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**Formation and Characterization
of Particles:
Report of the 1996 HEI Workshop**

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SUMMARY

Introduction

In the last few years, concerns have emerged regarding the health effects of exposure to low levels of ambient particulate matter (PM)[†], or particles. Ambient particles are derived from anthropogenic sources (stationary and mobile) and natural sources (soil erosion, sea spray, and organic debris), and vary in size and composition depending on the source and the chemical reactions they undergo in the atmosphere. The U.S. Environmental Protection Agency (EPA) regulates PM as a criteria pollutant for which a National Ambient Air Quality Standard (NAAQS) (expressed as the mass concentration in air) has been set to protect public health.

Combustion of fossil fuels contributes substantially to ambient particles of respirable size. The mass emission rate of particles from motor vehicles has been regulated, and to meet the increasingly stringent standards, manufacturers have continually decreased the mass emitted by improving engine designs, modifying fuel composition, and using exhaust control devices. However, other particle parameters (such as number, surface area, chemical composition), which may be more closely associated with health effects, are neither regulated nor routinely measured.

The Health Effects Institute organized this workshop to share current knowledge of the characteristics of particles in mobile-source emissions and to motivate scientists who measure particles to consider characterizing additional physical and chemical parameters that may be useful in assessing the potential health impacts of changes in fuel formulation, engine designs, and emission control systems. Another goal of the workshop was to build connections between the scientists who analyze particles and biologists who investigate the health effects of particles.

During the workshop speakers from academic institutions, the EPA, and the motor vehicle industry discussed the current understanding of the health effects of particles, the physical and

chemical combustion processes leading to particle formation, the atmospheric transformation of particles, the problems involved in generating relevant particulate atmospheres for animal and human exposure studies, and current results of particle characterization studies. This document summarizes the major points and conclusions from each presentation and lists research needs for particle characterization identified by the workshop participants. All the speakers had an opportunity to revise and edit the initial and final drafts of this document.

Current Understanding of the Health Effects of Particles and the Characteristics That Determine Dose or Effect

Joe Mauderly (Lovelace Respiratory Research Institute) presented a summary of epidemiologic studies of PM and discussed the implications of their findings for regulatory action and future research. The current NAAQS for PM is based on the concentration of material (measured in mass) in air collected by samplers with a collection efficiency of 50% for particles 10 μm in aerodynamic diameter (PM₁₀). These standards, 50 $\mu\text{g}/\text{m}^3$ (annual arithmetic mean) and 150 $\mu\text{g}/\text{m}^3$ (24-hour mean, not to be exceeded more than once per year), focus on the respirable fraction of PM ($\leq 10 \mu\text{m}$) because only a small portion of particles larger than 10 μm reaches the deep lung.

Several epidemiologic studies, using a time-series approach to data collection and analysis, have found a temporal relationship between daily or two-day increases in particle mass and an increased occurrence of respiratory illness and daily mortality (for a review, see U.S. Environmental Protection Agency 1996). These findings have been consistent in different countries and in cities with different weather patterns. The results of a meta-analysis of studies on particle-related mortality is shown in Table 1.

[†] A list of abbreviations appears at the end of this document.

Mauderly noted that, to date, the studies have not provided a clear description of the individuals affected (such as age and health status), possible biologic mechanisms involved, the personal exposures leading to the effect (the PM data are typically taken from area monitors), the role of PM independent of other pollutants, or the subclass of PM that might be most closely associated with the effect. However, the present findings suggest that older individuals with preexisting serious respiratory and cardiac diseases are at greatest risk, and that the finer fractions of PM are more strongly associated with the effects than the coarser fraction. More-

over, some evidence indicates that long-term exposure to PM may shorten the life span (from increased risk of cardiovascular disease or lung cancer) independently of the short-term hastening of death suggested by the daily mortality studies (Dockery et al. 1993; Speizer and Samet 1994; Cohen and Pope 1995; Pope et al. 1995). These results are of concern to developers of fuels, engines, and emission control systems because internal combustion engines contribute significantly to the ambient particle burden.

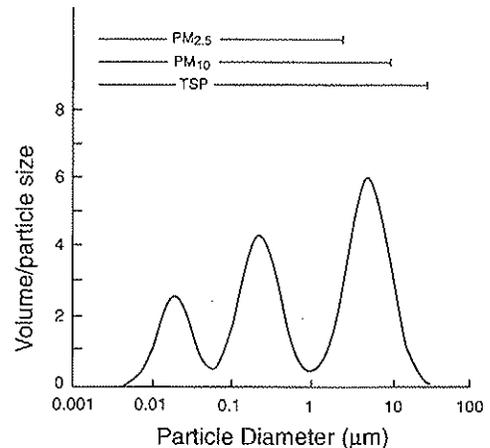
Mauderly commented that the independent causality of PM in these health effects has not been confirmed and is not yet supported by

MEASURING PARTICLES

Particles in ambient air comprise a mixture of pollutants. They originate from a variety of sources and differ in structure, size, and composition depending on their source. Some are solid and some are liquid.

The diameter is often used as a measure of particle size; however, the terminology was not uniform among the workshop presenters and participants. The most common size descriptor is the *aerodynamic diameter*, which depends on the particle density, and is defined as the diameter of a spherical particle (assumed to have a density of 1 g/m^3) with the same settling velocity as the particle being measured.

Ambient particles tend to fall into three size classes referred to as "modes." The Figure illustrates a typical volume-weighted size distribution for ambient particles (adapted from Wilson et al. 1977) and shows three commonly used measures of ambient particle concentration (based on the size cutpoint of the samplers). The Table gives the particle size classification (based on observed size distributions and formation mechanisms) most often used by presenters and in this document. Note that some presenters applied slightly different size ranges to the modes (for example, see Johnson or Cass). Particles from mobile-source combustion are primarily found in the nuclei and accumulation modes.



Modes	Also Described As	Most Common Size Range
Nuclei	Ultrafine	< 0.1 μm
Accumulation	Fine	0.1 – 1 μm
Coarse	(PM _{2.5} , PM ₁₀)	> 1 μm

Other important parameters used in this publication to quantify the amount of particles are:

- mass concentration ($\mu\text{g/m}^3$);
 - volume concentration ($\mu\text{m}^3/\text{m}^3$); and
 - number concentration (number/ cm^3).
- (Particle volume concentration closely approximates the mass concentration for typical exhaust particles.)

Table 1. Meta-Analysis of Particle-Related Changes in Daily Mortality^a

Location	Mean TSP ^b ($\mu\text{g}/\text{m}^3$)	Relative Risk for Mortality per 100- $\mu\text{g}/\text{m}^3$ Increase in TSP
TSP Highest in Cold Weather		
London (1952)	2000	1.06
Santa Clara County, CA	70	1.04
Utah Valley	94	1.08
TSP Highest in Warm Weather		
Birmingham, AL	96	1.06
Detroit, MI	84	1.06
Minnesota	76	1.06
Philadelphia, PA	77	1.07
St. Louis, MO	56	1.08
Steubenville, OH	111	1.04
Tennessee	60	1.09
Weighted Summary Estimate^c (Meta-Analysis)		1.06

^a Adapted from Schwartz 1994.

^b Total suspended particulates (TSP) is defined by the design of the high-volume sampler, which collects all the fine particles but only part of the coarse particles; its upper cut-off size depends on the wind's speed and direction, and may vary from 25 to 40 μm . TSP was the original indicator for PM when the NAAQS was first promulgated in 1971; it was replaced by PM_{10} in 1987 (U.S. Environmental Protection Agency 1996).

^c Calculated by method of inverse variance weighting.

either human or animal laboratory studies. Only recently has laboratory work focused on animal models of potentially susceptible humans, the mechanisms by which particles deposited in the lungs might cause harmful effects, the importance of reactive compounds borne on particle surfaces, and particle size.

The PM NAAQS has recently undergone review. The EPA has proposed that new standards for fine particles be established, which would consist of 24-hour and annual average concentrations of $\text{PM}_{2.5}$ (U.S. Environmental Protection Agency 1996). In the summer of 1997, either the current standard based on PM_{10} will be retained or a new standard based on $\text{PM}_{2.5}$ will be promulgated.^{*} The establishment of a fine-particle standard would increase the pressure to further reduce emission levels from sources of fine particles, such as engines.

Mauderly stressed the importance of close, iterative, continuing communication among

those scientists developing fuels, engines, and emission control technologies, who need to know which particle constituents and characteristics have the most impact on health, and those scientists studying the health effects of PM, who need to know the nature of emissions from contemporary and developing engine technologies (Figure 1). Mauderly suggested that

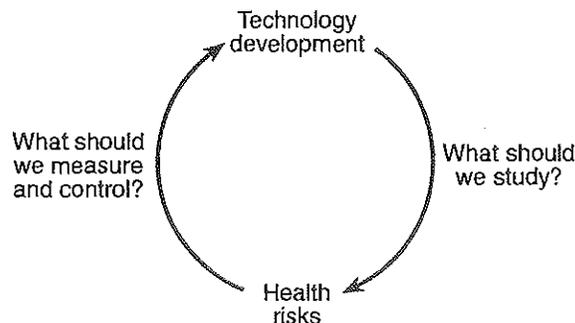


Figure 1. Communication loop among scientists in different disciplines. (Reprinted with permission from J. Mauderly.)

^{*} Editor's Note: On Thursday, July 17, 1997, the EPA announced its decision to retain the current PM_{10} standards, and to add new annual and 24-hour standards for $\text{PM}_{2.5}$ (Federal Register 1997).

control strategies based solely on reducing the mass of PM may not reduce—and, indeed, could increase—human health risks. For example, decreasing PM mass while increasing particle number or toxic chemical characteristics might prove to be a step in the wrong direction. He indicated that regulatory control of engine PM emissions might need to shift from a solely mass basis to include other parameters if the health research findings suggest that other characteristics are sufficiently important.

Günter Oberdörster (University of Rochester) focused on the particle parameters that have been associated with health effects. Dose-response relationships for inhaled particles are usually expressed using particle mass as the dose parameter. However, comparing the results of a number of studies of long-term effects of different types of particles has shown that mass concentration may not be the most appropriate indicator of dose; and that careful attention is needed when choosing which dose parameter might best describe the relationship between dose and effect. For example, parameters such as number concentration, surface area, or retained particle mass may be more directly linked to the effect observed.

In the group of studies Oberdörster evaluated, rats were exposed to high concentrations of particles of low toxicity, and cancer was the primary endpoint (see Heinrich 1995 for a re-

view of these studies). Oberdörster showed how the relative tumor-inducing potencies of the inhaled particles changed depending on whether the surface area of the retained particles or the mass of the retained particles was used as the measure of dose (Figure 2) (Oberdörster 1994, 1996). In the first case, the tumor-inducing potency would be the same for all particles; in the second case, two types of particles would be more carcinogenic than the other three. Moreover, the potency of those same particles to impair alveolar clearance function changed depending on whether the mass of the retained particles or the volume of the phagocytized particles was used as the measure of dose.

Oberdörster noted that the particle surface area is likely to be an important dosimetric parameter, especially when comparing effects of particles of different sizes. Target cells interact with the particle surface rather than with the volume or mass of a particle, and the surface area relative to a given mass increases as the size of the particle decreases.

Particle size also is an important dose parameter because fine or ultrafine particles may escape phagocytosis by alveolar macrophages, gain access into the respiratory epithelium and interstitium of the lung, and cause injury. Furthermore, the deposition of ultrafine particles seems to depend on whether these particles are

TUMORIGENICITY IN RATS

Retained Particle Surface Area

Toner = TiO₂ (pigment grade) = Talc = Carbon Black = Diesel Exhaust

Retained Particle Mass

Toner < TiO₂ (pigment grade) < Talc < Carbon Black = Diesel Exhaust

IMPAIRED CLEARANCE FUNCTION

Retained Particle Mass

TiO₂ (pigment grade) < Toner < Diesel Exhaust = Carbon Black < TiO₂ (ultrafine)

Phagocytized Particle Volume

TiO₂ (pigment grade) = Toner = Diesel Exhaust = Carbon Black < TiO₂ (ultrafine)

Figure 2. Toxicity ranking of inhaled particles for specific effects based on different dose parameters. (Pigment grade particles are ~ 250 nm; ultrafine are ~ 20 nm.) (Reprinted with permission from G. Oberdörster.)

inhaled as singlet particles or as aggregates. Inhaling singlet ultrafine particles can result in a very high deposition efficiency (or dose) in the peripheral lung, whereas aggregates of ultrafine particles behave like larger particles and may deposit more centrally in the lung. In addition, if aggregated ultrafine particles disaggregate in the lung, their overall effect on the lung could change.

It has been known for a long time that transition metals such as iron can amplify inflammatory responses in the lung via the Fenton reaction⁵ by generating highly toxic hydroxyl radicals. The importance of transition metals present in and on ambient particles, therefore, needs careful investigation. The concept that particles carry adsorbed materials on their surfaces is important because the particles may deposit toxic or reactive compounds on specific target cells via this mechanism.

Oberdörster stressed that a thorough understanding of exposure, dose, and effect relationships is necessary to support regulatory decisions, for example in establishing a fine-particle standard. Because the current NAAQSs are based on mass concentration, they primarily regulate coarse-mode and accumulation-mode particles, the two size groups in which the largest percentage of mass is found. Therefore, if the number of ambient ultrafine particles is found to be causally associated with the adverse health effects observed in epidemiologic studies, a fine-particle standard based on mass (e.g., PM_{2.5}) might prove ineffective because the nuclei-mode particles, although highest in number, contribute so little to overall mass concentration.

Oberdörster also hypothesized that because accumulation-mode particles act as a sink for ultrafine particles, decreasing their concentration in compliance with a fine-particle standard could result in increasing the number of ultrafine particles. This may have been the situation in Erfurt (in former East Germany), where clean-up measures resulted in lowering the ambient particulate mass concentration, but also in doubling the number of ultrafine particles (Tuch et al. 1997).

Particle Formation in Combustion

Jack Howard (Massachusetts Institute of Technology) provided an overview of the fundamental processes of particle formation in flames. He noted that understanding particle formation mechanisms has long been of scientific interest, but has been difficult to achieve because of the physical and chemical complexity of flames. Most information has been obtained using hydrocarbon flames, which have simple, one-dimensional flow fields that permit samples to be taken at different stages of particle formation. These studies have produced a time-resolved record of mass and number concentrations, size distribution of soot particles, and composition of the accompanying gas. Soot formation begins with particle nucleation or inception; mass increases as the particles react with gas-phase molecules or coagulate through particle-particle sticking collisions. Mass is removed from particles by eliminating functional groups through pyrolysis, dehydrogenation, carbonization of the condensed material, or oxidation. These processes are outlined below.

Particle Nucleation The molecular precursors of soot particles are heavy polycyclic aromatic hydrocarbons (PAHs) of molecular weight 500 to 1000, consisting of both five- and six-membered rings. The initial process of soot formation (nucleation) converts mass from the molecular to the particulate phase. The smallest soot particles observed under the electron microscope are about 1.5 nm in diameter, corresponding to a molecular weight of about 2000. At the onset of soot nucleation, the concentration (mass and number) of heavy PAH molecules rapidly decreases while the concentration (mass and number) of soot particles increases; the magnitudes of the two changes are consistent, in that the incipient particles are formed by combining two to four of the heavy PAH molecules. Thus, the chemical structure of the primary soot particles is similar to that of the PAHs.

Particle Growth Particles grow as a result of several processes. Growth is first accomplished by carbon being added from gas-phase unsaturated hydrocarbons (both stable molecules and radicals, among which PAHs and acetylene are important). This process increases the mass of individual particles, but does not af-

⁵ A reaction between iron(II) and H₂O₂.

fect the number of particles, so the mass concentration increases. Later, coagulation via reactive particle-particle collisions decreases the number of particles and increases the size of individual particles without changing the total particle mass concentration. Thus, as the mass concentration of particles increases, the number concentration increases at first (while the rate of nucleation exceeds the rate of coagulation) and later decreases (when the rate of nucleation falls below the rate of coagulation), largely because particle precursors are being depleted. During these processes, the PAH material forming the particles undergoes functional group elimination, cyclization, ring condensation, and ring fusion. These steps convert the initially amorphous soot material to a progressively more graphitic carbon material, with some decrease in particle mass but no change in particle number. Figure 3 is a schematic representation of soot particles growing in a hydrocarbon flame.

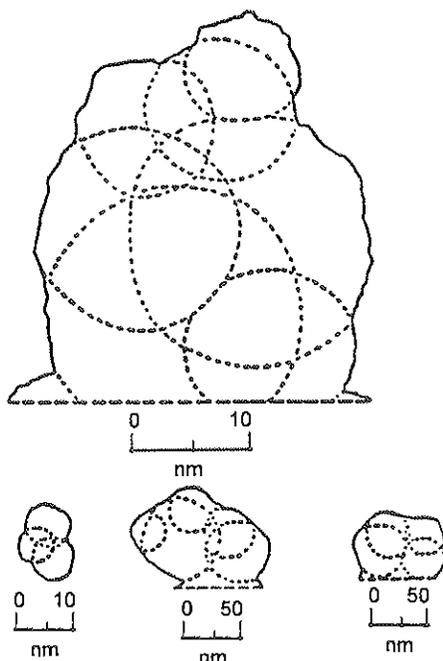


Figure 3. Outlines (solid lines) of actual soot particles from electron micrographs with hypothetical internal structure (dashed lines) representing possible primary, or nuclei-mode particles and surface growth. (Reprinted with permission from Battelle Press as published in Howard and Longwell 1983.)

Particle Mass Loss Particle mass decreases as soot is oxidized, which converts particulate carbon to gas. Oxidation can precede or overlap and compete with particle growth processes, depending on the type of flame and other combustion conditions. When oxidation occurs after particle formation, the number of particles increases substantially under fuel lean conditions (with 1% to 2% of excess oxygen) because reactions within the particle lead to particle fragmentation. Under fuel rich conditions, (i.e., more fuel than could be converted by oxygen to carbon dioxide and water), hydroxyl radical, rather than oxygen, is the main oxidation reactant, and the oxidation results in a monotonic decrease in particle size, whereas the number of particles remains constant.

The processes of soot formation and oxidation described above may terminate at different stages through dilution, thermal quenching, or other events that occur in combustion. The particles found in the exhaust may have characteristics of the formation stage, the destruction stage, or both, depending on the combustor design and operating conditions. For example, larger numbers of smaller particles could be produced by quenching the formation process at an early stage before particle number is extensively reduced by coagulation, or by quenching the oxidation process after break-up occurs but before the fragments are consumed by gasification. The composition of particles emitted from the formation stage would most likely be PAHs, whereas particles from the oxidative fragmentation stage would be graphitic, with stacked layers of carbon.

Gary Hunter (Cummins Engine Company) presented details of the soot formation and oxidation process in a diesel engine cylinder. This research was conducted at Sandia National Laboratory using an optically accessible heavy-duty diesel engine (rather than a simple flame as described by Howard). In this engine, a fuel jet penetrates into the combustion chamber (or cylinder) and the combustion process can be studied in detail. It is believed that, in the flame zone, fuel is pyrolyzed from its original molecular structures to form PAH compounds that collapse to form planar graphitic struc-

tures; as these structures grow they form spherical carbonaceous particles (or soot).

Besides soot, diesel particles contain organic compounds (from unburned or partially burned fuel and lubricants), trace amounts of ash (from oxidation of metals in lubricants and fuel additives), and sulfates (from sulfur present in the fuel). To decrease the total particle mass, strategies have focused on reducing each component of the particles. For example, the organic component from unburned fuel has been decreased by improving the fuel injector nozzle and optimizing the injection timing, whereas the contribution from lubricating oil has been reduced by improving piston ring design and incorporating valve-stem seals. Sulfate levels have been decreased by using low-sulfur fuel, which lowers the amount of sulfur oxides produced that can form sulfate particles in the exhaust stream and during dilution with air. Soot formation has been reduced by decreasing the amount of aromatic compounds in the fuel and enhancing oxidation processes (for example, by increasing the fuel injection pressure to mix fuel with air more efficiently).

In addition to particulate matter, diesel engines emit a substantial amount of NO_x , whose concentration in the exhaust also is regulated. A particularly challenging aspect of reducing both particles and NO_x emissions is that decreasing either one usually means increasing the other. The high flame temperature needed to oxidize and eliminate soot forms NO_x . The lower temperatures that reduce NO_x emissions leave more particles unoxidized. Nevertheless, Hunter noted that current heavy-duty diesel engines emit approximately 90% less particle mass than they did before emission standards were established; and this reduction has occurred simultaneously with reductions in NO_x emissions and improvements in engine fuel efficiency. Hunter also pointed out that further reductions in both soot and NO_x will be difficult to achieve because of the trade off between NO_x and particles. One way to reduce soot formation without affecting NO_x formation is by reducing the aromatic content of the fuel.

Hunter emphasized that understanding how technological changes may impact particle size distributions is vitally important, especially during transient emission testing, which is

more representative of on-road driving conditions than testing in steady-state modes.

The EPA Particle Emissions Testing Procedure

For the past 25 years, investigators at the EPA and other organizations have measured particulate emissions from mobile sources on the basis of total mass. *Joseph Somers* (U.S. Environmental Protection Agency, Office of Mobile Sources) described the methods specified in current regulations for measuring particle mass emissions from light-duty and heavy-duty diesel vehicles (Federal Register 1996); these methods were developed by the EPA in collaboration with scientists in the motor vehicle industry and academic institutions.

Regulations for visible smoke have been in effect since 1970. The initial diesel particulate regulations were instituted for the 1978-model-year light-duty vehicles, and for the 1988-model-year heavy-duty engines (regulations for heavy-duty vehicles apply only to their engines). The regulations have become increasingly stringent over the years; compared with vehicles manufactured before the 1978- and 1988-model-year regulations took effect, engines and vehicles currently being produced emit 90% less total particulate mass.

Heavy-duty diesel engines for motor vehicles are tested on a transient engine cycle designed to represent typical urban driving conditions for trucks. Before this transient engine test cycle was mandated, a 13-mode steady-state test cycle was used (and continues to be used for European certification). Light-duty diesel trucks are tested on the same Federal Test Procedure (FTP) used for passenger vehicles. Particulate mass emissions from nonroad engines (e.g., lawnmowers, tractors, snowmobiles) are presently measured using an 8-mode steady-state test cycle.

The EPA method for measuring exhaust particles starts by directing all of the exhaust through a long metal cylinder, or dilution tunnel, where it is diluted with sufficient air to simulate conditions in the ambient atmosphere. By controlling the amount of dilution air, water condensation is prevented and the temperature

of the exhaust-dilution air mixture is lowered to 125°C. Next, a small sample of the exhaust-dilution air mixture is drawn through an inert fluorocarbon-type filter to collect the particles. The tared weight of the particles on the filter is used to calculate the mass emission rate, which is commonly expressed as total particulate matter emitted by the engine per mile traveled (mg/mile).

Characterizing Particulate Matter in Motor Vehicle Exhaust

Diesel and Gasoline Engines

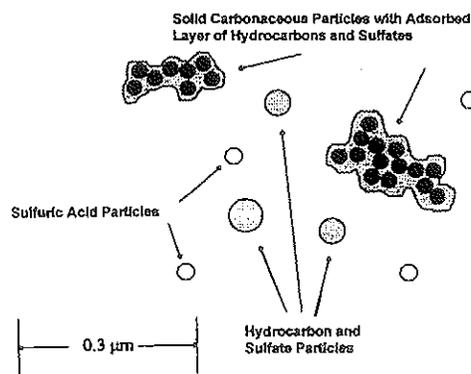
David Kittelson (University of Minnesota) presented the results of studies to characterize particles from diesel engines (selected references: Dolan and Kittelson 1978; Luo et al. 1989; Abdul-Khalek and Kittelson 1995). He has primarily used an electrical aerosol analyzer to measure number and volume

concentrations, surface area, and size distributions. With a condensation nucleus counter, he has independently measured total number concentration.

In describing the characteristics of diesel exhaust particles (see sidebar), Kittelson noted that particles also can be formed during the exhaust dilution and cooling processes by either nucleation or absorption into existing particles of volatile compounds present in the vapor-phase exhaust. The amount of material transformed into particles and the size of the particles formed depend on the details of the dilution and cooling processes. For example, under atmospheric conditions, the exhaust is rapidly diluted and cooled; this causes nucleation, condensation, and adsorption of materials that are in the vapor phase, but become supersaturated during the dilution and cooling process. Nucleation may lead to large concentrations of nuclei-mode particles. It is a highly nonlinear process and is very sensitive to the

COMPOSITION AND STRUCTURE

As described by Kittelson, most of the mass and volume of the exhaust is found in accumulation-mode particles, whereas the largest number of particles is in the nuclei mode. Nuclei-mode particles consist of volatile nuclei of sulfur or hydrocarbons, fragments of agglomerates, and traces of metals. The accumulation-mode particles consist mainly of solid carbonaceous agglomerates formed during combustion, with hydrocarbons, or sulfates, or both adsorbed onto their surfaces.



The coarse-mode particles consist mainly of accumulation-mode particles that have been deposited on the walls of the exhaust system and subsequently reentrained. The particle composition and structure of diesel exhaust emissions are schematically illustrated in the Figure (reprinted with permissions from D. Kittelson). Kittelson noted that spark-ignition engines produce qualitatively similar

particles, but smaller in diameter and in concentrations lower by two orders of magnitude than the levels produced by diesel engines.

degree of supersaturation. If high concentrations of nuclei-mode particles are formed, the coagulation process may become important, because the rate of coagulation is proportional to the square of the number concentration. As a result of these nonlinearities, measurements of ultrafine particles are very sensitive to sampling errors. Consequently, sampling and dilution systems should simulate atmospheric dilution as closely as possible.

Kittelson noted that over the past twenty years the typical volume concentration of particles in the exhaust of diesel engines (which is comparable to the mass concentration) has dropped from a range of 10,000 to 100,000 $\mu\text{m}^3/\text{m}^3$ to a range of 1,000 to 5,000 $\mu\text{m}^3/\text{m}^3$. During the same time, number concentration was in the range of 3 to 10×10^7 particles/ cm^3 and has fallen to the range of 5 to 20×10^6 particles/ cm^3 . Thus, on the basis of his experiments, Kittelson concluded that particle mass concentration has been reduced considerably more than particle number concentration, and particles are correspondingly smaller; in fact, the volume mean diameter of particles has fallen from about 0.12 to 0.08 μm . (The volume mean diameter of diesel particles is usually close to the mass mean diameter [Dolan et al. 1980].)

John Johnson (Michigan Technological University) summarized the results of a study, conducted in collaboration with Susan Bagley, to characterize and compare emissions from two Cummins heavy-duty diesel engines: a 1988 engine equipped with a ceramic particle trap and a 1991 engine equipped with an oxidative catalytic converter, both operated with low-sulfur fuel. (For this study, the engines were operated at steady-state, rated speed modes 9 and 11.) They found that particle mass concentration in emissions was substantially reduced (by 70% to 80%) using both the 1988 engine with a trap and the 1991 engine with a catalytic converter compared with the 1988 engine without the trap. However, the 1991 engine with the catalyst was up to 70% more effective in lowering emissions of total hydrocarbons than the 1988 engine with the particle trap (Bagley et al. 1996; Baumgard and Johnson 1996).

With the 1991 engine, the catalyst reduced the total particulate mass emitted by 25% to 50% compared with the mass emitted by the same engine without the oxidative catalytic converter, but had no effect on the number or size of the particles. The mass reduction by the oxidative catalytic converter was attributed to the decrease in particle-associated organic compounds.

When the 1988 engine without the trap and the 1991 engine without the catalytic converter were compared with each other, the total volume of particles from the 1991 engine was 78% to 85% lower than that from the 1988 engine; however, the 1991 engine generated more nuclei-mode particles (defined as smaller than 0.075 μm ; see Figure 4), thus shifting the particle number-weighted size distribution toward more ultrafine particles. Johnson attributed this finding to different pressures in the fuel injection systems in the two engines, and to the decrease in hydrocarbon emissions from the 1991 engine. A size distribution similar to that observed with the 1991 engine also was observed with a 1995 engine. Figure 4 shows the number-weighted size distribution for particles emitted from the three engines.

When comparing the particle number concentrations from the Johnson and Kittelson studies, several observations can be made. Whereas Johnson found ultrafine particles in emissions from 1991- and 1995-specification diesel engines at much higher number concentrations than he had found with an older engine design, Kittelson did not observe the same difference in particle number concentrations in the engines he studied. In fact, Kittelson reported that the particle number concentrations from a 1995-specification Perkins medium-duty engine were about one order of magnitude lower than number concentrations from older engine designs he had studied, and about two orders of magnitude lower than the data reported by Johnson. Kittelson noted that although the Cummins and Perkins 1995 engines were designed to meet the same emission standards, they have very different combustion designs. In the Cummins engine, most of the fuel-air mixing is produced by a very high-pressure fuel spray injected into quiescent air. The Perkins engine provides mixing energy by a combination of high-pressure

fuel injection and significant air swirl. In addition, Kittelson noted that the exhaust dilution systems differed between the two laboratories. This comparison suggests that modern low-emission engines designed to meet the same particle mass emission standard may emit significantly different quantities of ultrafine particles. These tiny particles contribute little to measurements of particle mass, but dominate measurements of particle number.

Johnson's laboratory also has pursued research to characterize the organic compounds adsorbed onto diesel exhaust particles. He summarized the results of a round-robin interlaboratory effort to compare methods for analyzing PAHs, conducted by four internationally recognized institutes. Each laboratory analyzed one portion of a single sample of Standard Reference Material (SRM) 1640 (the SRM for diesel exhaust, as determined by the National Institute of Standards and Testing [NIST]), and measured the amounts of selected PAHs (fluoranthene, pyrene, benzo[*a*]pyrene, and benzo[*g,h,i*]perylene) contained in the sample. Analysis methods included gas chromatography and mass spectrometry as well as high-pressure liquid chromatography. The results showed wide variation among the laboratories, both above and below the certified NIST values. The data demonstrated the diffi-

culty of making accurate and precise measurements of PAH levels in diesel exhaust. Johnson thought that additional research is needed to accurately characterize the organic compounds associated with diesel exhaust particles, and to investigate the role of both particle-associated and vapor-phase organic compounds in human health effects.

Klaus-Peter Schindler (Volkswagen AG) described work conducted in light-duty diesel engines to understand how soot forms. Soot formation occurs above a certain fuel-to-air ratio and when the air-fuel mixture is cooled by the cylinder walls. The load at which an engine is tested affects the mass concentration and size distribution of the particles, in that higher (heavier) loads generate more and larger particles. Schindler stressed, as did other speakers, that the time of sampling the exhaust is critical because, during soot formation, the particle number concentration increases until the coagulation phase starts, at which point the particle mass tends to increase (and the particle number decreases). Like Johnson's experience with heavy-duty diesel engines, Schindler noted that the more modern light-duty diesel engines shift the mass-weighted particle size distribution toward smaller particles (between 0.02 μm and 1.4 μm with a peak at 0.04 μm) than the size distributions from older engines.

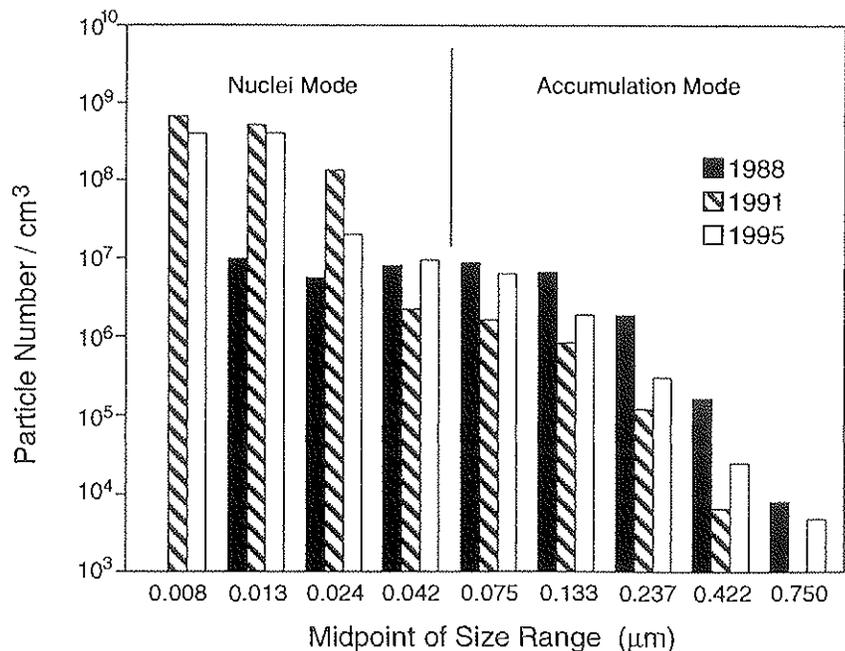


Figure 4. Comparison of particle size ranges from three different diesel engines operated at rated speed mode 9. (The data for the 1988 and 1991 engines are taken from Bagley et al. 1996 and Baumgard and Johnson 1996; the data for the 1995 engine are unpublished and reprinted with permission from J. Johnson.)

In contrast with Johnson, who had found virtually no difference in the particle size with and without the catalyst, Schindler observed that the size of particles from light-duty diesel engines tended to increase after the exhaust had passed through the catalyst. He thought the size increase might be due to an increase in volatile compounds, which tend to deposit onto the particles. Differences in light- and heavy-duty engine design, fuel composition (such as sulfur content), or sampling and operating procedures may explain the different results obtained by Johnson and Schindler.

With regard to control strategies, Schindler commented that it is better to prevent soot formation than to decrease the mass of soot by oxidation, which is accompanied by NO_x formation.

Matti Maricq (Ford Motor Company) described the work being conducted at the Ford Vehicle Emissions Research Laboratory to investigate new ways to examine the nature of vehicle emissions. The standard filter methods measure the total particulate mass integrated over particle size and duration of the driving cycle. The new techniques address the questions of "What sizes are the particles?" and "How do their emis-

sion levels vary over the transient driving cycle?" Future research will encompass investigations of the structure and chemical composition of particles.

Maricq noted that the principal instrument for particle size measurements has been the differential mobility particle sizer (DMPS) (for particles within an aerodynamic diameter range of 0.01 to 1 μm). This device separates charged particles according to their aerodynamic size using an electric field, and subsequently counts them using a condensation nucleus counter; thus, a number-weighted size distribution is measured by recording particle through-put versus electric potential. Because scanning the field requires a minute or more, this procedure is not appropriate for emission measurements during the transient driving cycle. To obtain transient measurements, the DMPS is set to transmit a fixed particle size, the emission rate of which is recorded throughout the drive cycle. The transient size distributions are subsequently built up from a number of fixed-particle-size emission measurements during successive drive cycles; this is demonstrated in Figure 5 for a gasoline vehicle driven during the cold-start phase of the FTP.

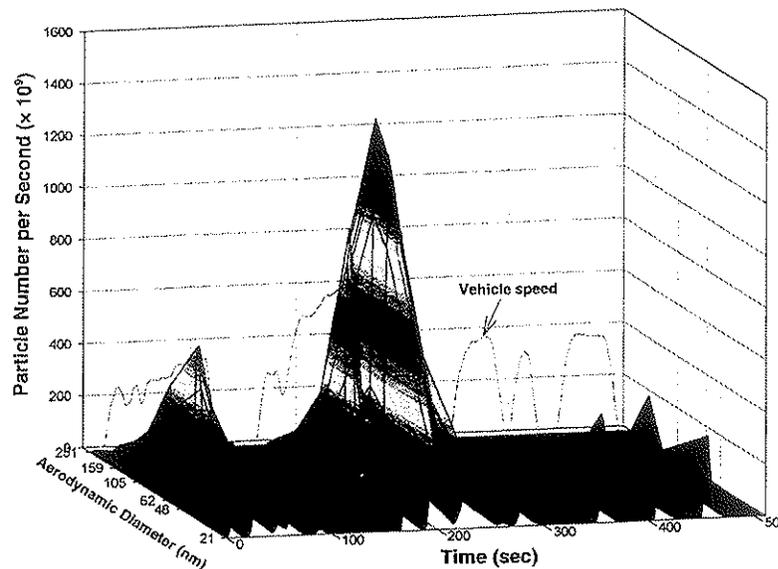


Figure 5. Size-resolved particle emissions from a gasoline engine for the cold-start phase of the FTP driving cycle. Particle emissions are measured as particle number per second, normalized by size. The vehicle speed (relative units) is given along the rear plane of the figure. (Reprinted with permission from M. Maricq.)

The Ford group is currently evaluating the usefulness of a new instrument for measuring particle sizes in the 0.04- to 10- μm range, the electrical low-pressure impactor (ELPI). With this apparatus, airborne particles are first charged and then passed through a cascade impactor, which segregates them into a number of size ranges (typically 12). Changes in the current deposited on each impactor stage yield the transient concentrations of particles of the corresponding aerodynamic size. The advantage of the ELPI over the DMPS is that particle concentrations at many sizes, rather than at a single size, are measured simultaneously; however, the ELPI cannot detect ultrafine particles with aerodynamic diameters less than 0.04 μm .

The principal results of the studies conducted by Maricq and collaborators are (a) the majority of particles emitted in tailpipe emissions from gasoline-fueled vehicles have aerodynamic diameters in the range of 20 to 200 nm, with a peak at about 50 nm; (b) particle emission is not uniform through time; rather, it occurs predominantly at a few discrete times during the driving cycle (see Figures 5 and 6); (c) particle emissions correlate strongly with vehicle acceleration and, to a lesser degree, with hydrocarbon and NO_x emissions; (d) particle emissions are higher for a cold start than for a hot start, indicating that catalyst temperature, or engine operating conditions, or both influence emission rates; and (e) particle mass can be estimated from the transient size distributions. This is accomplished as follows: the transient distributions are integrated over time to yield particle number versus size (for example, integrating the data in Figure 5 with respect to time yields the filled circles in Figure 6). The resulting number size distributions for each phase of the driving cycle are weighted by particle density and volume, and integrated with respect to size to yield the net mass for that phase. Maricq noted that the calculated masses (given in mg/mile in the Figure 6 legend) are in reasonable agreement (within about 50%) with the particle masses determined by weighing the filters.

Michael Hawkins (Ford Motor Company) presented some of the results of a large collaborative study characterizing particles

from gasoline and diesel vehicles and engines. The study (conducted at AEA Technology, Oxon, UK) was funded jointly by the United Kingdom Department of Transport, the Department of the Environment, and the Society of Motor Manufacturers and Traders. A related study assessed the sampling efficiency for particles and addressed critical design features of the dilution tunnel used for regulatory emissions testing. (The final reports for these studies are being prepared for publication.)

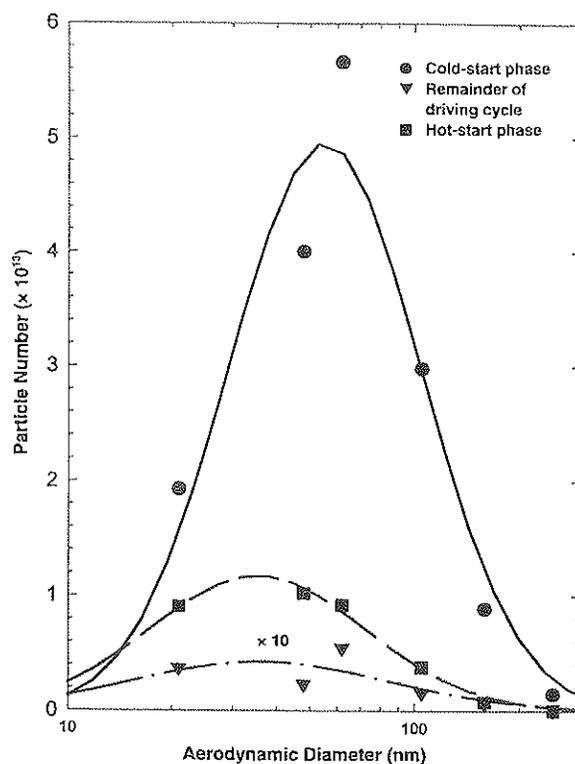


Figure 6. Time-integrated particle size distribution for the cold-start phase (bag 1), the remainder of the driving cycle (hot stabilized, bag 2), and the hot-start phase of the FTP (bag 3). For the cold-start phase, the total number of particles was 7.9×10^{13} and total mass emitted was 12 mg/mile. For the remainder of the driving cycle, the total number of particles was 9×10^{11} and total mass emitted was 0.15 mg/mile. For the hot-start phase, the total number of particles was 2.1×10^{13} and total mass emitted was 1.4 mg/mile. Note that the values for the remainder of the driving cycle were multiplied by 10 to make them visible on this graphic scale. (Reprinted with permission from M. Maricq.)

Before making actual measurements, two expert groups reviewed the literature and identified procedures for measuring particulate size and composition. The results showed that the scanning mobility particle sizing (SMPS) technique was reliable for measuring the size distribution of submicron ($< 1 \mu\text{m}$) particles. Instruments for studying mass concentrations of larger particle sizes ($> 1 \mu\text{m}$) require further investigation to overcome problems such as low collection efficiency and particulate charging. Compositional analysis techniques varied with respect to the repeatability of the results and require further validation. Evaluating the dilution tunnel design identified two key areas for improvement: conducting raw exhaust into the tunnel, and sampling dilute exhaust from the tunnel. The current design of the dilution tunnel produces low collection efficiency for particles larger than $2 \mu\text{m}$ in size; this may not be critical, however, because emissions are dominated by smaller-sized particles.

In the main study, nine light- and heavy-duty vehicles and engines were tested under steady-state and transient conditions. Within the particle size range from 16 to 270 nm, the SMPS measurement showed a single peak. The height and position of the peak varied with engine load, speed, and technology. The number-weighted size distribution of particles from various vehicles under one testing condition is shown in Figure 7.

Key findings from this work include:

- The test results from the limited range of vehicles and engines tested, although not necessarily representative of the UK vehicle fleet, suggested that modern light-duty vehicles, engines, fuels, and new particle trap technologies could substantially reduce the emission of submicron particles;
- Further research is needed to identify and validate techniques for correlating the regulatory measurement of particulate mass with the number-based and mass-based size distributions, and to refine and validate techniques for analyzing the composition of exhaust particles, especially those from low-emission vehicles and engines.

Hawkins concluded that this study has been of great value in demonstrating the suitability of some measuring techniques and in raising questions about others. It has provided valuable insight into the size distribution and composition of mobile-source particles, and has clearly indicated the need for further work. As a consequence, another test phase, which will examine the effects of different fuels, lubricants, and technologies, is being planned.

Motor Vehicles in Use

Glen Cass (California Institute of Technology) described ongoing research to characterize emissions from consumer-owned motor vehicles

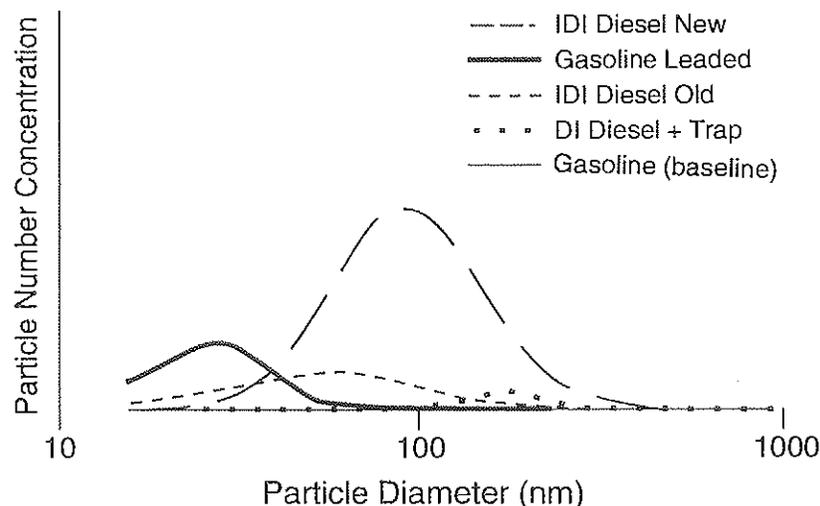


Figure 7. Size distribution of particles emitted from gasoline- and diesel-powered light-duty vehicles operated at a steady-state speed of 50 km/hr. (Reprinted with permission from M. Hawkins.)

and stationary sources, and to relate particle size distribution and chemical composition to the type of source. His sampling system dilutes effluents from different sources with purified air, allowing enough residence time for the gas-phase and particle-phase constituents of the exhaust to reach equilibrium at ambient temperature and pressure (Hildemann et al. 1989). Fine particulate matter ($\leq 2 \mu\text{m}$) emissions are measured gravimetrically. The particles also are sampled through a pair of multistage micro-orifice uniform deposit impactors (MOUDI), which aerodynamically separate particles by size. Their composition is determined using thermal evolution and combustion analysis for organic and elemental carbon, x-ray fluorescence or neutron activation for trace metals, ion chromatography and colorimetry for ionic species, and gas chromatography and mass spectrometry techniques for individual organic compounds. Fine and ultrafine particle size distributions are measured from the dilution tunnel using a scanning differential mobility analyzer combined with a condensation nucleus counter, a laser optical particle counter, or an electrical aerosol analyzer.

Two series of motor vehicle tests have been undertaken, one in the late 1980s (Hildemann et al. 1991) and one that is under way at present. In each case, approximately 15 in-use motor vehicles were sampled, including gasoline-powered vehicles with and without

catalysts and a few diesel trucks. The automobiles and light- and medium-duty trucks were tested using the FTP driving cycle, and the heavy-duty diesel trucks were tested on a less complex driving schedule. From these tests, Cass and coworkers saw that most of the particulate matter emitted from gasoline- and diesel-powered vehicles was largely carbonaceous, consisting of organic compounds adsorbed onto elemental carbon in varying proportions (Figure 8).

For the catalyst-equipped gasoline vehicles and the diesel vehicles in use in the late 1980s, the fine-particle mass distribution peaked at roughly $0.2 \mu\text{m}$, and the noncatalyst vehicles burning low-lead gasoline emitted particles over a much broader range of particle sizes (Figure 9).

Organic chemical analysis of vehicle exhaust samples revealed petroleum constituents in the family of the hopanes and steranes that can be used as molecular markers to trace the presence of vehicle exhaust aerosol in the Southern California atmosphere. Cass and coworkers developed a chemical mass balance model that uses molecular markers and the composition of ambient particle samples collected at four monitoring sites in Southern California to calculate the portions of the outdoor fine-particle concentrations that result from vehicle-related activities (Schauer et al. 1996). This model is

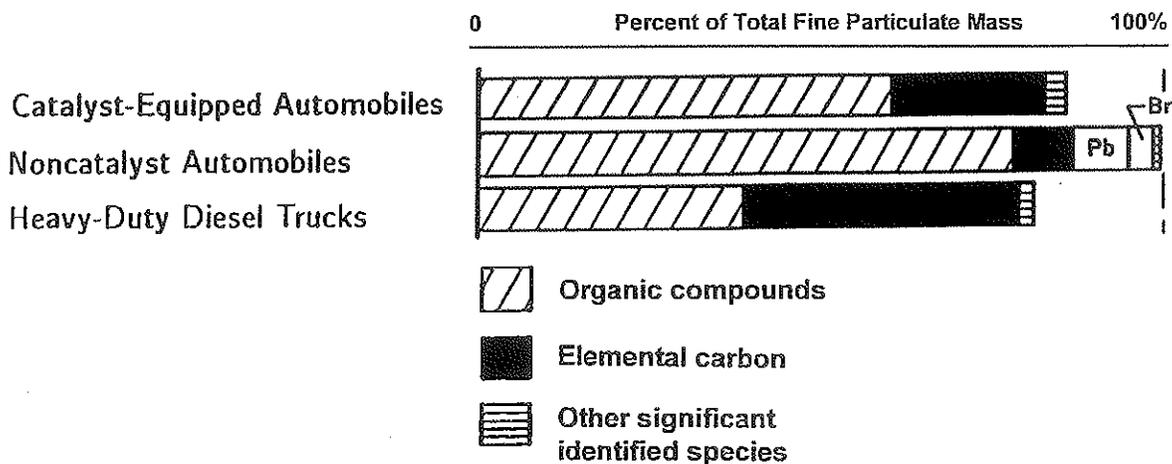


Figure 8. Average composition of particulate emissions from three types of engines. Bars show the average percentage of total mass for each compound or element from seven catalyst-equipped automobiles, six noncatalyst automobiles, and two heavy-duty diesel trucks. (Reprinted in part with permission from Environmental Science and Technology and G. Cass; copyright 1991 American Chemical Society.)

made possible by recent advances in source testing techniques that facilitate measuring the concentrations of hundreds of specific organic compounds in the emissions from various air pollution sources (Rogge et al. 1993a,b,c). Cass and coworkers (Schauer et al. 1991) found that, in the 1980s in downtown Los Angeles, the main sources of primary fine particles ($\leq 2 \mu\text{m}$) were diesel soot, paved road dust, gasoline-powered vehicle exhaust, food cooking operations, and wood smoke, with small but quantifiable contributions from sources such as cigarette smoke, natural gas combustion aerosols, tire-wear debris, and plant fragments.

In addition, Cass noted that motor vehicles add to atmospheric fine-particle concentrations through their contribution to secondary aerosols, which include sulfates, nitrates, and secondary organic compounds formed in part from gas-phase emissions from cars and trucks.

Steven Cadle (General Motors Corporation) presented a collaborative research program of particle characterization supported by General Motors, the Environmental Research Consortium (ERC; a consortium of auto and engine manufacturers), the Coordinating Research Council (CRC; an organization of auto and engine manufacturers and oil producers that funds research on vehicle performance, emissions, and resulting air quality), the EPA, and

the Desert Research Institute. Although the particulate emissions from light-duty gasoline-powered vehicles have decreased substantially over the years (from 200 mg/mile for vehicles using leaded gasoline in the early 1970s to the present rate of less than 5 mg/mile from properly functioning vehicles on the FTP driving cycle), Cadle noted that the current fleet of on-road vehicles contains a mix of both new and old vehicles in varying states of maintenance. To understand what this fleet contributes to the emissions inventory, the investigators examined emissions from a representative set of on-road vehicles in two separate studies (Cadle et al. 1997; Sagebiel et al. 1997). They classified vehicles as high-HC or high-CO emitters on the basis of remote sensor measurements, and tested them using a roadside chassis dynamometer and the Inspection/Maintenance IM240 driving cycle, which is designed to mimic the FTP but without cold- and hot-start emissions. These studies established that the in-use fleet contains vehicles emitting high levels of PM_{10} , all of which were at least 10 years old. Their average PM_{10} mass emission rates were more than 100 mg/mile in one study and 183 mg/mile in the other study. A few vehicles with visible smoke emissions averaged more than 300 mg/mile for PM_{10} . Analysis of the collected PM_{10} samples

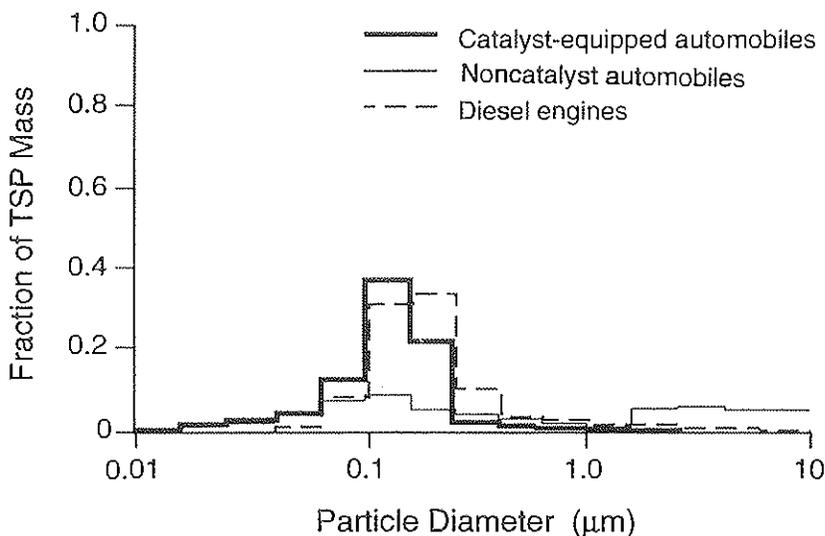


Figure 9. Relative size distribution of particulate emissions from three types of vehicles in use in the late 1980s. (Reprinted with permission from G. Cass.)

found that 77% of the material was organic and very little was sulfate. Several trace metals (corresponding to 3% of the total mass) were detected. The elemental composition of particles from these vehicles is shown in Figure 10.

Subsequently, the Center for Environmental Research and Technology of the University of California, Riverside, conducted a study of light-duty vehicles that emit smoke in Los Angeles sponsored by the South Coast Air Quality Management District and General Motors (Norbeck et al. 1996). Using the FTP driving cycle, this study found an average PM₁₀ emission rate of 408 mg/mile for gasoline-powered vehicles and a rate of approximately 367 mg/mile for diesel-powered vehicles. Correlation of emission rates between the FTP and the IM240 cycles was weak, primarily due to the importance of cold-start emissions in the FTP cycle. (MOUDI size distributions showed most of the mass was in particles smaller than 1 μm in diameter.) A field survey found that 1.1% to 1.7% of the in-use light-duty vehicles (including diesel) emitted some visible smoke, and researchers estimated that those vehicles contributed 24% to 35% of the total PM mass from the light-duty fleet.

The effects of ambient temperature and an oxygenated fuel (conventional gasoline with 10% ethanol) on PM emissions also were determined (using the FTP driving cycle), showing that PM increases significantly as temperature decreases and that oxygenated fuel reduces PM emissions (Mulawa et al. 1997).

The CRC is expanding these studies by funding three additional programs to examine PM emissions from in-use vehicles in Denver, Los Angeles, and San Antonio. All three studies will recruit a representative set of in-use vehicles for emissions testing on the FTP cycle. Measurements will include particle size distribution, particle count, and chemical characterization of the particles. The Denver study is being conducted in coordination with the Northern Front Range Air Quality (NFRAQ) study and will determine what portion of the total PM in Denver is contributed by gasoline-powered and light-duty diesel-powered vehicles that were manufactured between 1971 and 1996. The preliminary results from the first phase of the Denver program showed that much of the particle mass was 0.16 μm in size (determined using MOUDI), and that parti-

cle count varied substantially among test runs for the same vehicle.

In addition, the CRC is studying the production of secondary organic aerosols and the isotopic determination of contemporary carbon in the Denver atmospheric aerosol, and conducting a literature review of the contribution of mobile sources to PM₁₀ and PM_{2.5}.

William Pierson (Desert Research Institute) described the results of measuring emissions from in-use vehicles. For this study emissions were characterized in roadway tunnels because they offer substantial advantages for determining motor vehicle emission rates: Tunnels reflect real driving conditions, allow many vehicles to be sampled in a short time, and allow realistic mixing of emissions with ambient air in a relatively

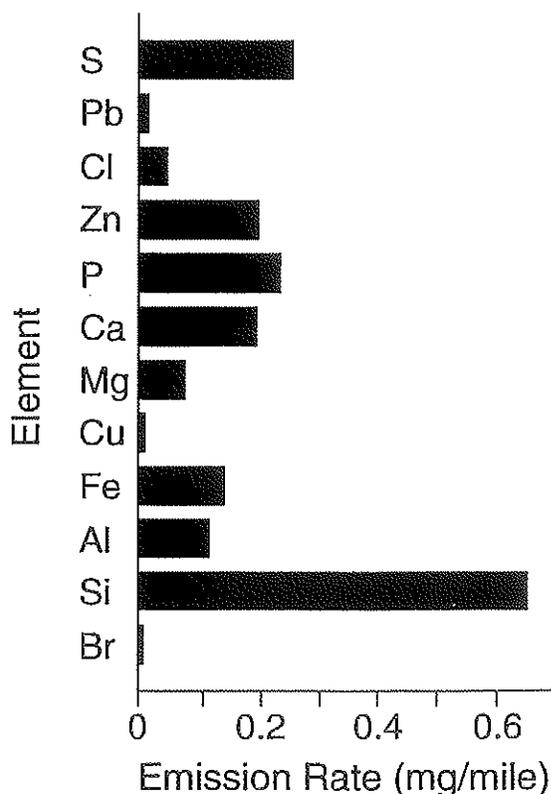


Figure 10. Average emission rates of elements in PM₁₀ from 63 prerepair vehicles identified as high-HC or high-CO emitters. (Reprinted with permission from S. Cadle.)

closed system; also, results from tunnel studies can be compared with emissions models. The disadvantages are that individual vehicles cannot be examined and that options of driving and test conditions are limited. Pierson described the procedure by which they calculated emission rates. In simple terms, the mass emission rate is obtained by dividing the total particle mass[¶] by the length of the tunnel and the number of vehicles passing through the tunnel for any given sampling period.

The analysis of the particulate matter collected in two tunnels on the Pennsylvania turnpike (from 1975 through 1979) showed that approximately 75% to 85% of the mass consisted of carbonaceous material (50% to 60% graphitic carbon plus 25% extractable organic material), which the investigators attributed chiefly to heavy-duty diesel engine exhaust (Pierson and Brachaczek 1983). The mass median aerodynamic (equivalent) diameter of the carbon particles was 0.15 μm (which is consistent with Cass' results from older in-use vehicles) (Pierson et al. 1983). Figure 11 shows the particle size distribution for certain constituents of the total mass of motor vehicle particles. Most metals (Sr, Ba, Fe, Ca, and Mn) were found in particles with a median aerodynamic diameter of 2.5 to 4 μm . Pb and Br were associated with particles smaller than 2 μm . More than half of the particles from tire-wear debris were smaller than 1 μm in size. (An estimated 1 μg of particles/ m^3 of air, or 2% to 7% of the total particle mass, was derived from tire debris.)

Pierson's tunnel studies showed that particulate mass emissions from heavy-duty diesel vehicles changed little between 1975 and 1981; but by 1993, emissions were lower than 1981 levels by a factor of two. In the same time span, CO emissions declined by a factor of five.

Atmospheric Aerosol Transformation

Spyros Pandis (Carnegie Mellon University) described the types of physicochemical transformations aerosol particles undergo after

[¶] Particle mass is calculated as [the product of (particle concentration) \times (volumetric airflow) at the outlet] minus [the product of (particle concentration) \times (volumetric airflow) at the inlet].

their emission into the atmosphere. These include coagulation with other particles (due to collisions), gas-to-particle conversion (due to condensation), processing by nonrain clouds, water absorption and growth, and removal by dry or wet deposition to the earth's surface. The half-life of particles in the atmosphere depends on their size: approximately 2 minutes for particles 5 nm in diameter and 20 minutes for particles 50 nm in diameter.

A significant fraction of ambient particulate matter is not emitted directly as particles, but rather is formed in the atmosphere by gas-to-particle conversion or by gas-phase compounds

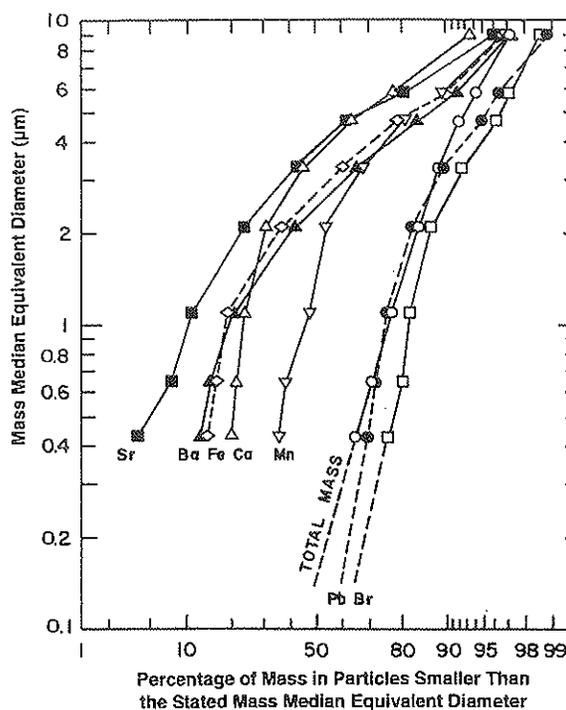


Figure 11. Log probability plot of particle size distribution of the vehicle aerosol and certain constituents; Allegheny Mountain Tunnel, August-September 1979. The mass median equivalent diameter approximates the median aerodynamic diameter. Size distribution of total mass is for the sum of all impactor runs (72.5% were gasoline-powered vehicles). Size distribution for Pb and Br are for traffic composition (90.3% gasoline-powered vehicles). Size distributions for Sr, Ba, Fe, Ca, and Mn are for traffic composition (35.3% gasoline-powered vehicles). (Reprinted with permission from W. Pierson and Elsevier Press, Inc., as published in Pierson and Brachaczek 1983. Copyright 1983 by American Association for Aerosol Research.)

attaching to already existing particles. Sulfates, nitrates, ammonium, and organic aerosols can be formed by gas-to-particle conversion either homogeneously or heterogeneously. The homogeneous production pathway starts with the compound (HNO_3 , H_2SO_4 , NH_3 , or a low-volatility organic compound) being formed and emitted in the gas phase, and then being converted to the aerosol phase by condensation or dissolution. The heterogeneous production pathway requires that the aerosol precursors (e.g., SO_2 , NO_x , HC) first be dissolved in the aerosol, or aqueous, phase (clouds, fogs, light rain, or wetted aerosols under conditions of high humidity), where they react to produce secondary aerosols. Substantial amounts of sulfate can be produced in the aqueous phase via a

variety of chemical reactions (involving O_2 , O_3 , OH^\bullet , or H_2O_2). According to Pandis, the aqueous-phase oxidation of SO_2 in clouds is the most important source of sulfate throughout the United States and on a global scale; preliminary data suggest that clouds also can be a source of nitrate (from NO_2 reacting with hydroxyl radicals or ozone). The atmospheric reactions leading to the production of sulfate and nitrate are schematically illustrated in Figures 12 and 13.

Pandis noted that during the last decade, significant progress has been made in understanding the processes that modify the size, composition, and distribution of emitted particles. However, lack of the same informa-

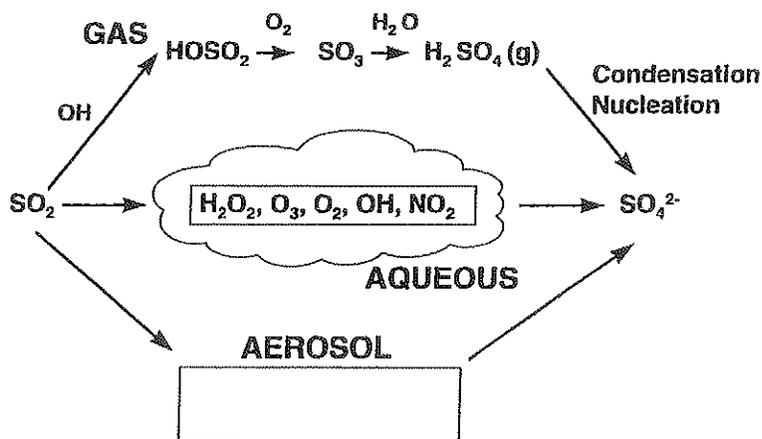


Figure 12. Schematic representation of atmospheric conversion of SO_2 to SO_4^{2-} . (Reprinted with permission from S. Pandis.)

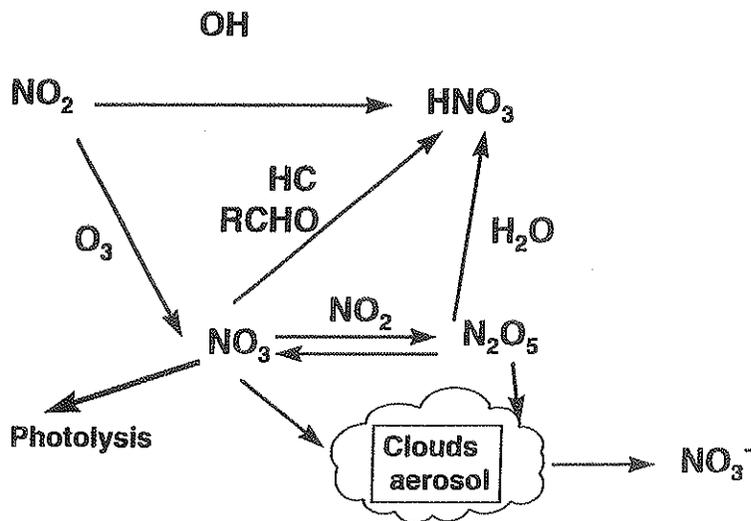


Figure 13. Schematic representation of atmospheric conversion of NO_2 to NO_3^- . (Reprinted with permission from S. Pandis.)

tion regarding gaseous precursors and the properties of emitted particles often inhibits further progress.

Generating Particles for Laboratory Studies

Yung-Sung Cheng (Lovelace Respiratory Research Institute) and Petros Koutrakis (Harvard School of Public Health) described some procedures for generating particles for laboratory studies of health effects. *Yung-Sung Cheng* focused on generating diesel exhaust and other insoluble particles. Because diesel exhaust is a complex mixture of soot particles, particle-associated organic compounds, and gases, special techniques are needed for generating and characterizing the exposure atmospheres. The engines are usually run in road-test cycles using a computer-controlled dynamometer to simulate driving in an urban area. The exhaust is diluted serially (in a dilution tunnel) to arrive at target concentrations in the animal exposure chambers. Dusts and dry powders are usually generated by resuspending them using a Wright dust feed, a fluidized bed, or an air jet mill.

Characterizing exposure atmospheres has included measuring the mass concentration and the size of diesel soot particles, organic compounds adsorbed onto particles, and gases. In a study conducted in the late 1980s using a light-duty engine, the mass-weighted size distribution of diesel soot particles had a mean diameter around 0.2 μm . The particle mass concentration is determined by weighing filter samples or by real-time measurements. The particle-associated compounds are usually characterized after extracting them with solvents from the filter samples. The gas-phase compounds (such as CO, CO₂, SO₂, NO_x, and total HC) are either collected in bags or are monitored with on-line real-time detectors in the exposure chamber. Cheng concluded that inhalation exposure systems that simulate engine exhaust require special designs, and stressed the need to apply appropriate characterization methods that address the complex nature of the engine exhaust.

Petros Koutrakis focused his presentation on the methods developed at the Harvard School of Public Health for generating concentrated ambient particles. He commented that the approaches used in the past for exposing animals to ambient particles (such as intratracheal instillation of resuspended particles) had limita-

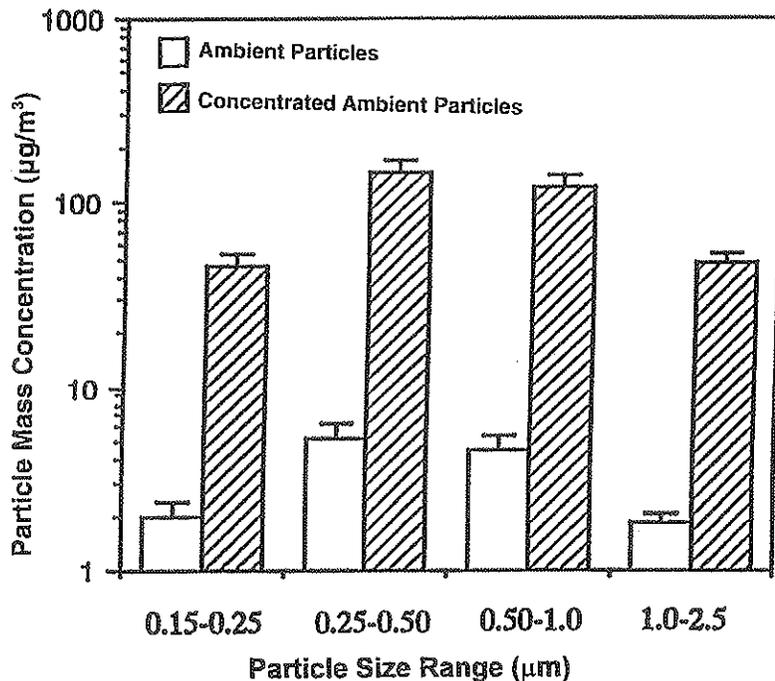


Figure 14. Mass concentration of ambient particles within a given size range compared with the mass concentration of concentrated particles (collected at the outlet of the concentrator) in the same size range. (Reprinted with permission from P. Koutrakis.)

tions, and the ability to conduct truly ambient exposures is an advantage. An effective particle concentrator needs to concentrate particles by a factor between 10 and 100, produce a low-pressure drop, ensure low distortion of the particle size distribution and composition, and adequately control humidity and temperature. In fulfilling these requirements, the Harvard concentrator aerodynamically separates particles from gases. It collects ambient particles between 0.15 and 2.5 μm in diameter and, by passing them through a series of virtual impactors, gradually increases the concentration approximately 25-fold. The concentrating power is constant over most of the size range, but is somewhat reduced (by about 18%) for particles between 0.15 and 0.25 μm (see Figure 14) (Sioutas et al. 1997). Further developments have enriched the particle concentration 70- to 80-fold. The particle concentrator is currently being used to generate particles for animal exposures. John Godleski (also of the Harvard School of Public Health) presented preliminary data from a small number of animals showing that dogs exposed to concentrated ambient particles display abnormal electrocardiographic profiles in some, but not all, experiments. Godleski interpreted these results as indicating that particle composition may play a role in particle-induced toxicity (Godleski et al. 1997).

Conclusion

Epidemiologic studies have suggested an association between exposure to low levels of ambient particles (10 μm or smaller) and both acute and long-term adverse health effects. Although the mechanisms by which particles cause harm are not yet understood, it is likely that size, shape, and composition of the particles may be important factors.

Motor vehicles are important direct contributors of fine particulate matter (soot), and indirect contributors because they emit oxides of nitrogen and sulfur, and hydrocarbons, all of which are precursors to nitrate, sulfate, and organic aerosols through atmospheric photochemical reactions. As a result of regulation, the mass of particles emitted from diesel and other engines has been substantially re-

duced. However, little attention has been paid to other parameters that may be more relevant than mass in causing health effects. The Health Effects Institute organized this workshop to bring together atmospheric, engine, and health effects researchers to discuss the needs for particle characterization, the current understanding of how particles are formed and how they behave, and the methods used to characterize them.

The workshop presenters described the chemical and physical processes that lead to combustion-generated particles, and the changes the particles undergo in the atmosphere; these affect both the size distribution and the composition of particles. They provided insights on the characteristics of particles generated by motor vehicles by describing laboratory, on-road, and tunnel measurements. Some (but not all) studies showed that the reduction in mass emissions from some modern diesel engines appears to have been accompanied by a large increase in the number of ultrafine particles emitted. Health effects researchers presented the problems they face in generating and characterizing particles for animal laboratory experiments. All of these studies highlighted the complexities involved with developing consistent protocols for characterizing particles, accounting for their atmospheric transformation, and resolving the problems encountered in generating and controlling laboratory animal exposures.

Issues and Research Needs for Particle Characterization

Historically, atmospheric particles have been quantified in terms of mass per unit of volume, either as TSP or, more recently, as PM_{10} . Adverse health effects have been associated with particles measured in these terms, and air quality standards and emission regulations (for both stationary and mobile sources) have been promulgated and complied with on the basis of these measurements. The epidemiologic evidence that associates both short-term and long-term exposure to particulate air pollution with increased morbidity and mortality suggests that

the particles of greatest concern are smaller than 2.5 μm in diameter. One recent epidemiologic study also suggests that respiratory effects are more closely correlated with ultrafine particles ($< 0.1 \mu\text{m}$ in diameter) than with fine particles (Peters et al. 1997). Other particle characteristics, such as chemical composition or surface area, also may play a role in determining health effects. Although a mechanistic understanding of how adverse health effects result from particle exposure is lacking, the importance of improved characterization of ambient particles, of emitted particles, and of particles used in laboratory exposures is certain. Assessing the toxicity of ambient particles and of their constituents, identifying important sources, and developing control strategies all would be greatly improved by characterizing particles in fuller detail and with more certain accuracy. Specifically:

1. Ambient particles must be characterized in terms of size distribution and other physical and chemical properties. These data will improve epidemiologic studies, provide a better assessment of the nature of the ambient particle air pollution problem, guide any needed mandates for regulation, and assist in identifying particle sources for reduction measures.
2. Personal exposure (both indoor and outdoor) must be characterized in terms of size distribution and other physical and chemical properties to assist in assessing dose and adverse health effects.
3. In real-world exposures, particles have been generated and then transformed through a variety of atmospheric processes. Therefore, particle size distributions and composition measured as they are emitted from the source may be different from the same characteristics measured a short distance away after undergoing the atmospheric processes in the ambient environment. Understanding these processes and the relationship between measurements at the source and measurements near the source is vital to assess the sources of primary particles and secondary particle precursors and relate them to eventual particle exposures and the health impacts that may follow.
4. Data on the size distribution, the chemical and physical properties related to the size of the particle, and particle sources are needed to: (a) assess the impact of emission controls and new technologies, (b) help in apportioning ambient particles to emission sources, and (c) assess the potential adverse health effects of primary particles. Instrumentation and other techniques designed to follow mobile-source particle emissions under transient conditions (particularly under driving conditions that include hard acceleration and speed changes, when most particles are formed) are needed to aid in developing control strategies.
5. The variety of techniques and instrumentation currently used for collecting particles, and determining size distributions and the chemical and physical properties need to be assessed for cross-correlations, precision, and sensitivity to sample conditioning and collection methods. The differences between methods that measure particle number and particle mass, and the appropriate conversion from one measurement to another need to be carefully described. Sample conditioning, collection, or in situ analyses, which mimic real-world conditions and avoid sampling artifacts, need to be developed.
6. Methods of generating, delivering, and characterizing particles for animal and human clinical studies need to be refined so that exposures relevant to real-world conditions can be produced.

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Abbreviations

Ba	barium	NH ₃	ammonia
Br	bromine	NIST	National Institute of Standards and Testing
Ca	calcium	NO _x	oxides of nitrogen
CO	carbon monoxide	NO ₂	nitrogen dioxide
CO ₂	carbon dioxide	NO ₃ ⁻	nitrate
CRC	Coordinating Research Council	O ₂	oxygen
DMPS	differential mobility particle sizer	O ₃	ozone
ELPI	electrical low-pressure impactor	OH [°]	hydroxyl radical
EPA	U.S. Environmental Protection Agency	PAHs	polycyclic aromatic hydrocarbons
ERC	Environmental Research Consortium	Pb	lead
Fe	iron	PM	particulate matter
FTP	Federal Test Procedure	PM _{2.5}	PM 2.5 μm or smaller in aerodynamic diameter
HC	hydrocarbon	PM ₁₀	PM 10 μm or smaller in aerodynamic diameter
HNO ₃	nitric acid	SMPS	scanning mobility particle sizing
H ₂ O ₂	hydrogen peroxide	SO ₂	sulfur dioxide
H ₂ SO ₄	sulfuric acid	SO ₄ ²⁻	sulfate
Mn	manganese	Sr	strontium
MOUDI	micro-orifice uniform deposit impactors	SRM	standard reference material
NAAQS	National Ambient Air Quality Standard	TSP	total suspended particulates

WORKSHOP AGENDA**Formation and Characterization of Particles:
Report of the 1996 HEI Workshop****TUESDAY, DECEMBER 3, 1996**

Welcome and Introduction *Robert Sawyer*
(Workshop Chairperson), University of California Berkeley

Current Understanding of Health Effects of Particles *Joe Mauderly*, Lovelace Respiratory Research Institute

Characteristics of Particles as Determinants of Dose or Effects *Günter Oberdörster*, University of Rochester

Fundamentals of Particle Formation in Combustion *Jack Howard*, Massachusetts Institute of Technology

Particle Formation from Engines and Impact of Design Features on Particle Formation *Gary Hunter*, Cummins Engine Company

The EPA Particle Emission Testing Protocol *Joseph Somers and Chris Lindhjem*, U.S. Environmental Protection Agency

Characterization of Diesel Particles *John Johnson*, Michigan Technological University

Characterization of Particulate Matter and Vapor-Phase Organic Emissions from Motor Vehicle Exhaust *Glen Cass*, California Institute of Technology

Engine Exhaust Particles: From the Cylinder to the Nose *David Kittelson*, University of Minnesota

Characterization of Particulate Matter from Gasoline Vehicles *Matty Maricq*, Ford Motor Company

Growth and Structure of Particles from Diesel Passenger Cars *Klaus-Peter Schindler*, Volkswagen AG

WEDNESDAY, DECEMBER 4, 1996

The CRC and Auto-Oil Research Program Relative to Particle Characterization: Results and Future Plans *Steven Cadle*, General Motors Corporation

A UK Particulate Emission Study *Michael Hawkins*, Ford Motor Company, UK

Alternative Ways to Make Exhaust Measurements: Tunnel Studies *William Pierson*, Desert Research Institute

Atmospheric Transformation: What Happens to Emitted Particles in the Atmosphere *Spyros Pandis*, Carnegie Mellon University

Generation and Characterization of Particles for Laboratory Experiments: Exposure to Resuspended Particles or Particles Emitted from an Engine *Yung-Sung Cheng*, Lovelace Respiratory Research Institute

Generation and Characterization of Particles for Laboratory Experiments: Exposure to Concentrated Ambient Particles *Petros Koutrakis*, Harvard School of Public Health

Workshop Summary *Robert Sawyer*, University of California, Berkeley

Workshop Conclusions: What We Know, What We Need to Know, and What Research Needs To Be Done Panel and Group Discussion Panelists: *Susan Bagley*, Michigan Technological University; *Nicholas Barsic*, John Deere; *Daniel Costa*, U.S. Environmental Protection Agency; and *Michael Spallek*, Volkswagen AG

WORKSHOP PARTICIPANTS

Praveen Amar
Northeast States for Coordinated Air Use
Management (NESCAUM)
129 Portland Street
Boston, MA 02114

Susan T. Bagley (Panelist)
Michigan Technological University
Department of Biological Sciences
1400 Townsend Drive
Houghton, MI 49931-1295

Alfred E. Barrington
U. S. Department of Transportation
Volpe Center
55 Broadway
Cambridge, MA 02142

Nicholas J. Barsic (Panelist)
John Deere
P. O. Box 8000
Waterloo, IA 50704-8000

Steven Cadle (Speaker)
Environmental Research Dept.
General Motors Corporation
30500 Mound Road
Warren, MI 48909-9055

Glen Cass (Speaker)
California Institute of Technology
Environmental Engineering Science Dept.
W. M. Keck Laboratories, Mail Code 138-78
Pasadena, CA 91125

Lung-Chi Chen
New York University Medical Center
Nelson Institute of Environmental Medicine
Long Meadow Road
Tuxedo, NY 10987

Yung-Sung Cheng (Speaker)
Lovelace Respiratory Research Institute
2425 Ridgcrest Drive, SE
Albuquerque, NM 87108-5127

Daniel Costa (Panelist)
U. S. Environmental Protection Agency
National Health and Environment Effects
Laboratory
Mail Drop 82
Research Triangle Park, NC 27711-2055

Maria Costantini
Health Effects Institute
955 Massachusetts Avenue
Cambridge, MA 02139

Kumkum Dilwali
Harvard School of Public Health
665 Huntington Avenue
Boston, MA 02115

John W. Fairbanks
U. S. Department of Energy
Office of Transportation Technology
1000 Independence Avenue, SW
Washington, DC 20585

Susan Field
Toyota Technical Center USA, Inc.
1588 Woodbridge Avenue
Ann Arbor, MI 48105

John E. Fisher
Detroit Diesel Corporation
13400 Outer Drive West
Detroit, MI 48239

Charles Freed
U. S. Environmental Protection Agency
Fuels and Energy Division
501 3rd Street, MC 6406J
Washington, DC 20005

John Godleski
Harvard School of Public Health
Department of Physiology
677 Huntington Avenue
Boston, MA 02115

Daniel S. Greenbaum
Health Effects Institute
955 Massachusetts Avenue
Cambridge, MA 02139

Michael Gurevich
U. S. Department of Energy
Office of Transportation Technology
Diesel Engines EE-33
1000 Independence Avenue, SW
Washington, DC 20585

Michael J. Hawkins (Speaker)
Brook Cottage, Camp Lane
Elberton
South Gloucestershire, BS12 3AQ
United Kingdom

Karl H. Hellman
U. S. Environmental Protection Agency
National Vehicle and Fuel Emissions
Lab/ATSD
2565 Plymouth Road
Ann Arbor, MI 48105

Simone Hochgreb
Massachusetts Institute of Technology
77 Massachusetts Avenue, 31-169
Cambridge, MA 02139

Jack B. Howard (Speaker)
Massachusetts Institute of Technology
Department of Chemical Engineering
77 Massachusetts Avenue, 66-454
Cambridge, MA 02139-4307

Gary Hunter (Speaker)
Cummins Engine Company, Inc.
P. O. Box 3005, M/C 50180
Columbus, IN 47203-3005

Bernard Jacobson
Health Effects Institute
955 Massachusetts Avenue
Cambridge, MA 02139

John Johnson (Speaker)
Michigan Technological University
Dept. of Mechanical Engineering and
Engineering Mechanics
Houghton, MI 49931

Meryl H. Karol
University of Pittsburgh
Center for Environmental and Occupational
Health Toxicology
260 Kappa Drive
Pittsburgh, PA 15238

David B. Kittelson (Speaker)
University of Minnesota
Department of Mechanical Engineering
111 Church Street, SE
Minneapolis, MN 55455-0150

Petros Koutrakis (Speaker)
Harvard School of Public Health
Environmental Exposure Assessment and
Engineering Program
665 Huntington Avenue
Bldg 1, Room G7
Boston, MA 02115-

Karl Loos
Shell Oil Company
P. O. Box 1380
Houston, TX 77001

Matti Maricq (Speaker)
Ford Motor Company
Scientific Research Laboratory
P.O. Box 2053, MD 3083
Dearborn, MI 48121

Joe L. Mauderly (Speaker)
Lovelace Respiratory Research Institute
2425 Ridgecrest Drive, SE
Albuquerque, NM 87108-5127

Kathleen Nauss
Health Effects Institute
955 Massachusetts Avenue
Cambridge, MA 02139

Günter Oberdörster (Speaker)
University of Rochester
Department of Environmental Medicine
575 Elmwood Avenue, Box EHSC
Rochester, NY 14642

Robert O'Keefe
Health Effects Institute
955 Massachusetts Avenue
Cambridge, MA 02139

Spyros Pandis (Speaker)
Carnegie Mellon University
Department of Chemical Engineering
Pittsburgh, PA 15213-3890

William C. Passie
Caterpillar, Inc.
100 NE Adams Street
Peoria, IL 61629-7150

William R. Pierson (Speaker)
Desert Research Institute
5625 Fox Avenue
Reno, NV 89506-0220

C. W. Robinson
Sandia National Laboratories
P. O. Box 969
Livermore, CA 94550

Margaret Round
Northeast States for Coordinated Air Use
Management (NESCAUM)
129 Portland Street
Boston, MA 02114

Robert F. Sawyer (Chairperson)
University of California, Berkeley
Department of Mechanical Engineering
72 Hesse Hall
Berkeley, CA 94720-1740

Klaus-Peter Schindler (Speaker)
Volkswagen AG
Wolfburg, Germany D-38436

Jamie Schauer
California Institute of Technology
391 S. Holliston, Kech 138-78
Pasadena, CA 91106

Warren Slodowske
Navistar
10400 West North Avenue
Melrose, IL 60160

Joseph H. Somers (Speaker)
U. S. Environmental Protection Agency
Assessment and Modeling Division
2565 Plymouth Road
Ann Arbor, MI 48105

Michael Spallek (Panelist)
Environmental Medicine
VDA/Volkswagen AG
P. O. 1774
Wolfsburg, Germany D-38436

Jane Warren
Health Effects Institute
955 Massachusetts Avenue
Cambridge, MA 02139

Tad Wysor
U. S. Environmental Protection Agency
Engine Program and Compliance Division
2565 Plymouth Road
Ann Arbor, MI 48105

Roy B. Zweidinger
U. S. Environmental Protection Agency
Office of Research and Development
MD-47
Research Triangle Park, NC 27711

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17	Studies on the Metabolism and Biological Effects of Nitropyrene and Related Nitro-polycyclic Aromatic Compounds in Diploid Human Fibroblasts	V.M. Maher	1988
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