The effects of water emulsified fuel on diesel particulate matter concentrations in underground mines

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ABSTRACT: In this study, we evaluated the ambient diesel particulate matter (DPM) concentrations (at the intakes and exhausts of the mine) as the entire vehicle fleet of a stone mine switched from using 35% biodiesel to using a water emulsified fuel (PuriNOx). Elemental carbon (EC) was reduced by 45% when a PuriNOx blend containing 10% water replaced 35% biodiesel and by 57% when a PuriNOx blend containing 20% water was used. Other factors such as engine duty cycle and production changes could potentially cause some day-to-day EC fluctuations, and no direct comparison to commonly used diesel fuels (No. 1 or No. 2) was achieved. Therefore, a second study was performed in a controlled "isolated zone" environment of a metal mine, comparing PuriNOx to No. 1 diesel fuel in a load haul dump vehicle. The EC fraction of the DPM was reduced by about 71% when the PuriNOx blend containing 10% water was used and by about 85% when the PuriNOx blend containing 20% water was employed. This study did not determine how the water emulsified fuel would affect the engine or power.

1 INTRODUCTION

Long-term exposure to diesel exhaust has become a concern because diesel emissions are believed to be a possible carcinogen by several organizations (IARC 1989, NIOSH 1988, EPA 2002). In addition, acute overexposure to diesel exhaust has been linked to deleterious health effects such as eye and nose irritation, headaches, nausea, and asthma (Kahn & Orris 1988, Rundell et al. 1996, Wade 1993). Measurements have shown that underground miners can be exposed to over 100 times the typical environmental concentrations of diesel exhaust and over 10 times the concentrations measured in other work environments where diesel engines are common (Cantrell & Watts 1997, Nauss 1998, Haney 1992).

In the United States, the Mine Safety and Health Administration (MSHA) has promulgated rules for regulating miners' exposure to diesel particulate matter (DPM) in underground metal/non-metal (MSHA 2001). In metal/non-metal mines, the MSHA rule limits personal exposure to DPM, measured by collecting air samples on quartz fiber filters and analyzing the filters for elemental carbon (EC) or total carbon (TC) (summation of organic carbon (OC) and EC) by NIOSH Method 5040. For the interim rule, miner exposure is limited to an average of 308 $\mu g/m^3$ EC for an entire shift (MSHA 2005). Due to this regulation, many types of control technologies are being investigated to reduce the DPM emitted from diesel-powered underground mining equipment.

Water-emulsified fuel is one such control technology being tried by the industry. The water in the fuel is believed (1) to reduce the combustion temperature which reduces the nitrogen dioxide (NO_2) production and (2) to alter combustion to inhibit soot formation.

Water emulsified fuels have been tried on several different types of vehicles, such as buses, fire trucks, tractors, etc. and mixed results were achieved (Rideout 1999, Rosenblatt 2000, Rosentblatt & Ainslie 1999, Howes 2000, EPA 2002, Matthews 2002, Matthews et al. 2002). For example, in a study done by Environmental Canada, a 24% total DPM reduction was observed in an International 4600 flatbed when the diesel fuel, used by the City of Houston, was replaced with PuriNOx (a water emulsified fuel made by Lubrizol) (Howes 2000). In the same study, a 69% reduction in total DPM was observed when PuriNOx was used in a John Deere road sweeper.

Common problems observed when using PuriNOx were power loss and increased fuel consumption

(Rideout 1999, Rosenblatt 2000, Rosentblatt & Ainslie 1999, Howes 2000, EPA 2002, Matthews 2002, Matthews et al. 2002). In some cases, PuriNOx affected the performance of the vehicle so much that it prevented its use, but in other cases PuriNOx was successfully used for years (Matthews et al. 2002). Due to the variation in these results, each type of engine with the duty cycles being used needs to be tested to determine the effects on the emission by the water emulsified fuels for that type of vehicle and use.

For the underground mining industry, Environment Canada showed some preliminary success in using PuriNOx. In an underground salt mine, Rosenblatt and Ainslie, from Environment Canada, reported a 46% reduction in DPM by mass when a PuriNOx blend replaced No. 2 diesel fuel in a front-end loader operating under a normal cycle (Rosenblatt 2000). This study does not give the effects on elemental carbon by the water emulsified fuel and was performed only on one vehicle. Therefore, in order to obtain additional information on the effects of PuriNOx on DPM from metal/nonmetal underground mining vehicles, we conducted two studies evaluating the effects of PuriNOx on DPM generated by diesel-powered underground mining equipment.

One study looked at the effect that PuriNOx had on DPM concentrations in a limestone mine. The limestone mine used a 35% biodiesel blend to reduce DPM exposure. The 35% biodiesel gave about a 30% reduction in EC and TC from DPM when compared to No. 2 diesel (Gerbec & Fields, 2003, Bugarski et al. 2003). The mine management had decided to switch from 35% biodiesel to PuriNOx blends. To evaluate this change, samples of EC and TC were obtained at the intakes and exhausts of the mine for three days when 35% biodiesel was used and again for three days when warm weather and cold weather blends of PuriNOx were being used. In this study, other factors such as engine duty cycle and production changes could potentially cause some day-to-day EC fluctuations. Three days of data were averaged in an attempt to minimize any effects that these factors would have on EC reduction. Nevertheless, these factors could not be totally accounted for. PuriNOx was also only compared to 35% biodiesel, and no direct comparison to commonly used diesel fuels (No. 1 or No. 2) was achieved.

Therefore, another study was conducted to confirm the results in the field by comparing PuriNOx to No. 1 diesel in a controlled environment. A loader was operated in an isolated zone (a long, sealed, entry supplied with fresh air). The isolated zone provided a controlled environment where the only source of DPM was the piece of equipment being investigated. The loader was operated over a duty cycle based on that used during actual mining. Downwind of the operating path of the vehicle, ambient EC, TC, and DPM mass measurements were obtained when No. 1 diesel fuel was used in the loader (baseline case) and then when a PuriNOx blend was used.

2 METHODS

2.1 *Fuels*

No. 1 Diesel: Cenex, Columbus, MT

Biodiesel: A 35% blend of Bio G-3000 biodiesel from Griffin Industries, produced from recycled restaurant grease with No. 2 diesel fuel. This fuel was used as the baseline.

Cold weather PuriNOx blend: 10% Water, 2.15% Lubrizol Emulsifier Additive, 2.15% Methanol, and 85.7% No. 2 diesel fuel.

Warm weather PuriNOx blend: 20% water, 3% Lubrizol Emulsifier Additive, and 77% No. 2 diesel fuel.

Sulfur content and other properties of the fuels can be found in publications by Bugarski et al. (2003, 2005).

2.2 *Sampling and analytical methods*

2.2.1 *EC-TC sampling train*

The EC-TC sampling train used for DPM sampling was identical to the one used by MSHA for DPM compliance monitoring (MSHA 2001). It consisted of a flow-controlled MSA Elf Model pump (Mine Safety Appliances Company, Pittsburgh, PA), a 10-mm Dorr-Oliver cyclone, and an SKC DPM cassette (SKC, Inc., Eighty Four, PA). The SKC DPM cassette contained a single-stage impactor and two 37 mm diameter tissue quartz filters, mounted in series. The pumps were operated at 1.7 lpm. The flow rate for each of the sampling pumps was measured and recorded at the beginning and end of each day using a Gilibrator II bubble flow meter (Sensidyne, Inc., Clearwater, FL). If the measured flow rates deviated more than 5% from 1.7 lpm, the pumps were recalibrated.

Exposed SKC DPM cassettes were taken to NIOSH Pittsburgh Research Laboratory (PRL) and analyzed in the laboratory for EC and TC content using the NIOSH Method 5040.

2.2.2 *High-volume sampling procedure*

When testing the efficiencies of control technologies in underground mines, the concentration of DPM can be low. To collect enough material to be at and above the limit of quantification for NIOSH Analytical Method 5040, one might have to sample for many hours. When doing research in the field, one does not always have this luxury. A high-volume (HV) sampling train was developed by Bugarski et al. (2003, 2005) to collect more material in less time. The HV flow rate was achieved by merging flows from five classifiers, each consisting of a 10-mm Dorr-Oliver cyclone followed by a U.S. Bureau of Mines (BOM) single stage diesel impactor, into a single stream. A flow rate of between 1.7–2.0 lpm was maintained through each cyclone and impactor pair. At this sampling flow rate only particles with geometric mean smaller then 0.8 μm were deposited on the filters. All five classifiers were attached to a symmetrical plenum that distributed a total flow rate of between 8.5–10 lpm uniformly among the five streams. Each of the classifier assemblies was connected to the plenum chamber by a 3-foot long section of conductive tubing. The outlet of the plenum was directly connected to a stainless steel 25 mm diameter filter holder containing a stack of two 25 mm tissue quartz fiber filters (Tissuequartz 2500QAT, Pall Corporation, Ann Arbor, MI). This design is described in detail in the Bugarski et al. reports (2003).

2.3 *Stone mine survey*

After vehicles in a stone mine had used 35% biodiesel for almost one year, we sampled EC, TC, and NO_2 one shift per day for three days. Each vehicle was equipped with a diesel oxidation catalyst. The fuel for the entire fleet was then changed from 35% biodiesel to the cold weather PuriNOx blend (supplied by Lubrizol). After running the new fuel for approximately one month, we again took three days of measurements. Following this evaluation the fuel was changed to the warm weather PuriNOx blend and run for about one month. Once again we sampled for one shift for three consecutive days.

This limestone mine had one main intake entry and two main exhaust entries. In the one main intake, one EC-TC sampling train (described earlier) was set up. The EC-TC sampling trains were chosen instead of the high volume sampling since we did not have electricity to run the high volume sampling and we were sampling for a long enough period (about 8 hours) to collect enough material using the EC-TC sampling train. Three EC-TC sampling trains were placed in each of the two main exhaust entries. In the exhaust entries, an ITX multi-gas monitor (Industrial Scientific Corp., Oakdale, PA) measured NO_2 and an anemometer measured air velocities.

Most of the vehicles in the mine (about 61%) had Caterpillar engines. A complete list of diesel engines is found in the report by Gerbec and Fields (2003).

EC and TC were chosen as surrogates for DPM, which consists of over 80% carbon (Heywood 1988, Pierson 1983). We could not directly measure the DPM since we believed that gravimetric or mass measurements of DPM on a filter would not be sensitive or precise enough to obtain reliable data and that even the small portions of dust that penetrate through the impactor (about 4–10%) may cause interference to mass measurements. As described later in this paper, we believed that we could account for TC interferences (e.g. cigarette smoke, oil mist, and vapor-phase OC) usually seen in underground mines. Unlike TC, EC is DPM-selective and would allow us to monitor DPM concentrations without being concerned about interferences.

2.3.1 *Ventilation normalization*

Factors other than fuels can cause different day-to-day DPM concentrations in a mine. These include ventilation changes, varying production, and different duty cycles on engines. To best evaluate the effects from the fuel change, we took measurements over three days to minimize the variable in-mine conditions and normalized the EC and TC concentrations to average ventilation rates to account for any ventilation changes. The normalization calculation is described in a report by Bugarski et al. (2003).

2.3.2 *Interferences*

There were no known interferences for the EC measurements. For OC from DPM there were possible interferences from mineral dust, cigarette smoke, oil mist, and vapor-phase OC.

The SKC DPM cassette was used for EC and OC measurements. This device allows only particles less than 0.8 μm to collect on the filter, eliminating any significant interference from airborne mineral dust.

We were also concerned with vapor-phase OC adsorbing onto the quartz filter and causing a positive bias to the particulate TC. To account for this, a second filter was placed in tandem (in series) with the primary filter. In theory, the second filter was exposed to the same concentrations of vapor OC as the first filter but does not collect any particulate. Thus, to correct for the adsorbed vapor-phase OC, results from the second filter were subtracted from the first filter OC values. In the literature, this is referred to as the tandem filter correction (Kirchstetter et al. 2001, Eatough et al. 1995, Turpin & Huntzicker 1994).

Oil mist should not be a significant interference by the time it arrives at the samplers in the exhaust entries. When compared to DPM, any cigarette smoke should be so diluted that interference should be minimal at the sampling locations used in this study (Haney 2000).

2.4 *Isolated zone study*

An isolated zone was set up in a metal mine as described in reports by Bugarski et al. (2003). In the isolated zone, the only source of diesel exhaust was the vehicle being tested. Air flowed in through one intake entry and out through one return entry.

A 344 Load Haul Dump (LHD) with a Caterpillar 3126B DITA engine was run with No. 1 diesel fuel using a duty cycle typical to this vehicle in production.

This was the same duty cycle described in reports by Bugarski et al. 2003 for an LHD.

Duplicate EC and TC samples were collected upstream and triplicate samples were obtained downstream of the operating vehicle using high-volume (HV) samplers described earlier and analyzed using NIOSH Method 5040 (Birch 2003). HV samplers were used in this case since we could only sample for about two hours. Therefore, we were not sure if we could collect enough material on the filter using the EC-TC sampling trains. An ultra sonic anemometer was set up to measure entry air velocities.

Duplicate DPM mass samples were collected using a design similar to the HV sampler described below. Instead of a quartz filter, a Teflon filter (Pall Corporation, East Hills, NY) was used. Instead of mass flow controllers, critical orifices were used to control the air flow rate. Prior to and after each test gravimetric samples were desiccated and equilibrated in a controlled environment (72°F and 50% relative humidity) before weighing. Balance precision was better than 6 μg.

No. 1 diesel fuel was replaced with a cold weather PuriNOx blend and the test was repeated. The vehicle was run for some time to allow the engine to consume the old fuel before the actual test began. Following this series, another evaluation was started using the warm weather PuriNOx blend.

2.4.1 *Interferences*

In the isolated zone a BOM impactor was used for EC, TC, and DPM mass measurements. This sampler should eliminate any significant interference from ambient airborne mineral dust in the mine. Samples were taken in the intake entry, upwind of the isolated zone, so that any analyte present in the incoming air could be determined and subtracted from its value measured downwind. Based on the experimental design, in the isolated zone the only source of DPM should be from the vehicle in this area.

Vapor-phase organic carbon (OC), generated from engine exhaust but not considered to be part of DPM, can adsorb onto the quartz filters and cause a positive bias of the particulate TC results in both upstream and downstream samples. As previously described, OC quantities on a secondary filter, located in tandem with the primary filter, were subtracted from the OC values to correct for the adsorption of vapor-phase OC.

Exposed filters were taken to NIOSH Pittsburgh Research Laboratory (PRL) and analyzed in the laboratory for EC and TC content using the NIOSH Method 5040.

2.5 *Confidence limits*

Each value for OC, EC, and TC was the average of triplicate samples for the isolated zone study and the average of three days of triplicate samples for the stone mine study. The 95% confidence limits for the carbon analysis for both the isolated zone and stone mine studies were calculated using the following equation (Skoog 1986):

$$confidence\ \lim it = \frac{t \times s}{\sqrt{N}} \tag{1}$$

where t is the factor for the confidence interval dependent on the degrees of freedom, s is the standard deviation, and N is the number of samples.

Since the DPM mass for the isolated zone study was only done in duplicate, the above equation cannot be used to give a reliable confidence limit. In this case, we calculated an accepted confidence limit for gravimetric samples by using the standard deviation obtained when hundreds of samples were weighed using the same procedure and balance used in this study. The 95% confidence limit for the DPM mass measurements was then calculated using the following equation (Skoog 1986):

$$accepted\ confidence\ \lim it = 1.96 \times s \tag{2}$$

where s is the standard deviation.

3 RESULTS AND DISCUSSION

3.1 *Stone mine study*

Significant reductions were observed when a mine used PuriNOx in its entire vehicle fleet. Table 1 shows the average concentrations of EC and TC for the three days of measurements at the two main exhausts of the mine.

When the cold weather PuriNOx blend was used instead of the 35% biodiesel, the average of the two locations showed a 45% reduction in the EC from DPM. There was no significant effect on the OC concentration, and the TC concentration was reduced by about 36%.

Substituting the warm weather PuriNOx blend for the 35% biodiesel, a 57% reduction in EC and a 43% reduction in TC was observed. There was again no significant effect on the OC concentration.

These emission reductions were observed when using 35% biodiesel as a baseline fuel. The diminutions would most likely be higher if PuriNOx blends were compared to No. 1 or No. 2 diesel fuel.

These numbers do have limitations. Other factors such as engine duty cycle and production changes could result in day-to-day EC fluctuations. Three days of data were averaged in an attempt to minimize any effect that these factors would have on EC reduction, but nevertheless, these factors could not be totally accounted for.

Table 1. Reduction in DPM from PuriNOx compared to 35% biodiesel at Black River Mine.

Location	Fuel	OC (μg/m^3)	EC (μg/m^3)	TC (μg/m^3)	Average Anemometer Readings (ft/min)	EC Reduction (%) - corrected for ventilation	TC Reduction (%) - corrected for ventilation
Exhaust 1	35 % biodiesel	61.47 ± 6	283.74 ± 23	345.21± 23	476		
	cold weather PuriNOx	61.31± 11	155.53 ± 27	216.85 ± 33	482	46	38
	warm weather PuriNOx	72.94 ± 6	119.56 + 12	192.50 ± 12	499	60	47
Exhaust 2	35 % biodiesel	52.23 ± 6	223.77 ± 21	276.00 ± 23	482		
	cold weather PuriNOx	53.95 ± 10	128.37 ± 11	182.32 ± 18	482	43	34
	warm weather PuriNOx	65.21 ± 7	104.95 ± 13	170.16 ± 16	482	53	39
average of two sites	cold weather PuriNOx					45	36
	warm weather PuriNOx					57	43

* There was no significant (average concentration <5 μg/m^3) EC or TC particulate collected on the intake samples.

The OC, EC, and TC concentrations were the concentrations measured after tandem filter correction without being normalized for ventilation. The reductions are after being normalized for ventilation.

Confidence limits were calculated as described in methods section.

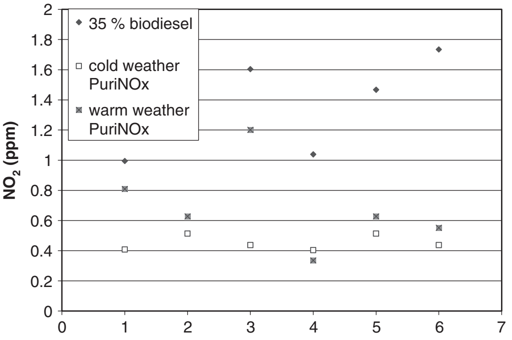

Figure 1. NO_2 concentrations observed in Black River Mine when each fuel was used. Each point represents the concentration at a location for each day.

3.1.1 *NO_2 measurements*

Figure 1 shows the daily NO_2 concentrations at each location and for each fuel. A reduction in NO_2 was observed.

3.1.2 *Problems*

A reduction in engine power was observed by operators with the use of PuriNOx fuels but did not seem to affect the production during the days of the study. However, this study was too short to determine how much this power loss would affect the use of the vehicles. That would have to be determined after a longer use of the fuel. It would also take a longer study to determine how the fuel would affect the engines. An odor was observed when the warm weather blend was used.

Table 2. The reduction of DPM in the isolated zone study.

Fuel	OC (μg/m^3)	EC (μg/m^3)	TC (μg/m^3)	DPM mass (μg/m^3)
No. 1 diesel	56.31 ± 2.7	254.30 ± 13.7	310.61 ± 16.2	366.52 ± 14
PuriNOx cold weather blend	79.70 ± 9.2	74.75 ± 7.6	154.45 ± 16.4	205.20 ± 14
PuriNOx warm weather blend	58.16 ± 6.6	35.65 ± 4.3	93.81 ± 10.2	157.09 ± 14
	Reduction (%) when compared to No. 1 diesel			
	OC	**EC**	**TC**	**DPM mass**
PuriNOx cold weather blend	-41.54	70.60	50.28	44.01
PuriNOx warm weather blend	-3.29	85.98	69.80	57.14

* There was no significant (<3 μg/m^3) EC or TC particulate collected on the upstream samples. Therefore, they were not subtracted from the data.

Confidence limits were calculated as described in methods section.

3.2 *Isolated zone study*

Use of the cold weather PuriNOx reduced EC by 71% relative to No. 1 diesel fuel; the warm weather formulation reduced EC by 86% (see Table 2).

The cold weather PuriNOx increased OC by 41% (no DOC was used) but the warm weather PuriNOx showed no significant change in OC. DPM mass was reduced by 44% with the cold weather PuriNOx and by 57% with the warm weather PuriNOx.

The ventilation did not change between tests. The duty cycle was the same and the same number of cycles were run for each test. Therefore, the effects of PuriNOx fuels should be the only cause of DPM reduction.

The operator and researchers did experience some burning of the eyes when the PuriNOx blends were used. This was not observed when running PuriNOx blends at Black River stone mine. This may have been because diesel oxidation catalysts were equipped on all vehicles in the stone mine but were lacking on the vehicle used in the isolated zone study. Some power loss was observed but not enough to prevent the vehicle from performing the duty cycle.

4 CONCLUSION

PuriNOx substantially reduced EC from DPM in two studies. The OC concentration was either not affected or increased (when no DOC was used). An odor and burning of the eyes can occur, but might be mitigated if DOCs (which probably should be used with PuriNOx) are also used on the vehicle. Power loss was observed and may inhibit the use of a water emulsified fuel on certain vehicles. These studies were too short to determine how this fuel will affect the engine.

Disclaimer: Mention of a company name or product does not constitute endorsement by the Centers for Disease Control and Prevention. The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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