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Submicrometer elemental carbon as a selective measure of diesel particulate matter in coal mines

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A monitoring method for diesel particulate matter was published as Method 5040 by the National Institute for Occupational Safety and Health (NIOSH). Organic and elemental carbon are determined by the method, but elemental carbon (EC) is a better exposure measure. The US Mine Safety and Health Administration (MSHA) proposed use of NIOSH 5040 for compliance determinations in metal and nonmetal mines. MSHA also published a rulemaking for coal mines, but no exposure standard was provided. A standard based on particulate carbon is not considered practical because of coal dust interference. Interference may not be a problem if an appropriate size-selective sampler and EC exposure standard are employed. Submicrometer dust concentrations found in previous surveys of nondieselized, underground coal mines were relatively low. If a large fraction of the submicrometer dust is organic and mineral matter, submicrometer EC concentrations would be much lower than submicrometer mass concentrations. Laboratory and field results reported herein indicate the amount of EC contributed by submicrometer coal dust is minor. In a laboratory test, a submicrometer EC concentration of 31 μg m^{-3} was found when sampling a respirable coal dust concentration over three times the US compliance limit (2 mg m^{-3}). Laboratory results are consistent with surveys of nondieselized coal mines, where EC results ranged from below the method limit of detection to 18 μg m^{-3} when size-selective samplers were used to collect dust fractions having particle diameters below 1.5 μm—submicrometer EC concentrations were $\approx$7 μg m^{-3}. In dieselized mines, submicrometer EC concentrations are much higher.

1. Introduction

1.1 Background

In the United States alone, over a million workers (*e.g.*, trucking, mining, railroad, agriculture workers) are occupationally exposed to diesel exhaust.[1] The widespread and growing use of diesel-powered equipment has raised concern because workers exposed to diesel exhaust show an elevated (20–50%) risk of lung cancer.[2] While environmental exposure is a concern, occupational exposure is a greater one because workplace exposures are generally much higher—especially among miners. In underground mines, diesel particulate concentrations[3–5] are usually more than 100 times higher compared with a typical environmental level (*e.g.*, 2 μg m^{-3}) and sometimes exceed 2 mg m^{-3}, which is one thousand times higher. The National Institute for Occupational Safety and Health (NIOSH) considers diesel exhaust a potential occupational carcinogen and recommends that employers reduce workers′ exposures.[1] Other organizations, including the International Agency for Research on Cancer (IARC),[6] the World Health Organization (WHO),[7] the California Environmental Protection Agency,[8] the US Environmental Protection Agency (US EPA),[9] and the National Toxicology Program[10] have reviewed the animal and human evidence, and each has classified diesel exhaust as a probable human carcinogen or similar designation. Non-cancer health effects also have been associated with diesel exhaust exposure. These include immunologic, respiratory, and cardiovascular effects.[11–15] Reviews on the health effects of diesel exhaust have been published previously.[1,2,6–10]

Assessment of exposure and the associated health risk is challenging because diesel exhaust is a highly complex and variable mixture of gases, vapors, and fine particles. Thus, a surrogate measure of exposure must be selected. NIOSH published Method 5040,[16,17] which targets the particulate carbon portion of diesel exhaust. In the analysis, the total carbon (TC) in a filter sample is quantified as *organic* and *elemental* carbon (TC = OC + EC). In the absence of interferences, TC is a logical surrogate for diesel particulate matter (DPM) because DPM is mostly ($>$80%) carbon,[18–20] but other OC sources make TC measurements interference prone. In contrast, EC (carbon in the soot particle core) is a selective measure of occupational exposure to DPM[17,21] and is therefore a better exposure surrogate. Fine EC particles are derived primarily from the combustion of fossil fuels, and diesel engines are major sources of these particles. Carbonaceous aerosols such as cigarette and wood smokes contain little, if any, EC.[17,21,22] Gasoline engines emit far less EC than diesels, so their relative contribution is usually small. In environmental settings, other sources can contribute to the EC background levels, which are typically 1–3 μg m^{-3},[21] but diesel engines are the primary emitters[23,24] of EC air pollution. In occupational settings, where diesel equipment is used in relatively close proximity to workers, the contribution of remote sources is negligible, especially when EC concentrations are elevated. EC concentrations in occupational settings[25–32] are ordinarily above background—in mines, they are well above it.[3–5,30]

In addition to selectivity, potential health effects were considered when an EC surrogate was proposed. Diesel particles and other insoluble fine particles are inhaled deeply into the lungs, where they can induce an inflammatory response.

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Further, EC particles increase the long-term retention[33,34] of adsorbed genotoxins and other chemical toxins because the particles have a high affinity for them.[35] In combination with an inflammatory response induced by the particles, genotoxic agents may promote tumorigenesis. Ultrafine ($<0.10\ \mu$m) particles may pose an even greater health risk. Results of toxicological studies on solid particles having aerodynamic diameters in this size range indicate ultrafine particles are especially toxic.[36] This is significant because by mass the majority of diesel particles are in the fine particle range, and most are in the ultrafine range by number.[20]

A review on NIOSH 5040, including detailed rationale for selection of an EC marker, is provided in a recent chapter of the NIOSH Manual of Analytical Methods (NMAM).[17] The method has been used in numerous industrial hygiene surveys,[25–32] and it was recently applied to an ongoing epidemiological study (NIOSH/National Cancer Institute [NCI]) of miners. Given the physical and chemical nature of EC particles emitted by diesel engines, monitoring and controlling exposures to these particles is prudent, especially in mines because DPM levels are high and EC is a large fraction of the DPM.

1.2 Mines

The Mine Safety and Health Administration (MSHA) proposed use of NIOSH 5040 for compliance determinations in metal and nonmetal mines. In its Final Rule,[3] an interim standard of 400 μg of TC per m^3 air was proposed. A standard of 160 μg TC per m^3 was to apply five years after publication of the Final Rule, but MSHA initiated limited new rulemaking[37,38] to revise specific provisions of the Final Rule. Among other amendments, MSHA proposed a change of the exposure standard from TC to EC. A change to EC was proposed because of potential OC interferences.

For sampling DPM in metal and nonmetal mines, MSHA recommends[3] a specialized impactor with a submicrometer *cutpoint* (diameter of particle collected with 50% collection efficiency, D_{50}) to minimize collection of carbonates and other carbonaceous dusts. The cutpoint (about 0.8 μm) of the impactor is based on particle size distributions found in coal mines. Impactors effect separation of particles according to their aerodynamic diameter through inertial impaction. Because diesel exhaust particles are mainly submicrometer,[20,39–46] their separation by size from larger, mechanically generated dust is possible. Given the recently proposed change to an EC exposure standard, an impactor having a submicrometer cutpoint would not be necessary for selective measurement of DPM EC in many metal and nonmetal mines because DPM is the only source of EC. Nonetheless, conditions in some metal and nonmetal mines may dictate its use (*e.g.*, to prevent filter overloading by inorganic and carbonaceous dusts, and potential interference of graphitic [EC] components in some ores). MSHA's recommendation regarding an impactor for metal and nonmetal mines considers these possibilities.

MSHA also published a rulemaking[47] on diesel equipment usage in underground coal mines, but an exposure standard was not provided. MSHA did not consider a standard based on particulate carbon feasible because of coal dust interference, but coal dust interference may not be an issue if an appropriate size-selective sampler and EC exposure standard are employed. Impactors with optimized cutpoints have been used for gravimetric measurements of DPM in coal mines.[48–51] Previous surveys in underground coal mines where no diesel-powered equipment was used indicated submicrometer dust concentrations were relatively low.[49,52,53]

Representative, submicrometer coal mine dust concentrations found in previous surveys of underground coal mines are plotted in Fig. 1. Three results[54] (Mutmanski and Consol Coal) were obtained by a commercial impactor (Marple 298); others were obtained by a prototype impactor.[51,52] Submicrometer coal mine dust concentrations ranged from 20 to 130 μg m^{-3}. If a large fraction of the submicrometer dust is organic, the corresponding EC concentrations would constitute a relatively small fraction of the submicrometer mass concentrations. Among other properties, coals are ranked according to their relative percentages of *fixed carbon*, which is the residual carbon remaining after volatile matter is removed thermally (fixed carbon = 100 − percentage of volatile matter).[55] Lower rank coals (*e.g.*, lignite) contain less fixed carbon than higher ranks (*e.g.*, anthracite). Presuming some fraction of the fixed carbon is quantified as EC, the OC–EC content of coals is expected to be rank dependent. In addition to its OC content, some of the submicrometer coal mine dust is mineral matter (*e.g.*, carbonates, sulfates, silicates, iron pyrites). Thus, the extent to which the submicrometer dust in coal mines interferes in the determination of DPM EC will depend on the coal type, dust concentration, particle size distribution, and the mineral content of the dust. In this paper, laboratory and field data on the potential EC contribution of submicrometer coal dust are reported. Our results indicate the amount of EC contributed by submicrometer coal mine dust is minor.

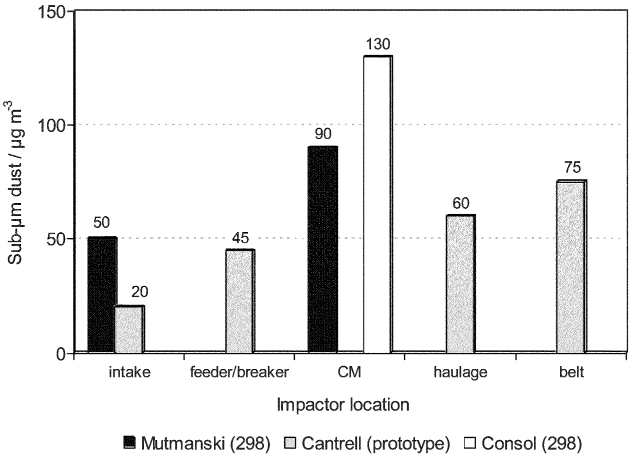

Fig. 1 Submicrometer dust concentrations in different locations of nondieselized mines (CM denotes continuous miner).

2. Methods and materials

2.1 Thermal-optical analysis

NIOSH 5040 is based on a thermal–optical technique for carbon. The thermal–optical analyzer (Sunset Laboratories, Inc., Forest Grove, OR) used for the NIOSH 5040 analysis has been described previously.[16,17,21] For the analysis, a filter portion (punch) of known area (normally 1.5 cm^2) was placed in the sample oven and the oven was tightly sealed. High-purity, quartz-fiber filters (Pallflex 2500QAT-UP, Pallflex Inc., Putnam, CN) were used. Quartz filters are required because temperatures in excess of 850 °C are employed in the analysis. Prior to use, all filters were cleaned in a muffle furnace or low-temperature asher.

The analysis proceeds in inert (helium) and oxidizing (oxygen–helium mix) atmospheres. OC (and carbonate, if present) is first removed under a constant flow of helium as the temperature is increased to a preset maximum. The thermally evolved carbon enters a heated catalyst bed, where it is oxidized to carbon dioxide (CO_2). The CO_2 then flows through a heated reduction catalyst that reduces it to methane (CH_4), and the CH_4 is quantified by a flame ionization detector (FID). After OC is removed, the gas is switched to an oxygen–helium (O_2–He) mix. The temperature is again stepped to a preset maximum, which effects combustion of the residual sample carbon. As with OC, the residual carbon is completely oxidized, reduced, and quantified as CH_4.

The thermal–optical analyzer is equipped with a pulsed diode laser and photodetector that permit continuous monitoring of the filter transmittance. This optical feature corrects for the *char* that is formed during the analysis of some materials. Char is formed through pyrolysis, which is a thermal decomposition process. When some organic substances are heated to elevated temperatures in an inert (non-oxidizing) atmosphere, carbonization (conversion to carbon) occurs. Both volatile products and char (thermal decomposition product containing mostly carbon) are formed in the process. As with EC initially present in the sample, char strongly absorbs the diode laser light. Thus, if charring occurs, the filter transmittance decreases as the temperature is stepped to the maximum in helium. After the gas is then switched to an O_2–He mix, the temperature is again stepped to the maximum. As the temperature increases, char and original EC are oxidized from the filter, which causes a concurrent increase in filter transmittance. The split between OC and EC is assigned when the initial (baseline) value of the filter transmittance is reached. All carbon removed before the OC–EC split is considered organic, and that removed after the split is considered elemental.

OC and EC results are reported in micrograms per square centimeter (μg cm^{-2}) of the sample deposit. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous deposit is assumed. The TC in the sample is the sum of OC and EC. (Note: if carbonate is present, the carbon in it is quantified as OC. Carbonate carbon can be estimated separately, if desired.[16,17])

2.2 Sample bank coals

Cans containing bags of −20 mesh (850 μm) coal (225–450 g) were purchased from the Penn State Coal Sample Bank at the Energy and Fuels Research Center, The Pennsylvania State University. At the Bank, the coals had been stored under argon in sealed polyethylene bags, and the bags were sealed in no. 2 cans. The coals originated from major coalfields of the United States. They were selected for inclusion in the Bank to achieve a representative distribution of seams (by rank, geologic province, maceral composition, sulfur content, ash yield, and composition, *etc*.). After receipt, the cans were stored at room temperature and remained unopened until ready for use.

The EC fractions and carbon (TC) contents (% carbon) of seven different coal ranks were determined by thermal–optical analysis (NIOSH 5040). Prior to analysis, the −20 mesh coals were sieved to less than 50 μm. Air samples of the sieved dusts were then collected in an in-house, dust generation system (see Section 2.5, Dust generation system). Quartz-fiber filters loaded into 37 mm, three-piece plastic cassettes were used for dust collection. Nylon cyclones (Dorr-Oliver) were attached to the inlets of the cassettes to select the respirable fraction. The filter samples of respirable coal dust were then analyzed to determine their EC content (an even filter deposit is required for the OC–EC split). The TC contents (% carbon) of the sieved dusts were determined by thermal–optical analysis of a known weight of the dust applied directly to a punch (1.5 cm^2) from the quartz filter media. Air samples were not used for this purpose because the dust mass on a punch from the loaded filter could not be determined with sufficient accuracy.

2.3 Impactors

Commercial, eight-stage, personal cascade impactors (Marple 298, Andersen Instruments, Inc., Smyrna, GA) and four prototype impactors were used to examine the potential EC contribution of submicrometer coal dust. All impactors were operated at 2 L min^{-1}. The four prototype impactors included: an in-house (NIOSH) design,[48] a MSHA design,[50] one designed jointly by the University of Minnesota (UMN) and the US Bureau of Mines (BOM),[53] and a BOM design.[51] As mentioned previously (Section 1.2), these impactors were developed for determination of DPM concentrations (as submicrometer mass) in underground coal mines. In mines, a nylon cyclone is used with the impactors to preselect the respirable dust fraction.

The in-house design[48] is a single-stage, single-jet impactor made from a three-piece, 37 mm cassette. The impaction substrate is held between the top and spacer ring portions of the cassette, and the cassette's inlet diameter is modified (reduced). The impactor was designed to provide an approximate cutpoint of 1 μm. The MSHA impactor[50] is based on a modified MSA (Mine Safety Appliances Company, PO Box 426, Pittsburgh, PA) cassette. It is similar to the in-house design (single stage and jet), but the filter cassette and jet-to-plate distance (*i.e.*, distance from inlet to impaction surface) differ. The impactor[53] designed jointly by researchers at UMN and BOM is a single-stage, four-jet design, as is the BOM impactor.[51] With the UMN/BOM device, the sample filter is located inside the impactor—with the BOM device, it is contained in a MSA cassette inserted into the outlet of the impactor. For the work reported in this paper, the BOM sampling train (*i.e.*, cyclone/impactor/cassette) and the MSHA impactor were modified slightly to better accommodate the quartz filter collection medium, which does not fit into the MSA cassette well. Specifically, a 37 mm cassette was used with the BOM impactor, and the bottom portion of the MSHA impactor was replaced with the base of a 37 mm cassette. To accommodate the base, the top portion (inlet piece and impactor substrate) of the MSHA impactor was glued to a 37 mm cassette spacer ring, and this piece was used with the cassette (37 mm) base.

2.4 Field samples

Field samples were collected in dieselized and nondieselized (electric-powered) coal mines. Personal sampling pumps were used to pull air (2 L min^{-1}) through the impactors. The sampling time varied from mine to mine (3–8 h). Two of each of the cascade impactors were assembled to include eight, seven, and six stages, which provided impactor cutpoints at 0.52 μm, 0.93 μm, and 1.5 μm, respectively. Different size cuts were examined to determine the impact of cutpoint on the EC results. Greased, stainless steel impaction substrates were used inside the impactors to prevent particle bounce to subsequent stages. A 37 mm cassette containing a quartz-fiber filter was attached to the outlet of each cascade impactor to collect the dust fractions. A short length (about 3 cm) of Tygon® tubing was used to attach the cassette. The quartz filter was not used inside the impactor, where a PVC (polyvinyl chloride) final filter is normally used, because an uneven deposit often formed. An even deposit is required for thermal–optical analysis.

Two additional cascade impactors were collocated with the others to determine the total, respirable, and submicrometer dust concentrations and particle size distribution. Pre-weighed, greased, stainless steel impaction substrates were used on the impactor stages, and a PVC filter was used inside the impactor as the final filter as usual. The dust masses on all impaction substrates and the final filter were used to calculate the total dust concentration and determine the particle size distribution. The dust masses for stages four through to the final filter were used to calculate the respirable dust (British Medical Research Council [BMRC] convention) concentration, while the dust masses for stages seven, eight, and the final filter were summed to calculate the submicrometer dust concentration. For comparison with the cascade impactors, an in-house impactor[48] previously used in preliminary field studies also was included.

Table 1 Carbon content of coals

		Reported values (%)		Thermal–optical results[a] (%)			
Rank	Origin	TC	Fixed C	TC (SD)[b]	TC[c]	Char + EC[c]	EC[c] (SD)
Lignite	ND	62.61	46.75	62 (5)	53	39	19
SubC[d]	WY	64.68	32.65	66 (3)	45	26	13.3 (0.3)
SubB[d]	MT	71.93	52.80	—	57	44	16.2 (0.8)
HvCb[d]	IL	66.23	46.92	—	45	33	1
HvAb[d]	PA	71.88	51.90	—	62	42	2 (2)
Lvb[d]	PA	79.67	71.96	—	76	46	29 (4)
Anthracite[e]	PA	88.85	89.52	78 (10)	80	76	76

[a] Where standard deviation (SD) is reported, $n = 3$ or 4. [b] As received. [c] Carbon content determined one year after opening coal sample. [d] Classified according to the American Society for Testing and Materials (ASTM) Standard Specification for Classification of Coals by Rank (ASTM D 388-77). SubC and subB are subbituminous coals; hvCb, hvAb, and lvb are bituminous. [e] Anthracite does not char.

2.5 Dust generation system

Laboratory samples were collected inside the dust chamber of an in-house, dust generation system. Details on the operation and design of the generation system have been described previously.[56] Briefly, coal dust (−20 mesh sieved to < 50 μm) was introduced to the chamber through a fluidized bed generator (Model 3400, Fluidized Bed Generator, TSI, Inc., St. Paul, MN) located outside the chamber. A stainless steel cyclone supplied with the generator was used for further size classification of the sieved dust. Air flow through the cyclone was adjusted to 9 L min^{-1}. The reported cutpoint (D_{50} value) of the cyclone at this flow rate is 3.5 μm. A tapered element oscillating microbalance (TEOM 1200 Mass Measurement Systems, Rupprecht and Patashnick Co., Inc., Albany, NY) was used to monitor the dust concentration, and an aerodynamic particle sizer (APS Model 3310, TSI, Inc., St. Paul, MN) monitored the particle size distribution.

2.6 Evaluation of prototype impactors

The performance of the four prototype impactors was evaluated at two dust concentrations. A bituminous coal dust (sieved to < 50 μm) and an in-house dust generation system (see Section 2.5, Dust generation system) were used for dust generation. Two of each prototype were included (eight total). Cascade impactors (two each) loaded with eight and seven stages (0.52 μm and 0.93 μm cutpoints, respectively) also were included for comparison. As with the field samples, 37 mm cassettes containing quartz-fiber filters were attached at the outlets of the cascade impactors to collect the dust size fractions.

For the evaluation, prototype impactors were positioned in a circular arrangement in a Plexiglas® holder at the base of the dust chamber. Prototype impactors of a given type (two each) were diametrically opposed. The two personal cascade impactors were operated in the center of the prototypes. Tygon® tubing was used to connect the impactor (all) outlets to critical orifices (2 L min^{-1}) mounted in the Plexiglas® holder. Air was pulled through the orifices by a high volume pump. The flow (2 L min^{-1}) through each orifice was measured to verify critical flow.

Prior to the evaluation, the homogeneity of the coal dust concentration within the chamber was confirmed in a separate experiment. To confirm an even distribution, eight nylon cyclones each in series with a 37 mm plastic cassette containing a pre-weighed PVC filter were used for dust collection. Two cascade impactors containing pre-weighed, stainless steel impaction substrates and a PVC final filter were used to determine the dust size distribution. The sampling flow rate (2 L min^{-1}), sampler placement (cyclone/cassettes in circular arrangement and two cascade impactors in center), and coal dust were identical to those used in the evaluation of the prototypes.

3. Results and discussion

3.1 EC–TC content of coals

The carbon contents of seven different ranks of coals purchased from the Penn State Coal Sample Bank are listed in Table 1. Thermal–optical results and the percentages of carbon and fixed carbon reported in the data sheet provided with each coal are listed. For comparison with the reported TC contents, thermal–optical results for three of the coal types (lignite, subC, and anthracite) were obtained shortly after they were received. Four others, and again the same three, were analyzed about one year later. Except for the low volatile bituminous (lvb) and anthracite ranks, significant volatile OC losses occurred. The TC content (TC mass/dust mass) of a lignite coal was about 10% lower than the reported value. TC contents of two subbituminous coals (subC and subB) were about 20% and 15% lower, and those of two high volatile bituminous coals (hvCb and hvAb) were 21% and 10% lower.

Char plus EC (Char + EC) and EC mass fractions are also reported in Table 1. Char plus EC is the total carbon removed in the oxidative mode (O_2–He atmosphere). It includes char carbon generated through pyrolysis of the organic matter in coal and EC initially present in the coal. Except for anthracite, the amount of EC initially present is lower than the Char + EC by up to 40%. Lignite and subC coals had a higher EC content than expected, but the EC in these coals can be distinguished from typical, diesel-source EC in mine samples because it is more readily oxidized (*i.e.*, removed in O_2–He at a lower temperature). In contrast, EC in anthracite cannot be distinguished from diesel-source EC because it is present originally (*i.e.*, not generated through pyrolysis) and removed over the same temperature range. Thermal–optical results for lignite and anthracite are shown in Fig. 2.

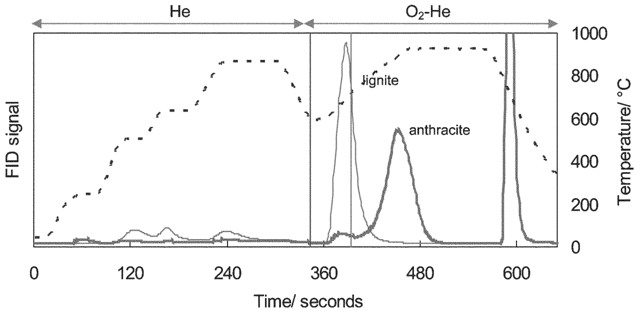

Fig. 2 Thermal–optical results for filter samples of lignite and anthracite dusts. Peak beginning at 360 s corresponds to lignite; vertical line through lignite peak is OC–EC split for lignite. Peak to immediate right of lignite is anthracite; OC–EC split for anthracite is vertical line at about 340 s (final peak is calibration peak; stepped dashed line is temperature).

Thermal behavior of the other coals was intermediate to that for lignite (and subC) and anthracite. Briefly, subB produced a peak in the same region as lignite and another where anthracite (and diesel-source) EC was oxidized. The magnitude of the two peaks was similar, and the OC–EC split was assigned slightly before the apex of the second peak. HvCb also produced two peaks, but the first was small relative to the second. HvAb's thermal behavior was similar to HvCb's, but the area of the first peak relative to the second was a bit smaller still.

Depending on the instrument and dust loading, the peak profiles and percentages of char carbon and EC may differ somewhat from those reported here, but the conclusion remains unchanged. Namely, optical correction for char and the different thermal properties (relative to diesel EC in mines) of most coals provide additional selectivity in the measurement of diesel-source EC. When the thermal behavior together with the selectivity provided by size-selective sampling (submicrometer dust) is considered, only low levels of coal-source EC are anticipated in coal mines. Results obtained in underground coal mines are discussed in the following section.

3.2 Underground coal mines

EC and TC concentrations found in nondieselized (electric-powered) underground coal mines are reported in Table 2. As described earlier (see Section 2.4, Field samples), commercial cascade impactors were used to collect three different dust size fractions ($<$0.52 μm, $<$0.93 μm, and $<$1.5 μm) for thermal–optical analysis, and an in-house impactor (PM1 in Table 2) was included for comparison. Two additional cascade impactors collocated with the others were used to determine the total, respirable (BMRC), and submicrometer dust mass concentrations (Table 2) and particle size distributions (Fig. 3 and Fig. 4) of the dusts.

Relatively low EC concentrations were found in nondieselized coal mines when impactors with submicrometer cutpoints were used. In five locations of four mines (D, E, G, and H), submicrometer ($<$0.93 μm) EC concentrations ranged from about 2 μg m^{-3} to 7 μg m^{-3}. EC concentrations found by the cascade impactors having a 1.5 μm cutpoint were higher, but they were still much lower than those in dieselized mines. EC concentrations found by an in-house prototype impactor (PM1, Table 2) were higher than those found by the 1.5 μm cutpoint impactor (cascade). The in-house device[48] was designed to produce a cutpoint near 1 μm. Based on the cascade impactor results, the apparent cutpoint is more likely to be closer to 2 μm.

The survey of Mine F was one of the first surveys where samples were collected for thermal–optical analysis. In this mine, only the in-house impactor was used. EC results for two locations (intake and haulage) of the mine were below the limit of detection (LOD). EC concentrations of about 20 μg m^{-3} and 50 μg m^{-3} were found in a very dusty area (return) of the mine, but the respirable dust levels there were quite high (6 and 16 mg m^{-3}) compared to the US compliance limit (2 mg m^{-3}).

EC concentrations in three dieselized mines—one limestone and two coal—also are reported in Table 2 (mines A–C). A dieselized limestone mine (A) was included to illustrate the effect of impactor cutpoint when a dust contains no EC. Here, EC results obtained with the 0.93 μm and 1.5 μm impactors were identical. Slightly lower results were obtained with the 0.52 μm impactor, which excluded a small fraction of the diesel DPM, while the in-house impactor[48] gave slightly higher results (possibly due to the presence of larger diesel agglomerates). As expected, EC concentrations in the three dieselized mines are much higher—about 200–560 μg m^{-3} for dust fractions $<$1.5 μm. Comparable EC results for metal and nonmetal mines have been reported elsewhere.[38]

3.3 Evaluation of prototype impactors

A test of the dust generation system indicated the coal dust concentration in the sample collection area of the system chamber was homogeneous. The RSD (n = 8) for the mean

Table 2 Fine particulate carbon (EC and TC) and dust (total, respirable, and submicrometer) mass concentrations in dieselized and nondieselized underground mines

			EC/µg m^{-3}				TC/µg m^{-3}				Dust concentration[e]/mg m^{-3}		
Mine type[a]	Sampling location[b]		PM1[c]	$<$1.5[d]	$<<$0.93[d]	$<$0.52[d]	PM1[c]	$<$1.5[d]	$<$0.93[d]	$<$0.52[d]	Total	Respirable	Sub-µm
Limestone	Haulage		235	198	197	168	462	428	443	308	—	—	—
Dieselized coal	Mine A	Return	531	427	—	313	706	626	—	564	4.17	1.15	0.51
		Intake	459	—	—	—	565	—	—	—	0.92	0.81	0.76
	Mine B	Haulage	651	558	—	356	964	866	—	522	1.82	1.31	1.10
		Intake	86	—	—	—	164	—	—	—	0.34	0.23	0.20
	Mine C	Haulage	539	—	—	—	674	—	—	—	2.15	1.39	0.93
Nondiesel coal	Mine D	Beltline	32	18	7	(3)[f]	125	81	33	24	5.03	0.67	(0.04)[f]
	Mine E	Shield	13	6	(4)[f]	—	426	186	104	—	21.51	2.27	(0.04)[f]
		Headgate	(2)[f]	—	ND[g]	—	58	—	66	—	4.16	0.63	ND[g]
	Mine F	Intake	ND[g]	Not sampled			50	Not sampled			3.72	1.13	0.41
		Haulage	ND[g]				48				4.07	1.42	0.52
		Return	50				1011				34.00	16.17	4.33
		Haulage	ND[g]				23				2.59	0.87	0.24
		Intake	ND[g]				18				1.44	0.44	0.22
		Return	20				121				14.38	6.11	0.85
	Mine G[h]	Shield	—	14	7	—	—	287	309	—	15.60	0.81	ND[g]
	Mine H[i]	Tailgate	—	—	(5)[f]	—	—	—	38	—	—	2.55	—
		Tailgate	—	—	ND[g]	—	—	—	ND[g]	—	—	1.27	—

[a] Mines A and B are located in UT; coals were bituminous with 37% (A) and 42% (B) fixed carbon. Mine C is located in KY (no information on coal type). Mine D is located in WV, E in PA, and F in OH. Mine D coal was bituminous with 75% fixed carbon, E was high volatile bituminous with 50–54% fixed carbon, and F was bituminous with 42% fixed carbon. Mine G coal was bituminous (fixed carbon unknown). [b] Except for mine G, sample volume ranged from 300–720 L, depending on location. [c] In-house (NIOSH) design. [d] Impactor cutpoint/µm. [e] Determined with cascade impactors; see text for details. [f] Parentheses indicate result is at or above limit of detection (LOD) and below limit of quantitation (LOQ). LOD = 3σ_b,where σ_b is standard deviation of blank; LOQ = 10σ_b. EC LOD = 2 µg m^{-3}; LOQ = 5 µg m^{-3}. TC LOD = 4 µg m^{-3}; LOQ = 14 µg m^{-3}. Dust concentration LOD = 20 µg m^{-3}; LOQ 68 µg m^{-3}. [g] Not detected (ND). [h] TC results blank corrected because of low sample volume (160 L). [i] Mine located in the UK; actual impactor cut was 0.8 µm.

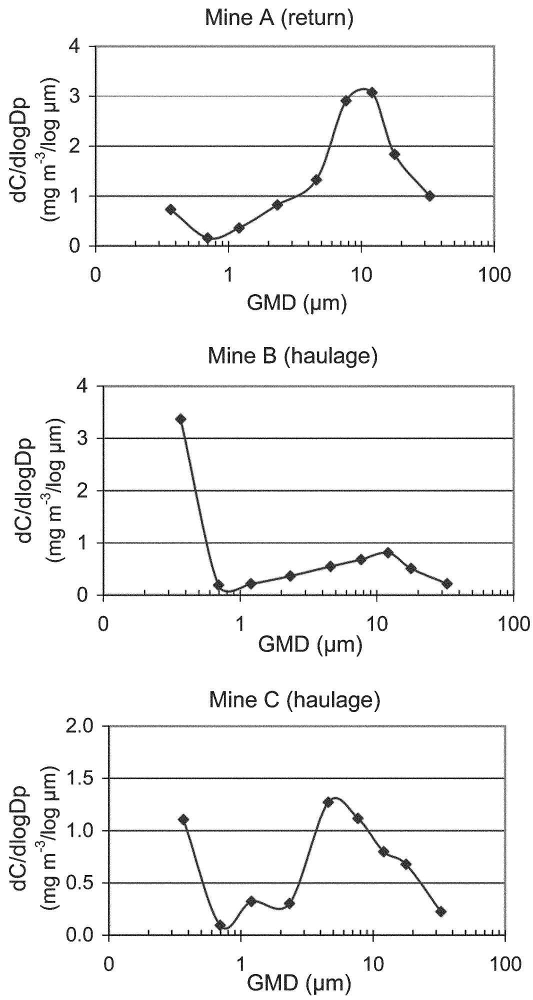

Fig. 3 Particle size distributions in dieselized underground coal mines (A–C). See Table 2 for details on mines. GMD is geometric mean diameter.

dust concentration (1.26 mg m^{-3}) found with the cyclone filter samplers was 4.6%. After verifying that the dust concentration was homogeneous, the performance of the four prototype impactors was evaluated at two respirable coal dust concentrations: about 2 mg m^{-3} and 5 mg m^{-3}. A bituminous coal

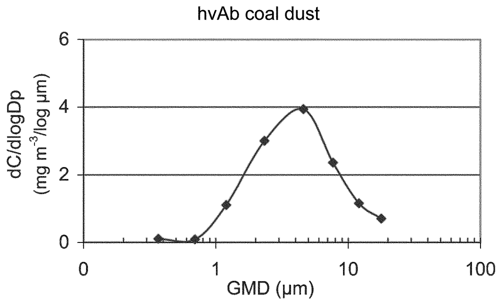

Fig. 5 Particle size distribution for laboratory generated coal dust. GMD is geometric mean diameter.

(hvAb) was used for the evaluation. The particle size distribution of the dust is shown in Fig. 5.

TC and EC results corresponding to the two dust concentrations are listed in Tables 3 and 4. The respirable dust concentrations reported (Tables 3 and 4) for the prototype impactors are the actual mass concentrations, not MRE (Mining Research Establishment) equivalents (used by MSHA). MRE equivalent concentrations can be calculated by multiplying the reported values (for prototypes) by 1.38.

At a respirable dust concentration of 1.75 mg m^{-3} (MRE equivalent = 2.42 mg m^{-3}), the TC concentrations found by the BOM, UMN/BOM, and MSHA impactors were: 44 μg m^{-3}, 61 μg m^{-3}, and 68 μg m^{-3} (Table 3). The EC concentrations found by these three impactors ranged from about 7 μg m^{-3} to 17 μg m^{-3}, and EC results for the Marple impactors were comparable. The TC concentration (304 μg m^{-3}) found by the in-house design (PM1) was about five times higher than the mean (58 μg m^{-3}) for the other three prototypes, while the EC concentration (40 μg m^{-3}) was about four times higher. As already mentioned, the in-house device was designed to have a 1 μm cutpoint, but the apparent cut was likely to be about 2 μm.

At a respirable dust concentration of 5 mg m^{-3} (MRE equivalent = 7 mg m^{-3}), only the BOM and UMN/BOM impactors, which are four-nozzle designs having cutpoints near 0.8 μm, effectively excluded coal dust. The mean TC concentration (Table 4) found with these two impactors was about 129 μg m^{-3}, and the corresponding EC concentration was about 31 μg m^{-3}. The TC on the final filter of the MSHA impactor was nearly six times higher than the mean for the BOM and UMN/BOM impactors, and the loading on the in-

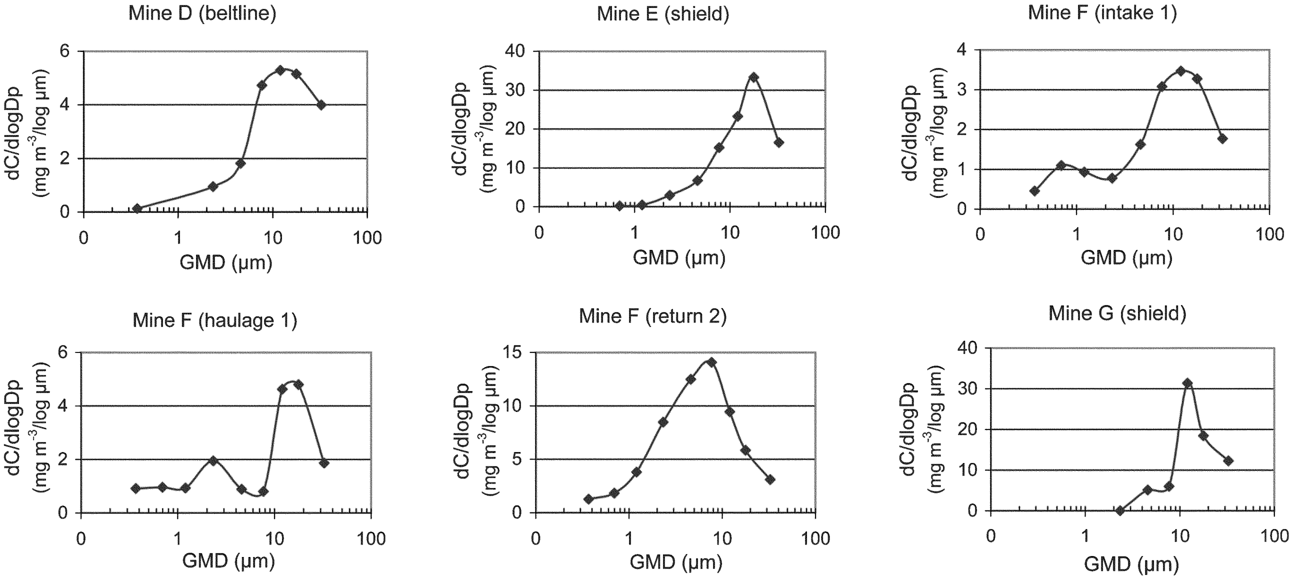

Fig. 4 Particle size distributions in nondieselized underground coal mines (D–G). See Table 2 for details on mines. GMD is geometric mean diameter.

Table 3 Coal-source, submicrometer carbon at respirable[a] coal dust concentration of 1.75 mg m^{-3}. Total[a] dust = 3.01 mg m^{-3}

Sampler	Cutpoint[b]/µm	EC[c] (RPD)[d]/µg m^{-3}	TC[c] (RPD)[d] /µg m^{-3}	Respirable dust/mg m^{-3}
Marple impactor[e]	0.5	6.34 (—)	69.48 (—)	1.84[f]
Marple impactor	0.9	17.40 (—)	101.35 (—)	1.66[f]
BOM impactor	0.8	9.09 (14)	44.45 (24)	1.18[g]
UMN/BOM impactor[h]	0.8	7.47 (30)	61.19 (17)	1.31[g]
MSHA impactor	0.8	17.13 (12)	67.99 (13)	1.28[g]
PM1 impactor[i]	1	39.90 (13)	303.98 (31)	—

[a] Average of two Marple impactor results. [b] Approximate 50% cutpoint (D_{50}). [c] Prototype impactor result is the average of two. [d] RPD is relative percent difference. [e] Seven stages used. [f] BMRC convention (see text). Final filter mass estimate is based on TC result and 62% carbon content of dust. [g] Respirable dust calculated as the sum of dust mass on impaction substrate and estimated mass on final filter (mass estimate based on TC result and 62% carbon content). MRE (Mining Research Establishment) equivalent concentration (used by MSHA) is 1.38 times the reported value. [h] Developed jointly by the University of Minnesota and US BOM. [i] In-house (NIOSH) design.

Table 4 Coal-source, submicrometer carbon at respirable[a] coal dust level of 5 mg m^{-3}. Total dust[b] = 12 mg m^{-3}

Sampler	Cutpoint[c]/µm	EC[d] (RPD)[e]/µg m^{-3}	TC[d] (RPD)[e]/µg m^{-3}	Respirable[d] dust/mg m^{-3}
298 Impactor[f]	0.5	—	301 (—)	—
298 Impactor[g]	0.9	23 (—)	595 (—)	—
BOM impactor	0.8	32 (1)	113 (4)	5.28 (0.06)
UMN/BOM impactor[h]	0.8	30 (8)	144 (15)	5.02 (0.04)
MSHA impactor	0.8	64 (13)	712 (18)	4.91 (0.03)
PM1impactor[i]	1	86 (16)	1327 (14)	4.97 (—)

[a] Average of four prototype impactors. Respirable dust calculated as the sum of dust mass on impaction substrate and estimated mass on final filter (mass estimate based on TC result and 62% carbon content). MRE equivalent concentration (used by MSHA) is 1.38 times the reported value ($1.38 \times 5 = 7$ mg m^{-3}). [b] Total dust based on TEOM result. [c] Approximate 50% cutpoint (D_{50}). [d] Result for prototype impactors is the average of two. [e] RPD is relative percent difference. [f] OC–EC spilt not valid due to laser problem. [g] Seven stages used. [h] Developed jointly by the University of Minnesota and US BOM. [i] In-house (NIOSH) design.

house impactor was ten times higher; EC results also were higher.

4. Summary and conclusions

Our results indicate that the amount of EC contributed by submicrometer coal dust is relatively small. In a laboratory test, even when the respirable coal dust concentration was as high as 5 mg m^{-3} (MRE equivalent = 7 mg m^{-3}, which is 3.5 times the US compliance limit), the average EC concentration found by two impactor designs (UMN/BOM and BOM) was only 31 μg m^{-3}. Laboratory results are consistent with those obtained in surveys of nondieselized, underground coal mines, where low levels ($\approx$7 μg m^{-3}) of submicrometer EC were found by commercial cascade impactors. In some mines, the EC background (from submicrometer coal dust) may be higher than a typical background (environmental) level, but it is still quite low relative to EC concentrations in dieselized mines. Thus, with an appropriate sampler design, NIOSH 5040 most likely can be used in many coal mines for DPM exposure monitoring and evaluation of emission controls. Monitoring DPM in underground coal mines is important because concentrations are often quite high.

A commercial version of the UMN/BOM and BOM impactors was recently introduced by SKC® (Catalog no. 225–317, SKC®, 863 Valley View Road, Eighty Four, PA 15330). MSHA recommended this impactor, called the DPM Cassette, for DPM sampling in metal and nonmetal mines. Given the intended application (*i.e.*, monitoring DPM mass concentrations in coal mines) of the original impactors on which the DPM Cassette design is based, it is likely well suited for use in underground coal mines. To this end, its efficacy for DPM EC sampling in the presence of coal dust was recently investigated. Results of this investigation will appear elsewhere.[57]

Mention of company name or product does not constitute endorsement by the Centers for Disease Control and Prevention.

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