Relationship between Elemental Carbon, Total Carbon, and Diesel Particulate Matter in Several Underground Metal/Non-metal Mines

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Elemental carbon (EC) is currently used as a surrogate for diesel particulate matter (DPM) in underground mines since it can be accurately measured at low concentrations and diesels are the only source of submicrometer EC in underground mines. A disadvantage of using EC as a surrogate for DPM is that the fraction of EC in DPM is a function of various engine parameters and fuel formulations, etc. In order to evaluate how EC predicts DPM in the underground mining atmosphere, measurements of total carbon (TC; representing over 80% of the DPM) and EC were taken away from potential interferences in four underground metal/non-metal mines during actual production. In a controlled atmosphere, DPM mass, TC, and EC measurements were also collected while several different types of vehicles simulated production with and without different types of control technologies. When diesel particulate filters (DPFs) were not used, both studies showed that EC could be used to predict DPM mass or TC. The variability of the data started to increase at TC concentrations below 230 μg/m² and was high (±20%) at TC concentrations below 160 μg/m³, probably due to the problem with sampling organic carbon (OC) at these concentrations. It was also discovered that when certain DPFs were used, the relationship between DPM and EC changed at lower DPM concentrations.

Introduction

Long-term exposure to elevated concentrations of diesel exhaust is a concern because diesel particulate matter (DPM) is believed to be a possible carcinogen (1–3). Exposure to elevated concentrations of diesel exhaust has also been linked to health effects such as eye and nose irritation, headaches, nausea, and asthma (4–6). 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 that are measured in other work environments where diesel engines are common (7–9).

In the United States, the Mine Safety and Health Administration (MSHA) has promulgated rules (10–14) limiting DPM concentrations to which underground metal/non-metal miners are exposed. In general, the rule stipulates using quartz fiber filters to collect DPM (15–17) and then analyzing the filters for elemental carbon (EC) and organic carbon (OC) content using NIOSH method 5040 (18–20). The total carbon (TC) content on a filter is obtained by adding EC and OC.

Initially, TC was considered by MSHA to be the most appropriate surrogate for DPM because it accounts for over 80% of the particulate matter in diesel exhaust (21–22). However, other sources, commonly present in underground mines, can interfere with the TC analysis (12, 14). These contaminants include EC and OC found on mineral dust, environmental tobacco smoke, and oil mist. EC and OC contamination from mineral dust has been shown to be effectively removed using size-selective samplers (15–17, 23–25). Unfortunately, these size-selective samplers are not effective in removing the submicrometer aerosols from cigarette smoke or oil mist. Because cigarette smoke and oil mist cannot always be avoided when taking personal samples, and because these contaminants only interfere with the OC analysis, MSHA proposed using submicrometer EC as a surrogate for DPM. There are no other known sources of submicrometer EC present in the metal/non-metal mining environment.

One potential issue with using EC as a surrogate for DPM is that the EC fraction of DPM may change depending upon factors such as engine duty cycle and fuel type, etc. For example, Burtscher et al. showed a black carbon (EC) to total mass ratio for DPM sampled from the tailpipe that ranged from 45 to 100%, depending upon the engine load conditions (26). The portion of EC in DPM in underground mining atmospheres could potentially vary, depending on how much engine conditions vary from day to day and mine to mine. It is necessary to investigate the relationship between DPM and EC in underground metal/non-metal mines to determine how well EC can be used to predict DPM concentrations across the industry. This will become especially important in 2008 when the exposure limit for underground metal/non-metal miners changes to the final exposure limit of 160 μg/m³ TC. MSHA plans on using EC as a surrogate for this final rule but has not yet determined the TC to EC conversion factor to be used to convert 160 μg/m³ TC to a comparable EC concentration.

In this study, we investigated the relationships between DPM and EC concentrations, and TC and EC concentrations, using results obtained through a series of tests conducted in an isolated zone in a metal mine. Additionally, the relationship between TC and EC concentrations was evaluated using results obtained from samples collected in two stone and two metal underground mines during actual production. This research will add to the current knowledge on the relationship between DPM and EC and may assist MSHA and other researchers in formulating proper conversion factors between the two.

Experimental Procedures

Testing Procedures. Isolated Zone Tests. Ambient concentrations of EC, TC, and DPM were measured during a series of tests in an isolated zone. The isolated zone, a section in a metal mine that is isolated from the remaining parts of the mine, was designed so that the only source of DPM and gases in the zone was from the vehicle being tested. A detailed description of the isolated zone is given in reports by Bugarski et al. (27, 28).

Six vehicles were used to test the emission control technologies (list of vehicles and control technologies in

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papers by Bugarski et al. (27, 28). Each vehicle was operated with and without emission control technologies. The vehicles were operated in the zone over simulated production duty cycles described in the reports by Bugarski et al. (27, 28).

During those tests, triplicate particulate samples for carbon analysis were collected upstream and downstream of the vehicle in the zone using a high-volume (HV) sampling method (air collected at 8.5 lpm with a 0.8 μm cutpoint (method described in detail in papers by Bugarski et al. (26, 27)). In parallel, the DPM concentrations were measured at the same locations (upstream and downstream) using a tapered element oscillating microbalance (TEOM; Thermo Electron, East Greenbush, NY). To avoid collecting mineral dust, a classifier, consisting of a Dorr-Oliver cyclone followed by a Bureau of Mines (BOM) impactor, was attached to the inlet of the TEOM. The TEOM measures the mass of material collected on a filter element mounted on a hollow tapered vibrating pedestal. To prevent condensation and ensure that the sample filter always collects particulates under similar conditions, the intake to the tapered element is heated and the sampling stream through the filter is maintained at 50 °C. The reported TPM concentration for each test was obtained from the net gain in mass that occurred over the same time period as that of the OC/EC sampling. Test equipment and procedures are described in detail in the reports by Bugarski et al. (27, 28).

Mine Surveys. The samples for carbon analysis were collected in two stone and two metal mines during normal mining production using the standard sampling method (described in the next section). The samples were analyzed using NIOSH method 5040.

The following precautions were taken to minimize the effects of potential interferences, such as cigarette smoke and oil mist: (1) area sampling stations were located in the mine returns, away from any potential sources; (2) a tandem filter correction (described later in this paper) was applied to correct for the adsorption of vapor-phase OC; (3) finally, only samples containing over 40 μg of TC were included in this data set to further minimize the potential effects on the TC to EC relationship from contributions of non-DPM OC (TC = OC + EC).

In addition to the area samples, seven personal samples were included in this data set. Because these samples were collected in areas where the average TC concentrations were greater than 900 μg/m^3 (i.e., areas with high DPM concentrations), any potential contamination from non-diesel sources should have a minor effect on the TC to EC relationship (29).

In each stone mine, triplicate samples were taken each day over a 3-day period. This procedure was repeated for each fuel type: No. 2 diesel, 50% recycled grease biodiesel, 10% PuriNox mixture (a water emulsified fuel produced by Lubrizol, Inc., of Wickliffe, OH), and 20% PuriNox mixture. Diesel oxidation catalysts were used on all equipment in the stone mines.

In one metal mine, where control technologies were not used and the vehicles were fueled with No. 2 diesel, the samples were collected once a day over a 4-h sampling period for 6 consecutive days. In the other metal mine, samples were collected over one, 2.5-h period when there were no control technologies on the vehicles. After DPF systems were installed on some of the vehicles, a second set of samples was collected for 2 days (involving about 4 h of sampling per day).

Sampling and Measurement Methods. Standard Sampling Procedure. In the standard sampling procedure, the sampling train, consisting of a DPM cassette (SKC, Inc., Eighty Four, PA), a Dorr-Oliver cyclone, and an Elf Escort personal pump (Mine Safety Appliances Co., Pittsburgh, PA), was used to collect ambient air samples at 1.7 L/min (liters per minute).

SKC DPM cassettes incorporate an impactor with a 0.8 μm cutpoint and two quartz fiber filters placed in tandem.

Analytical Methods. NIOSH Method 5040. NIOSH method 5040 was used to determine EC and TC concentrations. A detailed description of NIOSH method 5040 is found in the NIOSH Manual of Analytical Methods (20).

Tandem Filter Correction. Quartz filters have been found to adsorb vapor-phase OC, which is not traditionally recognized as part of DPM or other types of particulate carbon, and thereby contribute a positive bias in DPM TC results. A tandem filter correction procedure (30–32) was used to correct results and account for this phenomenon. This procedure requires a second filter to be placed behind the sample filter, resulting in two filters positioned in tandem. In theory, only the sample filter collects particulate OC but both filters adsorb about the same amount of vapor-phase OC. Results from the second filter were therefore subtracted from the sample filter OC values to correct for the adsorbed vapor-phase OC.

Data Analysis. A linear regression analysis was used to evaluate the relationship between DPM and EC and between TC and EC, where either DPM or TC was the dependent variable and EC was the independent variable. When the distribution of the dependent variables showed a significant departure from normality, a log-linear regression model was also investigated. If the overall fit of the models did not differ, only the results of the analyses using the untransformed data would be presented in this paper.

The coefficient of determination (R^2) was computed for each regression analysis. R^2 represents the fraction of total variation in the values of the dependent variables (DPM or TC) that can be explained by the linear relationship to the independent variable (EC).

An F-statistic was also computed for each model. This is the ratio of the model mean square divided by the error mean square. For a linear regression, it is used to test the hypothesis that the slope coefficient (β_1) is equal to zero. If the F-statistic results in a p-value of less than 0.05, this indicates that the linear model is appropriate for describing the relationship between DPM and EC or TC and EC.

Diagnostics were used to assess violations of linear regression assumptions. Studentized residuals (residuals divided by their standard errors) were calculated to identify outlying observations. Studentized residuals exceeding a value of 2.5 provide a way to pinpoint unusually large residuals. In addition, a Cook’s distance (Cook’s D) statistic was calculated for each point to determine its influence on the regression line. The Cook’s D number is the measure of change in the predicted values upon deletion of that point.
observation from the data set. If the Cook's $D$ number is above 1, that data point is considered to be highly influential. However, this does not necessarily indicate that the point should not be included in the regression model.

Once the regression equation was determined, the deviation of each point from the regression line was determined to see how well the equation predicted each data point. The following equation was used

$$\% \text{ deviation} = \left( \frac{V_{\text{calc}} - V_{\text{meas}}} {V_{\text{meas}}} \right) \times 100$$

where $V_{\text{calc}}$ is the dependent variable (DPM or TC) calculated from the regression equation and $V_{\text{meas}}$ is the dependent variable (DPM or TC) measured.

Results and Discussion

Blanks. At times in the laboratory it has been noticed that the second filter used to correct for the adsorption of vapor-phase OC can be contaminated. The second filter had significantly higher OC than the first filter for some blank samples. This could be due to some contamination from the backing pads used. To see if the second filter was contaminated for the samples in this study, samples from the intakes of the mine and in the upstream section of the isolated zone were studied. The concentration of particulate matter at these sites was very low (at times, even below the limit of detection for NIOSH method 5040). Therefore, if the second filter was contaminated, it would have higher OC than the first. If there was no contamination, then the first and second filter would either be approximately the same or the first filter would have a slightly higher OC, depending upon the concentration of OC particulate. As seen in Figure 1, contamination of the second filter was not a significant problem. Figure 1 shows the difference (TC(QQ2) - TC(QQ1)) between the second and first filter. For 92% of the samples the concentration of OC on the second filter did not exceed by more than 5 $\mu$g/m$^3$ OC that on the first.

Isolated Zone. As seen in Figure 2a, EC could be used to predict DPM for the conditions set in the isolated zone when diesel particulate filters (DPFs) were not used. There is a good overall fit for the linear regression model ($p$-value is $<0.0001$; $R^2 = 0.98$) between DPM and EC data obtained in the isolated zone, when diesel particulate filters were not
used. There was one outlying observation, but it was not influential. In addition, a log-linear model was investigated with these data, but the results did not differ significantly from those obtained using a linear model.

As illustrated in Figure 2a,b, the correlation between DPM and EC changes when noncatalyzed DPFs (high-temperature disposable DPF, ceramic DPF followed by DOC) were used in the isolated zone tests. In general, there is less than a 20% deviation between measured DPM and calculated DPM from EC (using the linear equation); however, at the lower DPM concentrations when noncatalyzed DPFs were used the data deviated from the line by over 50%. This deviation may have resulted from the use of noncatalyzed DPFs on the engine being tested in the isolated zone. DPFs are known to preferentially reduce EC over other DPM components. Bugarski et al. (27, 28) found 92, 92, and 70% reductions in EC corresponding to an 85, 69, and 62% reduction in DPM, respectively. It is important to note that the catalyzed DPFs also preferentially reduced EC over the other components of DPM (over 90% reduction in EC and around 75% reduction in DPM), but did not seem to affect the relationship between DPM and EC. This could be because the catalyzed DPFs can cause the formation of some non-EC DPM (sulfates) (32, 33). It is also important to note that some of the deviation could be due to experimental error when measuring at the lower DPM concentrations.

In this research the ratio between EC and TC was also analyzed. This EC to TC analysis was initiated for two reasons: (1) the mining community is interested in finding a conversion factor between TC and EC (13), and (2) it allows for a comparison with results from other field studies where gravimetric analysis was not possible. Figure 3a presents the regression model using EC to predict TC. The sample points included in this figure consisted of data collected when (1) no control technologies were used, (2) diesel oxidation catalysts (DOCs) were used, and (3) alternative fuels were used. The initial model contained a datum point that was highly influential (Cook's $D = 7$); this point was excluded from the analysis. The subsequent model resulted in an $F$-statistic that was significant at $p = 0.0001$ and an $R^2 = 0.99$. These results indicate that the linear model is appropriate for describing the relationship between TC and EC.
When certain DPFs were used, the results deviated from the linear regression and formed another trend. As seen in Figure 3b, the points deviated from the predicted TC by over 50% when certain DPFs were used. This could have been because the DPFs in this experiment preferentially reduced EC over OC (as mentioned previously).

We know that the DPFs used in the isolated zone substantially reduced all DPM components (for example, in the isolated zone when the data were normalized to a ventilation rate of 12,000 cfm, the DPM concentration (measured by TEOM) went from 600 µg/m³ (474 µg/m³ TC) with no control technology to 170 µg/m³ (53 µg/m³ TC) when a ceramic DPF, followed by a DOC, was used) (27) and caused deviations in the DPM and EC relationship at lower concentrations. Therefore, we would expect that if these certain DPFs were used in an underground mine that the DPM and EC relationship would not be affected until most of the DPM was generated from vehicles containing these DPFs. Since vehicles without DPFs would emit much more DPM than vehicles with these DPFs, the DPM and EC relationship would only be affected when a large number of the vehicles in the mine contained these DPFs. We would also expect the DPM concentration to be in the lower part of the concentration range when the DPM and EC relationship would change since the DPFs substantially reduce DPM. This is what was observed in the isolated zone.

The isolated zone results showed a linear relationship between EC and DPM when DPFs were not used; however, when the equipment was outfitted with certain DPFs, usually resulting in lower isolated zone DPM and EC concentrations, the relationship between DPM and EC was affected.

In the isolated zone tests we were limited to just several vehicles from one mine fleet. The next step was to utilize information gathered from many vehicles in actual mining production.

**Mine Surveys.** In this portion of the study, we sampled TC and EC concentrations in four operating mines. Due to the complexity of sampling DPM (interferences and precision of method, etc.) in real mining conditions, gravimetric samples could not be taken; therefore, only the relationship between TC and EC could be evaluated. Since TC represents over 80% of the DPM (as lower sulfur fuel is introduced, TC...
Literature Cited


(27) Bugarski, A.; Schnakenberg, G.; Noll, J. D.; Mischler, S.; Patts, L.; Hummer, J.; Vanderslice, S. Effectiveness of Selected Diesel Particulate Matter Control Technologies for Underground...


