# Characterization of Nanometer and Ultrafine Diesel Aerosols in the Underground Mining Environment

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Abstract

Despite extensive research efforts conducted in the past decades, occupational health risks associated with exposure to nano and ultrafine aerosols emitted by diesel power equipment are still not completely understood. The complexity of physical and chemical properties of diesel aerosols, constantly changing with the implementation of advanced diesel emissions control technologies, make this task rather challenging. The objective of this paper is to identify and characterize nanometer and ultrafine aerosols emitted by diesel engines in the underground environment and evaluate the effects of selected contemporary control technologies on physical properties, chemical composition, and in-vitro toxicology of diesel aerosols. The physical and chemical properties of the nanometer and ultrafine diesel aerosols are to be characterized through a test series in the NIOSH Lake Lynn Laboratory experimental mine. The crucial part of the study has been development of a facility that allows researchers to generate field results with precision and accuracy characteristics of a laboratory environment. The knowledge obtained from this study should strengthen our understanding of the health implications related to exposure to diesel particulate matter and aid in assessing the potential of various control technologies for reducing this exposure.

## Introduction

In recent years, health effects associated with exposure to diesel particulate matter (DPM) and other combustion-generated nanometer and ultrafine aerosols received substantial attention globally from public, academia, and government sources. Pope and coauthors (2002) established that long-term exposure to combustion-related fine particulate pollution is an important risk factor for cardiopulmonary and lung cancer mortality. Donaldson and Stone (2003) concluded that there is good toxicological evidence that ultrafine particles cause inflammation in the lungs, even when composed of relatively low toxicity material. There is growing evidence suggesting that particle number, surface area, size, or perhaps some associated structural properties may affect nanoparticle toxicity, in comparison with larger respirable particles of the same composition (Donaldson and Stone. 2003). In general, occupational health risks associated with exposure to nano and ultrafine aerosols are not yet clearly understood.

Diesel particulate matter (DPM) is a common term describing a complex mixture of solid and liquid aerosols emitted by diesel engines. Size distribution and chemical composition vary widely with a number of engine and aftertreatment parameters. The primary constituents of DPM are elemental carbon (EC), numerous organic carbon species (including several that are known carcinogens), sulfates, and transitional metals. A large portion of these aerosols, primarily generated due to incomplete combustion in diesel engines, ideally falls into the nanometer ($D_{50}$< 50 nm) and ultrafine ($D_{50}$<100 nm) size ranges (Kittelson 1998). Typically, ultrafine and nanometer aerosols emitted by diesel engines contribute between 1 and 20% of total DPM mass but comprise more than 90% of the total particle number and surface area.

Recent U.S. surveys revealed that, of all occupations, underground metal and nonmetal miners are exposed to the highest concentrations of diesel aerosols. Total carbon concentrations in underground metal mines were found to be as high as 3300 $\mu g/m^3$ (Cash and Baughman 2005). In January 2001, the U.S. Mine Safety and Health Administration (MSHA) promulgated rule 30

CFR 57.5060, which limited exposures of underground metal and nonmetal miners to DPM. The interim and final exposure limits are based on the feasibility of implementing various control strategies and technologies, rather than on established health effects of DPM. These limits are based on total DPM and EC mass concentrations. Mass-based exposure assessments are not always predictive of disease risk; in some cases respirable particle surface area and detailed surface compositional or morphological properties better correlate with toxicity or offer an explanation of seeming anomalies in epidemiological findings of disease risk (Wallace et al., 1990). Recent results (Donaldson et al. 2000, Tran et al. 2000, Oberdörster et al. 2000 and 2004, Englert 2004,) emphasize the importance of complementing mass-based monitoring exposure to nanometer and ultrafine aerosols with measurements of aerosol size, number, and surface area to better assess the adverse health impact of ultrafine aerosols.

Since the introduction of 30 CFR 57.5060, the U.S. underground mining community has been working on identifying and implementing technically and economically feasible strategies and technologies to curtail emissions from existing and new diesel-powered vehicles and reducing miners' exposures to DPM. Some tools available to control DPM emissions are the replacement of older diesel engines with cleaner powerplants, more efficient mine ventilation, advances in diesel engine maintenance, and the implementation of various diesel emission control methods.

As a result of the high demand for aftertreatment systems, a number of new emission control technologies have emerged to reduce diesel emissions from on- and off-road vehicles. Several studies (McGinn et al. 2002, Bugarski et al. 2006a and b) have shown that DPM concentrations can be substantially reduced by using modern engines, reformulated fuels, and exhaust aftertreatment technologies. The health effects of nanometer and ultrafine aerosols with altered size and chemical composition remain to be established.

Studies (Maricq et al. 1999, Khalek et al 2000, Kittelson et al. 2005) determined that the total mass, size distribution, size-resolved chemical composition, and genotoxicity of diesel aerosols depend on engine parameters, aftertreatment methods, and aerosol interaction with the environment. Since a majority of nanometer particles emitted by a diesel engine are volatile (Vaaraslahti et al. 2004), parameters such as dilution ratio, temperature, humidity, aerosol concentrations, and residence time were found to strongly influence their formation and transformation (Shi and Harrison 1999, Khalek et al. 2000). Although a majority of the work on characterizing diesel aerosol is done in the laboratory, this evidence suggests that the best way to characterize them is to sample directly in either an occupational setting or other environments where the aerosols are formed and transformed.

**Objective**

Through a Nanotechnology Safety and Health Research Program at the National Institute for Occupational Safety and Health (NIOSH), researchers from the Pittsburgh Research Laboratory (PRL) began an extensive study that characterizes the physical, chemical, and toxicological properties of diesel aerosols in an occupational setting. The specific objectives of the project are:

- Describing nano and ultrafine particles emitted in work environment by typical light- and heavy-duty diesel engines;

- Assessing the effects of selected control technologies on nanometer and ultrafine aerosol concentrations and their genotoxicity in occupational settings;
- Studying the effects of the aerosol aging process on diesel aerosol properties;
- Evaluating currently available instrumentation and methods for monitoring worker exposure to diesel aerosols
- Investigating the potential for establishing a new metric for monitoring worker exposure to DPM.

**Methodology**

Previous studies, conducted in operating underground metal mines (Bugarski et al. 2006 a, b), suffer from logistic and technical difficulties that prevent conducting detailed long-term studies on the characterization of DPM. Therefore, it was necessary to develop a facility capable of generating field results with precision and accuracy characteristics of a laboratory environment. The result of these efforts is the NIOSH Diesel Laboratory.

*NIOSH Diesel Laboratory*

The NIOSH Diesel Laboratory has integrated a transportable dynamometer into the NIOSH Lake Lynn Laboratory (LLL) experimental mine (Figure 1). LLL is an established underground limestone mine situated in Fairchance, Pennsylvania, about 97 km (60 miles) southeast of Pittsburgh, PA, and 16 km (10 miles) northeast of Morgantown, WV (Tribsch and Sapko 1990).

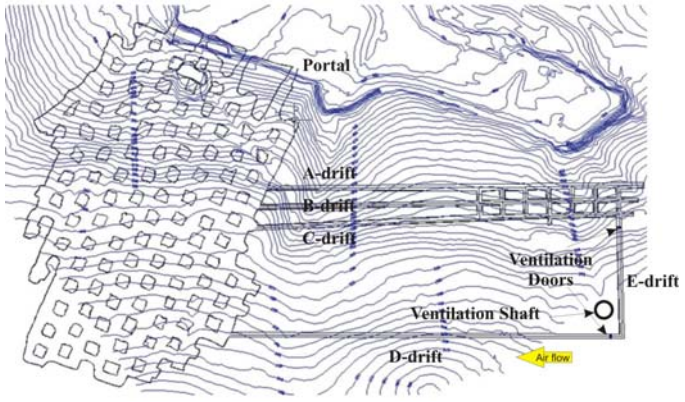


Figure 1. NIOSH Lake Lynn Laboratory Experimental Mine

The NIOSH Diesel Laboratory is located in the D-drift. This drift is approximately 530 m (1750 ft) long, 6 m (20 ft) wide, and 2 m (7 ft) high. A schematic layout of the laboratory is shown in Figure 2. The major components are engine/dynamometer systems, three sampling and measurement stations, and a ventilation measurement and control system.

*Dynamometer/Engine Systems*

Two dynamometer/engine systems are built around two water-cooled eddy-current dynamometers; a 150 kW (201 bhp) Model SE150 and a 400kW (536 bhp) Model SE 400 (SAJ, Pune, India). The 150 kW-dynamometer is coupled to a naturally aspirated, mechanically

controlled Isuzu C240 diesel engine (Figure 3). The Isuzu C240 is one of the most popular engines in U.S. underground coal mines and is primarily used to power light-duty vehicles. The

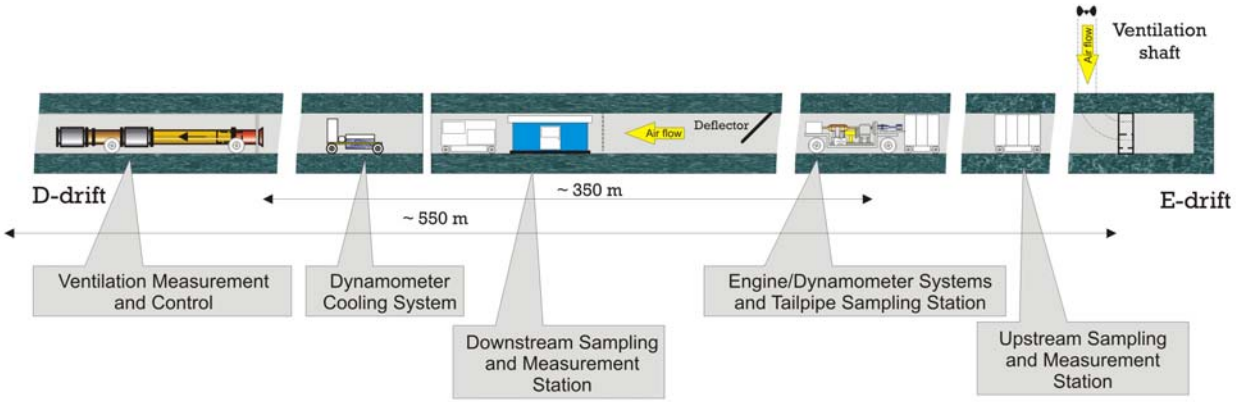


Figure 2. NIOSH Diesel Laboratory

Figure 3. 150 kW dynamometer/Isuzu C240 system

SE400 dynamometer is coupled to an electronically-controlled turbocharged Mercedes Benz OM 904 3MT32 engine.

*Measurement and Sampling Stations*

Ambient concentrations of selected gases and aerosols are sampled in the mine air upstream and downstream of the dynamometer. The upstream ambient monitoring and sampling station is located approximately 60 m (197 ft) inby the dynamometer. This station is designed to measure background aerosol concentrations. The downstream ambient monitoring and sampling station is located about 60 m (197 ft) downstream of the dynamometer. This station is designed to sample concentrations of aerosols, carbon monoxide (CO), carbon dioxide ($CO_2$), nitric oxide (NO), nitrogen dioxide ($NO_2$), sulfur dioxide ($SO_2$), and total hydrocarbons (HC). At both locations ambient concentrations of total particulate matter with aerodynamic diameters under 0.8 μm are monitored using a Series 1400a tapered element oscillating microbalance (TEOM) (Thermo Electron Corp., East Greenbush, NY).

Three sampling trains collect triplicate background DPM samples for carbon, ion, and metal analysis at both upstream and downstream locations. To minimize the effects of vertical and horizontal stratification, each sample is obtained at five different locations on the sampling grid (Figure 4). Five identical preclassifiers, each consisting of a 10-mm Dorr-Oliver cyclone followed by a single stage diesel impactor, are used to remove coarse aerosol. A flow rate of approximately 2.2 l/min (0.1 cfm) is maintained through each preclassifier. At this flow rate only particles with geometric mean diameters smaller then 0.75 μm are deposited on the filters (Olson 2001). The five preclassifiers are attached to a symmetrical plenum that distributes a total flow rate of about 11.0 l/min (0.4 cfm) uniformly to the five streams. Each preclassifier assembly is connected to the plenum chamber by a 0.9 m (3 ft) long section of conductive tubing. The plenum outlet is directly connected to either a 25 mm stainless steel filter holder or a 37 mm cassette. Sampling train airflow is maintained with a Model 1023 rotary vane pump (Gast Manufacturing Inc., Benton Harbor, MI).

Tissue quartz fiber (TQF) filters (Pall Corporation, Ann Arbor, MI) are used for collecting samples for carbon analysis. Teflon coated glass fiber (TCGF) filters (Pall Corporation) and 0.8 μm polyvinyl chloride (PVC) filters (Millipore Corp., Billerica, MA) collect DPM for ion and metal analysis. TCGF and PVC filters are conditioned in an environmental chamber/weighing room at 20 °C and 50% relative humidity for at least 8 hours, then pre- and post-weighed in a weighing room. When weighed, each filter is placed on an NRD model 2U500 anti static strip (NRD LLC, Grand Island, NY) and finally onto a Mettler Model MT5 balance (Mettler-Toledo, Inc., Columbus, OH).

Figure 4. Downstream sampling station

Downstream, aerosol size distributions and concentrations are measured using a Model 3936 Scanning Mobility Particle Sizer (SMPS) (TSI, St. Paul MN), a Model 3091 Fast Mobility Particle Sizer (FMPS) (TSI), and a Model DAS 3100 Electrical Low Pressure Impactor (ELPI), (Dekati, Finland). Samples for genotoxicity analysis are collected using a custom-designed system. Two sampling trains collect samples on two 90mm TCGF filters. Coarse particles (larger then 1 μm) are removed from the air stream by a URG-200-30EH cyclone (URG, Chapel Hill, NC). Sierra Model XXX mass flow controllers (Sierra Instruments, Inc., Monterey, CA) maintain a 50 l/min (1.8 cfm) flow rate in each sampling stream. A Gast Model 1023 rotary vane pump provides flow for both streams.

Downstream NO and $NO_2$ concentrations are quantified with a Model CLD 700 AL chemiluminescence analyzer (Eco Physics, Duernten, Switzerland). A Model 300 heated flame ionization detector (HFID) (California Analytical Instruments, Inc., Orange, CA) measures gaseous-phase hydrocarbons. A Model 1312 photoacoustic multi-gas monitor (INNOVA AirTech Instruments, A/S, Ballerup, Denmark) monitors CO, $CO_2$, and $SO_2$. Gases are recorded by a Model 34970A data acquisition system (Agilent Technologies, Inc., Santa Clara, CA).

The tailpipe monitoring station detects and records CO and $CO_2$ concentrations in the engine exhaust. A Model 602 non-dispersive infrared (NDIR) analyzer (California Analytical Instruments, Inc.) is used to measure CO and $CO_2$. Data from the analog outputs of this instrument are collected using a data acquisition system (Logic Beach Inc., La Mesa, CA).

Samples collected on TQF filters are analyzed for EC content at the PRL analytical laboratory using the NIOSH Analytical Method 5040 (NIOSH 1999, Birch and Cary 1996, Bugarski 2006). Samples collected on TCGF filters are analyzed by Clayton Laboratories (Clayton Group Services, Novi, MI) for various ions following NIOSH Method 6004 (NIOSH 1994). The same laboratory analyzes samples collected on PVC filters for metals following NIOSH Method 7300 (NIOSH 2003). Samples collected on 90 mm TCGF filters are assayed for standard in-vitro bacterial and mammalian cell genotoxicity by the NIOSH-Health Effects Laboratory Division-Molecular Biophysics Team, Morgantown, WV.

*Ventilation Measurement and Control*

Fresh ventilation air is supplied from the ventilation shaft located in E-drift, situated immediately upwind and normal to D-drift. Air quantities supplied to D-drift can be regulated with sliding air doors positioned at the upstream end of D-drift and downstream end of E-drift. The total flow through the D-drift is measured using a subsonic Venturi meter (Primary Flow Signal, Inc., Tulsa, OK). The engine-specific ventilation flow rate is maintained by a Series 2000 Model 48-26-1770 Axivane fan (Joy Technologies, Inc., New Philadelphia, OH).

**Preliminary Results**

Tests were conducted to establish sampling procedures. The objective of these was important to determine specific locations at the downstream sampling grid. SMPS downstream aerosol concentrations showed pronounced vertical stratification (Figure 5). These measurements indicated that the Isuzu C240 engine exhaust plume was strongly influenced by a strong vertical temperature gradient. Vertical stratification was minimized using a deflector curtain, installed 30.5 m (100 ft) downstream of the tailpipe. With the deflector curtain in position, results show minimal vertical and horizontal stratification at the downstream grid location.

SMPS and $CO_2$ studies of exhaust plume propagation in the drift were conducted at various cross-sectional locations downstream of the tailpipe. Figure 6 average size distributions and concentrations of diesel aerosols illustrate the change in peak and total concentrations as well as physical properties of aerosols relative to distance from the tailpipe. For a given condition, most particle formation and transformation processes occur within the first 30 m (100 ft).

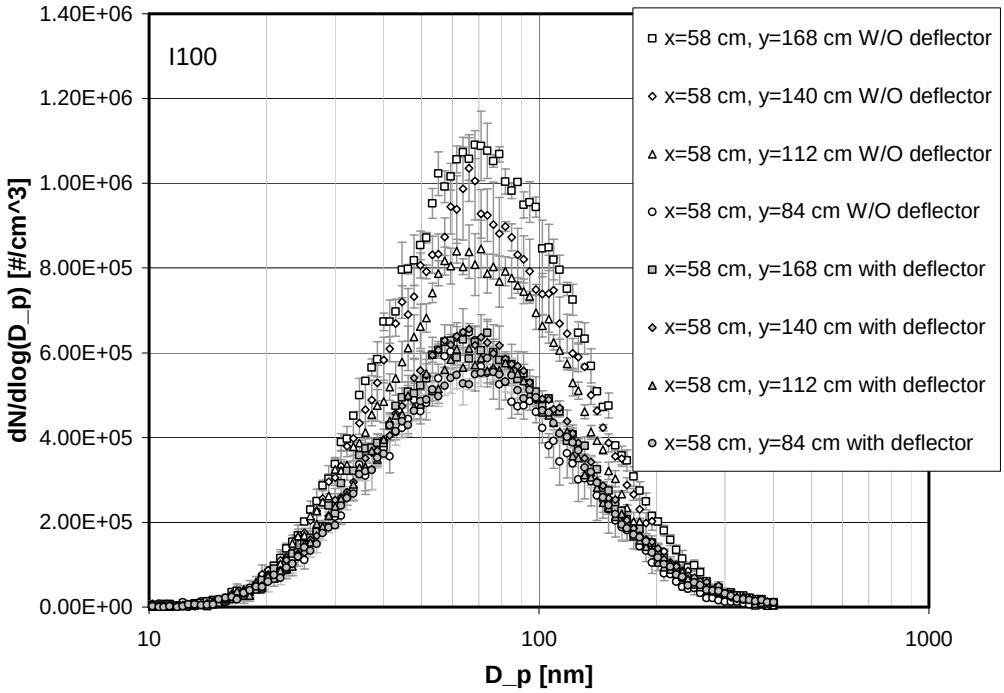


Figure 5. Diesel aerosol size distributions of Isuzu C240 engine emissions when operated at 2000 rpm and 107 Nm (79 lb-ft) measured 61 m (200 ft) downstream of the tailpipe with and without the deflector in place.

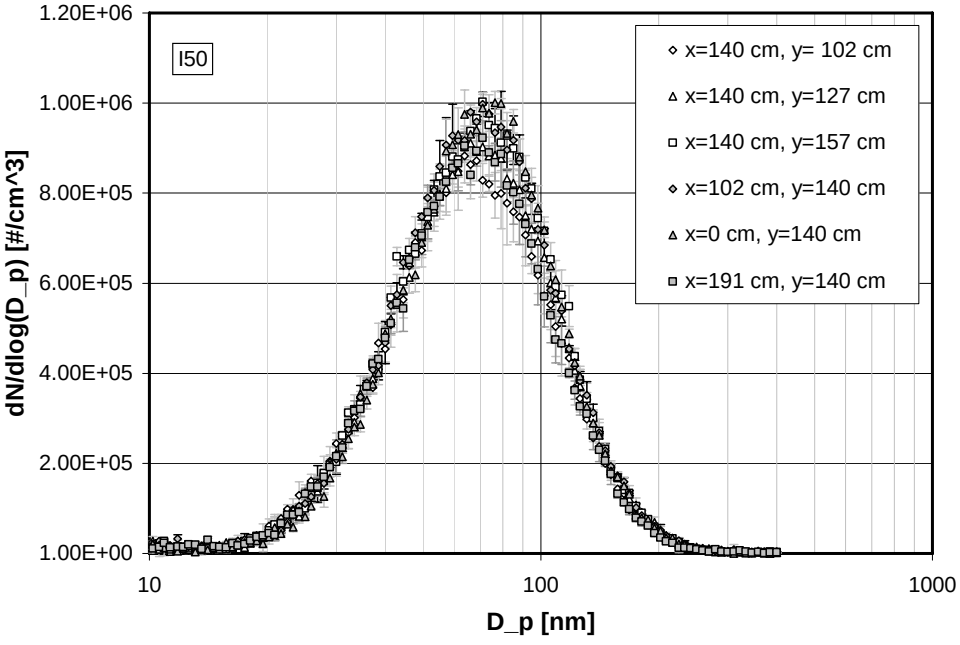


Figure 6. Diesel aerosol size distributions of Isuzu C240 engine emissions when operated at 2000 rpm and 36.6 Nm (27 lb-ft) at various locations 61 m (200 ft) downstream of the tailpipe

The NIOSH Diesel Laboratory enables diesel studies be conducted under field conditions with precision and accuracy characteristics of a laboratory environment. This approach should

minimize laboratory uncertainties and bridge the gap between inherently inaccurate real world field experiments and unrealistic laboratory investigations.

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