based remote sensing system is used to measure PM and a commercial remote sensor, the RSD3000 manufactured by Environmental Systems Products, Inc., to measure gaseous pollutants. The DRI LIDAR-based remote sensing system is a prototype for the measurement of on-road particulate matter emissions (Keislar et al, 2002). Using a measurement of CO₂ across the plume, the particulate mass emission factor (per fuel consumption) can be obtained. The University of Denver system used opacity measurements, at three different wavelengths, to measure the PM in the exhaust stream (Steadman and Bishop, 2002). In phase 1 of the project, the PM mass emissions and carbon composition for three vehicles (light and medium duty diesel trucks) were measured at steady state at the Colorado Department of Public Health and the Environment. In phase 2 of the study, the same vehicles were operated at steady state in a parking lot with a slight grade and measured with the two remote sensing systems. The vehicle and speeds were similar to the laboratory measurements, but the dilution conditions were not. At the PM levels measured by the remote sensors, 2.5 gm/kg of fuel, valid measurements could not be obtained by the remote sensing devices and the correlation between the remote sensors in the parking lot and the laboratory measurements were poor for both units. A poor correlation was also found for an on-board smoke detector. In phase 3, the same vehicles were tested on a freeway on-ramp at higher loads, speeds and accelerations. Under these conditions, valid measurements were only made for the highest emitting vehicle, with the DRI instrument somewhat better in distinguishing the higher PM emissions from the dirtiest vehicle. Overall, it was concluded that neither remote sensing instrument was ready for making PM measurements from an on-road vehicle fleet (Slott 2003).

Researchers at Oak Ridge National Laboratory have also developed an instrumentation system for remote sensing of PM emissions from trucks (Lenox et al. 2003). The PM measurement system is based on LIDAR. A UV absorption technique is also included in the system set-up for measurements of NO_x. This instrument will be deployed along the I-40/Watt Road corridor in Tennessee to evaluate truck emissions during actual operation. This project is a collaboration with the University of Tennessee. Remote sensing is also being utilized in various other regions of the world including Europe, Canada, Mexico, Australia, New Zealand, Taiwan, Hong Kong and India, although the most predominant application is for measurement of gaseous emissions from light-duty gasoline vehicles (Chan et al., 2002; Lan, 2002; Full et al., 2002; USAID India,

2004; McCrae et al., 2001; Kuschel et al., 2003). Some measurement so airplanes using remote sensing have also been conducted in Europe (Popp et al., 1998, 1999).

6. Summary and Conclusions

Particulate matter from diesel engines/vehicles has continued to be an important issue for the reduction of mobile source emissions inventories. Over the past 30 years, extensive studies have been conducted on PM emissions from vehicle exhaust. In the past decade, however, there has been an increased emphasis on reductions in not only particle mass, but also particle number and in better understanding size distributions. The goal of the present program was to conduct a thorough review and assessment of international and domestic literature to understand the changing nature of laboratory and other measurements of PM from vehicles and the state-of-the-art laboratory methods. A summary of this review is provided as follows:

- Roadside and chase studies have been conducted to evaluate the fate of vehicle exhaust PM in the ambient atmosphere under real-world conditions. These studies have included roadside studies and chase studies. These studies have shown a strong nuclei mode, and that atmospheric dilution is on the order of 1000:1 after 1 second, considerably higher than that obtained in the dilution tunnel measurements. Comparisons of particles in some chase studies have also shown considerably higher number of particles measured by a condensation particle counter (CPC) in comparison with an scanning mobility particle sizer (SMPS), which is attributed to a large number of particles <10 nm that can be detected by the CPC but not the SMPS.
- With the onset of new regulatory limits for 2007, essentially requiring the use of DPFs, more advanced PM sampling methodologies have been added to the current regulatory requirements for heavy-duty diesel engines. Specific changes to the regulation include increasing the balance precision from 20 to 2.5 μg , use of a PM classifier, a temperature range of $47\pm 5^\circ\text{C}$ for filter sampling, filter room specifications of $22\pm 3^\circ\text{C}$ ($\pm 1^\circ\text{C}$ at microbalance) and a dew point of $9.5\pm 1^\circ\text{C}$, and reference filter drift limits of 10 μg . These limits can provide COVs of ~10% for a 0.004 g/bhp-hr engine.
- Real-time PM can be measured by a variety of different methods including the Tapered Element Oscillating Microbalance (TEOM), Quartz Crystal Microbalance (QCM), Nephelometer, Aethalometer, Photoacoustic Instrument, Laser induced incandescence, and Fast FID. These instruments provide important information on the formation mechanisms of PM that cannot be obtained with traditional integrated filter techniques. The correlation with filter based systems can vary depending on the type/technique of the instruments, with systems based on mass generally correlating better than those based on black carbon, which can vary depending on the PM composition. Several of these techniques are currently being integrated into on-board measurement instruments.
- Size distributions can be measured by electrical mobility for sizing include the Electrical Aerosol Analyzer, the Differential Mobility Particle Sizer, the Scanning Mobility Particle Sizer, and the Nanometer Differential Mobility Analyzer or inertia sizing using a MOUDI, Electrostatic Low-Pressure Impactor, and Nano-MOUDI. Other available sizing techniques include the Aerosol Time-of-Flight Mass Spectrometer, Photoelectric Aerosol Sensor (PAS), the nephelometer, diffusion batteries, and time resolved laser induced incandescence.

- The Europeans have conducted an extensive program to evaluate PM measurement capabilities since the beginning of the decade. On the basis of this multinational study, technologies identified as promising for PM measurement include a Modified 2007PM (filter-based method), Raw exhaust + thermodenuder + electrical diffusion battery, Constant volume sampler + laser induced incandescence, Raw exhaust + laser induced incandescence, Constant volume sampler + thermodenuder + condensation particle counter, Constant volume sampler + photo acoustic soot sensor, Constant volume sampler + secondary dilution + MEXA (a filter-based method for determining PM mass with chemical analysis). Of these systems, the modified 2007PM method and the constant volume sampler + thermodenuder + condensation particle counter were recommended most strongly for further study.
- While the studies in Europe have shown promise in measuring PM number and size distributions, automobile manufacturers in Europe and elsewhere have expressed concerns about the reliability of the non-standard measurement techniques and do not consider them reliable for use in regulatory applications. At the very least, these arguments point out that factors such as nucleation and volatile organic carbon, which can contribute to experimental variability in PM number and size measurements, must be better controlled to achieve repeatability consistent with current regulatory measurements.
- In Japan, there are also a number of on-going particle programs conducted through the Japan Clean Air Program (JCAP), the Japanese National Traffic Safety and Environmental Laboratory (NTSEL), as well as Japanese universities, instrument companies, and automobile manufacturers. JCAP and NTSEL are both evaluating PM measurement methods for PM size as well as weight, including some inter-laboratory comparisons. Horiba has developed a fast FID methodology for real-time PM measurement and is also developing partial dilution and on-board measurement systems. The automobile manufacturers are more focused on engine and aftertreatment development for the reduction of PM.
- In standard laboratory practice, dilution ratio is one of the most important sampling parameters. In particular, the dilution ratio in typical dilution tunnel applications is in the range of 5 to 50:1, where saturation values are highest and there is a strong driving force for gas to particle conversion or nucleation. Suggestions for improving the sampling of PM under laboratory conditions include using a two-stage dilution system or, from a practical standpoint, the use of representative and repeatable laboratory procedures. This could include partial flow dilution systems where the dilution ratios and residence time can be more readily controlled or adjusting the dilution ratio in a full dilution tunnel to maintain a constant dilution ratio.
- A number of systems have been developed for measuring PM under in-use or non-laboratory conditions. Mobile emissions test facilities reviewed include units developed by CE-CERT, West Virginia University and the University of Minnesota. Portable systems reviewed include the MARI RPM-100 from WVU, the ROVER and SPOT systems from the EPA, and systems developed by Sensors, Clean Air Technologies

International, Inc. (CATI), and the RAVEN system. The BG-1, BG-2 mini-dilution system by Sierra Instruments, Inc./Caterpillar is also reviewed. The integration of PM measurements into on-board systems is still developing, although considerable progress in this area has been made recently, with several instruments showing the capability of measurements within 10% of dilution techniques.

- Diesel particle filters represent a considerable advance in the control of diesel PM. DPFs can typically achieve >90% reduction of both particulate mass and number. Diesel particle filters (DPFs) are expected to expand considerably in the near future, as these devices will essentially be required to meet regulatory standards for 2007. CARB, Switzerland, and EPA have also put programs in place to promote the extended use of DPFs in retrofit applications.

7. Bibliography

Aber, J.; McDowell, W.; Nadelhoffer, K; Magill, A.; Berntson, G.; Kamakea, M.; McNulty, S.; Currie, W.; Rustad, L.; Fernandez, I. (1998) “ Nitrogen Saturation in Temperate Forest Ecosystems.” *BioScience*, Vol. 48, No. 11, pp. 921-934.

Abgaszentrum Der Automobilindustrie (2002) Assessment of Particle Measurement Methods. October.

ACEA, (2002) ACEA Programme on the Emissions of Fine Particles from Passenger Cars. Brussels, Belgium, July.

ACEA, (1999) ACEA Programme on the Emissions of Fine Particles from Passenger Cars. Brussels, Belgium.

Ahlvik, P., Ntziachristos, L., Keskinen, J., Virtanen, A., (1998) Real-time Measurements of Diesel Particle Size Distribution with an Electrical Low Pressure Impactor. SAE Technical Paper No. 980410.

Ahlvik, P. and De Serves, C. (1999) Characterization of Particulate Emissions from 11 Gasoline and 5 Diesel-Fueled Cars. AVL-MTC report No. 9708B.

Aiyoshizawa, E., Hasegawa, M., Kawashima, J-I, and Muranaka, S. (1999) Combustion Characteristics of a Small DI Diesel Engine. SAE Technical Paper No. 1999-08-0019.

Akard, M., Oestergaard, K., Chase, R.E., Richert, J.F.O., Fukushima, H., and Adachi, M., (2004) Comparison of an Alternative Particulate Mass Measurement with Advanced Microbalance Analysis. SAE Technical Paper No. 2004-01-0589.

Alnslie, B., Rideout, G., Cooper, C., and McKinnon, D. (1999) The Impact of Retrofit Exhaust Control Technologies on Emissions from Heavy-Duty Diesel Construction Equipment. SAE Technical Paper No. 1999-01-0110.

An, F., M. Barth, M. Ross and J. Norbeck. (1997) The Development of a Comprehensive Modal Emissions Model: Operating Under Hot-Stabilized Conditions. *Transportation Research Board Record Series 1587: 52-62*, Washington DC, 1997.

Anderson, R. (2004) Development of a Novel On-Board Sampling and Conditioning System for the Measurement of Particulate Matter, Gases, and Air Toxics – Report on Phase 1. Proceedings of the 14th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, March.

Andersson, J.D., Wedekind, B.G.A., Hall, D., Stradling, R., Barnes, C., and Wilson, G. (2000) DETR/SMMT/CONCAWE Particle Research Programme: Sampling and Measurement Experiences. SAE Technical Paper No. 2000-01-2850.

Andersson, J.D., Wedekind, B.G.A., Hall, D., Stradling, R., Barnes, C., and Wilson, G. (2001) DETR/SMMT/CONCAWE Particle Research Programme: Light Duty Results. SAE Technical Paper No. 2000-01-3577.

Andersson, J. and Wedekind, B. (2001) DETR/SMMT/CONCAWE Particle Research Programme 1998-2001, May.

Andersson, J.D., Brown, A.J.M., Clarke, D.P., Lance, D.L., McGrath, N.J., and Savill, R.H., (2002) UK Particle Measurement Programme – Heavy Duty Methodology Development Final Report. Final report by Ricardo Consulting Engineers Ltd, West Sussex, UK for the UK Department of Transportation, August.

Andersson, J.D., Brown, A.J.M., Clarke, D.P., Jemma, C.A., McGrath, N.J., O’Leary, C.I., Savill, R.H., and Watson, J.A. (2003) UK Particle Measurement Programme Phase 2 – Heavy Duty Methodology Development Final Report. Final report by Ricardo Consulting Engineers Ltd, West Sussex, UK for the UK Department of Transportation, August.

Andrews, G.E., Clarke, A.G., Rojas, N.Y., Sale, T., and Gregory, D. (2001) Diesel Particle Size Distribution: The Conversion of Particle Number Size Distribution to Mass Distribution. SAE Technical Paper No. 2001-01-1946.

Ara, M. and Kishi, Y. (1994) Analysis of Diesel Particulate Matter. SAE Technical Paper No. 948375.

Arnott, W.P., H. Moosmuller, C.F. Rogers, T. Jin, and R. Bruch. (1999). Photoacoustic spectrometer for measuring light absorption by aerosol: instrument description. Atmospheric Environment, vol. 33, pp. 2845-2852.

Axelsson, B. and Wize, P.O. (2001) qualitative Laser-Induced Incandescence Measurements of Particulate Emissions During Transient Operation of a TDI Diesel Engine. SAE Technical Paper No. 2001-01-3574.

Ayala, A., Olson, B., Cantrell, B., Drayton, M., and Barsic, N. (2003) Estimation of Diffusion Losses when Sampling Diesel Aerosol: A Quality Assurance Measure. SAE Technical Paper No. 2003-01-1896.

Bagley, S.T., Baumgard, K.J., Gratz, L.D., Bickel, K.L. and Watts, W.F. (1991) Effects of a Catalyzed Diesel Particle Filter on the Chemical and Biological Character of Emissions from a Diesel Engine used in Underground Mines. SAE Technical Paper No. 911840.

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

Baikerikar, A. and Chaudhari, M.K., (2003) Emission Study and Evaluation of Emission Control Devices in Euro I/Euro II Compliant Indian Vehicles and Engines with Different Sulfur Content Fuel, SAE Technical Paper No. 2003-26-0018.

Baron, J. S.; Rueth, H. M.; Wolfe, A. M.; Nydick, K. R.; Allstott, E. J.; Minear, J. T.; Moraska, B. (2000) "Ecosystem Response to Nitrogen Deposition in the Colorado Front Range." *Ecosystems*, pp. 352-368.

Barth, M., F. An, J. Norbeck and M. Ross. (1996) "Modal Emissions Modeling: A Physical Approach", *Transportation Research Board Record Series 1520*: 81-88.

Baumgard, K.J. and Kittelson, D.B. (1985) *The Influence of a Ceramic Particle Trap on the Size Distribution of Diesel Particles*. SAE Technical Paper No. 850009.

Baumgard, K.J. and Johnson, J.H. (1992) *The Effect of Low Sulfur Fuel and a Ceramic Particle Filter on Diesel Exhaust Particle Size Distributions*. SAE Technical Paper No. 920566.

Bechmann, O., Carli, S., Engeler, W., Garbe, T., Lach, G., Ryan, L., Schindler, K-P, *Particulate Emissions and Their Measurement in Practice: Today and in the Future*. Volkswagen AG, Wolfsburg.

Bell, S.P., Dickens, C.J., Feest, E.A., Smith, A.P., and Tope, A.M., (1999) *Experimental Assessment of Particle Measurement Instrumentation*. Final report from AEA Technology, Oxfordshire, UK to the DGXI of CEC, UK.

Biancotto, D., Erol, T., Georges, H., Lavy, J., Martin, B., Blanchard, G., Macaudiere, P., Grellier, J-M, and Seguelong, T. (2004) *Retrofit Program of a Euro 1 and Euro 2 Urban Bus Fleet in La Rochelle, Using the Ceria-Based Fuel-Borne Catalyst for Diesel Particulate Filter Regeneration (Phase #1)*. SAE Technical Paper No. 2004-01-0821.

Booker, D. (2001) *Development of a Real-Time Transient Cycle Mass Monitor*. Proc. ETH Conference on Nanoparticle Measurement. Ed. By A. Mayer.

Brear, F., Fredholm, S.C.G., and Andersson, E.S., (1992) "The role of the Through Flow Oxidation Catalyst in the Development of a Low Emissions Specification HD Diesel Engine," SAE Technical Paper No. 920367.

Brown, J.E.; Clayton, M.J.; Harris, D.B.; King, Jr., F.G.; (2000) *Comparison of Particle Size Distribution of Heavy-Duty Diesel Exhaust Using a Dilution Tailpipe Sampler and In-Plume Sampler During On-Road Operation*; *Journal of the Air and Waste Management Association*, vol. 50, 1407-1416.

Brown, J.E. (2001) "Heavy-Duty Diesel Fine Particulate Matter Emissions: Development and Application of On-Road Measurement Capabilities". Environmental Protection Agency, Office of Research and Development, EPA/600/R-01/079.

Bryce, D.J., Ladommatos, N., Zhao, H. (2000) *Quantitative Investigation of Soot Distribution by Laser-Induced Incandescence*. *Appl. Opt.*, vol 39, pp. 5012-5022.

Buchholz, K. (2004) *Cleaner, Safer, Quieter*. *Automotive Engineering*. February.

Bureau of Mines (1992) Diesels in Underground Mines: Measurement and Control of Particulate Emissions. Proceedings of the Bureau of Mines Information and Technology Transfer Seminar, BuMines IC 9324, p 132.

Burtscher, H. and Siegmann, H.C. (1994) *Combust. Sci. Technol.*, vol. 101, pp 327-332.

Burtscher and Gross (1992) *Atmos. Envir.*, vol. 26a, 997-1003.

Burtscher, H. and Matter, U. (2000) Particle Formation Due to Fuel Additives. SAE Technical Paper No. 2000-01-1883.

Burtscher, H. (2001) Literature Study on Tailpipe Particulate Emission Measurement for Diesel Engines. Report for the Particle Measurement Programme (PMP) for BUWAL/GRPE.

Bytnerowicz, A.; Fenn, M. E. (1996) "Nitrogen Deposition in California Forests: A Review." *Environmental Pollution*, Vol. 92, No. 2, pp. 127-146.

Cadle, S.H., Mulawa, P., Ragazzi, R.A., Knapp, K.T., Norbeck, J.M., Durbin, T.D., Truex, T.J., and Whitney, K.A., Exhaust Particulate Matter Emissions from In-Use Passenger Vehicles Recruited in Three Locations CRC Project E-24, SAE Technical Paper No. 99FL-215.

California Air Resources Board. (2002) "Public Hearing to Consider Amendments to the Ambient Air Quality Standards for Particulate Matter and Sulfates"; Staff report available on California Air Resources Board site, <http://www.arb.ca.gov/research/aaqs/std-rs/std-rs.htm>. (Accessed January, 2004).

California Air Resources Board. (2000) Risk Reduction Plan to Reduce Particulate Matter Emissions from Diesel-Fueled Engines and Vehicles. Staff report available on California Air Resources Board site, www.arb.ca.gov/diesel/documents/rrpapp.htm, October.

California Environmental Protection Agency (1998) Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant. Calif. EPA, Office of Environmental Health Hazard Assessment, Sacramento, CA.

Cartus, T., Dorfer, F., Schindler, W., and Reischl, G.P. (1999) Messverfahren und Bewertung von Partikelemissionen, VDA – Technischer Kongress.

Chan, T.L., Dong, G., Ning, Z., Hung, W.T., Cheung, C.S., and Leung, C.W. (2002) Better Air Quality in Asian and Pacific Rim Cities, December, Hong Kong, SAR.

Chatterjee, S., McDonald, C., Conway, R., Windawi, H., Vertin, K., LeTavec, C.A., Clark, N.N., Gautam, M., (2001) Emission Reductions and Operational Experiences with Heavy Duty Diesel Fleet Vehicles Retrofitted with Continuously Regenerated Diesel Particulate Filters in Southern California; SAE Technical Paper No. 2001-01-0512.

Chen, D.R., Pui, D.Y.H., Hummes, D., Fissan, H., Quant, F.R., and Sem, G.J. (1996) Nanometer Differential Mobility Analyzer (Nano-DMA): Design and Numerical Modeling. *J. Aerosol Sci.*, Vol 27, S 1, pp S137-S138.

Chen, D.R., Pui, D.Y.H., Hummes, D., Fissan, H., Quant, F.R., and Sem, G.J. (1998) Design and Evaluation of a Nanometer Differential Mobility Analyzer (Nano-DMA). *J. Aerosol Sci.*, Vol 2, pp 497-509.

Cheng, Y.S. (1993) Condensation Detection and Diffusion Size Separation Techniques. In *Aerosol Measurement*, K. Willeke and P.A. Baron, eds. Van Nostrand Reinhold: New York, NY, pp. 427-451.

Cheng, Y.S. and Yeh, C.H., (1984) Analysis of Screen Diffusion Battery Data. *J. Am. Ind. Hyg. Assoc.*, vol. 45, pp. 556-561.

Cheng, Y.S., Yeh, H.C., and Brinsko, K.J., (1985) Use of Wire Screens as a Fan Model Filter. *Aerosol Sci. Tech.*, vol. 4, pp. 165-174.

Chow, J. (1995) Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles. *Journal of the Air and Waste Management Association*, Volume 45, pp 320-382.

Clark, N.N., Boyce, J.E., Xie, W., Gautam, M., Lyons, D.W., Vertin, K., LeTavec, C.A., Coburn, T.C., (2000) Class 8 Trucks Operating on Ultra-Low Sulfur Diesel With Particulate filter Systems: Regulated Emissions, SAE Technical Paper No. 2000-01-2815.

Clark, N.N., Gautam, M., Boyce, J., Xie, W., Mehta, S., Jarett, R., and Rapp, B. (2003) Heavy-Duty Vehicle Exhaust Plume Study in the NASA/Langley Wind Tunnel. SAE Technical Paper No. 2003-01-1895.

Cocker, D., Shah, S.D., Johnson, K., Miller, J.W. Norbeck, J.N., (2004) Development and Application of a Mobile Laboratory for Measuring Emissions From Diesel Engines 1. Regulated Gaseous Emissions, *Environ. Sci. Technol.*, vol 38, pp 2182-2189.

Code of Federal Regulations: *Protection of the Environment*, 40 CFR 86.

CONCAWE (1998) A Study of the Number, Size and Mass of Exhaust Particles Emitted from European Diesel and Gasoline Vehicles Under Steady-State and European Driving Conditions. Report No. 98/51. Brussels: CONCAWE.

CONCAWE (2001) A Study of the Number and Mass Weighted Size Distributions of Exhaust Particles Emitted from European Heavy Duty Engines. Report No. 01/51. Brussels: CONCAWE.

Cooper, B.J., and Thoss, J.E., (1989) Role of NO in Diesel Particulate Emission Control, SAE Technical Paper No. 890404.

Czerwinski, J., Jaussi, F., Wyser, M., and Mayer, A. (2000) Particulate Traps for Construction Machines Properties and Field Experience. SAE Technical Paper No. 2000-01-1923.

Damm, C.J., Lucas, D., Sawyer, R.F., and Koshland, C.P., Characterization of Diesel Particulate Matter with Excimer Laser Fragmentation Fluorescence Spectroscopy.

Das, R.N., Madhusoodana, C.D., Purushothama, M.E., Paramesh, S.K., and Ananda Roa, P.S., (2003) Development and Field Test of Ceramic-Based Diesel Particulate Filter (DPF) for Urban Transport Vehicle, SAE Technical Paper No. 2003-26-0004.

De Serves, C. (1999) Particulate Emissions from Six Different Fuels in Light-Duty Vehicles. AVL-MTC report No. 6809A.

De Serves, C. (2000) Particle Emissions from Gasoline Passenger Cars with Direct Injection and Multi-Point Injection Engines. AVL-MTC report No. 6905.

De Serves, C. and Westerholm, R. (2001) Emissions from a Diesel Passenger Car with Particle filter: Regulated Emissions, Particle Size and Number, PAH, and Nitro-PAH. AVL-MTC report No. 6026.

Dickens, C.J., Payne, E.L., Reading, A.H., and Feest, E.A., (2002) Particle Measurement Programme – final Report of Phase 1 of Module 3: Development of Candidate Systems – Light Duty Vehicles. Final report by AEA Technology, Oxfordshire, UK to the DTLR, January.

Dockery, D.W. Pope, C.A. III, Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Feris, B.G. Jr., and Spiezer, F.E. (1993) An Association Between Air Pollution and Mortality in Six US Cities. *N. England J. of Med.* Vol. 329, pp 1753-1759.

Dockery, D.W., and Pope, C.A. III (1994) Acute Respiratory Effects of Particulate Air Pollution. *Annu. Rev. Public Health*, Vol. 15, pp107-132.

Dolan, D.F. and Kittelson, D.B. (1979) Roadway Measurements on Diesel Exhaust Aerosols. SAE Technical Paper No. 790492. Society of Automotive Engineers, Warrendale, PA.

Dolan, D.F., Kittelson, D.B., and Liu, D.Y.H. (1980) Diesel Exhaust Particle Size Distribution Measurement Techniques. SAE Technical Paper No. 800187.

Drewnick, F., J. J. Schwab, J. T. Jayne, M. Canagaratna, D. R. Worsnop and K. L. Demerjian (2003b), Measurement of Ambient Aerosol Composition during the PMTACS-NY 2001 using an Aerosol Mass Spectrometer. Part I: Mass Concentrations. *Aerosol Sci. Technol.*, submitted.

Du, C.J. and Kittelson, D.B. (1983) Total Cylinder Sampling from a Diesel Engine: Part III – Particle Measurements. SAE Technical Paper No. 830243.

Durbin, T.D. and Norbeck, J.M., (2002) A Comparison of Emissions for Light-Heavy Duty Diesel Trucks Operated on California In-Use Diesel, ARCO's EC-Diesel, and ARCO EC-Diesel with a Diesel Particulate Filter. Final Report for the National Renewable Energy Laboratory and the Ford Motor Company prepared by the University of California at Riverside, Bourns College of Engineering – Center for Environmental Research and Technology.

Durbin, T.D., Zhu, X., and Norbeck, J.M. (2003) The Effects of Diesel Particulate Filters and a Low-Aromatic, Low-sulfur Diesel Fuel on Emissions for Medium-Duty Diesel Trucks. *Atmospheric Environment*. Vol 37, pp – 2105-2116.

Durbin, T.D., Norbeck, J.M., Smith, M.R., and Truex, T.J. (1999) Particulate Emission Rates from Light-Duty Vehicles in the South Coast Air Quality Management District. *Environmental Science and Technology*. Vol 33, pp 4401-4406.

Ecotraffic (1999) Emissions from Light-Duty Vehicles Driven on Different Fuels. Impact on Health, Environment, and Energy Use. 1999-12. (In Swedish)

Ecotraffic (2001) Emissions Between Bus and Car. Impact on Health, Environment, and Energy Use. 2001-06. (In Swedish)

Eden, G. (2002) Use of an On-Road, Real-World Particulate Analyzer to Characterize Emissions from Diesel Engines, Proceedings of the 12th CRC On-Road Emissions Workshop, San Diego, April.

Ensfield, C.D. and Shah, A. (2002) On-Road, Real-World Emission Testing of Gasoline and Diesel Pwered Vehicles Using On-Board Analyzers, Proceedings of the 12th CRC On-Road Emissions Workshop, San Diego, April.

Ensfield, C., Gordon, Jr., J., Lindner, J., (2003) Evaluation of a Low-Cost Transient Mass Measurement System in Vehicle Inspection and Maintenance Testing: Results of a Gordon-Darby Study *J. Air & Waste Manage. Assoc.*, vol.. 53, pp1098–1108.

European Conference of Ministers of Transport, Council of Ministers (2000). “Vehicle Emission Trends: Conclusions”. Council of Ministers, Sustainable Development, Vehicle Emission Trends: Conclusions. CEMT/CM(2000)6/Final.

Färnlund, J., Holman, C., Kageson, P., (2001) Emissions of Ultrafine Particles from Different Types of Light Duty Vehicles. Report for the Swedish National Road Administration, January.

Fenn, M. E.; Poth, M. A.; Aber, J. D.; Baron, J. S.; Borman, B. T.; Johnson, D. W.; Lemly, A. D.; McNulty, S. G.; Ryan, D. F.; Stottlemeyer, R. (1998) “Nitrogen Excess in North American Ecosystems: Predisposing Factors, Ecosystem Responses, and Management Strategies.” *Ecological Applications*, Vol. 8, No. 3, pp.706-733.

Frey, H.C., Roupail, N.M., , Unal, A., and Colyar, J.D. (2001) Measurement of On-Road Tailpipe CO, NO, and Hydrocarbon Emissions Using a Portable Instrument, Proceedings of the annual Meeting of the Air and Waste Management Association, June, Orlando, FL.

Friedlander, S.K. and Lippmann, M. (1994) *Environmental Science and Technology*, Vol. 28, 148A-150A.

Fukushima, H. (1999) Diesel Does It. In *Testing Technology International*.

Fukushima, H., Asano, I., Nalamure, S., Ishida, K., and Gregory, D. Signal Processing and Practical Performance of a Real-Time PM Analyser Using Fast FID's. (2000). SAE Technical Paper Series, 2000-01-1135. SAE International, Warrendale, PA.

Fukushima, H., Uchihara, H., Asano, I., Adachi, M., Nakamura, S., Ikeda, M., and Ishida, K. (2001) An Alternative Technique for Low Particulate Measurement. SAE Technical Paper No. 2001-01-0218.

Fukushima, H. and Adachi, M. (2001) Controlled Measures – Measuring Low Particulate Mass Need Never be a Chore Again. Engine Technology International., issue 2/01.

Fukushima, H. and Uchihara, H. (2002) MEXA-1370PM Super-Low-Mass PM Analyzer. Horiba Technical Reports, No. 23, pp 28-33.

Full, G., Vescio, N., Lenz, H.P., Stricker, P., and Nissler, W. (2002) Remote Sensing of Heavy-Duty Trucks in Flow Traffic. 12th CRC On-Road Vehicle Emissions Workshop, San Diego, April.

Gäggeler, H.W., Baltensperger, U., Emmenegger, M., Jost, D.T., Schmidt-Ott, A., Haller, P., and Hofmann, M. (1989a) J. Aerosol Sci., vol. 20, pp 557-564.

Gäggeler, H.W., Baltensperger, U., Jost, D.T., Emmenegger, M., and Nageli, W. (1989b) J. Aerosol Sci., vol. 20, pp 1225-1228.

Gautam, M., Clark, Lyons, D., Long, T. Jr., Howell, A., Loth, J., Palmer, G.M., Wang, W.G., and Bata, R. (1991) Design Overview of a Heavy-Duty Mobile Vehicle Emissions Testing Laboratory, ASME DE-Vol. 40, Advanced Automotive Technologies, ASME Winter Annual Meeting, Atlanta, CA, December, pp 199-207.

Gautam, M., Mehta, S., Bugarski, A., and Lyons, D. (2000) Size Distributions and Size-Selective Chemical Characterization of Particulate Matter from Heavy-Duty Diesel Engines, Proceedings of the 10th CRC On-Road Emissions Workshop, San Diego, March.

Gautam, M., Thompson, G.J., Carder, D.K., Clark, N.N., Shade, B.C., Riddle, W.C., and Lyons, D.W. (2001) Measurement of In-Use, On-Board Emissions from Heavy-Duty Diesel Vehicles: Mobile Emissions Measurement Systems, SAE Technical Paper No. 2001-01-3643.

Gautam, M., Wayne, S., Thompson, G., Clark, N., Lyons, D., Carder, D., Mehta, S. and Riddle (2002) Concentrations and Size Distributions of Particulate Matter Emissions from Catalyzed Trap-Equipped Heavy-Duty Diesel Vehicles Operating on Ultra-Low Sulfur EC-D Fuel, Proceeding of the 8th DEER Workshop, San Diego, March.

Gautam, M., McMillain, M., Cui, M., Keane, M., Ong, T-M, Wallace, W. and Robey, E. (2003a) Mutagenic Potential of Particulate Matter Emissions from a Diesel Engine Operating on Diesel No. 2 and Fischer-Tropsch Fuel: Effect of PM Size and Engine Operating Conditions, Proceeding of the 13th CRC On-Road Workshop, San Diego, April.

Gautam, M., Clark, N.N., Mehta, S., Boyce, J.A., Rogers, F., and Gertler, A. (2003b) Concentrations and Size Distributions of Particulate Matter Emissions from a Class-8 Heavy-Duty Diesel Truck Tested in a Wind Tunnel. SAE Technical Paper No. 2003-01-1894.

Gautam, M., Carder, D.K., Booker, D., and Gautam, S. (2003c) Real-time Measurement of Total Particulate Matter Emissions from On-Highway and Off-Road Vehicles Using the RPM-100, Proceedings of the 13th CRC On-Road Emissions Workshop, San Diego, April.

Gautam, M., et al. (2004) Measurement of Real-World Emissions from Heavy-Duty Diesel Vehicles: The State-of-the-Art, Proceeding of the 14th CRC On-Road Workshop, San Diego, March.

Gezelle, Jr., R., (2001) EPA's In-Use Test Program for Heavy-Duty Trucks—Putting the NTE to the Test., US EPA-SAE Government/Industry Meeting May 16.

Goto, Y. and Kawai, T. (2004) Real-Time Measurement of Particle Size Distribution from Diesel Engines Equipped with Continous Regenerative DPF under a Transient Driving Condition. SAE Technical Paper No. 2004-01-1984.

Graskow, B.R., Kittelson, D.B., Ahmadi, M.R., and Morris, J.E. (1999a) Exhaust Particulate Emissions from a Direct Injection Spark Ignition Engine. SAE Technical Paper No. 1999-01-1145.

Graskow, B.R., Kittelson, D.B., Ahmadi, M.R., and Morris, J.E. (1999b) Exhaust Particulate Emissions from Two Port Fuel Injected Spark Ignition Engines. SAE Technical Paper No. 1999-01-1144.

Graskow, B.R., Ahmadi, M.R., Morris, J.E., and Kittelson, D.B. (2000) Influence of Fuel Additives and Dilution Conditions on the Formation and Emission of Exhaust Particulate Matter from a Direct-Injection, Spark-Ignition Engine. SAE Technical Paper No. 2000-01-2018.

Graze, R.R. (1993) Development of a Miniaturized, Dilution-Based Diesel Engine Particulate Sampling System for Gravimetric Measurement of Particulates. SAE Technical Paper No. 931190.

Greenwood, S.J., Coxon, J.E., Biddulph, T., and Bennett, J. (1996) An Investigation to Determine the Exhaust Particulate Size Distributions for Diesel, Petrol, and Compressed Natural Gas Fueled Vehicles. SAE Technical Paper No. 961085.

Groblicki, P.J. and Begeman, C.R. (1979) Particle Size Variation in Diesel Car Exhaust. SAE Technical Paper No. 790421.

Gupta, S., Hillman, G., Shih, J., Sekar, R., Graze, R.R., Shimpi, S., Martin, W.T., and Pier, D., TG-1: Portable Instruments for Transient PM Measurements, Proceedings of DEER.

Hall, D.E., King, D.J., Morgan, T.B.D., Baverstock, S.J., Heinze, P., and Simpson, B.J. (1998) A Review of Recent Literature Investigating the Measurement of Automotive Particulate; The

Relationship with Environmental Aerosol, Air Quality, and Health Effects. SAE Technical Paper No. 982602.

Hall, D.E., Goodfellow, C.L., Heinze, P., Rickeard, D.J., Nancekievill, G., Martini, G., Hevesi, J., Rantanen, Merino, P.M., Morgan, T.D.B., and Zemroch, P.J. (1998) A Study of the Size, Number, and Mass Distribution of the Automotive Particulate Emissions from European Light Duty Vehicles. SAE Technical Paper No. 982600.

Hall, D. and Dickens, C. (1999) Measurement of the Number and Size Distribution of Particles Emitted from a Gasoline Direct Injection Vehicle. SAE Technical Paper No. 1999-01-3530.

Hall, D.E., Stradling, R.J., Zemroch, P.J., Rickeard, D.J., Mann, N., Heinze, P., Martini, G., Hagemann, R., Rantanen, L., and Szendefi, J. (2000) Measurement of the Number and Size Distribution of Particle Emissions from Heavy-Duty Engines. SAE Technical Paper No. 2000-01-2000.

Hall, D. and Dickens, C. (2000) Measurement of the Numbers of Emitted Gasoline Particles: Genuine or Artefact? SAE Technical Paper No. 2000-01-2957.

Hall, D. and Dickens, C. (2003) The Effect of Sulphur-Free Diesel Fuel on the Measurement of the Number and Size Distribution of Particles Emitted from a Heavy-Duty Diesel Engine Equipped with a Catalysed Particle Filter. SAE Technical Paper No. 2003-01-3167.

Hammerle, R.H., Ketcher, D.A., Horrocks, R.W., Lepperhoff, G., Hühwohl, G., Lüers, B. (1994) Emissions from Current Diesel Vehicles. SAE Technical Paper No. 942043.

Harris, S.J., and Maricq, M.M. (2001) Signature Size Distributions for Diesel and Gasoline Engine Exhaust Particulate Matter. *J. Aerosol Sci.*, vol. 32, 749.

Haywood, D.O. and Trapnell, B.M., (1964) *Chemisorption*. Butterworth, London.

Health Effects Institute. (1995) *Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects*. A Special Report of the Institute's Diesel Working Group. Health Effects Institute, Cambridge MA.

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

Hinds, W.C. (1999) *Aerosol Technology*, J. Wiley & Sons, New York.

Hirabayahi, N., Presentation by Tokyo Metropolitan Government, Countermeasures for particulate matter from diesel-powered vehicles in the Tokyo Metropolitan Area.

Hirabayahi, M., Matsuo, M., Tanabe, K., Kobayashi, S., and Nomura, M. (2002) Characterization of Sulfur in Airborne Particulate Matter by XANES Technique. Photon Factory Activity Report 2002 #20 Part B.

Hiranuma, S., Takeda, Y., Kawatani, T., Doumeki, R., Nagasaki, K., and Ikeda, T. (2003) Development of DPF System for Commercial Vehicle-Basic Characteristic and Active Regenerating Performance. SAE Technical Paper Series 2003-01-3182.

Hirofumi, O. and Yoshiharu, N., Air Quality Prospect for Metropolitan Areas. Research Trends and Accomplishments.

Hirokazu, Fukushima, Asano, I., Nakamura, S., Ishida, K., and Gregory, D., (2000) Signal Processing and Practical Performance of a Real-Time PM Analyzer using Fast FIDs, SAE Technical Paper No. 2000-01-1135.

Hirota, S., Tanaka, T., Takeshima, S., Itoh, K., Nakatani, K., and Dohmae, K. (2001) Simultaneous PM and NO_x Reduction System in Diesel Exhaust Gas, SAE Technical Paper No. 2001-08-0167.

Hosier, C. (2003) ACEA PM-3 Programme – Preliminary Results, Presentation in Milano, IT, December.

Hotta, Y., Nakakita, K., Inayoshi, M., Ogawa, T., Sato, T., and Yamada, M. (1998) Combustion Improvement for Reducing Exhaust Emissions in IDI Diesel Engine. SAE Technical Paper No. 980503

Human, D.M. and Ullman, T.L. (1992) Development of an I/M Short Emissions Test for Buses, SAE Technical Paper No. 920727.

Ikegami, M. (1990) Role of Flows and Turbulent Mixing in Combustion and Pollutant Formation in Diesel Engines. International Symposium, COMODIA, vol. 90, pp. 49-58.

Inoue, T., Masuda, Y-H, and Yamamoto, M., (1997) Reduction of Diesel Matter by Oil Consumption Improvement Utilizing Radioisotope Tracer Techniques, SAE Technical Paper No. 971630.

International Agency for Research on Cancer (1989) Monograph on the Evaluation of Carcinogenic Risks to Humans, Diesel, and Gasoline Engine Exhausts and Nitroarenes, vol. 46, pp 13-185.

International Organization of Motor Vehicle Manufacturers, (2003) Industry Comments on Proposed Particulate Measurement Techniques – OICA Contribution to PMP. January.

Itoyama, H., Uchida, M., and Miwa, H., (1997) A Study of an EGR Control System for Diesel Engines based on an Intake/Exhaust System Model. SAE Technical Paper Series 970621.

Japar, S.M. and Szkarlat, A.C. (1981) Measurement of Diesel Vehicle Exhaust Particulate Using Photoacoustic Spectroscopy. Combustion Science and Technology, Vol. 24, pp. 215-219. 0010-2202/81/2405-0215 \$06.50/0 Gordon and Breach Science Publishers, Inc. Printed in Great Britain.

Japar, S.M., Szkarlat, A.C., and Pierson, W.R. (1984) The Determination of the Optical Properties of Airborne Particle Emissions from Diesel Vehicles. *The Science of the Total Environment*, Vol. 36, pp. 121-130. Elsevier Science Publishers B.V., Amsterdam.

Jayne, J. T., D. C. Leard, X. Zhang, P. Davidovits, K. A. Smith, C. E. Kolb and D. R. Worsnop (2000), Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles. *Aerosol Sci. Technol.* 33: 49-70.

JCAP Test Methods WG Report (2002) Further Challenge in Automobile and Fuel Technologies For Better Air Quality. Presentation.

Jiménez, J. L., J. T. Jayne, Q. Shi, C. E. Kolb, D. R. Worsnop, I. Yourshaw, J. H. Seinfeld, R. C. Flagan, X. Zhang, K. A. Smith, J. Morris and P. Davidovits (2003), Ambient Aerosol Sampling Using the Aerodyne Aerosol Mass Spectrometer. *J. Geophys Res.* in press.

Johnson, J.H., and Baumgard, K.H. (1996) The Effect of Fuel and Engine Design on Diesel Exhaust Particle Size Distributions, SAE Technical Paper No. 960131.

Johnson, T., Caldown, R., Pöcher, A., Mirmem, A., and Kittelson, D., (2003) A New Electrical Mobility Particle Sizer Spectrometer for Engine Exhaust Particle Measurements, SAE Technical Paper No. 2004-01-1341.

Jung, H., Kittelson, D.B., and Zachariah, M.R. (2003) The Influence of Engine Lubricating Oil on Diesel Nanoparticle Emissions and Kinetics of Oxidation. SAE Technical Paper No. 2003-01-3179.

Kasai, Y., Miwa, S., Kuki, T., Senda, K., and Ogura, Y. (2004) New Cordierite Diesel Particulate Filter Material for the Diesel Particulate – NO_x Reduction System. SAE Technical Paper No. 2004-01-0953.

Kasper, M., Matter, U., Burtscher, H., Bukowiecki, N., and Mayer, A. (2001) NanoMet, a New Instrument for On-Line Size – and Substance – Specific Particle Emission Analysis. SAE Technical Paper No. 2001-01-0216.

Kasper, M. (2004) The Number Concentration of Non-volatile Particles – Design for an Instrument According to the PMP Recommendations. SAE Technical Paper No. 2004-01-0960.

Kawai, T., Y. Iuchi, S. Nakamura and K. Ishida: (1998) ‘Real-Time Analysis of Particulate Matter by Flame Ionization Detection,’ SAE 980048.

Kawatani, T., Mori, K., Fukano, I., Sugawara, K., and Koyama, T. (1993) Technology for Meeting 1994 USA Exhaust Emission Regulations on Heavy-Duty Diesel Engine. SAE Technical Paper Series 932654.

Kazakov, A. and Foster, D.E. (1998) Modeling of Soot Formation During DI Diesel Combustion Using a Multi-Step Phenomenological Model, SAE Technical Paper Series 982463

Keislar, R., Barber, P., Kuhns, H., Mazzoleni, C., Moosmüller, H., Robinson, N., and Watson, J. (2002) Measurement Of Diesel Particulate Emissions By UV Lidar Remote Sensing In Denver, Co, February 21-22, 2001. CRC Project E-56-1.

Kerminen, V-M, et al. (1997) *Environ. Sci. Technol.*, vol. 31, pp 1883-1889.

Keskinen, J., Pietarinen, K., and Lehtimäki, M. (1992) *J. Aerosol Sci.*, vol. 23, pp 353-360.

Khalek, I.A. and Ullman, T.L., (2002) Performance of Partial Flow Sampling Systems Relative to Full Flow CVS for Determination of Particulate Emissions under Steady-State and Transient Diesel Engine Operation, SAE Technical Paper No. 2002-01-1718.

Khalek, I.A. (2000) Characterization of Particle Size Distribution of a Heavy-Duty Diesel Engine During FTP Transient using ELPI. SAE Technical Paper No. 2000-01-2001

Khalek, I. A., Ullman, T. L., Shimpi, S. A., Jackson, C. C., Dharmawardhana, B., Silvis, W. M., Kreft, N., Harvey, R. N., Munday, D., Yamagishi, Y., Graze, R., Smitherman, J., and Adkins, A., (2002) Performance of Partial Flow Sampling Systems Relative to Full Flow CVS for Determination of Particulate Emissions under Steady-State and Transient Diesel Engine Operation, SAE 2002-01-1718; Society of Automotive Engineers: Warrendale, PA.

Kihara, N., Tsukamoto, T., Matsumoto, K., Ishida, K., Kon, M., and Murase, T. (2000) Real-Time On-Board Measurement of Mass Emission of NO_x, Fuel Consumption, Road Load, and Engine Output for Diesel Vehicles. SAE Technical Paper No. 2000-01-1141.

Kihara, N. and Tsukamoto, T. (2001) Real-Time On-Board Measurement of Mass Emissions of NO_x, THC, and Particulate Matters from Diesel Vehicles. Fifth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines, Hagoya.

Kihara, N. (2002) Opacimeter MEXA-130S. Horiba Technical Reports, No. 23, pp 35-39.

Kim, D-H, Gautam, M., and Gera, D. (2002) Effect of Ambient Dilution on Coagulation of Particulate Matter in a Turbulent Dispersing Plume. SAE Technical Paper No. 2002-01-0652.

Kimura, S., Matsui, Y., Kamihara, T., (1997) A New Concept of Combustion Technology in a Small DI Diesel Engines – 4th Report: The Effects of Fuel Injection Rates on MK Combustion. SAE Technical Paper Series 978224.

Kimura, S., Matsui, Y., Koike, M., (1997) A New Concept of Combustion Technology in Small DI Diesel Engines – Possibility of Expanding Low-Temperature, Premixed Combustion Range. SAE Technical Paper Series 978125.

Kimura, S., Muranaka, S., and Aoki, O., (1998) Development of a New Diesel Engine Concept Based on Second-Generation MK Combustion. SAE Technical Paper Series 988324.

Kimura, S., Aoki, O., Ogawa, H., Muranaka, S., and Enomoto, Y. (1999) New Combustion Concept for Ultra-Clean for High-Efficiency Small DI Diesel Engines. SAE Technical Paper Series 1999-01-3681.

Kimura, S., Aoki, O., Kitahara, Y., and Aiyoshizawa, E. (2001) Ultra-Clean Combustion Technology combining a Low-Temperature and Premixed Combustion Concept for Meeting Future Emission Standards. SAE Technical Paper Series 2001-01-0200.

Kishi, Y., Tohno, H., and Ara, M. (1992) Characteristics and Combustibility of Particulate Matter. SAE Technical Paper Series 920687.

Kitahara, Y., Kamijou, M., Akama, H., and Shinzawa, M., (1999) A Study of Next Generation Exhaust Aftertreatment Technique for Diesel Engine. SAE Technical Paper Series 1999-08-0572.

Kittelson, D.B., Dolan, D.F., and Verrant, J.A. (1978) Investigation of Diesel Exhaust Aerosol. SAE Technical Paper No. 780109.

Kittelson, D.B. and Dolan, D.F. (1980) Diesel Exhaust Aerosols. In Generation of Aerosols and Facilities for Exposure Experiments, Ed. K. Willeke, Ann Arbor Science, Ann Arbor, MI, p. 337-359.

Kittelson, D.B., (1988) Characterization of Diesel Particles in the Atmosphere. Coordinating Research Council. AP-2 Project Group Report.

Kittelson, D.B., Ambs, J.L., Hadjkacem, H. (1990) Particulate Emissions from Diesel Engines: Influence of In-Cylinder Surface. SAE Technical Paper No. 900645.

Kittelson, D.B., and Johnson, J.H. (1991) Variability in Particulate Emission Measurements in the Heavy Duty Transient Test. SAE Technical Paper Series, 910738, SAE International, Warrendale, PA.

Kittelson, D.B., Reinertsen, J., and Michalski, J. (1991) Further Studies of Electrostatic Collection and Agglomeration of Diesel Particles. SAE Technical Paper No. 910329.

Kittelson, D.B., Watts, W.F., and Arnold, M. (1998a) Review of Diesel Particulate Matter Sampling Methods, Supplemental Report #1, Diesel Exhaust Particulate Measurement Instruments. Prepared by the University of Minnesota for the U.S. Environmental Protection Agency.

Kittelson, D.B., Watts, W.F., and Arnold, M. (1998b) Review of Diesel Particulate Matter Sampling Methods, Supplemental Report #2, Aerosol Dynamics, Laboratory and On-Road Studies. Prepared by the University of Minnesota for the U.S. Environmental Protection Agency.

Kittelson, D.B., Watts, W.F., and Johnson, J.P. (2001) Fine Particle (Nanoparticle) Emissions on Minnesota Highways. Final report to the Minnesota Department of Transportation, May.

Kittelson, D.B., Watts, W.F., Ramachandran, G., Paulsen, D., and Kreager, C. (2002) Exposures to Diesel Exhaust Aerosol. In Health Effects Institute Report. Research Directions to Improve Estimates of Human Exposure and Risk from Diesel Exhaust. A Special Report of the Institute's Diesel Epidemiology Working Group, April, p 233, Health Effects Institute, Boston, MA.

Kittelson, D., Watts, W. and Johnson, J. (2002) Diesel Aerosol Sampling Methodology – CRC E-43. Final report to the Coordinating Research Council by the University of Minnesota, August.

Klingen, H.-J., and Roth, P. (1998) *J. Aerosol. Sci.*, vol. 20, pp 861-864.

Knobloch, S. Kock, H., and König, H.P., (1992) *J. Aerosol Sci.*, vol. 23, S257-S259.

Kohetsu, S., Mori, K., Sakai, K., and Nakagawa, H. (1996) Reduction of Exhaust Emission with New Water Injection System in a Diesel Engine. SAE Technical Paper Series 960033.

Krempf, P. Schindler, W., and Schiefer, E. (1985) Dynamic Measurements of Particulate Mass Emissions on Light-Duty Diesel Engines under Steady State and Transient Conditions. SAE Technical Paper No. 850269.

Kreso, A., Johnson, J., Gratz, L. Bagley, S. and Leddy, D. (1998) A Study of the Effects of Exhaust Gas Recirculation on Heavy-Duty Diesel Engine Emissions. SAE Technical Paper No. 981422.

Kruger, Luders, Luers, Kaufman, Kock, and Kauffeldt (1997) Influence of Exhaust Gas Aftertreatment on Particle Characteristics of Vehicle Diesel Engines. Research Report of the Forschungsvereinigung Verbrennungskraftmaschinen e. V. (FVV), MTZ Motortechnische Zeitschrift vol. 58, 27-30.

Kumagai, Y., Nakashima, N., Miyata, O., and Ikeda, T. (1996a) Development of PM Trap System for Urban Buses. SAE Technical Paper Series 960470.

Kumagai, Y., Nakashima, N., Miyata, O., and Ikeda, T. (1996b) Development of Diesel Particulate Filter System for Urban Buses. SAE Technical Paper Series 968023.

Kuschel, G., Bluett, J., Fisher, G., Xie, S., and Metcalfe, J. (2003) Remote Sensing of Vehicle Emissions (Its Monitoring, Jim – but not as we know it!). Presented at the 29th Australian Transportation Research Forum, Wellington, NZ, October.

Lan, P. (2002) Remote Sensing in Taiwan. Presented at the 18th Mobile Sources/Clean Air Conference, September.

Lanni, T.R. and Vojtisek-Lom, M. (2003) Portable Emissions Monitoring of Diesel Construction Equipment at the World Trade Center #7 Site; Proceedings of the 13th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, April.

Lapuerta, M., Aramas, O., Ballesteros, R., and Durán, A. (1999) Influence of Mini-Tunnel Operating Parameters and Ambient Conditions on Diesel Particulate Measurement and Analysis. SAE Technical Paper No. 1999-01-3531.

Lapuerta, M., Aramas, O., and Gómez, A. (2003) *Aerosol Sci. & Technol.*, vol. 37, pp 369-381.

Lenaers, G., Verlaak, J., and Reimersma, I. (2002) Emissions Control Technology for Heavy Duty Vehicles. VITO – Flemish Institute for Technological Research.

Lenaers, G., (2003) An On-Board Emission Measuring System for (S)ULEV's. Proceedings of the 13th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, April.

Lenox, K., McGill, R., Akerman, A., Ayers, C., Dam, T., Goedeke, S., Richards, R., Simpson, M., Storey, J., and Cheng, M. (2003) Further Development of Emissions from Heavy-Duty Trucks. Proceedings of the 13th CRC On-Road Emissions Workshop. San Diego, CA, March.

Lepperhoff, G., Hüthwohl, G., and Lüers-Jongen, B. (1994) Methods to Analyze Non-Regulated Emissions from Diesel Engines. SAE Technical Paper No. 941952.

LeTavec, C., Uihlein, J., Segal, J., Vertin, K., (2000) ECDiesel Technology Validation Program Interim Report, SAE Technical Paper No. 2000-01-1854.

LeTavec, C.; Uihlein, J., Vertin, K., Chatterjee, S., Hallstrom, K., Wayne, S., Clark, N., Gautam, M., Thomspson, G., Lyons, D., Chandler, K., Coburn, T., (2002). Year-Long Evaluation of Trucks and Buses Equipped with Passive Diesel Particulate Filters, SAE Technical Paper No. 2002-01-0433.

Lev-On, M., LeTavec, C., Uihlien, J., Kimura, K., Alleman, T.L., Lawson, D.R., Vertin, K., Gautam, M., Wayne, W.S., Thompson, G.J., Clark, N., Okamoto, R., Rieger, P., Yee, G., Zielinska, B., Sagebiel, J., Chatterjee, S., Hallstrom, K., (2002). Speciation of Organic Compounds from Exhaust of Trucks and Buses: Effect of Fuel and After-treatment on Vehicle Emission Profiles, SAE Technical Paper No. 2002-01-0432.

Liu, B.Y.,H. and Pui, D.Y.,H. (1974) J. of Aerosol Sci., vol. 6, pp 249-264.

Lloyd, A.C. and T.A. Cackette (2001) "Diesel engines: Environmental Impact and Control" *Journal of the Air and Waste Management Association*, 51 (6): 809-847.

Lu, H. (1999) Regulated and Unregulated Emissions from a Flexible-Fuel SAAB Passenger Car Driven with Seven Different Fuels. AVL-MTC report No. 6907 B.

Luo, L., Piphon, M.J., Ambs, J.L., Kittelson, D.B. (1989) Particle Growth and Oxidation in a Direct-Injection Diesel Engine. SAE Technical Paper No. 890580.

Lyons, D., Bata, R., Wang, W.G., Clark, N., Palmer, G.M., Gautam, M., Howell, A., Loth, J., Long, T., Jr. (1992) Design and Construction of a Transportable heavy-Duty Vehicle Emissions Test Laboratory. ISATA Paper No. 920450. 25th International Symposium on Automotive technology and Automotion (ISATA), Florence, Italy, June.

McCrae, I.S., Boulter, P.G., Barlow, T.J., and Hickman, A.J. (2001) Remote Sensing and Vehicle Emission Inspection and Maintenance Programmes. Report to DTLR, Report No. PR/SE/177/2000.

Maher, E.F. and Laird, N.M., (1985) EM Algorithm Reconstruction of Particle Size Distributions from Diffusion Battery Data. *J Aerosol Sci.*, vol. 16, pp. 557-570.

Maricq, M.M., Podsiadlik, D.H., and Chase, R.E. (1999a) *Environ. Sci. Technol.* vol. 33, 1618.

Maricq, M.M., Podsiadlik, D.H., and Chase, R.E. (1999b) *Environ. Sci. Technol.* vol. 33, 2007.

Maricq, M.M., Chase, R.E., Podsiadlik, D.H., and Vogt, R. (1999c) Vehicle Exhaust Particle Size Distributions: A Comparison of Tailpipe and Dilution Tunnel Measurements. SAE 1999-01-1461.

Maricq, M.M., Podsiadlik, D.H., and Chase, R.E. (2000) *Aerosol Science and Technology*, vol. 33, pp 239-260.

Maricq, M.M., Chase, R.E., and Xu, N. (2001) A Comparison of Tailpipe, Dilution Tunnel, and Wind Tunnel Data in Measuring Motor Vehicle PM, *J. Air & Waste Manage. Assoc.*, vol. 51, pp 1529-1537.

Maricq, M.M., Chase, R.E., Podsiadlik, D.H., and Xu, N. (2002a) The Effects of the Catalytic Converter and Fuel Sulfur Level on Motor Vehicle Particulate Emissions: Gasoline Vehicles, *Environ. Sci. Technol.*, vol. 36, p. 276.

Maricq, M.M., Chase, R.E., Podsiadlik, D.H., and Xu, N. (2002b) The Effects of the Catalytic Converter and Fuel Sulfur Level on Motor Vehicle Particulate Emissions: Light-Duty Diesel Vehicles, *Environ. Sci. Technol.*, vol. 36, p. 283.

Marjamäki, M., , Ntziachristos, L., Viranen, A., Ristimäki, J., Keskinen, J., Moisio, M., Palonen, M. and Lappi, M. (2002) Electrical filter Stage for the ELPI. SAE Technical Paper No. 2002-01-0055.

Marple, V.A., Rubow, K.L., and Behm, S.M. (1991) *J. Aerosol. Sci. Technol.*, vol. 14, pp 434-446.

Marple, V.A., Rubow, K.L., and Olson, B.A. (1994) Low Pressure Stages for the Microorifice Uniforma Deposit Impactor (MOUDI). Fourth International Aerosol Conference, vol. 2, p 6.

Mase, K., Ohmiya, Y., Yamada, K., Yamamoto, M., and Masuda, Y. (1996) Reduction of Diesel Particulate Matter by Oil Consumption Utilizing Radioisotopes Measuring Technique. SAE Technical Paper No. 968393.

Mayer, A., Czerwinski, J., and Scheidegger, P. (1996) Trapping Efficiency Depending on Particle Size. SAE 960472.

Mayer, A., Czerwinski, J., Matter, U., Wayer, M., Scheidegger, Kieser, D., and Weidhofer (1998) VERT: Diesel Nano-Particulate Emissions: Properties and Reduction Strategies. SAE Technical Paper No. 980539.

Mayer, A., Matter, U., Czerwinski, J., and Heeb, N. (1999) Effectiveness of Particulate Traps on Construction Site Engines: VERT Final Measurements. Available at www.dieselnet.com.

Mayer, A., Evéquo, R., Wyser-Heusi, M., Czerwinski, J., Matter, U., and Graf, P. (2000) Particulate Traps Used in City-Buses in Switzerland. SAE Technical Paper No. 2000-01-1927.

Mayer, A., Nöthiger, P., Zbinden, R., and Evéquo, R. (2001) Particulate Trap Selection for Retrofitting Vehicle Fleets based on Representative Exhaust Temperature Profiles. SAE Technical Paper No. 2001-01-0187.

Mayer, A., Heeb, N., Czerwinski, J., and Wyser, M. (2003) Secondary Emissions from Catalytic Active Particle Filter Systems. SAE Technical Paper No. 2003-01-0291.

Mayer, A., Czerwinski, J., Petermann, J-L., Wyser, M., and Legerer, F. (2004) Reliability of DPF-Systems: Experience with 6000 applications of the Swiss Retrofit Fleet. SAE Technical Paper No. 2004-01-0076.

McAughey, J. (2002) Particle Measurement Programme: Final Report of Phase 1 of Module 1: Literature Review. Final report by AEA Technology, Oxfordshire, UK for the DTLR, March.

McGill, R., Oak Ridge National Laboratory, mcgillrn@ornl.gov.

Mewes, B. and Seitzman, J.M., (1997) Soot Volume Fraction and Particle Size Measurements with Laser-Induced Incandescence. *Appl. Opt.* Vol. 36, pp 709-717.

Miller et al., (1974) The Size Distribution and Volume Concentration of Aerosols Attributable to Automobiles. 67th Annual Meeting of the Air Pollution Control Association, Denver, CO.

Miller, W., Johnson, K., Lee, J., Mueller, M., Soriano, B., and Welch, B., (2003) The California Demonstration Program for Control of PM from Diesel Backup Generators (BUGS), 9th DEER conference, Newport, RI, August.

Mkilaha, I.S.N. and John, G.R. (2001) *Africitation Journal of Science and Technology*, vol. 1, pp 91-99.

Moon, D.P. and Donald, J.R. (1997) UK Research Program on the Characterization of Vehicle Particle Emissions. (Contract Report for the Department of the Environment, Transport, and the Regions and the Society of Motor Manufacturers and Trader by ETSU – group within AEA. ETSU-R98.

Moosmüller, H., Arnott, W.P., Rogers, C.F., Bowen, J.L., Gillies, J.A., Pierson, W.E., Collins, J.F., Durbin, T.D., and Norbeck, J.M., (2001a) Time Resolved Characterization of Diesel Particulate Emissions. 1. Instruments for Particle Mass Measurements. *Environ. Sci. Technol.*, vol 35, 781-787.

Moosmüller, H., Arnott, W.P., Rogers, C.F., Bowen, J.L., Gillies, J.A., Pierson, W.E., Collins, J.F., Durbin, T.D., and Norbeck, J.M., (2001b) Time Resolved Characterization of Diesel

Particulate Emissions. 2. Instruments for Elemental and Organic Carbon Measurements. Environ. Sci. Technol., vol 35, 781-787.

Mohr, M. and Lehmann, U. (2003) Comparison Study of Particle Measurement Systems for Future Type Approval Application, Swiss contribution to GRPE Particle Measurement Programme. EMPA Dubendorf, May.

Mori, K., Kamikubo, H., Kawatani, T., Obara, T., Fukano, I., and Sugawara, K. (1990) Technology for Meeting the 1991 USA Exhaust emission Regulations on Heavy-Duty Diesel Engines. SAE Technical Paper Series 902233.

Mostafa, K., Gautam, M., and McMillian, M. (2001) Effect of Sulfur Content of Lubricant and Diesel Fuel on Concentrations and Size Distributions of Exhaust Particulate Matter Emissions, Proceeding of the 11th CRC On-Road Workshop, San Diego, March.

MTC Motorestcenter (1997) New Methods for In-Use Testing of Heavy-Duty Vehicles. Report No. MTC 9610.

Mueller, E. and M. Zillmer (1998), Modeling of Nitric Oxide and Soot Formation in Diesel Engine Combustion, SAE Technical Paper Series 982457.

Nakatani, K., Hirota, S., Takeshima, S., Itoh, K., Tanaka, T., and Dohmae, K. (2002) Simultaneous PM and NO_x Reduction System for Diesel Engines. SAE Technical Paper No. 2002-01-0957.

Nakamura, S. (2002) The Development of PM Measurement Systems at Horiba. Horiba Technical Reports, No. 23, pp 17-21.

Nakamura, H., Kihara, N., Adachi, M., and Ishida, K. (2002) Development of a Wet-based NDIR and Its Application to On-Board Emission Measurement System. SAE Technical Paper No. 2002-01-0612.

Nakamura, S., Fukuma, T., Matsunaga, A., Miyake, T., and Wakimoto, T. (2003) A New Dynamic Combustion Control Method Based on Charge Oxygen Concentration for Diesel Engines. SAE Technical Paper No. 2003-01-3181.

Noble, C.A. and Prather, K.A. (1996) Environ. Sci. Technol., vol. 30, pp 2667-2680.

Noble, C.A. and Prather, K.A. (1998) Appl. Occup. Environ. Hyg., vol. 13, pp 439-443.

Ntziachristos, L., Giechaskiel, B., Pistikopoulos, P., Samaras, Z., Mathis, U., Mohr, M., Ristimaki, J., Keskinen, J., Mikkanen, P., Casati, R., Scheer, V., and Vogt, R. (2004) Performance Evaluation of a Novel Sampling and Measurement System for Exhaust Particle Characterization. SAE Technical Paper No. 2004-01-1439.

Ogawa, T., Daisho, Y., Kurata, O., and Saito, T. (1990) Particulate Formation in Compression-Ignited Fuel-Rich Mixtures. International Symposium COMODIA, vol. 90, pp 633-638.

Ohki, H., Ishiyama, S., Asano, A. (2002) DPNR Control Technology of Diesel Engine for Passenger Car. SAE Technical Paper No. 2002-08-0101.

Ohki, H., Ishiyama, S., Asano, A. (2003) Control Technology for a Passenger Car Diesel Engine Equipped with the DPNR System. SAE Technical Paper No. 2003-01-1880.

Ostro, B.D., Broadwin, R., and Lipsett, M.J. (2000) Coarse and Fine Particles and Daily Mortality Rates in the Coachella Valley, California: A Follow-up Study. *J. Expo Anal. Environ Epidemiol*, Vol. 10, pp. 412-419.

Padgett, P. E.; Bytnerowicz, A. (2001) "Deposition and Adsorption of the Air Pollutant HNO₃ Vapor to Soil Surfaces." *Atmospheric Environment*, Vol. 35, pp. 2405-2415.

Panne, U., Petzold, A., Niessner, R. (1992) *J. Aerosol Sci.*, vol. 23, S659-S660.

Panyacosit, L. (2000). "A Review of Particulate Matter and Health: Focus on Developing Countries". Interim Report, IR-00-005. International Institute for Applied Systems Analysis, Laxenburg, Austria.

Patschull, J. and Roth, P. (1992) *J. Aerosol Sci.*, vol. 23, S229-S232.

Pierson, W.R. and Brachaczek, W.W. (1976) Particulate Matter Associated with Vehicles on the Road, *SAE Transactions*, vol. 85, pp 209-227.

Pierson, W.R. and Brachaczek, W.W. (1983) *Aerosol Sci. & Technol.*, vol. 2, pp 1-40.

Pipho, M.J., Ambs, J.L., Kittelson, D.B. (1986) In-Cylinder Measurements of Particulate Formation in an Indirect Injection Diesel Engine. SAE Technical Paper No. 860024.

Popp, P.J., Bishop, G.A., and Stedman, D.H. (1998) Remote Sensing of Emissions from Commercial Aircraft. 8th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, April.

Popp, P.J., Bishop, G.A., and Stedman, D.H. (1998) *Environ. Sci. Technol.*, vol. 33, pp 1542-1544.

Rattary, G.; Sievering, H. (2001) "Dry Deposition of Ammonia, Nitric Acid, Ammonium, and Nitrate to Alpine Tundra at Niwot Ridge, Colorado." *Atmospheric Environment*, Vol. 35, pp. 1105-1109.

Rautenberg-Wulff, A., Isreal, G.W., Pesch, M., and Schlums, C. (1995) Bestimmung des Beitrags von Reifenabrieb zur Russemission an stark befahrenen Strassen. *VDI Berichte* 1228, 81-92.

Ravikumar, T.S., Basar, P.D., and Attfield, M.J., (2001) Emulsified Diesel – An Intermediate and Effective Solution for Diesel Exhaust Emission Reduction, SAE Technical Paper No. 2001-28-0037.

Reading, A. R., Eden, G., Ensfield, C. (2001) The Design and Implementation of a Portable Analytical System (SEMTECH) for the Measurement of In-Use Diesel Engine Emissions; Proceedings of the 11th CRC On-Road Vehicle Emissions Workshop; San Diego, CA.

Reavell, K., Hands, T., and Collings, N., (2002) A Fast Response Particulate Spectrometer for Combustion Aerosols, SAE Technical Paper No. 2002-01-2714.

Reichardt, T. (1995) Weighing the Health Risks of Airborne Particulates. Environmental Science and Technology, Vol. 28, No. 9, pgs 360-364, 1995.

Richards, P.J., Vincent, M.W., and Cook, S.L. (2000) Operating Experience of Diesel Vehicles Equipped with Particulate Filters and Using Fuel Additive for Regeneration. SAE Technical Paper No. 2000-01-0474.

Rickeard, D.J., Bateman, J.R., Kwon, Y.K., McAughey, J.J. and Dickens, C.J. (1996) Exhaust Particle Size Distribution: Vehicle and Fuel Influences in Light Duty Vehicles. In Diesel Engine Combustion and Emission Control (SP-1206), SAE Technical Paper 961980.

SAE International, Diesel Engine Modeling, SAE SP-1450, 1999.

Saito, S., Shinozaki, R., Suzuki, A., Jyoutaki, H., and Takeda, Y. (2003) Development of Urea-SCR System for Commercial Vehicle-Basic Characteristics and Improvement of NOx Conversion at Low Load Operation. SAE Technical Paper Series 2003-01-3248.

Sakai, T. and Kashiwakura, K. (2002) Basic Investigation of Particulate Matters (O-PM) and Polycyclic Aromatic Hydrocarbons Emitted by Two-Stroke Motorcycles. SAE Technical Paper Series 2002-32-1846.

Sakamoto, S., Saito, J., Kishimoto, T., and Ishida, K. (1997) Particulate Characterization of Automotive Emissions by Helium Microwave-Induced Plasma Atomic Emission Spectrometry. SAE Technical Paper Series 971017.

Samaras, Z. (2002) The EU DG TREN "Particulates" Project: Characterization of Exhaust Particulate Emissions from Road Vehicles. Proceedings for the CRC PM workshop, San Diego, CA, October.

Sandström-Dahl, C. (2003) Emission testing of Light Vehicles Equipped with Modern Combustion Engines. AVL-MTC report No. 5205.

Sawyer, R.F, and Johnson, J.H. (1995) Diesel Emissions and Control Technology in Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects, Health Effects Institute, Cambridge, MA.

Schaberg, P.W., Zarling, D.D., Waytulonis, R.W., and Kittelson, D.B. (2002) Exhaust Particle Number and Size Distributions with Conventional and Fischer-Tropsch. SAE Technical Paper No. 2002-01-2727.

Schindler, W. and Silvis, W. (2000) Einflussfaktoren von Systemparametern bei verdünnter gravimetrischer Partikelmessung. Forum Partikelemissionen 2000, AVL-Deutschland GmbH, 55252 Mainz.Kastel.

Schindler, W., Haisch, C., Beck, H.A., Niessner, R., Jacob, E., and Rothe, D. (2004) A Photacoustic Sensor System for Time Resolved Quantification of Diesel Soot Emissions. SAE Technical Paper No. 2004-01-0968.

Schraml, S., Dankers, S., Bader, K., Will, S., and Leipertz, A., (2000a) Soot Temperature Measurements and Implications for Time-Resolved Laser-Induced Incandescence (TIRE-LII), Comb. Flame, vol. 120, pp. 439-450.

Schraml, S., Will, A., Leipertz, A., Zens, T., and D'Alonso, N., (2000b) Performance Characteristics of TIRE-LII Soot Diagnostics in Exhaust Gases of Diesel Engines. SAE 2000-01-2002.

Schuetzle, D. (1983) *Sampling of Vehicle Emissions of Chemical Analysis and Biological Testing*. Environ. Health Perspect., Vol. 47, pp. 65-80.

Schuetzle, D., Jensen, T.E., and Ball, J.C. (1985) *Polar Polynuclear Aromatic Hydrocarbon Derivatives in Extracts of Particulates: Biological Characterization and Techniques for Chemical Analysis*. Environment International, Vol. 11, pp. 169-181

Schwarz, J. (1994) What are People Dying of on High Air Pollution Days? Environmental Research, Vol. 64, pp. 26-35.

Senda, J., Okui, N., Tsukamoto, T., and Fujimoto, H. (2004) On-Board Measurement of Engine Performance and Emissions in Diesel Vehicle Operated with Bio-diesel Fuel. SAE 2004-01-0083.

Sensors, Inc., (2002) new bulletin "Sensors Lands EPA Contract", August.

Sensors, Inc., (2003) Clean Skies News, vol. 3.4, October.

Siegmann, K. and Siegmann, H.C. (1999) Die Entstehung von C-Partikeln bei der Verbrennung organischer Treibstoffe, HdT-Tagung Feinpartikelemissionen von Verbrennungsmot, October.

Silvis, W.M., Marek, G., Kreft, N., and Schindler, W. (2002) Diesel Particle Measurement with Partial Flow Sampling Systems: A New Probe and Tunnel Design that Correlates with Full Flow Tunnels. SAE Technical Paper No. 2002-01-0054.

Sioutas, C. (2002) Transformation of Vehicle Exhaust Particulate Matter in the Atmosphere. Proceedings for the CRC PM workshop, San Diego, CA, October.

Slott, R.. (2003) Remote Sensing Measurements of On-Road Heavy-Duty Diesel NO_x and PM Emissions – E56. CRC Project E-56-1. January.

Smallwood, G.J., Snelling, D.R., Gülder, Ö.L. Clavel, D., Gareau, D., Sawchuk, R.A., and Graham, L. (2001) Transient Particulate Matter Measurements from the Exhaust of a Direct Injection Spark Ignition Automobile. SAE Technical Paper No. 2001-01-3581.

Soltic, P. and Rutter, J. (2003) On-Road and Engine Dynamometer Measurement of Heavy-Duty Engine Emissions. Presentation at the Euro V Conference.

Spears, M.W. (2001) Portable Emission Measurement Strategy; Proceedings of the 11th CRC On-Road Vehicle Emissions Workshop; San Diego, CA, March.

Spears, M.W. (2002) Portable Emission Measurement Strategy – Update on Recent Activities; Proceedings of the 12th CRC On-Road Vehicle Emissions Workshop; San Diego, CA, April.

Spears, M.W. (2003) On-Vehicle Emissions Measurements and Test Procedures; future Worldwide Emission Requirements for Passenger Cars and Light Duty Vehicles and EURO V; December.

Stedman, D.H. and Bishop, G.A. (2002) Opacity Enhancement of the On-Road Remote Sensor for HC, CO, and NO. CRC Project E-56-1.

Stein, H.J. (2002) Consequences of ACEA Heavy-Duty Vehicle Emissions Program for Future PM Measurement. Proceedings of the CRC Particulate Measurement Workshop, San Diego, October.

Stern, A.C., et al., (1984). “Fundamentals of Air Pollution”, Orlando, Florida. Academic Press.

Suryanarayana Setty, K.L., (1999) Application of Fuel Injection Equipment to Meet India 2000 and Euro II Emission – Hands on Experience, SAE 990028.

Tahara, J., Ohtsubo, Y., Aoyama, T., Ito, T., Matsuoka, H., and Fujimura, T. (2002) Development of an Exhaust Aftertreatment System for Diesel Passenger Cars – Simultaneous Reduction System of NO_x and Particulate Matter. SAE Technical Paper Series 2002-08-0098.

Takahashi, Y., Kishi, Y., Fukano, I., Sasaki, K., and Shinozaki, R. (1995) A Study of the Durability of Diesel Oxidation Catalysts. SAE Technical Paper Series 952650.

Takeda, Y., Fukano, I., Yamasaki, A., and Suzuki, T. (1990) Measurement of Diesel Particulate using Multi-Tube Type Mini-Dilution Tunnel. SAE Technical Paper Series 908226.

Takemoto, B. K.; Bytnerowicz, A.; Fenn, M. E. (2001) “Current and Future Effects of Ozone and Atmospheric Nitrogen Deposition on California’s Mixed Conifer Forests. “ Forest Ecology and Management, Vol. 144, pp. 159-173.

Taskinen, P. Von Hollen, P. Karvinen, R. Liljenfeldt, G., and Salminen, H.J., (1998) Simulation of Combustion, Soot and NO_x-emissions in a Large Medium Speed Diesel Engine, SAE Technical Paper Series 981449.

Thaller, W., Schindler, W., and Singer, W. (2000) Transiente Erfassung niedriger Rauchwerte mittels Opazimetrie. Forum Partikelemissionen 2000, AVL-Deutschland GmbH, 55252, Mainz.Kastel.

Thompson, G.H., Clark, N. N., Gautam, M., Carder, D. K., Lyons, D. W., (2002) Inference of Torque and Power from Heavy-Duty Diesel Engines for On-Road Emissions Monitoring, SAE 2002-01-0614.

Traver, M. (2002) Interlaboratory Crosscheck of Heavy-Duty Vehicle Chassis Dynamometers. Proceedings of the 12th CRC On-Road Vehicle Emissions Workshop. San Diego, CA.

Trivedi, N.K., Husain, A.S., Chaudhari, M.K., Pirangute, V.G., Vora, K.C., Dias, C.F., Diewald, R., and Reck, A., (1999) Emission Reduction from a Heavy-Duty 6 Seater, 3-Wheeler Employing Metallic Converter, SAE 990018.

Truex, T.J. and Anderson, J.E. (1979) Mass Monitoring of Carbonaceous Aerosols with a Spectrophone. Atmos. Environ., vol. 13, 507.

Uchiyama, S., (2003) Results of JCAP I Studies and Outline of JCAP II Program, JRC Conference, December.

University of Biel, Switzerland, (2003) Literature of the Laboratory for IC-Engines and Exhaust Emission Control of the Biel School of Engineering, October, (www.hti.bfh.ch/fileadmin/img/Auto/Literaturverzeichnis_CSJ.PDF).

USAID-India (2004) Delhi Tests Remote Vehicle Emissions Sensor, press release, April.

U.S. Environmental Protection Agency (2000) National Air Pollutant Emission Trends, 1900-1998. Prepared by the Office of Air Quality Planning and Standards, Research Triangle Park, NC, document No. EPA-454/R-00-002, March.

U.S. Environmental Protection Agency (2002) Health Assessment Document for Diesel Engine Exhaust. Prepared by the National Center for Environmental Assessment, Washington D.C., for the Office of Transportation and Air Quality, EPA/600/8-90/057F.

VDI (1996) Chemisch-analytische Bestimmung des elementaren Kohlenstoffes nach Extraktion und Thermodesorption des organische Kohlenstoffes. VID 2465.

Verrant, J.S. and Kittelson, D.A. (1977) Sampling and Physical Characterization of Diesel Exhaust Aerosols. SAE Technical Paper No. 770720.

Vertin, K., Chandler, K., LeTavec, C., Goguen, S., Keske-Hynnilla, D., Chatterjee, S., Smith, G., Hallstrom, K., (2000) Class 8 Trucks Operating on Ultra-Low Sulfur Diesel with Particulate Filter Systems: A Fleet Start-Up Experience; SAE Technical Paper No. 2000-01-2821.

Viranen, A., Ristimäki, J., Marjamäki, M., Vaaraslahti, K., Keskinen, J., and Lappi, M. (2002) Effective Density of Diesel Exhaust Particles as a Function of Size. SAE Technical Paper No. 2002-01-0056.

Vogt, R. and Scheer, V. (2002) Particle in Diesel Exhaust: A Comparison of Laboratory and Chasing Experiments. Proceedings of the 11th International Symposium Transport and Air Pollution. Graz, pp 79-84.

Vojtisek-Lom, M. and Allsop, J.E. (2003) Six Years On – and Off – the Road: Exhaust Sampling and Exhaust Flow Measurement in Non-Traditional Settings; Proceedings of the 13th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, April.

Wanabe, H., Enhancing Next Generation Product Development, Toyota Development and Design.

Weaver, C.S. and Balam-Almanza, M.V. (2001) Development of the ‘RAVEM’ Ride-Along Vehicle Emission Measurement System for Gaseous and Particulate Emissions; SAE 2001-01-3644; Society of Automotive Engineers: Warrendale, PA.

Weaver, C.S., Chan, L-M, Makartchouk, A., and Petty, L. (2003) Reproducibility and Accuracy of On-Board Vehicle Emission Measurements using the RAVEM System; Proceedings of the 13th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, April.

Wedekind, B.G.A., Andersson, J.D., Hall, D., Stradling, R., Barnes, C., and Wilson, G. (2000) DETR/SMMT/CONCAWE Particle Research Programme: Heavy Duty Results. SAE Technical Paper No. 2000-01-2851.

Wei, Q., Kittelson, D.B., and Watts, W.F., (2001) Single-Stage Dilution Tunnel Performance, SAE Technical Paper No. 2001-01-0207.

Wei, Q., Kittelson, D.B., and Watts, W.F., (2001) Single-Stage Dilution Tunnel Design, SAE Technical Paper No. 2001-01-0201.

Weiss, S. B. (1999) “Cars, Cows, and Checkerspot Butterflies: Nitrogen Deposition and Management of Nutrient-Poor Grasslands for a Threatened Species.” Conservation Biology, Vol. 13, pp. 1476-1486.

Whitby, K.T., et al. (1975) Characterization of California Aerosols – 1. Size Distributions of Freeway Aerosol. Atmosph. Environ., vol. 9, p 463-482.

Whitby, R., Gibbs, R., Johnson, R., Hill, B., Shimpi, S., and Jorgenson, R. (1982) Real-Time diesel Particulate Measurement Using a Tapered Element Oscillating Microbalance. SAE Technical Paper No. 820463.

Wilson, W.E., et al. (1977) General Motors Sulfate Dispersion Experiment: Summary of Epa Measurements. Journal of Air Pollution Control Association. Vol. 27, p 46-51.

Witze, P.O. (2002) High-Energy, Pulsed-Laser Diagnostics for Real-Time Measurements of Reciprocating Engine PM Emissions. Proceedings of the 8th DEER conference, August.

Witze, P.O., Chase, R.E., Maricq, M.M., Podsiaklik, D.H., and Xu, N. (2004) Time-Resolved Measurements of Exhaust PM for FTP-75: Comparison of LII, ELPI, and TEOM Techniques. SAE Technical Paper No. 2004-01-0964.

Wolfe, A. P.; Baron, J. S.; Cornett, R. J. (2001) "Anthropogenic Nitrogen Deposition Induces Rapid Ecological Changes in Alpine Lakes of the Colorado Front Range (USA)." *Journal of Paleolimnology*, Vol. 25, pp. 1-7.

World Bank Group (1998). "Airborne Particulate Matter". Pollution Prevention and Abatement Handbook, Project Guidelines: Pollutants, pp. 201-207

Woshni, V.G. Schwarz, C., und Klaus Zeilinger, K., (1995), Laengsdynamiksimulation von Kraftfahrzeugen mit dieselmotorischen Antrieb, *Motortechnische Zeitschrift*, 56:206-211.

Yamagishi, Y. and Ohtsuki, S. (2000) Tunnel Vision – A Particulate Matter Sampling System using a Partial Flow Dilution Method has been Designed to Perform Sampling during a Transient Test Cycle. *Testing Technology International*, pp 95-99.

Yamagishi, Y. (1999) The MDLT-1302T Partial-Flow Dilution Tunnel for Transient Test Cycle PM Sampling. Horiba Technical Reports, No. 19, pp 45-49.

Yamagishi, Y. and Otsuki, S. (2002) Evaluation and Testing of the Partial Flow Sampling System for PM Measurement. Horiba Technical Reports, No. 23, pp 40-44.

Yamamoto, T., Kusaka, J., Daisho, Y., Kihara, R., Saito, T. (1999) The Effects of Polycyclic Aromatic Hydrocarbons on Particulate Matters in Fuel-Rich Mixtures. SAE Technical Paper Series 1999-08-0343.

Yanowitz, J., McCormick, R.L., and Graboski, M.S., (2000) "In-Use Emissions from Heavy-Duty Diesel Vehicles"; *Environmental Science and Technology*, 34 (5), 729-740.

Yusheng Zhang G. T. Reader, (1999) Simulation and Experimental Studies on Closed-Cycle Diesel Engines, SAE Technical Paper Series, 1999-01-1536.

Zelenka, P., Kriegler, W., Herzog, P.L., and Cartellieri, W.P., (1990) "Ways Toward the Clean Heavy-Duty Diesel," SAE Technical Paper No. 900602.

Zhu, J., Lee, K.O., Sekar, R., and Choi, M.Y., Morphological Study of the Particulate Matter from a Light-Duty Diesel Engine, Proceedings of the Third Joint Meeting of the US Section of the Combustion Institute.

Zhu, X, Durbin, T.D., Cocker, D., and Norbeck, J.M. (2004) Internal Combustion Engine Air Toxic Emissions. Final Report to the California Air Resources Board, May.

Appendix A. Certification Standards for Heavy-Duty Diesel Engines

Table A-1 California and US EPA on-road heavy-duty diesel standards since 1985

Model Year	Federal				California			
	HC	CO	NO _x *	PM	HC	CO	NO _x *	PM
1985-86	1.3	15.5	10.7	---	1.3	15.5	5.1	---
1987-89	1.3	15.5	10.7	0.60	1.3	15.5	6.0	0.60
1990	1.3	15.5	6.0	0.60	1.3	15.5	6.0	0.60
1991-93	1.3	15.5	5.0	0.25	1.3	15.5	5.0	0.25
1994-97	1.3	15.5	5.0	0.10	1.3	15.5	5.0	0.10
1998-02	1.3	15.5	4.0	0.10	1.3	15.5	4.0	0.10
2003-06	---	15.5	2.4	0.10	---	15.5	2.4	0.10
2007	0.14	15.5	0.20	0.01	0.14	15.5	0.20	0.01

* = NMHC+NO_x for 2003-06 and later engines; units = (g/bhp-hr)

Table A-2 EU heavy-duty diesel Engine standards (g/kW-hr)

Tier	Model Year	Test Cycle	CO	HC	NO _x	PM	Smoke
Euro I	1992, <85 kW	ECE R-49	4.5	1.1	8.0	0.612	---
	1992, >85 kW		4.5	1.1	8.0	0.36	---
Euro II	1996.10	ESC/ETC/ELR	4.0	1.1	7.0	0.25	---
	1998.10		4.0	1.1	7.0	0.15	---
Euro III	1999.10*		1.5	0.25	2.0	0.02	0.15
	2000.10		2.1	0.66	5.0	0.10	0.8
Euro IV	2005.10		1.5	0.46	3.5	0.02	0.5
Euro V	2008.10		1.5	0.46	2.0	0.02	0.5

*Enhanced environmentally friendly vehicles only; ECE – old steady state cycle;
 ESC – European Stationary Cycle; ETC – European Transient Cycle;
 ERL - European loaded response (smoke opacity)

Table A-3 Japanese heavy-duty diesel Engine Standards (g/kW-hr)*

Model Year	Test Cycle	CO	HC	NO_x	PM
		mean (max)	mean (max)	mean (max)	mean (max)
1988/89	6 mode	790 (980)	510 (670)	DI: 400 (520) IDI: 260 (350)	
1994	13 mode	7.40 (9.20)	2.90 (3.80)	DI: 6.00 (7.80) IDI: 5.00 (6.80)	0.70 (0.96)
1997		7.40 (9.20)	2.90 (3.80)	4.50 (5.80)	0.25 (0.49)
2003		2.22	0.87	3.38	0.18
2005	JE05	2.22	0.17	2.0	0.027

GVW>2500 kg (>3500 beginning 2005)

* 1988/89 units in ppm

ERL - European loaded response (smoke opacity)