Diesel Particulate Matter Exposure and Concentration Monitoring in Underground Mines: Practices and Challenges

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Monitoring personal exposures to diesel particulate matter (DPM) plays an important role in efforts to reduce exposure of workers to diesel aerosols and gases.

- Monitoring is critical to:
  - Protection of workers health;
  - Identification of potential risks;
  - Selection, implementation and monitoring effectiveness of control technologies and strategies…
- Regular monitoring personal exposure to TC and EC, as surrogates to DPM, is a major pillar of a performance or risk based approaches toward reducing exposures of underground miners to diesel aerosols and gases in the U.S.A. [30 CFR 57.5061], Ontario [OHSA 2017], Australia [AIOH 2013], and some other countries.
- In the U.S.A. and Ontario monitoring is done primary in underground metal, nonmetal, and stone mines.
- In Australia, monitoring is done also in underground coal mines [Noll et al. 2015].

- 30 CFR 57.5061. Compliance determinations. Safety and Health Standards. Underground metal and nonmetal mines. Mine Safety and Health Administration, Department of Labor, Code of Federal Regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.
- OHSA [2017]. Occupational Health and Safety Act, Ontario Regulation 854. Mines and Mining Plants. Ontario Ministry of Labor.
- AIOH [2013]. Diesel Particulate Matter & Occupational Health Issues. Position Paper. Australian Institute of Occupational Hygiene. AIOH Exposure Standards Committee.
- Noll J, Gilles S, Wu HW, Rubinstein E [2015]. J. Occup. Environ. Hyg. 12, 205-211.

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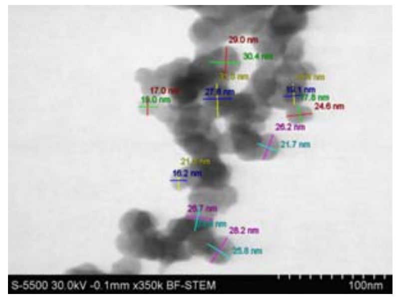
Monitoring diesel aerosols is challenging due to complex, diverse, and dynamic nature of aerosols and gases emitted by diesel engines.

- Submicron diesel aerosols have complex physical and chemical structure [Bugarski et al. 2012].
- Typical diesel engines emit aerosols made of elemental carbon, sulfates, nitrates, ash and hundreds of different volatile (primarily gas phase), semivolatile (gas and particle bound phase), and nonvolatile organic compounds (primarily particle bound phase) [Lowenthal et al. 1994, Zielinska et al. 2002. Khalek et al. 2011, Khalek et al. 2015].
- It is important to note that the distinctions between volatile, semivolatile, and nonvolatile organic fractions are not very well defined [Võ and Morris 2014].



- Bugarski AD, Janisko SJ, Cauda EG, Noll JD, Mischler SE [2012]. ISBN-13: 9780873353601.
- Lowenthal DH, Zielinska B, Chow JC, Watson JG, Gautam M, Ferguson DH, Neuroth GR, Stevens KD [1994].. Atmos. Environ., 28(4), 731–743.
- Zielinska B, Sagebiel J, McDonald J, Rogers CF, Fujita E, Mousset-Jones P [2002]. Special Report. Heath Effect Institute, Boston MA. April. 181-232.
- Khalek IA, Bougher TL, Merritt PM, Zielinska B [2011]. J. Air & Waste Manage. Assoc., 61, 427–442.
- Khalek IA, Blanks MG, Merritt PM, Zielinska B [2015]. J. Air & Waste Manage. Assoc., 65, 987–1001.
- Võ Y-YT, Morris MP [2014]. J. Air & Waste Manage. Assoc., 64, 661-669.

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For practical reasons, elemental carbon (EC) and total carbon (TC) were adopted as surrogates for monitoring DPM.

- Current methods based on carbon analysis have an advantage over previously used methods involving gravimetric analysis (size-selective gravimetric (SSG), respirable combustible dust (RCD)) in terms of sensitivity and selectivity for monitoring DPM on targeted PEL levels [Ramachandran and Watts 2003].
- Since EC and organic carbon (OC), collectively known as TC (TC=EC+OC), make the major part of the pre-Tier 4 DPM, carbon has been deemed a logical choice of surrogate for the DPM exposure monitoring [Verma et al. 1999, Birch et al. 2002, NIOSH 2016].
- Mining Safety and Health Administration (MSHA) and Ontario Ministry of Labor (OMOL) adopted TC PEL standard [MSHA 2016, OHSA 2017].
- Australian Institute of Occupational Hygienists (AIOH) recommended EC standard [AIOH 2013].

- Ramachandran G, Watts W [2003]. AIHA Journal 64(3): 329-337.
- Verma DK, Shaw L, Julian J, Smolynec K, Wood C, Shaw D [1999]. App. Occup. Environ. Hyg., 14(10), 701-714.
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- NIOSH [2016a]. Diesel Particulate Matter (as Elemental Carbon). In: NIOSH Manual of Analytical Methods (NMAM), 5th Edition, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.
- MSHA [2016]. Carbon (Diesel Particulate Matter) by Thermal/Optical Analysis. MSHA P-13. Revision #003. Mine Safety and Health Administration, Department of Labor.
- OHSA [2017]. Occupational Health and Safety Act, Ontario Regulation 854. Mines and Mining Plants. Ontario Ministry of Labor.

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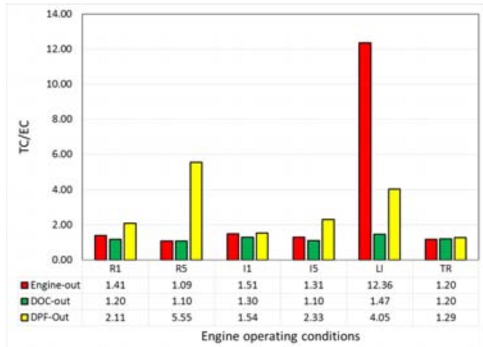
TC, which typically makes the majority of DPM mass emitted by pre-EPA Tier 4 technology engines, appears to represent better DPM surrogate than EC.

- However, composition of DPM at workplace [Verma et al. 1999, Stephenson et al. 2006, Noll et al. 2007] can vary substantially with type of engines operated, engine operating conditions, use of exhaust aftertreatment and other factors.

- TC/EC ratio for DPM emitted by Tier 2 engine operated at R1 (rated speed/100% load), R5 (rated speed/50% load), I1 (intermediated speed/100% load), I5 (intermediated speed/50% load), LI (low idle), and TR (transient) conditions was examined for different exhaust configurations:
  - muffler,
  - low NO_2 diesel oxidation catalytic converter (DOC), and
  - low-NO_2 diesel particulate filter (DPF)



- TC/EC ratio was found to vary widely with selected engine operating conditions and exhaust configurations.

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- Stephenson DJ, Spear TM, Lutte MG [2006]. Min. Eng. 58(8): 39–44.
- Noll JD, Bugarski AD, Patts LD, Mischler SE, McWilliams L [2007]. Environ. Sci. Technol., 41, 710–716. .

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Dynamic developments in engine, exhaust aftertreatment, and fuel technologies resulted in major changes in composition of diesel aerosols.

- EC is substantially less present than OC in DPM for:
  - some of the older technology engines [Verma et al. 1999]
  - contemporary engines equipped with c-DPFs or DOC/c-DPF/SCR exhaust aftertreatment systems [Khalek et al. 2011, Khalek et al. 2015].
  - engine operated on FAME biodiesel [Bugarski et al. 2009].
  - the mines that use DPFs [Noll et al. 2007].

- Sulfates are dominant component of DPM emitted by engines equipped with c-DPFs (2007-technology engine) [Khalek et al. 2011].

- Verma DK, Shaw L, Julian J, Smolynec K, Wood C, Shaw D [1999]. App. Occup. Environ. Hyg., 14(10), 701-714.
- Khalek IA, Bougher TL, Merritt PM, Zielinska B [2011]. J. Air & Waste Manage. Assoc., 61, 427–442.
- Khalek IA, Blanks MG, Merritt PM, Zielinska B [2015]. J. Air & Waste Manage. Assoc., 65, 987–1001.
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Monitoring OC, and consequently TC, is much more challenging than monitoring EC.

- NIOSH Method 5040, off-line analytical method used for quantification of carbon content on sampling filters, is devised for EC quantification [NIOSH 2016a].
- In underground mines, the number of sources that could interfere with the results of sampling and analysis is much larger for OC than for EC [Noll et al. 2015].
- That could be the primary reason why EC is used in Australia as a surrogate (AIOH, Peters et al. 2017.

- NIOSH [2016a]. Diesel Particulate Matter (as Elemental Carbon). In: NIOSH Manual of Analytical Methods (NMAM), 5th Edition, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health https://www.cdc.gov/niosh/nmam/pdfs/NMAM_5thEd_EBook.pdf.
- Noll J, Gilles S, Wu HW, Rubinstein E [2015]. J. Occup. Environ. Hyg. 12, 205-211.
- AIOH [2013]. Diesel Particulate Matter & Occupational Health Issues. Position Paper. Australian Institute of Occupational Hygiene. AIOH Exposure Standards Committee.
- Peters S, de Klerk N, Reid A, Fritischi L, Musk AW, Vermulen R [2017]. Occup. Environ. Med 74, 282-289.

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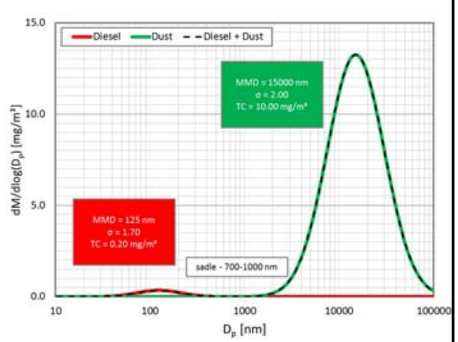
Monitoring diesel aerosols in underground mines is even further complicated due to a number of environmental factors.

- Potential presence of OC and/or EC in mechanically generated dust;
- Presence of OC and EC in submicron aerosols from other than diesel sources:
  - Hydraulic oil,
  - Welding,
  - Cigarette smoking….
- Potential interaction of diesel aerosols with other aerosols and gases present in the environment.



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Practices of monitoring exposures of underground miners in the U.S.A., Australia, Ontario, Quebec, and some other places are founded on the adaptations of off-line analysis [NIOSH 2016a] and sampling methodology based on NIOSH Method 5040 [NIOSH 2016b].

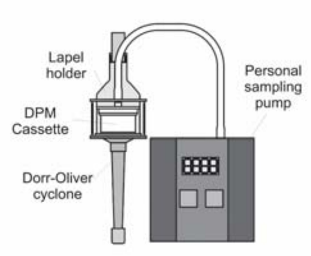
- Methodology [NIOSH 2016a] and guidance [NIOSH 2016b] was adopted with some modifications by MSHA [MSHA 2006, MSHA 2016] and OMOL [OMOL 2015] for compliance DPM sampling.
- Additionally, various adaptations of the methodology were used for engineering or research purposes.
- **However, there are major differences in interpretation of the sampling and analytical practices.**

- NIOSH [2016a]. Diesel Particulate Matter (as Elemental Carbon). In: NIOSH Manual of Analytical Methods (NMAM), 5th Edition, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health DHHS (NIOSH) Publication No. 2014-151.
- NIOSH [2016b]. Monitoring diesel exhaust in the workplace. In: NIOSH Manual of Analytical Methods (NMAM), 5th Edition, Chapter DL, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health https://www.cdc.gov/niosh/nmam/pdfs/NMAM_5thEd_EBook.pdf
- MSHA [2006]. Metal/nonmetal health inspection procedures handbook number PH06-IV-1(1). In: MSHA handbook series. U.S. Department of Labor, Mine Safety and Health Administration, Metal and Nonmetal Mine Safety and Health.
- MSHA [2016]. Carbon (Diesel Particulate) By Thermal/Optical Analysis - Method P13. Revision #3. Department of Labor. Mine Safety and Health Administration.
- OMOL [2015]. Sampling for Diesel Particulate Matter in Mines. Ontario Ministry of Labor. [https://www.labour.gov.on.ca/english/hs/pubs/gl_dparticulate.php].

Sampling Subtleties

Compliance sampling in underground M/NM miners in the U.S. for purpose of enforcement of DPM PEL standard [30 CFR Part 57.5061] is performed using methodology described in and PH06-IV-1 [MSHA 2006].

- The sampling apparatus consists of:
  - cassette (SKC, 225-317), made of conductive plastic with incorporated four-nozzle single-stage impactor, and primary and secondary quartz fiber filters (QFFs) (Noll et al. 2005)
  - 10 mm Dorr-Oliver style cyclone;
  - lapel holder;
  - personal sampling pump (1.7 lpm).
- Therefore, the procedure results in tandem QFFs with submicron DPM samples.



- 30 CFR 57.5061. Compliance determinations. Safety and Health Standards. Underground metal and nonmetal mines. Mine Safety and Health Administration, Department of Labor, Code of Federal Regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.
- MSHA [2006]. Diesel Particulate Matter Sampling. Metal/nonmetal health inspection procedures handbook. PH06-IV-1(1). U.S. Department of Labor, Mine Safety and Health Administration, Metal and Nonmetal Mine Safety and Health. (https://arlweb.msha.gov/READROOM/HANDBOOK/HANDBOOK.HTM)
- Noll JD, Timko RJ, McWilliams LJ, Hall P, Haney R [2005]. J Occup Environ Hyg 2, 29–37.

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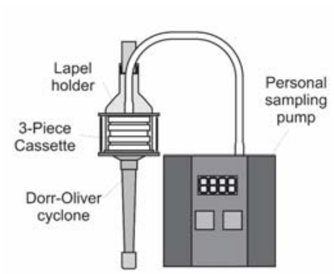
Sampling in underground M/NM miners in the Ontario for purpose of enforcement of DPM PEL standard [OHSA 2017] is performed using methodology described in OMOL [2015].

- The sampling apparatus consists of:
  - 3-piece cassette with 37 mm pre-ashed QFF (such as SKC Cat. No. 225-401),
  - 10 mm Dorr-Oliver style cyclone;
  - lapel holder;
  - personal sampling pump (1.7 lpm).
- Therefore, the procedure results in single QFF with respirable DPM samples.



- OHSA [2017]. Regulation 854. Occupational Health and Safety Act, Mines and Mining Plants. Ontario Ministry of Labor. Ontario
- OMOL [2015]. Sampling for Diesel Particulate Matter in Mines. Ontario Ministry of Labor. [https://www.labour.gov.on.ca/english/hs/pubs/gl_dparticulate.php]

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DPM sampling in diluted exhaust at NIOSH PMRD Diesel Laboratory [Bugarski et al. 2016a, Bugarski et al. 2016b]

- The sampling apparatus consists of:
  - 5-piece cassettes
  - 11 lpm critical orifices
  - Leybold SV25B sampling pump.
- Due to absence of mechanically generated aerosols (parallel measurements with ELPI), the cyclone and impactor are not necessary.
- When compared with 3-piece cassette, 5-piece cassette allows for more uniform deposition of the aerosols on the sampling filters.

- Bugarski, A.D., Hummer, J.A., Miller, A., Patts, L.D., Cauda, A.G., Stachulak, J.S. [2016a]. Ann. Occup. Hyg. 60(2):252-262.
- Bugarski, A.D., Hummer, J.A., Vanderslice, S [2016b]. J. Occup. Environ. Hyg. 13(4):297-306.

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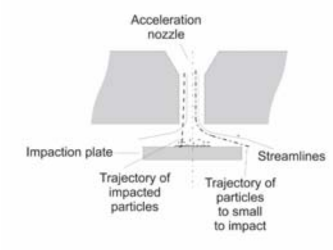
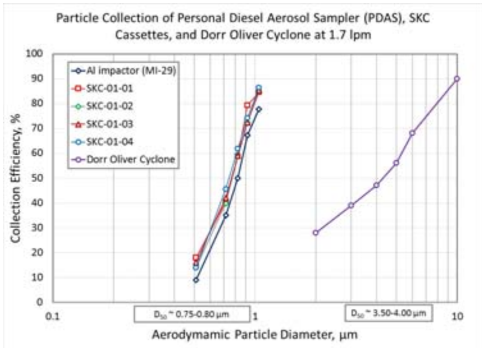
In industrial hygiene sampling, the Dorr-Oliver cyclone is extensively used as a primary pre-selector [MSHA 2006, OMOL 2015].

- The cyclone is used to remove coarse aerosols from a sample.
- Door-Oliver cyclone has D_{50} ~ 3.50-4.00 µm (ACGIH/ISO/CEN respirable curve).
- The removal of coarse dust improves performance and life of the impactor and removes some of the interfering elements.





- MSHA [2006]. Metal/nonmetal health inspection procedures handbook number PH06-IV-1(1). In: MSHA handbook series. U.S. Department of Labor, Mine Safety and Health Administration, Metal and Nonmetal Mine Safety and Health.
- OMOL [2015]. Sampling for Diesel Particulate Matter in Mines. Ontario Ministry of Labor. [https://www.labour.gov.on.ca/english/hs/pubs/gl_dparticulate.php].

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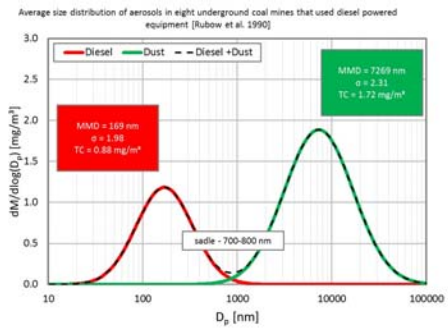
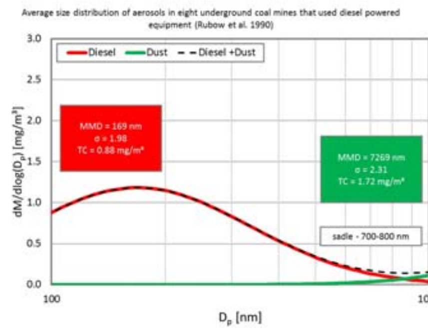
Impactor in the SKC DPM cassette was designed using the results of size distribution and concentration measurements of diesel aerosols and dust in haulage ways in nine underground coal mines in the U.S.A. in late 1980s [Rubow et al. 1990].

- Diesel aerosols and dust were measured using micro orifice uniform deposit impactor (MOUDI).
- The distributions in mines that used diesel-powered equipment were found to be bimodal with a saddle point at 800 nm.
- Cantrell et al. [1991] estimated that if 0.8 µm impactor is used, 0.2-8.4 % of mass of DPM sample might be lost, and dust that penetrate the impactor can contribute 0.1 to 3.6 % to the mass.

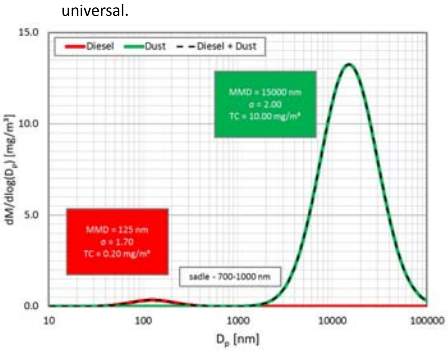


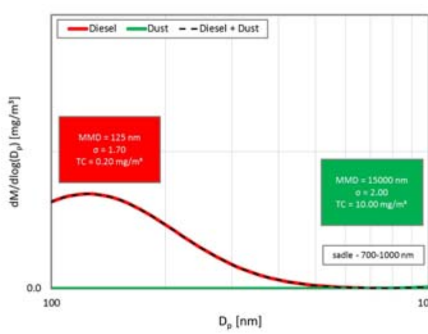


- Rubow KL, Marple VA, Tao Y, Liu D [1990]. SME Preprint No. 90-132.
- Cantrell BK, Rubow KL [1991]. Min Eng 43(2): 231–236.

Size distribution and concentration of diesel aerosols and dust in underground mines very widely.

- Advancement in engine technologies and exhaust aftertreatment over past three decades resulted in the substantial changes in properties of aerosols emitted by diesel engines in the underground mines [Bugarski et al. 2012].
- Size distribution and concentration of dust depends on the sources present in the particular in underground mines [Potts et al. 1990].
- However, separation between diesel aerosols and dust, with saddle point around 0.8 µm, appears to be rather universal.

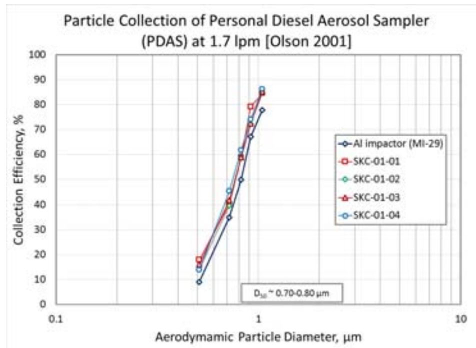




- Bugarski AD, Janisko SJ, Cauda EG, Noll JD, Mischler SE [2012]. ISBN-13: 9780873353601.
- Potts JD, McCawley MA, Jankowski RA [1990]. App. Occup. Environ. Hyg., 5, 440-447.

Impactor with D_{50} ~ 700-800 nm is integrated in the SKC DPM Cassette.

- The impactor in the SKC DPM cassette was modeled after the Personal Diesel Aerosol Sampler (PDAS) [Rubow et al. 1990, Cantrell and Rubow 1991]
- Aluminum (Al) impactor in PDAS was designed to separate diesel aerosols from respirable dust.
- The collection efficiency curves for the PDAS impactor and SKC DPM cassettes were evaluated by Olson [2001].
- Even distribution of the samples on the filter was a very important cassette design factor.



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- Cantrell BK, Rubow KL [1991]. Min. Eng., 43, 231–236.
- Olson B [2001]. Particle calibration of the disposable personal diesel aerosol sampler (PDAS). Report submitted to the National Institute for Occupational Safety and Health. Minneapolis, MN: University of Minnesota, Particle Calibration Laboratory.

CDC NIOSH

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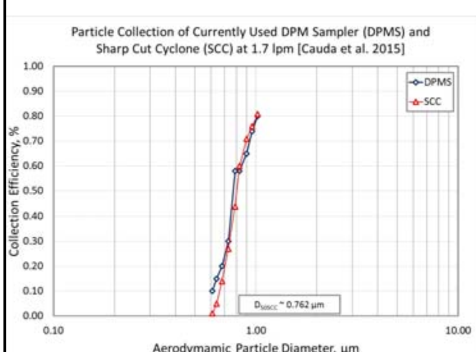
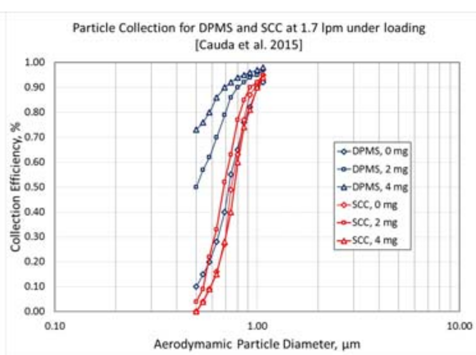
Prolonged sampling in dusty environments might change performance characteristics of the impactor in the SKC DPM cassette [Cauda et al. 2014].

- The buildup of the dust under the impactor nozzle was shown to result in lower penetration through the sampler [Cauda et al. 2014].
- Cauda et al. [2014] suggested that DPM sampling in dusty environments could be done using single-stage sharp-cut cyclone [BGI by Mesa Lab, Model SCC0.695] in place the two-stage impactor and cyclone setup used in the SKC DPM cassette.





- Cauda E, Sheehan M, Gussman R, Kenny L, Volkwein J [2014]. Ann. Occup. Hyg., 58, 995–1005.

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Ambient and occupation particulate samples for carbon analysis are collected exclusively on QFFs.

- QFF are suited for thermal carbon analysis which require heating samples as high as 900°C.
- Additionally, the QFF can be easily extracted [Turpin et al. 2000].
- The downside of using QFFs is that those are not inert [Verma et al. 1999, Kirchstetter et al. 2001].
- Collection of EC and OC samples on QFF have been extensively studied for high-volume atmospheric sampling [Fitz 1990, Turpin et al. 2000, Kirchstetter et al. 2001, Mader et al. 2003, Subramanian et al. 2004] and less extensively for low-volume occupational sampling [Olson and Noriss 2005, Noll and Birch 2008].

- Turpin BJ, Saxena P, Andrews E [2000]. Atmos. Environ., 34, 2983–3013.
- Verma DK, Shaw L, Julian J, Smolynec K, Wood C, Shaw D [1999]. App. Occup. Environ. Hyg., 14, 701-714.
- Kirchstetter TW, Corrigan CE, Novakov T [2001]. Atmos. Environ. 35, 1663-1671.
- Fitz DR [1990].Aerosol Sci. Technol. 12, 142-148.
- Mader BT, Schauer JJ, Seinfeld JH, Flagen RC, Yu JZ, Yang H, Lim H-J, Turpin BJ, Deminter JT, Heidemann G, Bae MS, Quinn P, Bates T, Eatough DJ, Huebert BJ, Bertram T, Howell S [2003]. Atmos. Environ. 37, 1435–1449.
- Subramanian R, Khlystov AY, Cabada JC, Robinson AL [2004]. Aerosol Sci. Technol. 38 (S1), 27–48.
- Olson DA, Norris GA [2005]. Atmos. Environ. 39, 5437–5445.
- Noll JD, Birch ME [2008]. Environ. Sci. Techol. 42(14): 5223–5228.

DPM sampling on QFF is affected by positive and negative artifacts [Turpin et al. 2000, Kirchstetter et al. 2001, Mader et al. 2003].

- **Positive artifact:**
  - adsorption of gas-phase volatile organics by QFF media and collected particle-bound material;
  - contamination of filters with volatile, semivolatile, and nonvolatile organics (before and after sampling).
- Limited information is available on the chemical nature of the organics adsorbed by quartz filters [Vecchi et al. 2009, Li et al. 2016].
- **Negative artifacts** are associated with evaporation of:
  - semivolatile organic compounds (SVOCs) collected on the primary filter, and
  - volatile and semivolatile contaminants.

- Turpin BJ, Saxena P, Andrews E [2000]. Atmos. Environ., 34, 2983–3013.
- Kirchstetter TW, Corrigan CE, Novakov T [2001]. Atmos. Environ., 35, 1663-1671.
- Mader BT, Schauer JJ, Seinfeld JH, Flagen RC, Yu JZ, Yang H, Lim H-J, Turpin BJ, Deminter JT, Heidemann G, Bae MS, Quinn P, Bates T, Eatough DJ, Huebert BJ, Bertram T, Howell S [2003]. Atmos. Environ., 37: 1435–1449.
- Li X, Dallmann TR, May AA, Tkacik DS, Lambe AT, Jayne JT, Croteau PL, Presto AA [2016]. Environ. Sci. Technol. 50, 12146−12155.
- Vecchi R, Valli G, Fermob P, D'Alessandro D, Piazzalunga A, Bernardoni V [2009]. Atmos. Environ., 43, 1713–1720.

If not accounted for, the positive artifacts due to adsorption of gas phase organics onto QFF would lead to overestimation of OC concentrations [Kirchstetter et al. 2001, Mader et al. 2003].

- In the case of nanometer-size aerosols mass of organic aerosols might be much higher in gas phase than in the particle-bound phase [Parshintsev et al. 2011].
- If single QFF filter is used, the particle bound phase OC concentrations could be overestimated by as much as 100 % [Kirchstetter et al. 2001, Mader et al. 2003, Vecchi et al. 2009]
- Several methods of correcting or eliminating artifacts due to adsorption of gas phase organics are reported in literature:
  - Dynamic blank correction using OC on the secondary QFF in QFF before QFF filter arrangement (QBQ) [Fitz 1990, Turpin et al. 2001, Olson and Noriss 2005];
  - Dynamic blank correction using OC on the secondary QFF in Teflon membrane filter (TMF) before QFF filter arrangement (TBQ) [Turpin et al. 2001, Olson and Noriss 2005];
  - Removing gas-phase OC by XAD-coated and activated carbon impregnated filter lined denuders [Mader et al. 2003, Subramanian et al. 2004, Olson and Noriss 2005].

- Kirchstetter TW, Corrigan CE, Novakov T [2001]. Atmos. Environ. 35, 1663-1671.
- Mader BT, Schauer JJ, Seinfeld JH, Flagen RC, Yu JZ, Yang H, Lim H-J, Turpin BJ, Deminter JT, Heidemann G, Bae MS, Quinn P, Bates T, Eatough DJ, Huebert BJ, Bertram T, Howell S [2003]. Atmos. Environ. 37, 1435–1449.
- Parshintsev J, Ruiz-Jimenez J, Petäjä T, Hartonen K, Kulmala M, Riekkola M-L [2011]. Anal. Bioanal. Chem. 400, 3527–3535.
- Vecchi R, Valli G, Fermob P, D'Alessandro D, Piazzalunga A, Bernardoni V [2009]. Atmos. Environ., 43, 1713–1720.
- Fitz DR [1990]. Aerosol Sci. Technol. 12, 142-148.
- Turpin BJ, Saxena P, Andrews E [2000]. Atmos. Environ., 34, 2983–3013.
- Olson DA, Norris GA [2005]. Atmos. Environ. 39, 5437–5445.
- Subramanian R, Khlystov AY, Cabada JC, Robinson AL [2004]. Aerosol Sci. Technol. 38 (S1), 27–48.

Addressing Adsorption of Gas Phase Organics on Compliance DPM Samples Collected in Underground Mines

- NIOSH [NIOSH 2016b] suggests that the dynamic blank correction using OC on the secondary QFF in QBQ configuration might provide better correction for the adsorption of gas phase organics than the field blank typically used in the other analyses.
- MSHA [MSHA 2016] also suggests that the adsorption of OC on primary QFF filter should be corrected using OC determined for the secondary QFF dynamic blank in QBQ configuration.
- Ontario MOL [OHSA 2017] which requires only single filter does not provide any reference to the correction for adsorbed gas phase organics onto QFF.

- NIOSH [2016a]. Diesel Particulate Matter (as Elemental Carbon). In: NIOSH Manual of Analytical Methods (NMAM), 5th Edition, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health https://www.cdc.gov/niosh/nmam/pdfs/NMAM_5thEd_EBook.pdf.
- MSHA [2016]. Carbon (Diesel Particulate Matter) by Thermal/Optical Analysis. MSHA P-13. Revision #003. Mine Safety and Health Administration, Department of Labor.
- OHSA [2017]. Occupational Health and Safety Act, Ontario Regulation 854. Mines and Mining Plants. Ontario Ministry of Labor.

Advantages and Disadvantages of Methods Used to Correct for Adsorption of Gas Phase Organics

- The QBQ method is the easiest to implement, however, in order for the secondary QFF in QBQ configuration to provide a good estimate of the positive artifact, both primary and secondary QFFs adsorbed equal amount of OC and reached equilibrium [Kirchstetter et al 2001, Mader and Pankow 2001].
- The adsorption of gas-phase compounds on the filters does not always depend on vapor pressure, but may be influenced by the aerosol layer formed on the filter acting as chromatographic stationary phase [Parshintsev et al. 2011].
- Mader end Pankow [2001] suggested that minimum air sampling volume required to reach gas/filter sorption equilibrium can be calculated if the partitioning coefficient of a targeted compound and face area of filter are known.
- Subramanian et. al. [2004] found that the equilibrium can be expected in the case of long (24 hr), but not of short (4-6 hr) duration atmospheric sampling.

- Kirchstetter TW, Corrigan CE, Novakov T [2001]. Atmos. Environ. 35, 1663-1671.
- Mader BT, Pankow JF [2001]. Environ. Sci. Tech. 35, 3422–3432.
- Parshintsev J, Ruiz-Jimenez J, Petäjä T, Hartonen K, Kulmala M, Riekkola M-L [2011]. Anal. Bioanal. Chem. 400, 3527–3535.
- Subramanian R, Khlystov AY, Cabada JC, Robinson AL [2004]. Aerosol Sci. Technol. 38 (S1), 27–48.

Advantages and Disadvantages of Methods Used to Correct for Adsorption of Gas Phase Organics

- Several researchers suggested that the dynamic blank correction using OC determined for the secondary filter in concurrently collected TBQ is more appropriate than the one done using OC determined for the secondary filter in QBQ [Turpin et al. 2001, Kirchstetter et al. 2001, Mader et al. 2003, Olson and Noriss 2005].
- When compared with QBQ approach, TBQ and denuder approaches are more complex and costly.
- Using TBQ correction would require collection of additional TBQ sample concurrently with QBQ sample and additional carbon analysis on the secondary QFF in TBQ sample.
- Since the level of OC on the backup filter of QBQ configuration were shown to be lower than those on the backup filter of TBQ configuration [Mader et al. 2003], the samples corrected using QBQ dynamic blank correction should provide higher estimates of exposure.

- Turpin BJ, Lim HJ [2001]. Aerosol Sci. Technol. 35, 602–610.
- Kirchstetter TW, Corrigan CE, Novakov T [2001]. Atmos. Environ. 35, 1663-1671.
- Mader BT, Schauer JJ, Seinfeld JH, Flagen RC, Yu JZ, Yang H, Lim H-J, Turpin BJ, Deminter JT, Heidemann G, Bae MS, Quinn P, Bates T, Eatough DJ, Huebert BJ, Bertram T, Howell S [2003]. Atmos. Environ. 37, 1435–1449.
- Olson DA, Norris GA [2005]. Atmos. Environ. 39, 5437–5445.

Methods based on removing gas-phase OC by denuders were deemed as an alternative method for obtaining representative particle-bound OC samples.

- In order for this method to provide accurate estimate of particle-bound OC denuder effectiveness in removing gas-phase OC under variety of conditions must be 100% or accurately known [Turpin et al. 2000].
- Mader et al. [2003] reported that XAD-coated and carbon-impregnated denuders were not always 100% efficient in removing gas phase OC from ambient aerosols, but, nonetheless, such denuders minimize gas adsorption artifacts.
- Olson and Norris [2005] reported that observed average efficiency for XAD denuders of 82 % can very with sources.
- Personal sampling with denuder is technically challenging and might not be very practical.

- Turpin BJ, Saxena P, Andrews E [2000]. Atmospheric Environment 34, 2983–3013.
- Mader BT, Schauer JJ, Seinfeld JH, Flagen RC, Yu JZ, Yang H, Lim H-J, Turpin BJ, Deminter JT, Heidemann G, Bae MS, Quinn P, Bates T, Eatough DJ, Huebert BJ, Bertram T, Howell S [2003]. Atmos Environ 37: 1435–1449.
- Olson DA, Norris GA [2005]. Atmos Environ 39: 5437–5445.

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Contamination of the filters with volatile, semivolatile, and nonvolatile organics compounds present the major analytical problem.

- Baking of the QFFs prior to sampling is critical to reducing contamination but preparation of QFF for sampling is not standardized:
  - Researchers reported preparing QFFs for various atmospheric and laboratory studies by baking those at 550 °C for 16-20 hours [Mader et al. 2003], 650 °C for at least 4 hours [Olson and Noriss 2005], 700 °C for at least 6 hours [Kirchestetter et al. 2001];
  - MSHA requires baking at 800 °C for 2 hours [MSHA 2016].
  - NIOSH PMRD bakes QFFs at 800 °C for 2 hours.
  - SKC “heat-treat” QFFs in DPM cassettes to assure low carbon background [SKC 2017].
- Storage and handling could be also source of contamination of the QFFs:
  - QFFs were stored in a freezer (-10 to -5 °C) [Fritz 1990]
  - MSHA and NIOSH do not have any requirements for storage of SKC DPM cassettes and QFFs.

- Mader BT, Schauer JJ, Seinfeld JH, Flagen RC, Yu JZ, Yang H, Lim H-J, Turpin BJ, Deminter JT, Heidemann G, Bae MS, Quinn P, Bates T, Eatough DJ, Huebert BJ, Bertram T, Howell S [2003]. Atmos. Environ. 37, 1435–1449.
- Olson DA, Norris GA [2005]. Atmos. Environ. 39, 5437–5445.
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- SKC [2017]. Diesel Particulate Matter (DPM) Cassettes. SKC Inc. Publication 1643 Rev 1706. http://www.skcinc.com/catalog/pdf/instructions/1643.pdf
- Fitz DR [1990].Aerosol Sci. Technol. 12, 142-148.

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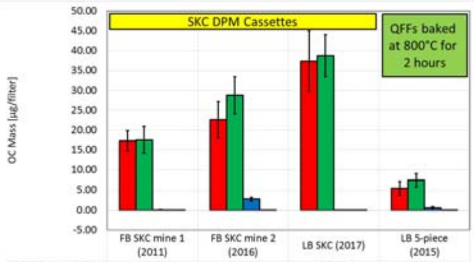
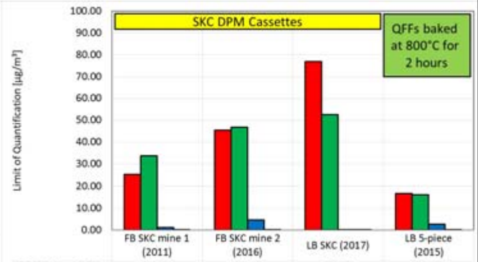
High OC contamination on QFFs is detrimental to efforts to quantify OC concentrations in DPM samples.

- The results of NIOSH 5040 analysis on 18 SKC DPM cassettes used as field blanks in 2011 and 2016 studies, 8 unused SKC DPM cassettes (close to the end of shelf life), and 9 sets of tandem QFFs from 5-pice cassettes used as a laboratory blanks were use to assess the extent of contamination of QFFs in SKC DPM cassettes.
- Substantial contamination of QFFs might result in relatively high LOQ (10* σ) rendered quantification of OC impossible.
- At this time sources of contamination are not known.
- EC contamination was found to be insignificant.



	FB SKC mine 1 (2011)	FB SKC mine 2 (2016)	LB SKC (2017)	LB 5-piece (2015)
OC Primary QFF	17.39	22.69	37.36	5.48
OC Secondary QFF	17.58	28.79	38.79	7.47
EC Primary QFF	0.04	2.80	0.01	0.63
EC Secondary QFF	0.01	0.01	0.01	0.01

Sampling Campaign



	FB SKC mine 1 (2011)	FB SKC mine 2 (2016)	LB SKC (2017)	LB 5-piece (2015)
OC Primary QFF	25.34	45.44	76.82	16.73
OC Secondary QFF	33.70	46.83	52.61	16.26
EC Primary QFF	1.08	4.72	0.14	2.75
EC Secondary QFF	0.06	0.04	0.11	0.05

Sampling Campaign

Negative Artifacts Associated with Evaporation

- The information on the methodologies for quantification of the negative artifacts due to evaporation of semi-volatile OC from particles collected on the primary QFF is rather limited.
- Primary reason for that is that the evaporation of semi-volatile OC from collected ambient particles is much less likely than the adsorption of gaseous phase OC on the QFF [Mader and Pankow 2001] .
- Subramanian et al. [2004] found that negative artifacts for atmospheric samples are typically less than 10% of the ambient particle-bound OC.
- Quantification of the negative artifacts is complicated by large variety of semi-volatile compounds adsorbed onto diesel aerosols and complex interactions with environment.

- Mader BT, Pankow JF [2001]. Environ. Sci. Tech. 35, 3422–3432.
- Subramanian R, Khlystov AY, Cabada JC, Robinson AL [2004]. Aerosol Sci. Technol. 38 (S1), 27–48.
- Vecchi R, Valli G, Fermob P, D'Alessandro D, Piazzalunga A, Bernardoni V [2009]. Atmos. Environ. 43, 1713–1720.

Several other issues can affect sampling on QFFs and consequent analysis using NIOSH Method 5040.

- In spite of the similar appearance, QFFs from different suppliers and even from the same supplier, but different batches (lots) might have different surface areas and therefore adsorption characteristics [Kirchstetter et al. 2001].
- Sampling artifacts depend on filter face velocity, sampling duration, and atmospheric conditions [Turpin et al. 2000, Vecchi et al. 2009].
  - Ambient monitoring – 47 mm filters, 12 to 24 hour sampling at (filter face velocity of 20-80 cm/s)
  - Personal exposure monitoring – 37 mm, 8 to 12 hr sampling at 1.7 lpm (filter face velocity 3.5 cm/s)
- Uniform filter deposit of the sample is critical for the analysis.

- Kirchstetter TW, Corrigan CE, Novakov T [2001]. Atmos. Environ. 35, 1663-1671.
- Turpin BJ, Saxena P, Andrews E [2000]. Atmos. Environ. 34, 2983–3013.
- Vecchi R, Valli G, Fermob P, D'Alessandro D, Piazzalunga A, Bernardoni V [2009]. Atmos. Environ. 43, 1713–1720.

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Analysis

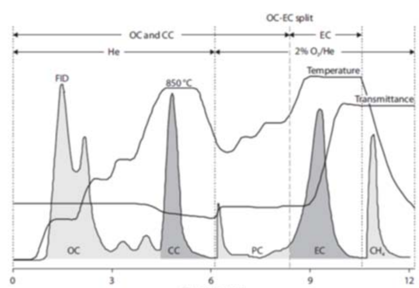
DPM monitoring samples collected in underground mines in the U.S.A., Australia, Ontario, Quebec, and some other places are analyzed using the NIOSH Method 5040 [NIOSH 2016a].

- NIOSH Method 5040 is based on thermal-optical transmittance - evolved gas analysis (TOT-EGA) performed on the punch made out of quartz fiber filter sample [Birch and Cary 1996, Birch 2002, NIOSH 2016a].
- The analysis is done using OCEC Aerosol Analyzer made by Sunset Laboratory Inc. (Portland, OR).
- The NIOSH Method 5040 is designed for analysis of nonvolatile solid portion of the DPM, EC [NIOSH 2016a].
- At 22nd MDEC Conference, Mr. Stoyanoff of Golder Associates reviewed the analytical part of the NIOSH Method 5040.

- Birch ME, Cary R [1996]. Analyst 121, 1183–1190.
- Birch ME [2002]. App. Occup. Environ. Hyg. 17, 400-405.
- NIOSH [2016a]. Diesel Particulate Matter (as Elemental Carbon). In: NIOSH Manual of Analytical Methods (NMAM), 5th Edition, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health DHHS (NIOSH) Publication No. 2014-151.
- Stoyanoff R [2016]. A review of NIOSH Manual of Analytical Methods Chapter DL – Monitoring Diesel Particulate Exhaust in Workplace. 22nd Annual MDEC Conference, Toronto, October 4-6.

Analysis is done using off-line thermal optical transmittance-evolve gas analysis (TOT-EGA) known as a NIOSH Method 5040 [NIOSH 2016a].

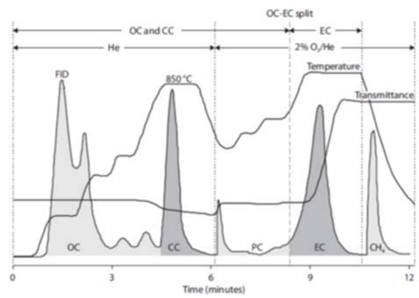
- Analysis has two phases:
  - Organic carbon (OC) (and carbonate carbon (CC)) phase - four temperature steps in pure helium (He)
  - Elemental carbon phase - four temperature steps in a mixture of 10% oxygen in helium (10% O_2/He).
- Temperature protocol is critical to the results:
  - Four temperature steps for OC phase are between 250°C and 900°C.
  - Six temperature steps for EC phase are between 550°C and 900°C.
- Dwell times at different temperatures, typically 45 to 190 sec, need to be extended if samples are heavily loaded.
- The EC loading of QFFs should be not less than 3 µg/cm^2 [Noll et al. 2015] and less than 20 µg/cm^2.



- NIOSH [2016a]. Diesel Particulate Matter (as Elemental Carbon). In: NIOSH Manual of Analytical Methods (NMAM), 5th Edition, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.
- Noll J, Gilles S, Wu HW, Rubinstein E [2015]. J. Occup. Environ Hyg., 12, 205-211.

Split between OC and EC

- The discrimination between OC and EC is done via monitoring transmission of light through the filter.
- If not accounted for, pyrolysis (charring) of OC in the first phase of the analysis might result in overestimate of EC [Chow et al. 2001].
- In some cases, the split between EC and OC needs adjustment:
  - Overloaded samples;
  - Presence of oxygenated species (e.g. biodiesel);
  - Presence of metal oxides (e.g. metallic fuel additives) [Chow et al. 2001]
  - …



- Chow JC, Watson JG, Crow D, Lowenthal DH, Merrifield T [2001]. Aerosol Sci. Technol. 34, 23-34.

The working range and accuracy of the analytical method were found to be adequate for monitoring exposures of underground miners [NIOSH 2016 b].

- The working range for the NIOSH Method 5040 is approximately 6 to 630 µg/m^3 [NIOSH 2016a].
- The LOD of NIOSH Method 5040 for EC is 2 µg/m^3 for 960 l sample collected on 37 mm QFF with at 1.5^2 cm punch.
- MSHA adopted modified NIOSH Method 5040 as a method MSHA P-13 [MSHA 2016] to enforce TC standard [30 CFR 57.5061].
- The working range for the MSHA P-13 is approximately 30 to 668 µg/m^3 [MSHA 2016].
- The LOD of MSHA-P13 is 0.7 µg/m^3 for EC and 0.5 µg/m^3 for OC and TC.

- NIOSH [2016a]. Diesel Particulate Matter (as Elemental Carbon). In: NIOSH Manual of Analytical Methods (NMAM), 5th Edition, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.
- NIOSH [2016b]. Monitoring diesel exhaust in the workplace. In: NIOSH Manual of Analytical Methods (NMAM), 5th Edition, Chapter DL, Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health https://www.cdc.gov/niosh/nmam/pdfs/NMAM_5thEd_EBook.pdf
- MSHA [2016]. Carbon (diesel particulate) by thermal/optical analysis (MSHA P-13). U.S. Department of Labor, Mine Safety and Health Administration.
- 30 CFR 57.5061. Compliance determinations. Safety and Health Standards. Underground metal and nonmetal mines. Mine Safety and Health Administration, Department of Labor, Code of Federal Regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

The LOQ of whole process is substantially larger.

- Actual LOQs of the whole method, accounting for other aforementioned uncertainties (with low contamination QFFs), might be closer to:
  - EC: 30 μg/m^3 TWA
  - TC: 40 μg/m^3 TWA
- Noll et al. [2015] concluded that TC can be determined in underground metal/nonmetal mines in the U.S. within 18% using EC as a surrogate and single TC/EC conversion factor (1.27).
- Noll et al. [2015] concluded that TC can be determined in coal mines in Australia within 19% using EC as a surrogate only if EC > 50 μg/m^3.

- Noll J, Gilles S, Wu HW, Rubinstein E [2015]. J. Occup. Environ. Hyg. 12, 205-211

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MSHA develop method specific error factors to assure that a personal exposure results are more than likely to represent an overexposure at the MSHA PEL [MSHA 2008].

- The error factors (EF) for EC and TC were calculated to account for potential systematic errors and ensure noncompliance with at least 95-percentile confidence.
- The EFs accounts errors in quantification of sample volume, deposited surface area, and analytical procedure.
- The coefficient of variation for directly measured EC and TC, and TC determined by multiplying EC with mine specific TC/EC ratio were estimated to be 5.7%, 11.7%, and between 7.4 and 15.7 % (depending on the number of ambient samples used for establishing TC/EC ratio), retrospectively.
- Taking in account EFs the citations for personal overexposure to DPM are issued for 8-hour shift when:
  - EC * EF(1.095) ≥ 160 μg/m³ (EC ≥ 176 μg/m³), and
  - EC * EF (1.095) < 160 μg/m³, but TC*EF (1.192) ≥ 160 μg/m³ (191 μg_{TC}/m³) or EC*TC/EC*EF (1.259-1.121) ≥ 180 - 202 μg/m³ (depending on the number of ambient samples)

- MSHA [2008]. Enforcement of diesel particulate matter final limit at metal and nonmetal underground mines. U.S. Department of Labor, Mine Safety and Health Administration, Program policy letter No. P08-IV-01.

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Due to relative complexity and cost, sampling for DPM in underground mines has been performed relatively sparsely.

- In the U.S.A., compliance sampling is done by MSHA inspectors [2017].
- MSHA compliance samples are designated as:
  - Contaminant Code (CD) 560 - elemental carbon (EC)
  - CD 561 - total carbon (TC) directly measured or calculated using EC data and mine specific TC/EC ratio established on a number of ambient samples.
- MSHA noncompliance samples are designated as:
  - CD 562 – used to establish mine specific TC/EC ratio.
- The sampling strategy is executed on discretion of the inspectors.

- MSHA [2017]. The DPM personal sampling compliance data. [https://arlweb.msha.gov/OpenGovernmentData/OGIMSHA.asp]

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Relatively small number of samples were collected every year [MSHA 2017].

- In 2016, DPM samples were collected at 46.83 % of 252 mines [MSHA 2017, NIOSH 2017]:
  - 21.74 % of 92 underground metal mines
  - 25.00 % of 44 nonmetal mines, and
  - 75.00 % of 116 underground stone mines.
- In 2016, DPM samples were obtained only for single shift for 5.04 % of 11001 miners [MSHA 2017 NIOSH 2017]:
  - 1.86 % of 6391 workers in underground metal mines were sampled for one shift,
  - 0.98 % of 2652 workers in underground nonmetal mines were sampled for one shift, and
  - 20.89 % of 1958 workers in underground stone mines were sampled for one shift.

Year	Number of Compliance Samples [MSHA 2017]
2012	566
2013	452
2014	545
2015	503
2016	524

- MSHA [2017]. The DPM personal sampling compliance data. [https://arlweb.msha.gov/OpenGovernmentData/OGIMSHA.asp]
- NIOSH [2017]. Annual Collection of Statistical graphics .General Statistics for Metal and Nonmetal mines in the U.S. for CY2015. NIOSH Mining Program Intranet (based on MSHA data) [https://esp.cdc.gov/sites/niosh/DLO/OMSHR/_layouts/15/WopiFrame.aspx?sourcedoc=/sites/niosh/DLO/OMSHR/Documents/SST/PowerPoint/2015GraphicsPresentations.pptx&action=default&DefaultItemOpen=1]

In summary…

- Therefore, the currently used methodologies allow for accurate determination of exposures of underground miners to EC in almost all underground work places.
- In spite of seemingly simple and well defined methodologies, accurate determination of exposures underground miners to OC require extremely careful preparation, sampling, and analysis.
- The methodology for establishing TC/EC ratio via the ambient samples needs careful consideration.
- The methodology is relative complex, slow, and costly.
- The interpretation of the results requires intimate knowledge of sampling and analytical methodology.
- As a result, the publically available information on exposures of underground miners are relatively sparse are often not well documented.

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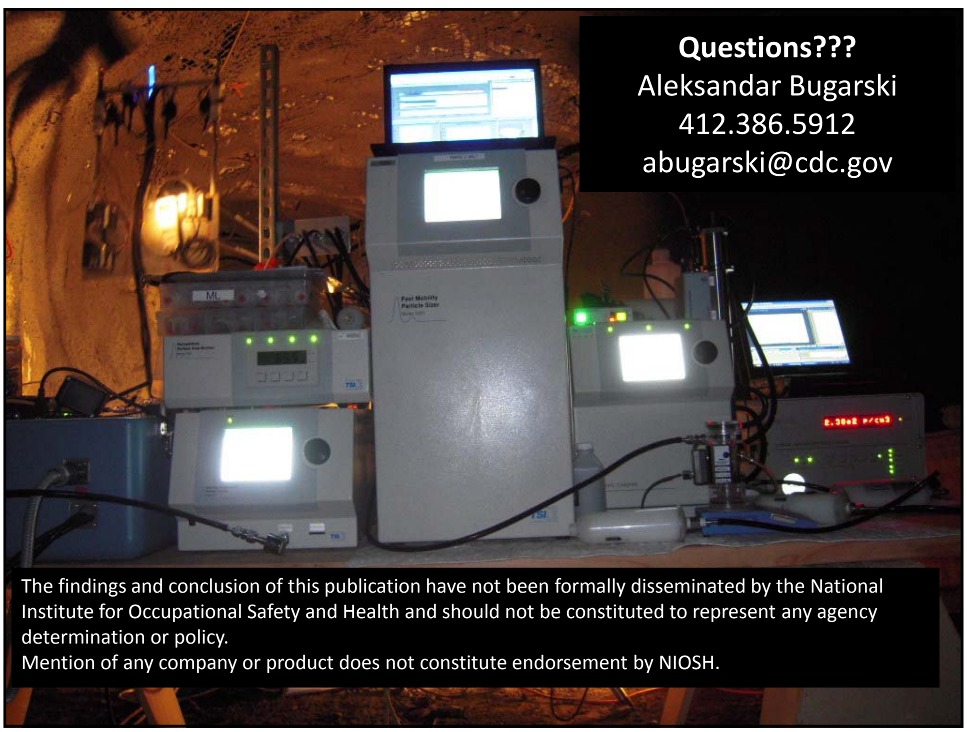

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Abstract

Monitoring concentrations of total carbon (TC) and elemental carbon (EC) using filter-based sampling and off-line carbon analysis is critical to controlling exposure of underground miners to diesel particulate matter (DPM) in the U.S.A. [30 CFR 57.5061], Australia [AIOH 2013], Ontario [OHSA 2017], and other jurisdictions, and to conducting DPM control research. Several iterations of the sampling and analytical methods known as NIOSH Method 5040 [NIOSH 2016a, NIOSH 2016b] are currently used for sampling, analysis, and data interpretation for TC and EC monitoring. Comprehensive knowledge and understanding of the sampling, analysis methodology is crucial for interpretation of DPM monitoring data gathered for compliance, research, and other purposes [MSHA 2016, Bugarski et al. 2016a, Bugarski et al. 2016b, Noll et al. 2015]. Several challenges and potential remediation for reducing uncertainties pertinent to sampling, analysis, and data interpretation of DPM monitoring samples are discussed. The emphasis is given to the following issues: (1) sampling in presence of mechanically and combustion generated aerosols, (2) effects of contamination of filter media; (3) dynamic blank correction as a tool for addressing adsorption and desorption of the gas-phase volatile and semi-volatile organic species on the quartz filter media, (4) establishing a mine-specific TC/EC ratio, (5) using EC and TC surrogate for DPM, and similar. The general trends in DPM exposure were studied using the MSHA compliance and non-compliance samples in underground metal and nonmetal in the U.S.A.

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