



## Underground Coal Mine Air Quality in Mines Using Disposable Diesel Exhaust Filter Control Devices

D. H. Carlson , J. H. Johnson , S. T. Bagley & L. D. Gratz

To cite this article: D. H. Carlson , J. H. Johnson , S. T. Bagley & L. D. Gratz (1996) Underground Coal Mine Air Quality in Mines Using Disposable Diesel Exhaust Filter Control Devices, Applied Occupational and Environmental Hygiene, 11:7, 703-716, DOI: [10.1080/1047322X.1996.10389960](https://doi.org/10.1080/1047322X.1996.10389960)

To link to this article: <https://doi.org/10.1080/1047322X.1996.10389960>



Published online: 24 Feb 2011.



Submit your article to this journal [↗](#)



Article views: 13



View related articles [↗](#)

# Underground Coal Mine Air Quality in Mines Using Disposable Diesel Exhaust Filter Control Devices

D.H. Carlson,<sup>A</sup> J.H. Johnson,<sup>B</sup> S.T. Bagley,<sup>C</sup> and L.D. Gratz<sup>B</sup>

<sup>A</sup>Department of Mining Engineering, <sup>B</sup>Department of Mechanical Engineering-Engineering Mechanics, and <sup>C</sup>Department of Biological Sciences, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931-1295

As part of a collaborative study with the U.S. Bureau of Mines, in-mine studies have been conducted to assess the effects of a low temperature disposable diesel exhaust filter. The mines have been designated as mines R and S in U.S. Bureau of Mines publications. Each mine operated three to four Jeffrey 4110 ramcar haulage vehicles in the test section. The ramcars were equipped with MWM D916-6 diesel engines, rated at 74.6 kW (100 hp), and were operated for 3 days with the disposable diesel exhaust filter and 2 days without in both mines. Average diesel particulate matter control efficiencies, as measured by samplers located on the coal haulage vehicle, were 80 percent in mine R and 76 percent in mine S. Diesel particulate matter average control efficiencies, as measured in the diesel engine tailpipe, were 52 percent for mine R (for two ramcar vehicles) and 86 percent for mine S (for four ramcar vehicles). The air quality index control efficiencies, as measured by samplers located on the coal haulage vehicle, were 48 percent in mine R and 51 percent in mine S. The exhaust quality index control efficiencies from tailpipe measurements were 45 percent for mine R and 63 percent for mine S. As measured by a high volume sampler in mine S, diesel particulate matter and associated organics and mutagenic activity were reduced approximately 50 percent with the use of the disposable diesel exhaust filter. Similar results were found with modified personal samplers in mine R. Little effect was found on relative removal of semivolatile organics. The disposable diesel exhaust filter resulted in about a 50 percent reduction in the most volatile polynuclear hydrocarbons; however, there appeared to be little effect on the less volatile polynuclear hydrocarbons. The disposable diesel exhaust filter appears to be very effective in reducing the levels of all the diesel exhaust particulate components, while having minor effects on the relative breakdown of the individual components of the particulate. CARLSON, D.H.; JOHNSON, J.H.; BAGLEY, S.T.; GRATZ, L.D.: UNDERGROUND COAL MINE AIR QUALITY IN MINES USING DISPOSABLE DIESEL EXHAUST FILTER CONTROL DEVICES. *APPL. OCCUP. ENVIRON. HYG.* 11(7):703-716; 1996.

The versatility and safety of diesel-powered coal haulage vehicles compared to electric equipment with trailing cables have resulted in increased acceptance of diesels by U.S. underground coal mines. Currently over 2200 diesel units are used in over 160 coal mines.

In recent years, diesel particulate matter (DPM) has become

the priority pollutant in efforts to control underground mine diesel emissions. This concern is justified by studies in underground mine areas using diesel-powered coal haulage vehicles, which have shown that respirable coal dust, as measured to evaluate compliance with federal standards, is almost always more than half DPM. In addition, the National Institute for Occupational Safety and Health (NIOSH) currently regards whole diesel exhaust to be "a potential occupational carcinogen."<sup>(1)</sup> About 90 percent of the DPM encompasses a size range from 0.0075 to 1.0  $\mu\text{m}$ .<sup>(2)</sup> DPM, therefore, is important in terms of potential health impacts due to the ability of particles to be inhaled and eventually trapped in the bronchial passages and alveoli of the lungs. The carcinogenic effect of DPM is now considered likely to be related to at least two DPM components: the solid carbon core and the organics adsorbed to solid carbon core which are known as the soluble organic fraction (SOF). The SOF and its components, such as polynuclear aromatic hydrocarbons (PAHs), have been shown to be mutagenic and carcinogenic.<sup>(3)</sup> The health significance of the diesel-derived organics has been more difficult to assess, although mutagenic and carcinogenic compounds and mutagenic activity have been detected in laboratory studies with diesel engines.<sup>(4,5)</sup>

The Mine Safety and Health Administration (MSHA) is considering adopting a DPM standard for a personal exposure limit (PEL) that will affect all underground operations using diesel equipment.<sup>(6)</sup> However, because the current federal method for monitoring compliance does not distinguish DPM from respirable coal dust, the mine ambient air DPM concentration is limited by the 2 mg/m<sup>3</sup> PEL-time-weighted average (TWA) respirable coal dust standard, minus any contained respirable coal dust and whatever reductions in this standard result from silica contained in the coal dust. For respirable coal dust (including DPM) containing greater than 5 percent free silica, the 0.1 mg/m<sup>3</sup> PEL-TWA respirable quartz standard must also be complied with; thus, for example, if the dust contains 10 percent quartz, the DPM plus respirable coal dust concentration would be limited to 1.0 mg/m<sup>3</sup>.

The effects of a low temperature disposable diesel exhaust filter (DDEF) on coal haulage vehicle diesel tailpipe emissions and the effects of the DDEF on the mine ambient air during production operations were studied in two U.S. underground coal mines (designated as mines R and S by the Bureau of Mines). The study was a joint effort by participating universities (Pennsylvania State University, University of Minnesota,

and Michigan Technological University) in the Generic Technology Center for Respirable Dust, the U.S. Department of the Interior, Bureau of Mines, and MSHA. The key objectives for this portion of the study were to:

1. determine the concentration of DPM, carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, and sulfur dioxide, and the air quality index (AQI) and exhaust quality index (EQI) in the coal mines using diesel-powered coal haulage vehicles;
2. determine the control efficiencies of the DDEF for DPM from mine ambient air and tailpipe measurements; and
3. evaluate the chemical and biological characteristics of the DPM and vapor phase organics with and without the DDEF by quantifying levels of selected key PAH and mutagenic activity.

## Methods

### Description of Diesel Equipment and Mines Studied

The studies were conducted in the continuous miner section of mines R and S. In both mines, the Jeffrey 4110 ramcar diesel trucks, referred to as ramcars, were used to haul coal from the continuous miner to the conveyor feeder breaker. Each mine produces highly volatile, bituminous coal, with production levels ranging from 272 to 604 metric tons/shift. Usually three ramcars, operating simultaneously in a section, perform the coal haulage operation, with one loading, one dumping, and one in transit. Seam heights ranged from 1.5 to 2.4 m. Mine R used continuous mining to develop longwall panels. Mine S was a room-and-pillar operation. Both of the mines used the control devices in the vehicle exhaust system downstream of the water bath scrubbers required by the federal regulations<sup>(7)</sup> to cool the exhaust prior to discharging it into the mine air. The ramcars in the test section were equipped with MWM D916-6 diesel engines, rated at 74.6 kW (100 hp).

The DDEF has been described elsewhere.<sup>(8)</sup> The Bureau of Mines and Donaldson Company, Inc., collaborated in the development and testing of the device for permissible diesel vehicles. The ramcars were operated in the mine section under study with and without the DDEF installed. Tests in mine S involved two work shifts of measurements without and three work shifts with the DDEF installed. In mine R, two work shifts each of control-off and control-on measurements were made. Diesel exhaust pollutant concentration measurements were made both in the mine ambient air and in the tailpipes of the individual coal haulage vehicles. The mine ambient air measurements involved placing portable samplers in at least two underground locations. One set of portable samplers was placed in a mine drift through which the coal haulage vehicles passed in hauling coal from a continuous miner to a conveyor feeder, and this was designated the downstream location. The other set was placed on one of the coal haulage vehicles in the section as near to the operator as possible, and this was designated as the vehicle location. The pollutant concentrations measured included DPM, carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, and sulfate.

Among the primary requirements for underground coal mine diesel use set by Title 30 of the Code of Federal Regulations<sup>(7)</sup> is the requirement that the exhaust temperature be

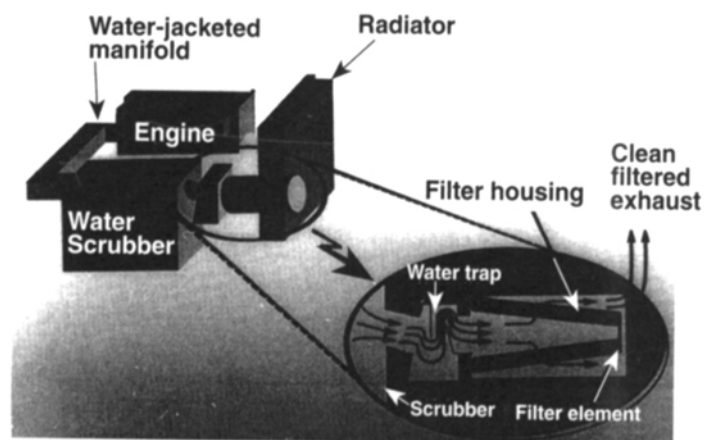


FIGURE 1. DDEF Illustrated. (Drawing by Bureau of Mines Twin Cities Research Center, Minneapolis, Minnesota.)

limited to 77°C. A water bath scrubber is used on the Jeffrey 4110 ramcars for the purpose of performing as both a flame arrestor and an exhaust cooler. The DDEF also requires that the exhaust be cooled or the media will burn, thereby destroying its capability to filter DPM from the exhaust and possibly creating an explosion hazard.

Figure 1 is a schematic showing how the DDEF was mounted on the Jeffrey ramcar underground mine coal haulage trucks used in these studies. As illustrated in Figure 1, the exhaust passes through a water scrubber, where it is cooled to a temperature of about 82°C, and then through a short section of exhaust pipe and into the pleated media filter through the larger open end. A seal on the large end of the filter presses against a flange on the end of the exhaust pipe. A seal on the opposite small end of the filter presses against the canister cover. To exit the filter, the exhaust must flow through the filter wall from the inside to the outside, which is open to the atmosphere.

The pleated media used in the DDEF is similar in appearance to pleated media used in automobile air filters. However, while a cylindrical automobile air filter is usually less than 4 cm high, the DDEF is conical and is 0.6 m long with a corresponding increase in surface area. Figure 2 is a photograph showing the Jeffrey ramcar with the DDEF filter located in the foreground ready for installation. The round filter canister cover is located on the upper right-hand side of the motor grillwork. The DDEF is installed in this canister located on the downstream end of the exhaust pipe.

### Mine Ambient Air Measurement Locations

The following mine ambient air sampling equipment and methods were used at the upstream, vehicle, and downstream locations: modified personal respirable dust samplers with dichotomous impactors for DPM; gas sampling bag and Fuji ZFP5 instrument for carbon dioxide; gas sampling bag and Ecolyzer 2600 instrument for carbon monoxide; and Palmes passive personal sampler for nitric oxide and nitrogen dioxide.

Measurements were made at up to four underground locations as selected in discussions by the joint study participants. The measurement locations using portable sampling devices included:

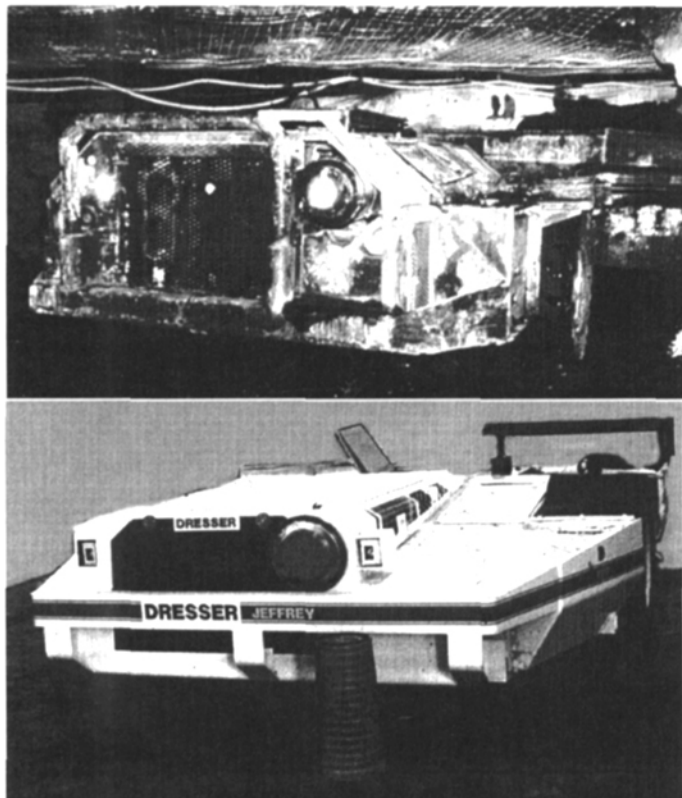


FIGURE 2. Photo of Jeffrey ramcar in mine S with DDEF in operation in mine (top) and ramcar with DDEF shown in front of ramcar (bottom).

1. an upstream location to determine the background concentrations which are subtracted from concentrations measured in the vicinity of the ramcars;
2. an on-vehicle location where instruments sampled air in the vicinity of the ramcar operator;
3. a downstream location along the route the ramcars travel while moving coal from the milling type continuous miner to the conveyor feeder breaker; and
4. the return location where air from the section under test was exhausted.

Each location was sampled over as large a portion of the 8-hour work shift as possible, typically 5 to 6 hours, thereby allowing time for setup and dismantling of the sampling equipment.

Measurements in the return location were made with the permissible portable samplers, but the data are not presented here because the return air was unusually high in coal dust and not typical of concentrations inhaled by miners. Thus, mining and ventilation systems are designed to direct uncaptured coal dust and diesel exhaust emissions, along with any methane gas released by mining coal, away from mine personnel and into the returns where personnel spend very little time. Larger, less portable instruments, such as the high volume samplers used to collect DPM for chemical and biological characterization studies and samplers used for other purposes by other team members, are not permissible and therefore could not be used in the returns due to the danger of methane and/or coal dust explosions.

Locations were selected for instrument placement based upon the known conveyor feeder location, predicted mining locations, travel routes, and air flow directions. Some difficulty in finding good locations for making representative diesel emission measurements is nearly always experienced in production mines as a result of on-the-spot changes in face ventilation and vehicle travel routes that are inherent in mining.

#### *Measurements of DPM and Gaseous Pollutants*

On each day of sampling, DPM and gaseous pollutants were measured simultaneously at each location.

1. Triplicate TWA DPM and respirable coal dust concentration measurements were made using personal dichotomous samplers which separate respirable DPM from respirable coal dust.<sup>(9-11)</sup>
2. Triplicate TWA nitric oxide and nitrogen dioxide concentrations were measured using nitric oxide and NO<sub>x</sub> (Palmer) personal passive samplers.<sup>(12)</sup>
3. TWA carbon monoxide and carbon dioxide concentrations were measured using one gas sample collection bag which was filled by a constant low flow sampler drawing in mine air throughout the sampling period. At the end of the sampling period, the bag is connected to carbon dioxide and carbon monoxide instruments to measure the concentrations.
4. A fuel sample was collected and analyzed for its sulfur mass content and the ratio of hydrogen to carbon atoms in the fuel. This hydrogen to carbon ratio and the sulfur content were needed to calculate the theoretical quantity of sulfur dioxide per unit of carbon dioxide produced by combustion of the fuel.<sup>(13,14)</sup>

For the personal dichotomous samplers, a personal constant-flow sampling pump draws mine air at 2 L/min through a 10-mm nylon cyclone preseparator to remove coarse, nonrespirable coal dust particles, and then through the dichotomous sampler. In the dichotomous sampler, the air passes through an inertial impaction plate where the particles coarser than 1  $\mu$ m are collected in a coating of petroleum jelly, and then through a 37-mm diameter polyvinylchloride back-up filter (MSHA FWSB) which collects the <1- $\mu$ m particles that pass through the impaction plate. The 10-mm nylon cyclone preseparator and the 2 L/min flow rate provide the same conditions as used to measure respirable coal dust by the federal procedure specified for determining compliance with the respirable coal dust standard of 2 mg/m<sup>3</sup> (Title 30, Code of Federal Regulations).<sup>(7)</sup>

The weights of particles on the impactor and on the back-up filter were determined by conditioning in a constant relative humidity chamber (44  $\pm$  3% relative humidity and 23°  $\pm$  1°C) and weighing the impactors and back-up filters in our laboratory before and after sampling.

Several of the dichotomous sampler back-up filters which had been collected when the DDEF was not installed were analyzed for sulfate to determine the fraction of the fuel sulfur that is converted to sulfate. The two fractions (sulfate and sulfur dioxide) are assumed to add up to 100 percent. The resulting percentage conversion to sulfate is then used to calculate the sulfur dioxide concentration at the particular sampler location.

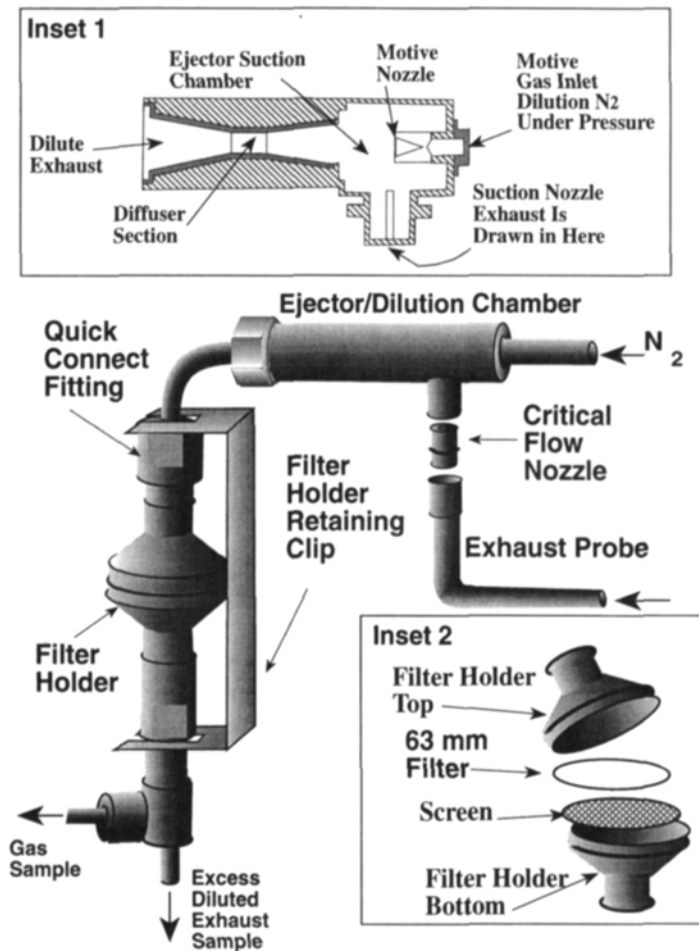


FIGURE 3. Schematic of EMA as used in mines R and S. Inset 1 shows cross-section of ejector; inset 2 shows parts of filter cassette.

#### Tailpipe Measurements of DPM and Gaseous Diesel Emissions

The emissions measurement apparatus (EMA) was used to measure the raw exhaust concentrations of DPM, carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, and sulfate out the tailpipe for each coal haulage vehicle in the section under study with and without the DDEF installed.<sup>(15-19)</sup> For these tests, the vehicle was parked and the engine was operated at the vehicle torque converter engine stall condition.

The EMA<sup>(15-19)</sup> is designed to determine the concentrations of DPM, carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, and sulfate in the raw exhaust from a diesel mine vehicle. Figure 3 is a schematic of the EMA. Figure 4 is a photograph showing the EMA as it was used in the mine tailpipe sampling. The EMA consists of: (1) a cylinder of compressed nitrogen gas, (2) a special, high flow rate, two-stage regulator on the cylinder, equipped with a special valve to turn the gas on and off instantaneously, (3) an ejector, using compressed nitrogen as the motive gas, (4) a critical flow motive nozzle in the ejector which can be replaced by a nozzle of a different size to control the flow rate of dilution nitrogen (or air), (5) a critical flow suction gas nozzle which can be replaced by a nozzle of a different size to control the flow rate, (6) a thermocouple on the suction inlet port to measure the exhaust temperature so that the exhaust flow rate can be

accurately calculated, (7) a Teflon-coated glass fiber filter to collect DPM from the dilute exhaust (the filter is inserted in a cassette holder specially designed to minimize back pressure from the relatively high (>200 L/min) flow rates of dilute exhaust), (8) a gas sampling bag to collect the dilute exhaust, and (9) instruments to measure the concentrations of nitric oxide, nitrogen dioxide, carbon monoxide, and carbon dioxide collected in the gas sampling bag.

The EMA was used in tandem with other instruments, as follows: the Fuji ZPF5 instrument for carbon dioxide; the Ecolyzer 2600 instrument for carbon monoxide; and the Ecolyzer 7000 instrument for nitric oxide and nitrogen dioxide.

The EMA samples a known volume of raw exhaust from the mine vehicle tailpipe, instantaneously dilutes it with a known volume of nitrogen, filters the dilute mixture, collecting a sample of DPM for subsequent weighing, and collects a sample of the dilute filtered exhaust in a gas sample bag for immediate analysis of the concentrations of nitric oxide, nitrogen dioxide, carbon dioxide, and carbon monoxide using portable instruments. These measurements were made with and without the control device installed to determine the effect of the DDEF

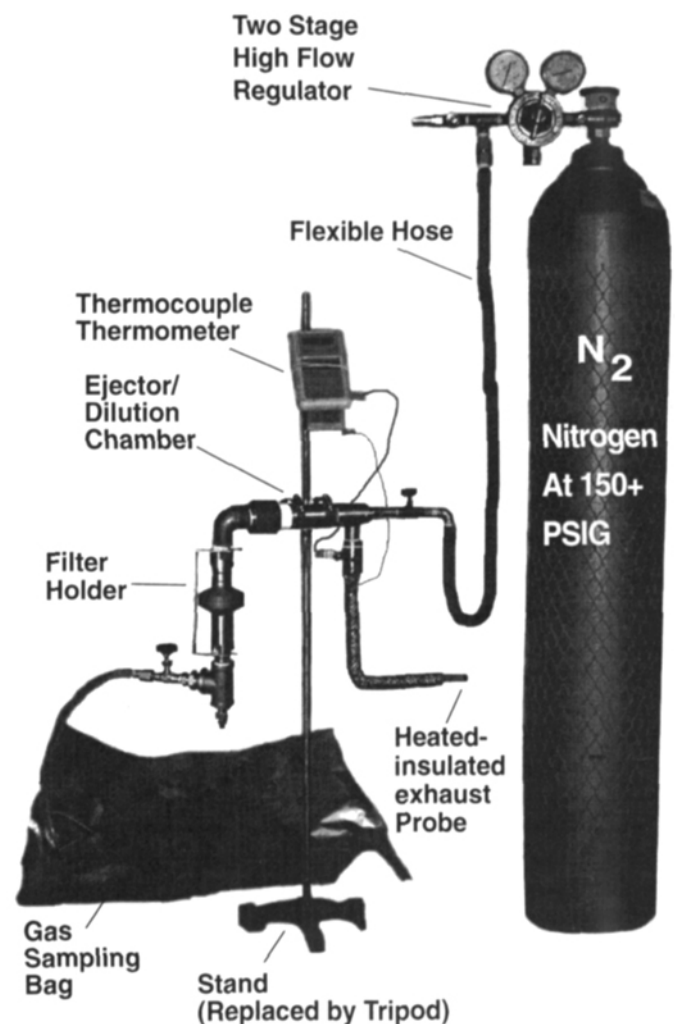


FIGURE 4. Photo of EMA in typical configuration for tailpipe pollutant measurement as used in mines R and S. An adjustable tripod has replaced the metal stand.

on the concentrations and to calculate the control efficiency of the device for each pollutant measured. The vehicle torque converter engine stall condition was produced by locking the vehicle brakes, shifting the vehicle transmission into the highest gear, and holding the accelerator pedal to the floor. Two to six measurements were made per vehicle, with the number determined by how long it took to obtain repeatable readings. The accuracy of the EMA and associated instrumentation has been evaluated in three separate comparisons with laboratory-grade instruments in the Bureau of Mines Twin Cities Research Center Diesel Emissions Laboratory.<sup>(17-19)</sup> These earlier tests demonstrated that the EMA can provide accurate and precise measurements of the concentrations of DPM, carbon monoxide, carbon dioxide, nitric oxide, and nitrogen dioxide, and resulted in some modifications which have greatly improved the device.

### Chemical and Biological Characterization

**SAMPLE COLLECTION.** In-mine samples for chemical and biological characterization were collected at each of the mines by Bureau of Mines personnel. Samples were collected on five days in mine S (three with the DDEF and two without) and four days in mine R (two with the DDEF and two without). The locations for these samplers were downstream and upstream from the vehicle location in mine S. In mine R the location was in the haulageway for the first day and return location for the second day of the control device-off condition; when the control device was on in mine R, the location for samples was the return location. However, because of ventilation in mine R, these locations were essentially downstream of the work area and are considered to be equivalent in this article. No upstream samples were collected in mine R.

The mine S samples were collected using the same procedures as for previous studies in underground coal mines where specific DPM control devices were not used.<sup>(20,21)</sup> High volume samplers with size-selective impactors, operated at a flow rate of 1.13 m<sup>3</sup>/min, were used to collect submicrometer (<1.0  $\mu$ m) particles, with slotted impactors having cut sizes of 3.5, 2.0, and 0.95  $\mu$ m removing coal and rock dust. Teflon-coated, glass fiber, 20  $\times$  25-cm back-up filters (Pallflex TX40HI20-WW) collected particles less than 0.95  $\mu$ m, which were considered to be primarily diesel in origin. The filters had previously been equilibrated in a constant relative humidity chamber (44  $\pm$  3% relative humidity and 23 $^{\circ}$   $\pm$  1 $^{\circ}$ C) and weighed in our laboratories. These samplers were placed in the same upstream and downstream locations as the other samplers reported on in this article. Because of the low levels of DPM expected when the DDEF was used, two high volume samplers were placed side by side at each sampling location and operated for the same time periods. In the downstream area, the samplers were operated primarily when diesel haulage vehicles were traveling past the sampling point, with collection times for individual filters varying from 11 to 68 minutes. Data from these samples, therefore, represent potential maximum diesel-related emissions in the downstream haulageway areas. The upstream samplers were for the most part operated continuously (from 3 to 6 hours). Data from these samples represent potential upstream (background) contributions to diesel emissions in the downstream haulageway areas due to emissions from diesel vehicles operating in other areas of the mine.

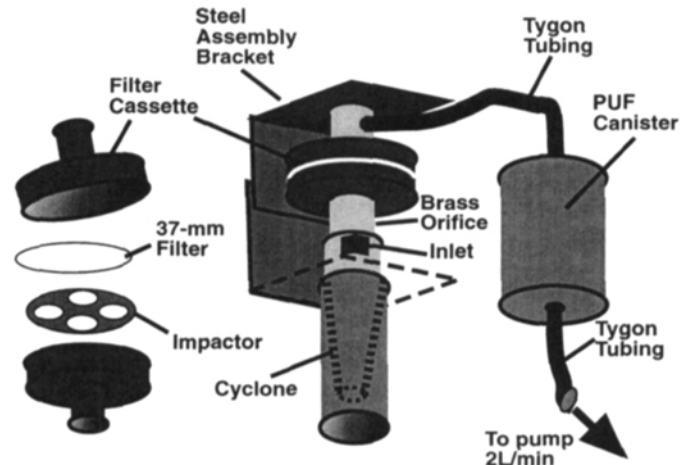


FIGURE 5. Modified MSHA personal sampler used for collecting samples in mine R for use in chemical and biological characterization studies.

Different samplers were used in mine R in an attempt to collect both diesel-derived particles and vapor phase organics using modified personal-type samplers. To this end, low flow rate (2.0 L/min) MSHA personal dichotomous particle samplers having 0.8- $\mu$ m cut points<sup>(22)</sup> were modified to allow for the simultaneous collection of vapor phase hydrocarbons or volatile organic component (VOC) which passed through the 37-mm filters (Pallflex TX40HI20-WW filters, preequilibrated and preweighed in our laboratories) and were collected on polyurethane foam (PUF). The cylindrical PUF plugs were cut from 5.08-cm stock, trimmed to fit commercially available canisters, washed with distilled, deionized water, 2-propanol, and acetone, and then Soxhlet-extracted with dichloromethane prior to use. After exposure, the PUF plugs were extracted with dichloromethane in the same manner as the exposed filters. A schematic of this modified sampler is shown in Figure 5. Ten of these samplers were placed in either the downstream (1 day) or return areas (3 days) at mine R, with samples collected continuously over 5- to 6-hour time periods.

After sample collection, the back-up filters were placed in paper folders, wrapped in aluminum foil, and kept refrigerated at the mine sites until shipment (packed in dry ice) to our laboratories. Similar refrigeration procedures were used for the foam from mine R.

**DETERMINATION OF DPM AND SOF LEVELS.** At our laboratories, all filters were reequilibrated in the constant relative humidity chamber and reweighed for gravimetric determination of the DPM mass. The SOF was removed from the 20  $\times$  25-cm filters by Soxhlet extraction for 24 hours with dichloromethane. All of the 37-mm filters or PUFs from the same day were placed together in the Soxhlet apparatus and extracted with dichloromethane for 4 hours to obtain SOF and VOC, respectively. The mass of SOF was determined gravimetrically on a small (100  $\mu$ L) aliquot of the total extract, which was brought to dryness. All extracts were stored in the freezer (-18 $^{\circ}$   $\pm$  4 $^{\circ}$ C) until they were divided into aliquots for mutagenicity assay and PAH quantification. Unexposed filters were also extracted and the masses of extractables were used to

TABLE 1. HPLC Method Parameters for the Quantification of Selected PAH in Diesel Exhaust Extracts

HPLC instrument:	HP 1090 capable of microbore chromatography and gradient elution	
Column:	Vydac 201TP52, 2 mm i.d. × 25 cm	
Mobile phase:	65% CH <sub>3</sub> OH, 35% H <sub>2</sub> O; linear gradient to 95% CH <sub>3</sub> OH in 20 minutes, isocratic for 15 minutes	
Flow rate:	200 μL/min	
Injection volume:	2 to 5 μL	
Fluorescence detector wavelengths and expected retention times:		
Compound	RTR <sup>A</sup>	Ex/Em, nm <sup>B</sup>
Fluoranthene	0.858	232/440
Pyrene	0.904	232/440
Benz[a]anthracene	1.11	289/413
Chrysene	1.14	267/389
Benzo[b]fluoranthene	1.28	247/418
Benzo[k]fluoranthene	1.33	247/418
Benzo[a]pyrene	1.38	247/418

<sup>A</sup>Relative retention time, relative to 2-chloranthracene (used as internal standard), which elutes at approximately 17.2 minutes and is detected at 242/440 nm.

<sup>B</sup>Excitation (Ex) and emission (Em) wavelengths are given for the HP 1046A detector and may not be appropriate choices for other detectors.

correct the exposed samples for upstream contributions on a mass basis. For PAH and biological activity determinations, the individual extracts from all downstream or upstream filters from the same day from mine S were pooled to reflect average levels over each day's entire sampling period.

**DETERMINATION OF PAH LEVELS.** The PAH compounds in the SOF and VOC chosen for quantification and reported on in this study are fluoranthene (FLU), benz[a]anthracene (BaA), and benzo[a]pyrene (BaP). These compounds were selected on the basis of their activities as mutagens or carcinogens.<sup>(23-25)</sup> These PAH compounds were also known to be components of diesel exhaust, and pure reference standards were commercially available for accurate quantification. These compounds, typically found in DPM in the parts per million range, are part of a complex sample composed of the products of incomplete combustion of fuel and lubricating oil. Methods employed for the analysis of PAH in diesel emission samples must, therefore, effectively separate the compounds to be quantified from interferences in the matrix and provide a means for detection of the compounds with adequate selectivity and sensitivity for reliable quantification.

The SOF and VOC samples were prepared for PAH quantification by separation using a two-column procedure.<sup>(5)</sup> The PAH fraction was then analyzed via high performance liquid chromatography (HPLC) with fluorescence detection. A polymeric C<sub>18</sub> column (Vydac 201TP52; The Separations Group, Hesperia, California) was used with a Hewlett Packard (HP; Avondale, Pennsylvania) model 1090 HPLC instrument and HP 1046AX programmable fluorescence detector to achieve baseline resolution of the isomers BaA and chrysene, which typically coelute on monomeric reverse phase materials. A methanol/water mobile phase gradient was used in place of the usual acetonitrile/water for the purpose of reducing both the initial cost and the expense of hazardous waste disposal associated with acetonitrile. A standard reference material (SRM 1647) from the National Institute for Standards and Technology (NIST, Gaithersburg, Maryland) containing certified levels of the PAH of interest was used as an HPLC calibration standard (diluted 1:250). NIST SRM 1650, certified DPM,

was used as a control sample and was subjected to Soxhlet extraction and column separation procedures prior to analysis by HPLC. Method details are summarized in Table 1.

**DETERMINATION OF BIOLOGICAL ACTIVITY.** Biological activity of the SOF and VOC fractions was determined using a modification of the microsuspension version of the *Salmonella typhimurium*/microsome mutagenicity bioassay or Ames assay.<sup>(4,20,26)</sup> Assays were conducted only with tester strain TA98 without S9 metabolic activation due to the limited amount of sample mass available. Test samples were grouped together to eliminate day-to-day variability in response by the tester strains. Controls were run on each test date for spontaneous revertant levels (in dimethyl sulfoxide), genotypic checks, positive controls ±S9, and sterility checks on assay components. Spontaneous revertant levels (mean ± SD of two assays) were 35 ± 1.9 revertants/dish. Responses with 2-nitrofluorene (mean ± SD of two assays) were 1100 ± 56 revertants at 400 ng/dish.

**DATA ANALYSIS.** All DPM, SOF, PAH, and biological activity data were converted to a volumetric concentration basis using the total volume flow (in cubic meters) for each sample (mine S) or for the combined samples (mine R). Means of daily mean values were calculated from the DPM and SOF data from each sampling location. A mean for each mine and sampling location was calculated from the PAH and biological activity data.

#### Air Quality Index and Exhaust Quality Index

The AQI<sup>(27)</sup> was calculated from mine ambient air measurements at upstream, vehicle, and downstream locations for each day's measurements. The AQI was developed by Canadian researchers<sup>(27)</sup> to make it possible to evaluate diesel emission controls based on the combined health effects of DPM, carbon monoxide, nitric oxide, nitrogen dioxide, and sulfur dioxide concentrations. Special methods were developed in this study to collect the data used in the AQI equation. These included: (1) substitution of the DPM concentration measured by personal dichotomous samplers for respirable combustible dust (RCD) in the AQI equation and (2) calculation of the sulfur



dioxide concentration from the fuel sulfur content, the measured carbon dioxide concentration, and the percentage of the fuel sulfur converted to sulfur dioxide (determined by calculation using measured sulfate data).

The AQI,<sup>(27)</sup> originally developed in the 1980s, estimates quantitatively the health effects of concentrations of diesel exhaust in the environment. According to Reference 27, the primary purpose for its development was to make possible the evaluation of diesel emission control devices based on their combined effect on all pollutants of concern (at the time the index was developed) and not on a single pollutant. The AQI was originally called the health effects index and was calculated by the following formula:

$$V = \frac{CO}{50} + \frac{NO}{25} + \frac{RCD}{2} + 1.5 \left( \frac{SO_2}{3} + \frac{RCD}{2} \right) + 1.2 \left( \frac{NO_2}{3} + \frac{RCD}{2} \right) \quad (1)$$

All of the gaseous constituents are measured in parts per million, and RCD is measured in milligrams/cubic meter. It had been estimated by the developers of the index that a value of 3 or less for V would minimize the risk to the health of workers in dieselized underground mines. They suggested that the risk at a level between 3 and 4 could be alleviated by the use of personal protective equipment, but that a level in excess of 4 would indicate that the quantity of ventilation air should be increased.

Reference 28 also shows how an EQI would be applied:

"V" was formulated as an ambient criterion; it follows logically that substitution of the concentrations of the same substances in the raw exhaust in the expression will yield  $V_{\text{exhaust}}$ . As the ambient goal is a value of 3,  $V_{\text{exhaust}}$  divided by 3 yields the number of equivalent volumes of fresh air which must be added to the exhaust to achieve the recommended ambient level: a ventilation criterion. If "V" is recalculated for exhaust levels after a treatment device is fitted, the impact of the treatment device may be quantified by comparison with "V" for the untreated exhaust, and dividing by 3 as before yields a ventilation recommendation for the treated exhaust.

$V_{\text{ambient}}$  was named the Air Quality Index, or AQI, and  $V_{\text{exhaust}}$  was designated the Exhaust Quality Index, or EQI. The EQI was adopted as the agreed method of ranking the effectiveness of exhaust control technologies by the Collaborative Diesel Research Advisory Panel.<sup>(28)</sup>

In the current study, DPM concentrations measured using personal dichotomous samplers were substituted for RCD in the AQI equation. Up until only recently, no generally accepted method had been available by which to determine the DPM concentration in the mine aerosol mixture. RCD had, therefore, been used to estimate the DPM concentrations in metal mines, but the presence of other materials in the particulate matter, which are also evaporated in heating the particulate sample as in the RCD test method, resulted in overestimation of the DPM concentrations. Because RCD did not distinguish coal from DPM, the AQI has not been used previously to evaluate coal mine ambient air diesel emission concentration measurements.

The sulfur dioxide concentration needed to calculate the

AQI was determined by a combination of sulfate measurements and calculations as discussed above. The EQI<sup>(27)</sup> was calculated using the same equation, but substituting the diesel engine tailpipe raw exhaust concentrations into Equation 1.

### Control Efficiency Calculations

Control efficiencies (percentage decreases in pollutant concentrations due to the DDEF) were calculated for DPM, for the various gases, and for chemical species and biological activity of the DPM and vapor phase organics. The mine ambient air concentrations were normalized using a procedure developed earlier<sup>(5)</sup> to minimize the effects of mine ventilation and vehicle use variables on the calculated control efficiencies. A control efficiency is also calculated for the AQI. A positive AQI control efficiency indicates that the control device has a positive overall effect on the mine air quality. A positive AQI control efficiency minimizes the concern that a device may be lowering the concentration and reducing the health effects of one pollutant, while at the same time having the opposite effect on another more harmful pollutant. Unfortunately, the AQI does not make use of the chemical and biological data associated with the vapor phase organics and the SOF associated with the DPM.

Note that a concentration cannot be reduced more than 100 percent, and therefore positive control efficiencies greater than 100 percent indicate suspect data in the measurements or calculations. Such errors can occur as a result of changes taking place between the measurements with and without the control device installed or inability to locate the upstream sampling location in air that is the same air that flows by the diesel equipment to the downstream sampling location. However, because concentrations may be increased by several hundred percent, negative control efficiencies of several hundred percent are not impossible.

Because the sulfur dioxide concentrations are calculated from the carbon dioxide concentrations, any reductions in sulfur dioxide due to control are not accounted for in the calculated values. Therefore, the control efficiency for sulfur dioxide cannot be determined. However, the DDEF would not be expected to significantly affect the concentrations of sulfur dioxide emitted, since it was not designed with a catalyst or with other processes that would change the sulfur dioxide concentration. Therefore, the assumption used was that sulfur dioxide control by the DDEF is zero.

Because ventilation and vehicle operating conditions frequently change in a mine, it is important to normalize the measured concentrations prior to using them to calculate the control efficiency. Normalization was accomplished here by dividing the concentrations of diesel-produced pollutants by the concentrations of diesel-produced carbon dioxide emitted at the same time.<sup>(29)</sup> This carbon dioxide normalization expresses the pollutant concentrations in terms of concentration per percent carbon dioxide. The normalized concentrations are largely unaffected by either vehicle use or ventilation variables, as can perhaps be most easily understood from the following example: If the vehicle operates twice as much, the carbon dioxide concentration as well as the concentrations of the other pollutants would be expected to double (same quantity emitted, but emitting during twice as much time). However, the normalized concentrations would remain unchanged.



TABLE 2. Average Mine Ambient Air Gaseous and DPM Concentrations at Upstream, Vehicle, and Downstream Locations in Mines R and S With and Without the DDEFs

Component	Mine R <sup>A</sup>		Mine S <sup>A</sup>	
	Control Off <sup>B</sup>	Control On <sup>B</sup>	Control Off <sup>B</sup>	Control On <sup>C</sup>
Carbon dioxide (%)				
Upstream	0.062 ± 0.01	0.046 ± 0.001	0.05	0.05
Vehicle	0.12 ± 0.03	0.105 ± 0.01	0.19 ± 0.04	0.16 ± 0.01
Downstream	0.12	0.093 ± 0.04	0.15 ± 0.01	0.15 ± 0.03
Carbon monoxide (ppm)				
Upstream	0	0	1.5	0.83 ± 0.76
Vehicle	4.5	5	4.75 ± 0.35	4.83 ± 1.15
Nitric oxide (ppm)				
Upstream	0.12 ± 0.06	0.1	0.25 ± 0.03	0.3 ± 0.15
Vehicle	2.98 ± 1.08	2.99 ± 0.77	6.23 ± 0.26	5.79 ± 0.65
Nitrogen dioxide (ppm)				
Upstream	0.13	0.13 ± .03	0.23 ± 0.09	0.33 ± 0.16
Vehicle	1.76 ± 0.1	1.86 ± 0.38	0.76 ± 0.05	0.6 ± 0.11
Sulfur dioxide (ppm)				
Upstream	0.13	0.05 ± 0.004	0.21	0.19 ± 0.04
Vehicle	0.33 ± 0.11	0.26 ± 0.04	2.12 ± 0.05	1.78 ± 0.15
DPM (mg/m <sup>3</sup> )				
Upstream	0.065 ± .007	0.29 ± 0.071	0.005 ± 0.035	0.043 ± 0.09
Vehicle	0.945 ± 0.21	0.47 ± 0.04	1.53 ± 0.28	0.35 ± 0.1
AQI				
Upstream	0.244 ± 0.02	0.62 ± 0.14	0.243 ± 0.03	0.335 ± 0.1
Vehicle	2.83 ± 0.44	1.96 ± 0.28	4.54 ± 0.53	2.11 ± 0.22

<sup>A</sup>Presented as mean (±SD) for two to three sampling dates per condition; one to six values per sampling date.<sup>B</sup>Average of samples on two sampling dates.<sup>C</sup>Average of samples on three sampling dates.

Likewise, if dilution ventilation air doubles, the carbon dioxide concentration would be reduced by half, as would the concentrations of the other diesel pollutants, and the normalized concentration would remain unchanged. The normalized concentration would, however, be reduced by half if a given pollutant concentration were reduced by half by control and the carbon dioxide concentration was unchanged. None of the control devices tested to date affects the carbon dioxide concentration significantly.

## Results

### Control of DPM by the DDEF from Mine Ambient Air Data

The mine air vehicle and upstream location data for mines R and S are presented in Table 2, showing the mine air vehicle location average gaseous and DPM concentration data along with the calculated AQI. The downstream carbon dioxide concentration is also given because these data are used to normalize the chemical and biological characterization data collected at the downstream location. Table 3 shows the tailpipe data.

Figure 6 compares mine R (left) and mine S (right) DPM vehicle location average ambient concentrations with the DDEF off and on. These data indicate that the vehicle location mine air DPM concentration was reduced from 0.95 to 0.50 mg/m<sup>3</sup> in mine R and from 1.53 to 0.35 mg/m<sup>3</sup> in mine S. Control efficiencies were calculated using normalized upstream-corrected data.

A control efficiency based on these mine air data represents the calculated average percentage reduction in the upstream-corrected, normalized mine air concentration attributable to the DDEF when the vehicle engine is operating in its normal production load speed cycle. Control efficiencies based on tailpipe measurement data represent the percentage reduction in normalized tailpipe concentrations for the vehicles during the steady-state test at the torque converter stall speed and load. Control efficiencies for tailpipe measurements using pure nitrogen as the dilution gas do not require the upstream correction and normalization procedures used for mine ambient air concentrations. Some differences between mine air and tailpipe control efficiency percentages would be expected, mainly because the mine air concentrations were dependent upon the part of the coal haulage cycle from which the measurements were taken, which vehicles have the greatest effect on the instruments, and how each vehicle is operated (fraction of time operating, fraction of time at idle and at full load, operating speed, engine condition, stops, starts, etc.).

Figure 7 compares mines R and mine S control efficiencies calculated from vehicle location mine ambient air DPM measurements with those calculated from tailpipe DPM measurements. The average control efficiency from mine R ambient air measurements was 80 percent, compared with 52 percent from tailpipe measurements (second from the left). The mine air control efficiency calculations are heavily influenced by differences in upstream DPM and carbon dioxide values. The

TABLE 3. Average Tailpipe Gaseous and DPM Concentrations for Mine Vehicles in Mines R and S With and Without the DDEFs

Component	Mine R <sup>A</sup>		Mine S <sup>A</sup>	
	Control Off <sup>B</sup>	Control On <sup>B</sup>	Control Off <sup>C</sup>	Control On <sup>D</sup>
Carbon dioxide (%)	9.05 ± 0.11	9.05 ± 0.16	9.66 ± 0.71	8.99 ± 1.17
Carbon monoxide (ppm)	924 ± 63	948 ± 125	336 ± 158	324 ± 163
Nitric oxide (ppm)	250 ± 64	246 ± 58	308 ± 30	275 ± 31
Nitrogen dioxide (ppm)	63 ± 7.4	51 ± 0.31	15.3 ± 4.1	12.01 ± 2.9
Sulfur dioxide (ppm)	26.5 ± 0.29	37 ± 0.77	140 ± 8	137 ± 4.5
DPM (mg/m <sup>3</sup> )	215 ± 38.7	108 ± 20	184 ± 89	37 ± 63
EQI	436 ± 215	268 ± 40	436 ± 167	153 ± 120

<sup>A</sup>Presented as mean (±SD).

<sup>B</sup>Average of five samples of two vehicles, 1700 rpm engine speed.

<sup>C</sup>Average of two samples each of four vehicles, engine speed 1450 to 1500 rpm.

<sup>D</sup>Average of two to four samples each of four vehicles, engine speed 1450 to 1500 rpm.

tailpipe values are not influenced by these variables and are therefore more repeatable. For mine S, the DDEF control efficiency for DPM was 76 percent from mine air measurements and 76 percent from tailpipe measurements.

In mine S some insight was gained into why DDEF control efficiencies for DPM vary from vehicle to vehicle. Visual observation of tailpipe sampling filters collected with the DDEF installed revealed some darkening on the filters from one ramcar, indicating that more DPM was passing through the DDEF than would be expected. For other mine S ramcars, use of the DDEF resulted in little, if any, evidence of particulate on the DPM sample collection filter. To help determine the cause, the DDEF was removed. Inspection revealed burn holes in the filter media. Discussions with mine personnel indicated that such burn holes are a result of scrubber dry-out, making it possible for the hot, unconditioned exhaust to come into contact with and initiate combustion of the filter media.

When the burned DDEF was replaced with a new one, another set of measurements revealed minor darkening of the EMA sample filter, indicating that DPM was still bypassing the DDEF. Inspection of the DDEF canister revealed that the seal on the larger filter diameter was not touching the exhaust pipe flange all the way around its circumference. The flange was straightened and a third set of tests provided no more visible darkening of the EMA sample collection filters.

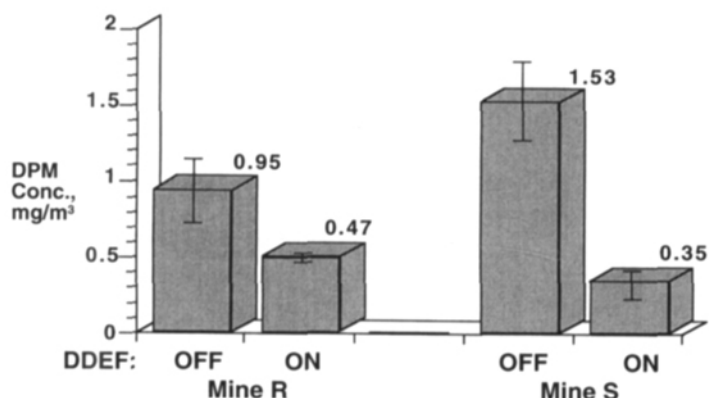


FIGURE 6. DPM concentration at vehicle location in mines R and S with DDEF off and on.

Figure 8 shows the DPM concentrations measured by the EMA sample filters during these observations for the following conditions: (1) no DDEF installed (249 mg/m<sup>3</sup>), (2) burn holes in the DDEF (209 mg/m<sup>3</sup>), (3) a new DDEF in the bent canister (81 mg/m<sup>3</sup>), and (4) a new DDEF in the straightened canister (18 mg/m<sup>3</sup>).

Figure 9 shows the calculated DPM control efficiencies of the DDEF from tailpipe measurements by the EMA. The no-DDEF condition represents zero control efficiency. The burned DDEF provides 16 percent DPM control, the new DDEF in the bent canister provides 65 percent DPM control, and the new DDEF in the straightened canister provides 92 percent DPM control, which is in the range of a new, properly operating DDEF. This demonstrates the importance of tailpipe measurements and vehicle inspection for the maintenance of properly working control devices.

#### Effect of the DDEF on Other Diesel Exhaust Gaseous Pollutants and the AQI/EQI

Control efficiencies were also calculated for the gaseous pollutants of interest: nitrogen dioxide, nitric oxide, and carbon monoxide, as well as for the AQI and EQI. These data address the concern about whether the DDEF, in controlling DPM, increases the concentration of other pollutants of concern. The control efficiencies presented for the tailpipe data include range bars which represent the range of control efficiencies among all of the vehicles that were monitored to calculate the average. Table 3 shows the number of vehicles for each mine and the

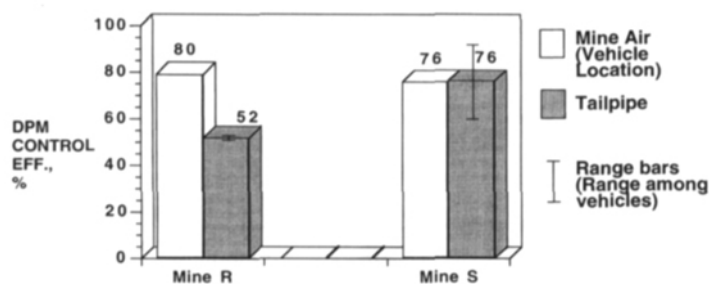


FIGURE 7. Control efficiency for DPM at vehicle location in mines R and S (corrected for upstream levels and normalized for carbon dioxide levels) and from tailpipe measurements.

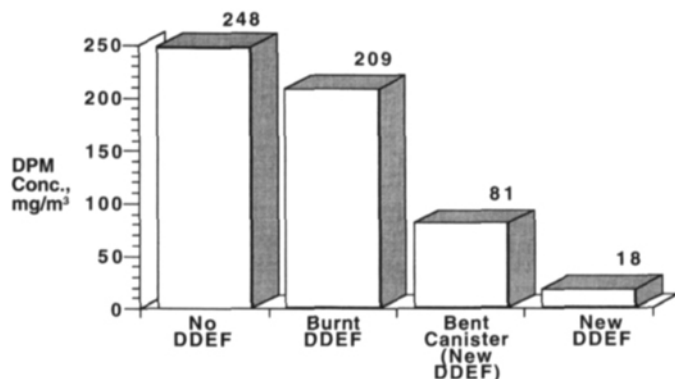


FIGURE 8. DDEF and canister condition effect on mine S vehicle 3 tailpipe DPM concentration.

number of samples taken, as well as engine speed. Range bars are not presented for the mine ambient air control efficiencies since the control efficiency value is calculated from the average DPM concentration with the control off and on.

The DDEF is designed to reduce the DPM concentration. The data in Tables 2 and 3 indicate, as would be expected, that the nitrogen dioxide, nitric oxide, and carbon monoxide concentrations with and without the DDEF are not significantly different for either the ambient or the tailpipe data.

The calculated AQI values for the mine R and mine S data are shown in Figure 10. Figure 11 presents the control efficiencies based on the EQI data (measured in the tailpipe) with those based on the AQI data measured in the mine air. The control efficiencies are seen to be all in the area of 50 percent, with individual averages ranging from 45 to 63 percent. This positive effect on the AQI indicates that, for the pollutants considered in the AQI/EQI equations, the DDEF has an overall positive effect. The DDEF has virtually no effect on the gaseous pollutants, but has a marked effect on DPM, which the AQI/EQI equation weighs heavily; however, the AQI/EQI doesn't take the chemical characteristics or biological activity of the DPM into consideration.

#### Effect of DDEF on PAH Concentrations and Biological Activity

A summary is presented in Table 4 of the actual downstream ambient air data obtained from the high volume samplers from

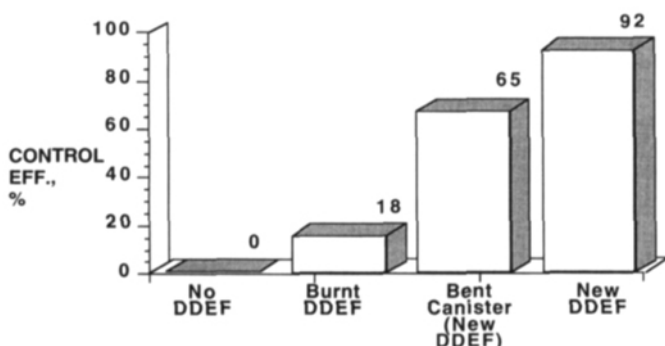


FIGURE 9. DDEF and canister condition effect on mine S vehicle 3 tailpipe DPM control efficiency.

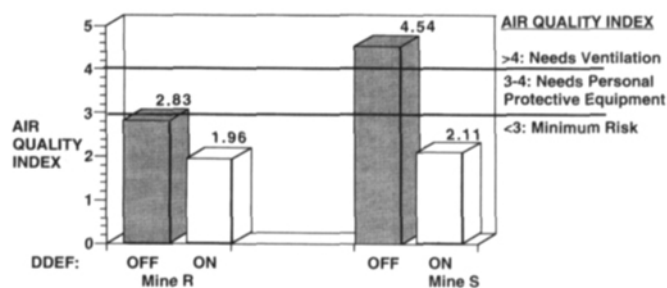


FIGURE 10. AQI at vehicle location in mines R and S with DDEF off and on.

mine S and from the modified personal samplers used in mine R. These data have not been corrected for upstream levels or normalized using carbon dioxide levels in the sampling areas. The primary intent of this sampling was to obtain DPM samples (and VOC from mine R) to determine the levels of selected PAH and mutagenic activity associated with the SOF and VOC in the underground mine environment. Estimates were also to be made of DPM, other DPM components, and VOC collectable with these sampling systems.

The downstream DPM levels obtained with the modified personal samplers from mine R represent nearly full-shift average values and are similar to those found with and without the DDEF using similar types of sampling systems in the same mine.<sup>(30)</sup> However, the DPM levels found from the high volume sampler for mine S are considerably higher than those found with the other sampling systems. The reasons for the elevated levels include operating the high volume samplers for much shorter time periods, primarily when there was diesel activity in the sampling area (as little as 1 hour when the DDEF was not in use), and having a slightly larger filtration cut point (0.95 versus 0.8  $\mu\text{m}$  for the personal samplers). Therefore, the high volume samplers collected more of the heavier diesel-derived particles and also some of the smaller coal particles. Another possible contributor to the elevated levels is the reentrainment of coarser coal or rock particles collected on the slotted filters associated with the impactor upstream of the back-up filter, and redeposition of this larger-sized dust on the back-up filter.

Although submicrometer or larger coal or rock dust particles might contribute to the DPM levels found with the high

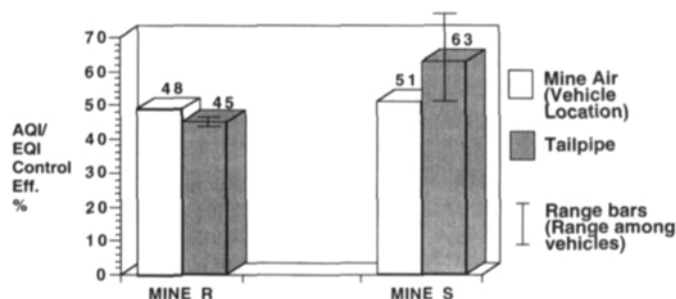


FIGURE 11. Control efficiency for AQI at vehicle location (corrected for upstream levels and normalized for carbon dioxide levels) and for EQI from tailpipe measurements in mines R and S.

TABLE 4. Actual Diesel-Related Emissions Obtained from Mines R and S Using Personal or High Volume Samplers, Respectively, With and Without the DDEFs

Component	Mine R <sup>A</sup>		Mine S <sup>B</sup>	
	Control Off	Control On	Control Off	Control On
DPM (mg/m <sup>3</sup> )	0.92 ± 0.02	0.40 ± 0.19	2.76 ± 0.99	1.43 ± 0.17
SOF (mg/m <sup>3</sup> )	0.14 ± 0.01	0.07 ± 0.04	0.28 ± 0.05	0.18 ± 0.01
FLU (ng/m <sup>3</sup> )	26.8 ± 7.42	2.00 ± 0.64	12.5 ± 4.75	5.49 ± 3.07
BaA (ng/m <sup>3</sup> )	16.4 ± 0.56	4.44 <sup>C</sup>	2.48 ± 0.60	2.61 ± 2.01
BaP (ng/m <sup>3</sup> )	19.6 ± 1.20	2.56 ± 1.79	1.11 ± 0.16	4.13 ± 4.01
Activity (rev/m <sup>3</sup> )	320 ± 85	86 ± 41	110 ± 24	51 ± 27
VOC (mg/m <sup>3</sup> )	0.41 ± 0.06	0.24 ± 0.06	ND <sup>D</sup>	ND
FLU (ng/m <sup>3</sup> )	12.2 <sup>E</sup>	<BL <sup>F</sup>	ND	ND
BaA (ng/m <sup>3</sup> )	3.76 ± 3.0	2.11 <sup>C</sup>	ND	ND
BaP (ng/m <sup>3</sup> )	2.07 ± 0.81	0.76 ± 0.72	ND	ND
Activity (rev/m <sup>3</sup> )	NA <sup>D</sup>	NA <sup>D</sup>	ND	ND

Data uncorrected for upstream values and not normalized for carbon dioxide levels.

<sup>A</sup>One pooled value per sampling date; two to three sampling dates per condition.

<sup>B</sup>Presented as mean (±SD) for two to three sampling dates per condition; one to six values per sampling date.

<sup>C</sup>Value from first day's pooled sample; the value for the second day's sample was <0.6 ng/m<sup>3</sup>.

<sup>D</sup>ND = not determined; NA = no activity above spontaneous revertant levels detected.

<sup>E</sup>Value from second day's pooled sample; value for first day's sample was less than the blank.

<sup>F</sup>Level in the exposed sample was equal to or less than the blank.

volume samplers, they should make only a slight contribution, at most, to DPM component levels. In a previous study,<sup>(20)</sup> analyses of submicrometer coal dust indicated that there should typically be less than a 1 percent contribution to SOF, PAH, and mutagenic activity levels even if 10 percent of the material on the back-up filter was from coal. The organics collected on the PUF (VOC) are also expected to be diesel and not coal derived. Therefore, the levels of these DPM components presented in Table 4 should represent diesel-derived emissions regardless of which sampling system was used.

Based on the data in Table 4, the effect of the DDEF in each mine was to reduce DPM and SOF levels by about 50 percent. The modified personal sampler was also successful in collecting VOC in mine R, with approximately twice as much organic solvent-extractable mass recovered from the vapor phase (VOC) as that associated with the DPM (SOF). The VOC levels were also reduced about 50 percent with DDEF use in mine R.

For mine R, the levels (nanograms/cubic meter) of all measured PAH compounds were higher in the DPM than in the corresponding VOC samples, with FLU being detected in only one of the VOC samples. Use of the DDEF in mine R was associated with generally reduced levels of all three PAH compounds in the DPM and VOC. The exception was FLU, for which the levels in the VOC were generally less than or equal to levels from the unexposed PUF (both with and without the DDEF). In mine S, DPM-associated FLU levels were reduced, BaA levels were unchanged, and BaP levels increased when the DDEF was used. However, the standard deviations were high for the measurements made with the DDEF; for BaP, in particular, the measurements for 2 days' samples were not repeatable, with one value the same as the mean without the DDEF, and one value much higher than this mean. The PAH levels detected in the mine S downstream area without the DDEF were also somewhat lower than those measured in mine R.

The repeatability for PAH quantification (for, in most cases, duplicate samples representing different dates) was generally better for the DPM samples collected with the personal sampler than for those collected with the high volume sampler. This was probably due to the fact that there was only one value per test date for the personal samplers, as this equipment was operated during most of the operating shift and all filters were pooled before extraction. Thus, the PAH level obtained represented the concentration integrated over a larger period of time with less inherent variability.

Mutagenic activity was detected for DPM collected in both mines, with the levels at least 50 percent less with the DDEF installed (Table 4); all activity was direct-acting in nature (data not presented). The DDEF did not appear to affect the activities on a mass basis (revertants/microgram), as these values were similar with and without the DDEF in each mine. The mutagenic activity levels (revertants/cubic meter) found in the downstream areas of each mine without the DDEF were generally within the range of values found in a previous study of underground coal mines where no specific diesel emission control devices were in use.<sup>(21)</sup> In contrast to the DPM results, no activity was detected with mine R VOC samples despite the fairly large mass collected.

SOF associated with particles collected in the DDEFs in each mine had about 50 times the mutagenic activity (revertants/microgram SOF) as SOF collected in the downstream ambient mine air on the same days. No activity was detected in the small amount of organic material extracted from unexposed DDEFs. This higher activity for material collected by the DDEF could be expected as the trapped particles are exposed to diesel exhaust throughout the 10- to 32-hour lifetime of the DDEFs in these mines.<sup>(30)</sup>

Control efficiencies for the DDEF in mine R could only be calculated by normalizing the downstream data using the carbon dioxide concentrations determined over approximately the same time periods in essentially the same sampling areas, as

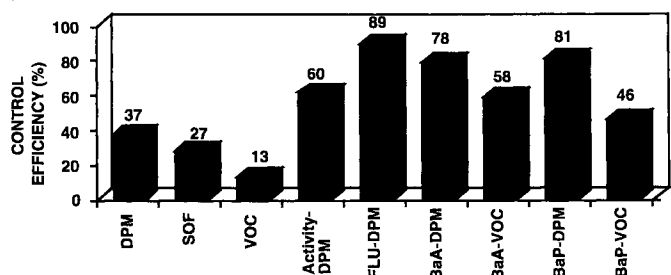


FIGURE 12. Control efficiency at downstream location in mine R using modified personal samplers, as normalized for carbon dioxide levels.

no upstream samples were obtained with the modified personal samplers. The results for most of the diesel-related components are shown in Figure 12. No calculated efficiencies are presented for VOC mutagenic activity levels, as no activities above spontaneous revertant levels were detected; no efficiencies are presented for VOC-associated FLU levels, as the unexposed or blank PUFs contained relatively high FLU levels and three of the four daily samples did not contain FLU above these levels.

As indicated in Figure 12, DDEF use reduced all diesel emission components measured with the modified personal samplers. The greatest effects were on the DPM and DPM-associated components. When normalized for carbon dioxide levels, the DDEF had much less effect on VOC removal and on removal of the vapor phase-associated PAH. However, the effect of upstream levels on these control efficiencies is unknown for this mine.

For mine S, the control efficiencies in the downstream areas are presented in two ways, first with the downstream data corrected by subtraction of the upstream concentrations (Figure 13) and then as normalized for the downstream carbon dioxide concentrations (Figure 14). For these data, both correction and normalization are only approximations as the upstream DPM component and upstream and downstream carbon dioxide concentrations typically were obtained using much longer sampling periods than were the downstream high volume sampler filters.

As shown in Figures 10 and 11, normalizing or correcting the data had little effect on most of the calculated control

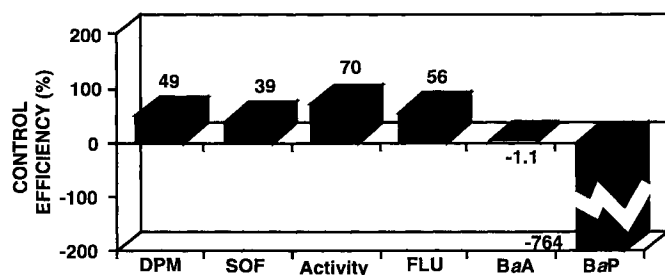


FIGURE 13. Control efficiency at downstream location in mine S using the high-volume samplers as corrected for upstream values and normalized for carbon dioxide levels.

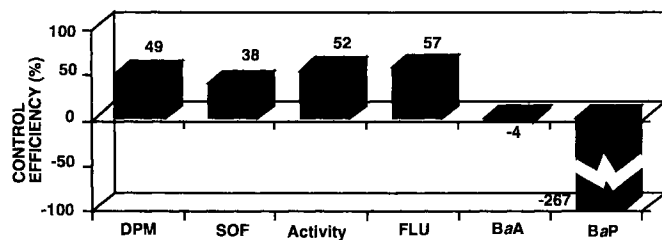


FIGURE 14. Control efficiency at downstream location in mine S using high volume samplers as normalized for carbon dioxide levels.

efficiencies; the control efficiencies calculated for downstream location data that were both corrected and normalized (figure not presented) were virtually identical to those presented in Figure 10. In mine S, the carbon dioxide levels did not vary throughout the total sampling time period at either the downstream or upstream sampling locations. The downstream measured concentrations were also very low and similar on all sampling dates, thus having little influence on the downstream data. The exception to the above was for BaP, where a negative control efficiency became much less negative when the data were both normalized and corrected for the upstream data. However, as noted earlier, there was poor repeatability for the 2 days' BaP measurements. Due to the low number of samples, the control efficiencies can only be estimated. The DDEF was estimated to be approximately 50 percent effective in reducing DPM and DPM-associated SOF, FLU, and mutagenic activity. No effect was found on BaA levels, and BaP levels increased with DDEF use.

## Discussion

In spite of the difficulties that are experienced in obtaining mine air pollutant concentration data, the study results indicate that the DDEF efficiently removes DPM as well as its constituents from the exhaust emitted from a diesel-powered mine vehicle. Because the device is no more than a high surface area filter, it would not be expected to increase the concentrations of any of the pollutants of concern. This is verified by the data indicating that DPM and its constituent parts were reduced by the DDEF, while none of the gaseous pollutants increased and both the AQI and EQI were reduced.

The study did raise some important concerns about the potential for ignition of the DDEF when the water scrubber dries out. While water scrubber dryout is not supposed to occur because the exhaust temperature may then exceed the standard, water scrubber dryout occurred during our short study and resulted in burn holes in the filter. There is the obvious concern that ignition of the DDEF may result in ignition of the methane or coal dust in the vicinity of the vehicle. However, scrubber dryout itself produces a situation that should not occur where exhaust temperatures are controlled to minimize the explosion hazard.

As shown in mine R, the modified personal samplers used in this study can be used to obtain sufficient mass to conduct chemical and biological characterization of potentially health-related diesel-derived emissions, provided sufficient filters or PUFs were collected and pooled together. The levels obtained

may, therefore, more closely represent the average, daily levels found in the actual work areas than the data obtained from the high volume samplers. The control efficiency of the DDEF on downstream DPM levels in mine R was similar to the normalized-only DPM control efficiency found for the vehicle location sampling in this same study (data not presented). However, both of these values were lower than the value reported from the same location in Reference 30. The other data<sup>(30)</sup> were corrected for the upstream concentrations, but were normalized using ventilation and production changes, not carbon dioxide levels.

The use of the DDEF in mine R was associated with at least 70 percent reductions in PAH levels for the three compounds measured in the DPM. The PAH concentrations were also lower in the VOC samples when the DDEF was used, although not to a great extent. Since the DDEF functions basically as a low temperature particle filter, one would expect to see reductions in these PAH compounds along with the reductions in DPM, SOF, and VOC. The PAH compounds which have relatively low vapor pressures at the operating temperatures typical for the DDEF would be expected to be mostly adsorbed onto the DPM; therefore, filtration is an effective means of removal of these compounds. Conversely, those compounds with relatively high vapor pressures will remain either in the vapor phase exclusively or partitioned between the particle and vapor phases. Although one does not expect to remove PAH in the vapor phase with a clean DDEF, it may be that the efficiency of PAH removal from the vapor phase increases as DPM collects in the DDEF and it subsequently becomes a more efficient organic adsorber.

The DDEF control efficiency data from mine S more conclusively indicate that this control device appears to primarily affect the concentrations of some of the key DPM components and does less to change which components are present (i.e., quantitative rather than qualitative changes). As noted above, these results support the concept of the DDEF as a low temperature, physical filter. The levels of DPM-associated PAH were not consistently reduced with DDEF use. The control efficiency for FLU was positive, however, possibly due to FLU adsorption to DDEF-collected particles (as discussed above for mine R). FLU concentrations are generally higher as well, which makes trends easier to detect.

The control-off PAH and activity levels were also somewhat lower in mine S than in mine R and at four other underground coal mines where no control devices were used and filters were also collected with a high volume sampler.<sup>(21)</sup> This may be attributed to differences in engine operating conditions and quality of engine and vehicle maintenance between the mines which resulted in higher DPM but lower SOF and associated PAH and activity. The lower levels without the DDEF may also have made it more difficult to detect DDEF effects on these PAH compounds; the levels measured with the DDEF installed were associated with relatively high variabilities (particularly BaP, for which there was a 97% coefficient of variation with the control on compared with 14% with the control off). In any case, the control efficiencies found with the DDEF in mine S probably represent the minimum reductions that would occur.

## Conclusions

1. Use of the DDEF in two U.S. underground coal mine production diesel haulage operations successfully reduced the mine ambient air DPM concentrations with control efficiencies of 80 and 76 percent.
2. The DPM control efficiency calculated from tailpipe measurements for mine R was 52 percent, as compared with 80 percent for mine air measurements. The DPM control efficiency from tailpipe measurements for mine S was 76 percent, as compared with 76 percent for mine air measurements.
3. The EQI control efficiency from tailpipe measurements for mine R was 45 percent, compared with the AQI control efficiency of 48 percent for mine air measurements. The EQI control efficiency from tailpipe measurements for mine S was 63 percent, compared with the 51 percent AQI control efficiency. These slight differences may be due to various causes, including differences in engine operating conditions and the effect of these differences on the control efficiencies of the devices, improper weighting of the effects of the different vehicles making contributions to the average, and difficulty in interpreting mine ambient air measurement data.
4. The AQI at both mines R and S was reduced from levels that required protective equipment and/or ventilation to minimum risk levels with the use of the DDEF.
5. Analyses with both the high volume and modified personal samplers indicate that the DDEF use showed approximately 50 percent (and often greater) reductions in some of the potentially health-related diesel exhaust components associated with the DPM and VOC, although fewer effects may be found for the VOC than for the DPM components.
6. Particle-associated PAH concentrations, and mutagenic activity in particular, apparently can be reduced in the mine with the DDEF. The DDEF effects appear to be due more to physical removal and reduction in DPM, in particular, than to changes in DPM composition. Whether or not the reductions in measured concentrations are significant probably depends in part on the levels with the control off (i.e., engine operating conditions, engine maintenance, and the effectiveness of the ventilation system are parameters that affect baseline levels and determine, to some extent, whether or not the use of the DDEF will give measurable reductions in these levels).
7. The particles retained by the DDEF, however, have greatly elevated levels of mutagenic activity associated with them, and they may have enhanced potential to adsorb vapor phase hydrocarbons, including some PAH, as the DDEF is loaded with DPM.

## Acknowledgments

The authors acknowledge the effort of personnel from the U.S. Bureau of Mines Twin Cities Research Center for their collaboration in designing and conducting these studies, including collecting the high volume samples. In particular, we acknowledge the efforts of Dr. Winthrop Watts, Jr. and Dr. Bruce Cantrell. At our laboratories, Barbara Heard carried out portions of the chemical analysis laboratory work and Donna Becker assisted in conducting the mutagenicity analyses.

This research has been supported by the Department of the Interior's Mineral Institute Program administered by the U.S. Bureau of Mines through the Generic Mineral Technology Center for Respirable Dust under grant G1115142 and NIOSH under grant ROI OH02611.

## References

1. National Institute for Occupational Safety and Health: Carcinogenic Effects of the Exposure to Diesel Exhaust. Current Intelligence Bulletin 50, NIOSH Pub. No. 88-116. NIOSH, Cincinnati, OH (1988).
2. Baumgard, K.J.; Johnson, J.H.: The Effect of Low Sulfur Fuel and Ceramic Particulate Filter on Diesel Exhaust Particle Size Distribution. Transactions of the Society of Automotive Engineers 101:691-699 (1992).
3. International Agency for Research on Cancer: Diesel and Gasoline Engine Exhaust and Some Nitrosarenes. In: IARC Monographs on the Evaluation and Carcinogenic Risks to Humans, Vol. 46. IARC, Lyons, France (1989).
4. Bagley, S.T.; Baumgard, K.J.; Gratz, L.D.; et al.: Effects of a Catalyzed Diesel Particle Filter on the Chemical and Biological Character of Emissions from a Diesel Engine Used in Underground Mines. SAE Technical Paper Series, No. 911840 (1991).
5. McClure, B.T.; Bagley, S.T.; Gratz, L.D.: The Influence of an Oxidation Catalytic Converter and Fuel Composition on the Chemical and Biological Characteristics of Diesel Exhaust Emissions. SAE Technical Paper Series, No. 920371 (1992).
6. Mine Safety and Health Administration: Permissible Exposure Limit for Diesel Particulate. Federal Register 57(3):500-503 (1992).
7. U.S. Code of Federal Regulations: Title 30, Chapter I, Subchapter B, Part 36 (1991).
8. Ambs, J.L.; Hillman, T.L.: Disposable and Reusable Diesel Exhaust Filters. In: Diesels in Underground Mines: Measurement and Control of Particulate Emissions. Proceedings of the Bureau of Mines Information and Technology Transfer Seminar, September 29-30, 1992, Minneapolis, MN, pp. 67-73 (1992).
9. Cantrell, B.K.; Rubow, K.L.: Development of Personal Diesel Aerosol Sampler Design and Performance Criteria. Min. Eng. Mag., Soc. Min. Eng., AIME February: 232-236 (1991).
10. Rubow, K.L.; Marple, V.A.; Tao, Y.; et al.: Design and Evaluation of a Personal Diesel Aerosol Sampler for Underground Coal Mines. Soc. Min. Eng., AIME preprint 90-132 (1990).
11. Marple, V.A.; Rubow, K.L.; Behm, S.M.: A Micro-Orifice Uniform Deposit Impactor (MOUDI): Description, Calibration, and Use. Aerosol Sci. Technol. 14:434-446 (1991).
12. Palmes, E.D.; Gunnison, A.F.; Dimattio, J.; et al.: Personal Sampler for Nitrogen Dioxide. AIHA J. 37:570-577 (1976).
13. Johnson, J.H.; Carlson, D.H.; Renders, C.F.: Underground Laboratory Evaluation of a Venturi Scrubber and a Catalyzed Corn-ing Ceramic Particulate Filter. Task Report submitted to U.S. Bureau of Mines, Department of the Interior, Washington, DC, for contract JO145007, pp. 15-16 (January 15, 1987). (Copies available through NTIS or by writing to Dr. J.H. Johnson, ME-EM Department, Michigan Technological University, Houghton, MI 49931.)
14. Cantrell, B.K.; Rubow, K.L.; Watts, Jr., W.F.; et al.: Pollutant Levels in Underground Coal Mines Using Diesel Equipment. Transactions of the Society for Mining, Metallurgy, and Exploration, Inc. 290:1901-1907 (1992).
15. Chan, L.M.; Carlson, D.H.; Johnson, J.H.: Apparatus and Methodology for Controlling Mine Ambient Air Quality Based on Vehicle Tailpipe and Ambient Air Pollutant Measurements. In: Proceedings of the 6th U.S. Mine Ventilation Symposium, June 21-23, 1993, Salt Lake City, UT. Society of Mining, Metallurgy, and Exploration, Inc., Littleton, CO (1993).
16. Chan, L.M.; Carlson, D.H.; Johnson, J.H.: Deterioration Criteria for Servicing Mine Diesel Vehicles Based on Tailpipe Pollutant Concentration Data. Mining Engineering 44(12):1472-1476 (1992).
17. Chan, L.M.; Carlson, D.H.; Johnson, J.H.: Evaluation and Application of a Portable Tailpipe Emissions Measurement Apparatus for Field Use. SAE Technical Paper Series 921647. In: Diesel Combustion Emissions and Exhaust Aftertreatment, SAE Special Publication, Vol. SP 931 (1992).
18. Carlson, D.H.; Taubert, T.R.; Johnson, J.H.: Apparatus for Measuring Diesel Tailpipe Emissions in Underground Mines. U.S. Department of the Interior, Bureau of Mines Pub. No. 9422. Bureau of Mines, Washington, DC (1992).
19. Carlson, D.H.; Johnson, J.H.; Taubert, T.R.: Apparatus for Sampling and Measuring Diesel Tailpipe Emissions. Office of Technology Transfer, Bureau of Mines, Washington, DC (1994).
20. Bagley, S.T.; Baumgard, K.J.; Gratz, L.D.: Comparison of In-mine and Laboratory-generated Diesel Particulate Matter, Biological Activity, and Polynuclear Aromatic Hydrocarbon Levels. In: Respirable Dust in the Mineral Industries, pp. 61-70. R.L. Franz and R.V. Ramani, Eds. (1990).
21. Cantrell, B.K.; Rubow, K.L.; Watts, Jr., W.F.; et al.: Pollutant Levels in Underground Coal Mines Using Diesel Equipment. In: Proceedings of the 6th U.S. Mine Ventilation Symposium, Salt Lake City, UT, 1993, pp. 60-64. R. Bhaskar, Ed. Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO (1993).
22. Tomb, T.F.; Haney, R.A.; Gero, A.J.; et al.: Evaluation of Two Diesel Particulate Sampling Devices. In: Proceedings of the 3rd Symposium on Respirable Dust in the Mineral Industries, October 17-19, 1990, Pittsburgh, PA. Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO (1991).
23. Busby, W.F.; Goldman, M.E.; Newberne, P.M.; et al.: Tumorigenicity of Fluoranthene in a Newborn Mouse Lung Adenoma Bioassay. Carcinogenesis 5:1311-1316 (1984).
24. Cavalieri, E.; Rogan, E.; Sinha, D.: Carcinogenicity of Aromatic Hydrocarbons Directly Applied to Rat Mammary Gland. J. Cancer Res. Oncol. 114:3-9 (1988).
25. Cook, J.W.; Hewett, C.L.; Hieger, I.: The Isolation of a Cancer-Producing Hydrocarbon from Coal Tar. J. Chem. Soc. 395-405 (1933).
26. Kado, N.Y.; Guirguis, G.N.; Flessel, C.P.; et al.: Mutagenicity of Fine (<2.5  $\mu$ m) Airborne Particles: Diurnal Variation in Community air Determined by a *Salmonella* Micro Preincubation (Microsuspension) Procedure. Environ. Mutagen. 8:53-66 (1986).
27. Mogan, J.P.; Dainty, E.D.: Development of the AQI/EQI Concept—a Ventilation Performance Standard for Dieselized Underground Mines. In: Heavy Duty Diesel Emission Control: A Review of Technology, CIM Special Volume 36, pp. 364-367. The Canadian Institute of Mining and Metallurgy, Montreal, Quebec, Canada (1986).
28. Dainty, E.D.; Mitchell, E.W.; Schnakenberg, Jr., G.H.: Organization, Objectives and Achievements of a Three-Government Collaborative Program on Diesel Emissions Reduction Research and Development. In: CIM Special Volume 36, pp. 3-20. The Canadian Institute of Mining and Metallurgy, Montreal, Quebec, Canada (1986).
29. Schnakenberg, Jr., G.H.; Johnson, J.H.; Schaefer, P.: Use of CO<sub>2</sub> Measurements in Monitoring Air Quality in Dead-End Drifts. Heavy Duty Diesel Emission Control: A Review of Technology. In: CIM Special Volume 36, pp. 291-297. The Canadian Institute of Mining and Metallurgy, Montreal, Quebec, Canada (1986).
30. Ambs, J.L.; Cantrell, B.K.; Watts, Jr., W.F.; et al.: Evaluation of a Disposable Diesel Exhaust Filter for Permissible Mining Machines. Bureau of Mines Pub. No. RI 9508. Bureau of Mines, Washington, DC (1994).