

Measuring diesel particulate matter in underground mines using submicron elemental carbon as a surrogate

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ABSTRACT: Elemental carbon (EC) is used as a surrogate for regulating the exposure to diesel particulate matter (DPM) of underground metal/non-metal miners. EC was chosen as a surrogate because EC is selective to DPM and is a major component of DPM. Using EC as a surrogate also gives one the advantages of no sampling artifacts and being able to sample at all locations in the mine. Currently, EC represents DPM well in underground mines. Some control technologies have been shown to possibly alter the relationship between DPM and EC and characteristics of DPM. Therefore, future work will investigate the relationship between DPM and EC as new control technologies are implemented.

1 INTRODUCTION

1.1 Background

Long-term exposure to diesel exhaust has become a concern because diesel emissions are believed to be a potential carcinogen (NIOSH, 1988). 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 and 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 and Watts, 1997; Nauss, 1998; Haney, 1992).

In the United States, the Mine Safety and Health Administration (MSHA) has promulgated rules to limit the exposure of metal/non-metal underground miners to diesel particulate matter (DPM) to 500 $\mu\text{g}/\text{m}^3$ for an interim limit and 200 $\mu\text{g}/\text{m}^3$ for a final limit (MSHA, 2001, 2005). One issue that had to be overcome was how to measure for DPM.

1.2 Difficulties in measuring DPM in underground mines

DPM is a complex mixture of particulate elemental carbon (EC) or soot, particulate and particle bound organic carbon (OC), sulfates, some metals, etc. (Kittelson, 1998). Mass measurements of DPM are prone to interferences from other sources of aerosols

(mineral dust, cigarette smoke, etc.) in the mining environment and are not sensitive enough for the concentrations near the proposed final limit (below 200 $\mu\text{g}/\text{m}^3$). Therefore, a surrogate was needed to determine DPM exposure.

Initially, total carbon (TC) was considered by MSHA to be the most adequate surrogate for DPM because TC accounts for over 80% of the DPM (MSHA, 2001; Pierson and Brachaczek, 1983; Kittelson, 1998). However, the EC and OC particles from mineral dust and OC aerosols from the other sources commonly present in underground mines, such as environmental tobacco smoke and oil mist, were found to interfere with the TC analysis.

A size selective sampler (Cantrell and Rubow, 1991; McCartney and Cantrell, 1992; Cash et al., 2003; Noll et al., 2005) has been shown to effectively segregate the coarse mineral dust from the generally submicron DPM. Unfortunately, the size selective samplers are not very efficient in removing cigarette smoke and oil mist (OC aerosols that generally belong to the same size category as diesel aerosols). Therefore, cigarette smoke and oil mist cannot always be avoided when taking personal samples. For example, when TC vs. EC was plotted from personal samples below 400 $\mu\text{g}/\text{m}^3$ from smokers and non-smokers from two stone mines (samples corrected for adsorbed vapor phase OC), there is greater variability in the TC and EC relationship as samples are potentially exposed to more interferences (smokers). The R^2 goes from about 0.7 to 0.9 when the data from smokers are taken out. Figure 1 also shows that at the same EC values when

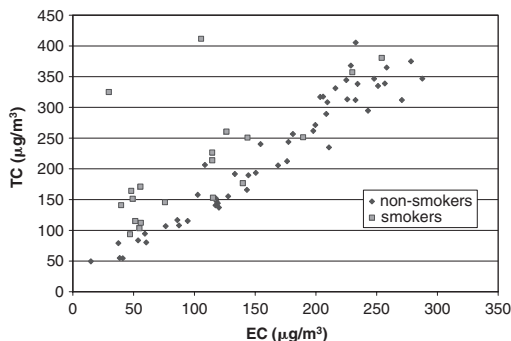


Figure 1. TC vs. EC of personal samples from smokers and non-smokers in two stone mines.

the majority of the samples were exposed to potentially more cigarette smoke that a larger TC value was measured. This is probably due to the additional OC from the cigarette smoke.

At this time, no method to correct for these interferences has been found. NIOSH did some studies on using solanesol as a possible surrogate for cigarette smoke but solanesol was found to be too unstable (Tucker and Pretty, 2005).

As a result, MSHA turned to using EC as a surrogate for DPM for the interim limit since no other sources of submicron EC are known to exist in the metal/non-metal mining environment and EC is a major component of DPM (MSHA, 2005). This paper gives an overview of the sampling and analytical methods presently used to measure EC and some issues when using EC as a surrogate.

2 SAMPLING AND ANALYTICAL METHODS

2.1 Sampling methods

2.1.1 Personal sampling

For taking personal samples, a personal sampling pump, a 10-mm Dorr-Oliver cyclone, a submicron impactor, and two quartz filters placed in tandem (in series) are used. The pump is operated at 1.7 lpm.

The submicron impactor segregates the mineral dust from the DPM. This is necessary when using EC as a surrogate because it avoids overloading a filter with mineral dust, some mineral dusts contain EC, and it provides a cleaner sample. When impactors were first being used, the mining industry brought up concerns with cassette performance and possible defects (MSHA, 2003). The submicron impactor has been shown to be efficient in collecting DPM while allowing less than 10% of mineral and coal dust to penetrate in both laboratory and field studies (Noll et al., 2005;

Birch and Noll, 2004; Noll and Birch, 2004). For example, at a dust concentration equivalent to 8-hr time weighted average of 3 mg/m³, a sub micron impactor was shown to collect only 2% of the respirable dust (Noll et al., 2005).

2.1.2 High volume sampling

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 sufficient material for the analysis of TC and EC using the Method 5040 while still avoiding mineral dust for control technology studies. 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. Flow rates between 1.7 and 2.0 lpm were maintained through each cyclone and impactor pair. At this sampling flow rate only particles with geometric mean smaller than 0.8 µm were deposited on the filters. All five classifiers were attached to a symmetrical plenum that distributed a total flow rate 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 two stacked 25 mm tissue quartz fiber filters. As seen in Table 1, the high volume method gave similar results as the personal sampling methods when collecting samples in an isolated zone of a metal mine (these were when no control technologies or just alternative fuels were used).

This high volume sampling method used mass flow controllers or critical orifices to control the flow rate and needed electricity to run. However, electricity may not always be available at sampling locations in the underground mine being tested. Therefore, we are currently testing a more portable assembly using a high flow personal pump with a cyclone with a 1 µm cutpoint at around 8 lpm (see Figure 2).

2.2 NIOSH analytical method 5040

After a sample is collected, it is sent to a laboratory and analyzed for elemental and total carbon using NIOSH Method 5040 (Birch, 2004). This analytical method analyzes for OC and EC in two different stages. In the first stage, the OC is measured by ramping the oven temperature over four progressively higher temperature steps programmed into the instrument, with the last step being at about 870 °C in a pure helium (He)

Table 1. High volume (9.7 lpm) sampling vs. standard sampling at 1.7 lpm.

EC concentration between high volume sampling and personal sampling method		
HV ($\mu\text{g}/\text{m}^3$)	Standard method ($\mu\text{g}/\text{m}^3$)	% difference
181	172	5
205	167	20
287	257	11
319	289	10
401	353	13
414	376	10
311	296	5
213	198	7

HV – high volume sampling

Standard method – personal sampling method

% difference = (HV – standard method)/average(HV – standard method) \times 100



Figure 2. A high volume setup consisting of a cyclone with a $1\ \mu\text{m}$ cutpoint at 8 lpm, filter to collect particulate and a high flow rate (5–15 lpm) personal pump.

atmosphere. The EC does not evolve because there is no oxygen (O_2) available for it to react. The evolved OC is oxidized to carbon dioxide (CO_2), reduced to methane (CH_4), and finally measured using a flame ionization detector (FID). In the second stage, the EC is measured by reducing the oven temperature to about $600\ ^\circ\text{C}$ and then again raising the temperature to about $900\ ^\circ\text{C}$ in a He/O_2 atmosphere (O_2 is now present to react with the EC to form CO_2). The EC is then measured in the same way as the OC. TC is simply the sum of OC and EC. The NIOSH Method 5040 also optically corrects for pyrolysis (charring) of OC.

NIOSH 5040 has been shown to meet the NIOSH accuracy criteria and has given good results for inter-laboratory testing (Birch, 2004).

3 EC AS A SURROGATE

3.1 Selectivity of EC

As mentioned earlier, submicron EC (after using an impactor) is selective to DPM in the underground metal/non-metal mining environment. This gives us the advantage of sampling for DPM and taking personal samples in all areas of the mine. If one tried to use TC as a surrogate, one might have to develop a complicated sampling strategy to avoid the interferences. A complicated sampling strategy could preclude areas with the highest concentration of DPM.

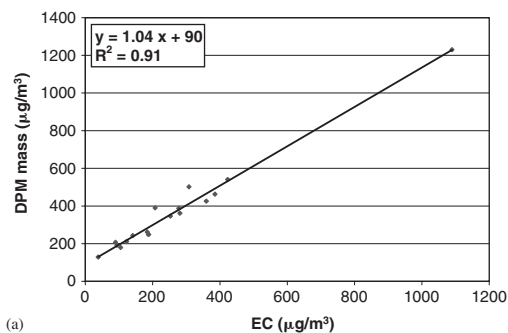
In addition to avoiding interferences, known OC sampling artifacts when using quartz filters (Eatough et al., 1995; Kirchstetter et al., 2001; Turpin et al., 1994) do not affect EC based methods. Quartz filters are known to adsorb vapor-phase OC (not part of DPM). We routinely observe between $30\text{--}40\ \mu\text{g}/\text{m}^3$ vapor-phase OC adsorbed by the quartz filter in mining samples. This could cause a 19–25% error in a TC result at the proposed final limit of $160\ \mu\text{g}/\text{m}^3$ TC if not corrected. There is also a possibility of some OC semi-volatiles evaporating and causing a negative bias relative to the TC results. These artifacts do not affect the EC results.

Coal dust also has less of an effect on EC results than TC or DPM mass results since a smaller portion of coal dust is EC (Birch and Noll, 2004; Noll and Birch, 2004). In both field and laboratory studies, when using a sub micron impactor, coal dust contributed relatively minimal (<25%) to the EC results when measuring $160\ \mu\text{g}/\text{m}^3$ TC concentrations, but in a few instances, even when using the impactor, the coal dust contributed significantly (>25%) to the TC values when measuring DPM at $160\ \mu\text{g}/\text{m}^3$ TC (Birch and Noll, 2004; Noll and Birch, 2004).

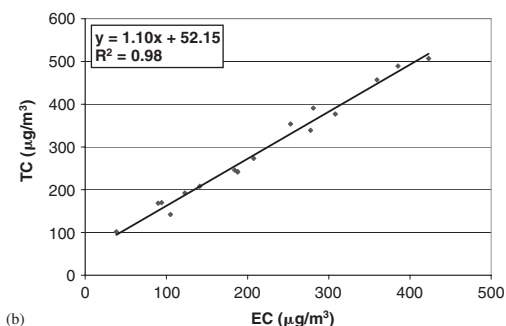
3.1.1 How is DPM represented by EC

The strong points of using EC as a surrogate are that it is a major part of DPM, is selective to DPM, and can be sampled and measured accurately. One potential issue when using EC as a surrogate for DPM is that the EC fraction of DPM may change depending upon various factors such as engine duty cycle, fuel type, control technology, etc.

Some preliminary data demonstrates that, at this time, EC represents DPM in underground mines well but may change as new control technologies are implemented. Bugarski et al. 2003, 2005 collected DPM mass (measured using TEOM), TC, and EC samples in an isolated zone in a metal mine. The isolated zone was a section in the mine where only clean air entered and ventilation could be controlled. This allowed measuring the diesel emissions from a vehicle without interferences. As seen in Figures 3a and 3b, a linear relationship existed between DPM and EC and



(a)



(b)

Figure 3. (a) DPM (mass) vs. EC for vehicles in the isolated zone. (b) TC vs. EC for vehicles in the isolated zone study.

between TC and EC for the types of vehicles tested in this mine (Noll et al., 2005).

This data was obtained when the vehicles ran No. 2 diesel fuel, diesel oxidation catalytic converters (DOCs), biodiesel, or water emulsified fuels. These conditions are present in operating underground mines.

This relationship was confirmed when sampling in four mines during actual production (see Figure 4) (Noll et al., 2005). The sampling was done at the main exhausts of the mine where oil mist and cigarette smoke should be so diluted compared to diesel that they have minimal effect on the TC results. SKC DPM cassettes were used to prevent the collection of mineral dust. The tandem filter was used to correct for the adsorption of vapor phase OC (Eatough et al., 1995; Kirchstetter et al., 2001; Turpin et al., 1994).

DPM mass was not measured during these field studies but since DPM consists of over 80% TC, most DPM and EC samples were shown to have a linear relationship.

It is important to note that the relationship between TC and EC looks very well with the above data when interferences were minimized. However, as shown in Figure 1, when taking personal samples, cigarette smoke can provide a substantial interference. Even when taking precautions, the variability

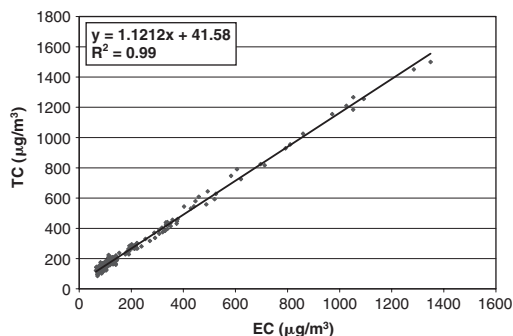


Figure 4. TC vs. EC for data from four different mines during actual production (trying to avoid interferences).

between TC and EC increases at the lower concentrations (<230 $\mu\text{g}/\text{m}^3$) of TC which could be the result of interferences or at least partially.

Some preliminary data has shown that as certain control technologies are implemented in underground mines, the DPM and EC relationship and even the characteristic of the DPM may change (Bugarski et al., 2003). In the Bugarski et al. 2003, 2005 studies, diesel particulate filter (DPF) systems were shown to preferentially reduce EC over OC and non carbon DPM (e.g. a platinum (Pt)-catalyzed DPF reduced EC by 95% and OC by 80%) which could cause the relationship between DPM and EC to change when these DPF systems are implemented. The characteristics of DPM were also shown to change (e.g. the mass of particulate decreased but the number of nanoparticles increased when some DPF systems were used). Even though the DPM and EC relationship changed, EC still could be measured accurately and followed the trend of DPM (as DPM decreased so did the EC). The DPF system that preferentially reduced EC over OC reduced both substantially; therefore the concentration of DPM or the contributions of the DPM from vehicles with these control technologies may be low enough that the potential change in DPM and EC relationship may not be a concern.

We do not know at this time the magnitude that the different control technologies effects will contribute to the future DPM and EC relationship in underground mines. We do not know what type of control technologies will be eventually implemented in the mines, how the characteristic of DPM could change, and at what concentration. Future work will be needed as new control technologies are introduced into the mines to determine the characterization of DPM.

4 CONCLUSION

EC is selective to DPM in underground mines and can be sampled and measured accurately. Using EC

as a surrogate allows one to measure in all areas of the mine. It also gives the benefit of being free of OC sampling artifacts and makes it easier to sample in coal mines. Under present conditions, EC represents DPM well and is a major component. As some control technologies are implemented, such as diesel particulate filter systems, the relationship between DPM and EC may change, may vary between mines, and the characteristics of DPM itself may change. EC can still be measured accurately and it will still follow the trend of DPM. Future work will be needed as new control technologies are introduced into the mines to determine the characterization of DPM. At this time the benefits of using EC as a surrogate outweigh the problems.

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REFERENCES

- Birch, M. E. 2004. In NIOSH Manual of Analytical Methods (NMAM), ed. O'Connor P.F., Third Supplement to NMAM, 4th Edition. Cincinnati, OH: Department of Health and Human Services, Public Health Service, Center for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS(NIOSH) Publication No. 2003-154.
- Birch, M. E. & Noll, J. D. 2004. Submicrometer elemental carbon as a selective measure of diesel particulate matter in coal mines. *Journal of Environmental Monitoring*, 6, 799–806.
- Bugarski, A., Schnakenberg, G., Noll, J. D., Mischler, S., Crum, M. & Anderson, M. 2005. Evaluation of Diesel Particulate Filter Systems and Biodiesel Blends in an Underground Mine. *Society of Mining and Metallurgical Engineers Transactions*, vol. 318.
- Bugarski, A., Schnakenberg, G., Noll, J. D., Mischler, S., Patts, P., Hummer, J., Vanderslice, S., Crum, M. & Anderson, R. 2003. The Effectiveness of Selected Technologies in Controlling Diesel Emissions in Underground Mine – Isolated Zone Study at Stillwater Nye Mine. <http://www.msha.gov/01%2D995/dpmdocs/stillwater.pdf>
- Cantrell, B. K. & Watts, W. F. 1997. Diesel Exhaust Aerosol: Review of Occupational Exposure. *Appl. Occup. Environ. Hyg.*, vol. 12, pp 1019–1026.
- Eatough, D. J., Tang, H., Cui, W. & Machir, J. 1995. Determination of the Size Distribution and Chemical Composition of Fine Particulate Semivolatile Organic Material in Urban Environments Using Diffusion Denuder Technology. *Inhalation Toxicology*, vol. 7, pp 691–710.
- EPA. Impacts of Lubrizol's PuriNOx Water/Diesel Emulsion on Exhaust Emissions from Heavy-Duty Engines EPA420-P-02-007, 2002.
- Haney, R. A. 1992. Diesel particulate exposures in underground mines. *Mining Engineering*, pp 173–176.
- Haney, R. 2000. Sampling and Interferences for Diesel Particulate Matter in Underground Metal/Non-metal Mines. <http://www.msha.gov/S&HINFO/TECHRPT/diesel/haneyimvc7.pdf>
- Heywood, J. B. Internal Combustion Engine Fundamentals. McGraw-Hill, Inc. New York (1988).
- Howes, P. 2000. City of Houston Diesel Field Demonstration Project. ERMD Report 01–36.
- Kahn, G., Orris, P. & Weeks, J. 1988. *Am. J. Ind. Med.*, 13, 405.
- Kirchstetter, T. W., Corrigan, C. E. & Novakov, T. 2001. Laboratory and field investigation of the adsorption of gaseous organic compounds onto quartz filters. *Atmospheric Environment*, vol. 35, pp 1663–1671.
- Kittelson, D. B. 1998. *J. Aerosol Sci.*, 29, 575–588.
- Mine Safety and Health Administration. 1998. Diesel Particulate Matter Exposure of Underground Metal and Non-metal Miners; Proposed Rule. *Federal Register* 30:57. pp 58103–58270.
- McCartney, T. C. & Cantrell, B. K. 1992. A cost-effective personal diesel exhaust aerosol sampler. In: Diesels in underground mines: Measurement and control of particulate emissions (Information circular 9324). *Proceedings of the Bureau of Mines Information and Technology Transfer Seminar, Minneapolis, MN*, September 29–30, pp 24–30.
- Mine Safety and Health Administration. (January 19, 2001) 30 CFR Part 57 Diesel Particulate Matter Exposure of Underground Metal and Nonmetal Miners; Final Rule. *Fed. Reg.*, vol. 66, No. 13, 5706.
- Mine Safety and Health Administration. (June 6, 2005) 30 CFR Part 57 Diesel Particulate Matter Exposure of Underground Metal and Nonmetal Miners; Final Rule. *Fed. Reg.*, vol. 70, No. 107, 32868.
- Mine Safety and Health Administration. Diesel Particulate Matter Exposure of Underground Metal and Nonmetal Miners; Proposed Rule. *Federal Register*. 30:57 (2003). pp 48668–48721.
- Nauss, K. 1998. Diesel exhaust: A critical analysis of emissions, exposure, and health effects. *HSA Bulletin*, November, pp 10–13.
- NIOSH. Carcinogenic Effects of Exposure to Diesel Exhaust. Current Intelligence Bulletin No. 50. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Pub., 1988, No. 88–116.
- Noll, J. D., Bugarski, A. D., Schnakenberg, G. H., Patts, L. D., Mischler, S. E. & McWilliams, L. 2005. The Relationship between Elemental Carbon, Total Carbon, and Diesel Particulate Matter in Several Underground Metal/Non-metal Mines. Submitted to Mining Engineer.
- Noll, J. D., Timko, R. J., McWilliams, L., Hall, P. & Haney, R. 2005. Sampling Results of the Improved SKC Diesel Particulate Matter Cassette. *Journal of Occupational and Environmental Hygiene*, 2, 29–37.
- Noll, J. D. & Birch, M. E. 2004. Evaluation of SKC DPM Cassettes for Monitoring Diesel Particulate Matter in Coal Mines. *J. Environ. Monit.*, 6, 973–978.
- Pierson, W. R. & Brachaczek, W. W. 1983. *Aerosol Sci. Technol.*, 2:1.
- Rideout, G. Impact of Lubrizol's PuriNOX Low-emissions Diesel Fuel on the Exhaust Emissions from a Heavy-duty Off-road Diesel-powered Vehicle, ERMD Report 99–37, October, 1999.
- Rundell, B, et al. *Occup. Environ. Med.*, 1996, 53, 658.

- Tucker, S. P. & Pretty, J. R. 2005. Identification of oxidation products of solanesol produced during air sampling for tobacco smoke by electrospray mass spectrometry and HPLC. *The Analyst*, vol. 130, issue 10, pp 1414–1424.
- Turpin, B. J., Huntzicker, J. J. & Hering, S.V. 1994. Investigation of organic aerosol sampling artifacts in the Los Angeles Basin. *Atmospheric Environment*, vol. 28, pp 3061–3071.
- Wade, J. F., III & Newman, L. S. *J. Occup. Med.*, 1993, 35, 149.