SWCNT, MWCNT AND CNF EXPOSURE SUMMARY

By Lisa Cashins, Sc.D., CIH

QUESTIONS TRYING TO ANSWER

- How does CNF physically compare to SWCNT and MWCNT?
- How does the CNT and CNF physically relate to asbestos?
- How does the CNT and CNF exposures relate to asbestos exposure?
- How is CNF processed?
- Is there employee exposure to CNF?

PARTICLE DEPOSITION IN THE LUNG

- Particles with =/< 10 um diameter will deposit somewhere in the respiratory system if inhaled (inhalable)
- Particles with =/< 4 um diameter will deposit in the respirable region of the lung, lower region (respirable)
- Size-selective sampling devices
- NIOSH REL for CNT and CNF is 1.0 ug/m3 of the mass of the sample that contains elemental carbon in the respirable size range, using NISOH Method 5040 (elemental carbon), 8-hour TWA

HINDS, 1982

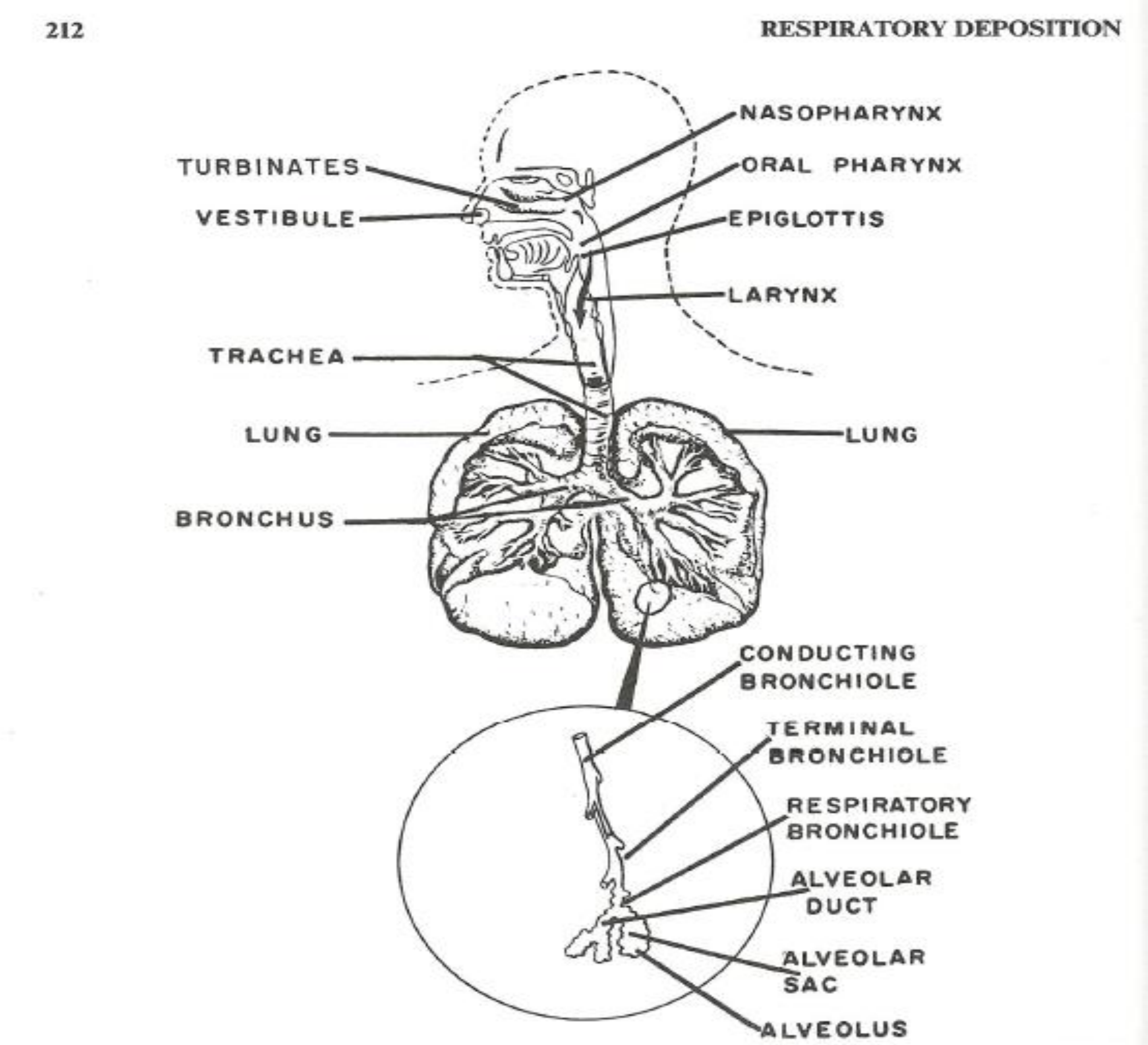


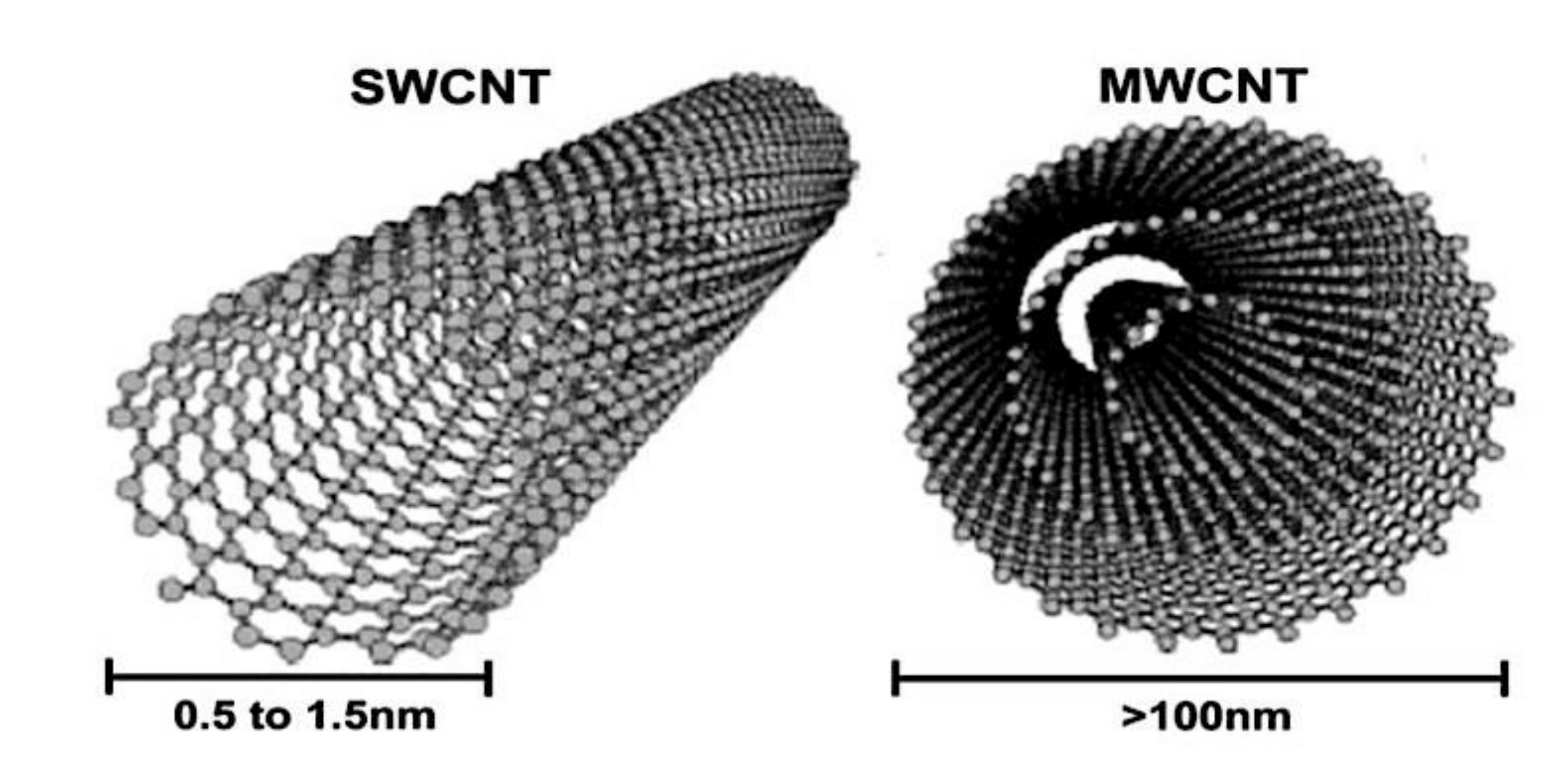
Figure 11.1 The respiratory system. Adapted from *Handbook of Air Pollution* USPHS 999-AP-44 (1968).

PICTURE OF RESPIRABLE CYCLONE WITH MEDIA

HINDS, 1982

- 1 um = 1000 nm (particle with diameter of 4000 nm or less is respirable)
- Nanomaterial – one dimension is less than 100 nm in size
- Diameter of an air molecule – 0.37 nm (0.00037 um)
- Mean free path – average distance traveled by an air molecule between successive collisions
- Mean free path – 66 nm
- Nanoparticles (NP) fall or "slip" in between air molecules
- NP settle slightly faster than particles in um size range

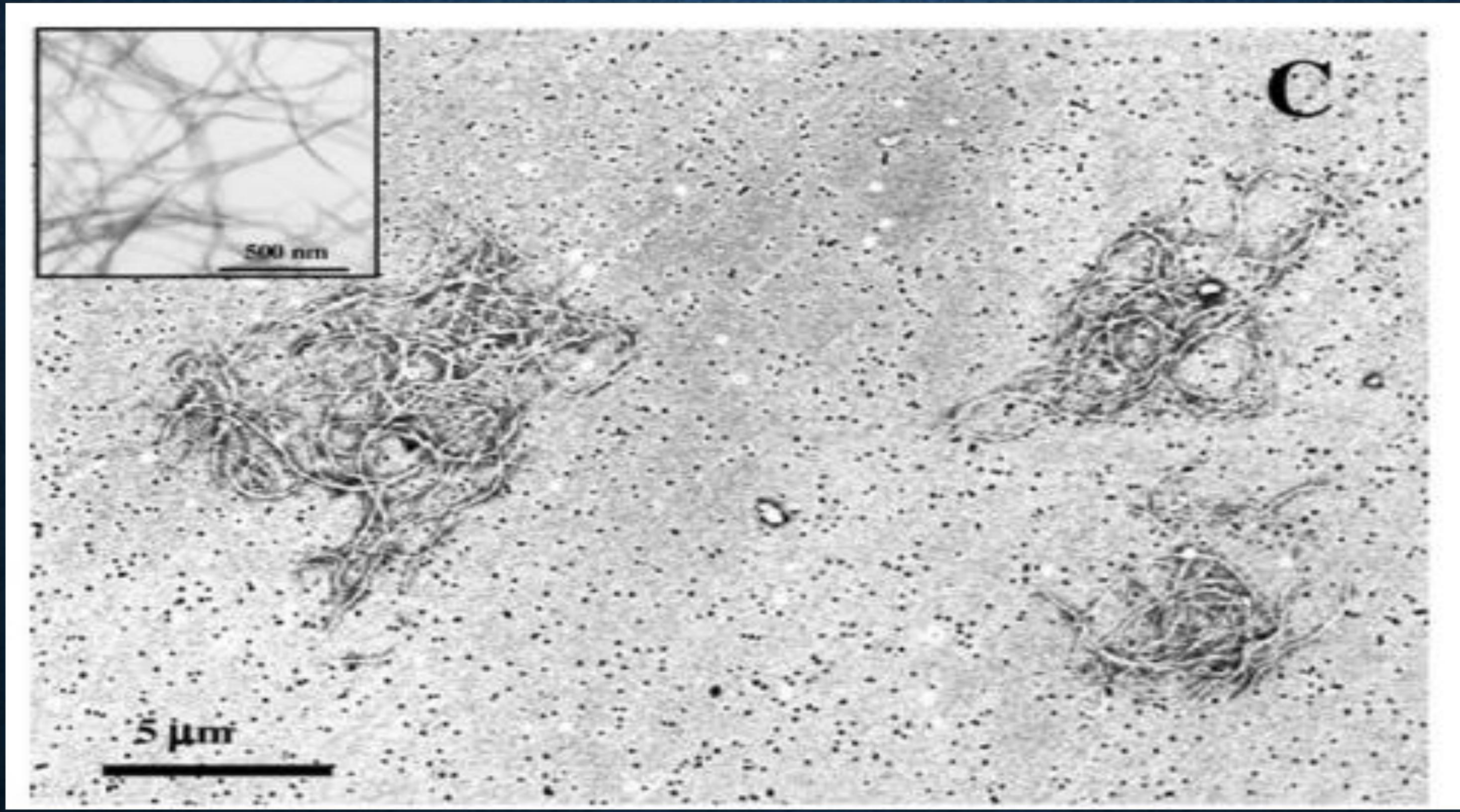
HTTPS://WWW.RESEARCHGATE.NET/FIGURE/SCHEMATIC-REPRESENTATION-OF-SINGLE-WALLED-CARBON-NANOTUBE-SWCNT-AND-MULTI-WALLED-CARBON_FIG1_319966218



SWCNT

- 1 to 10 mn diameters (NIOSH) individual fibers
- Up to 1 mm in length (1,000,000 nm)
- 20 to 50 nm diameters in bundles (Maynard et al, 2004)
- Form tight nest-like bundles or ropes (Birch et al, 2011)

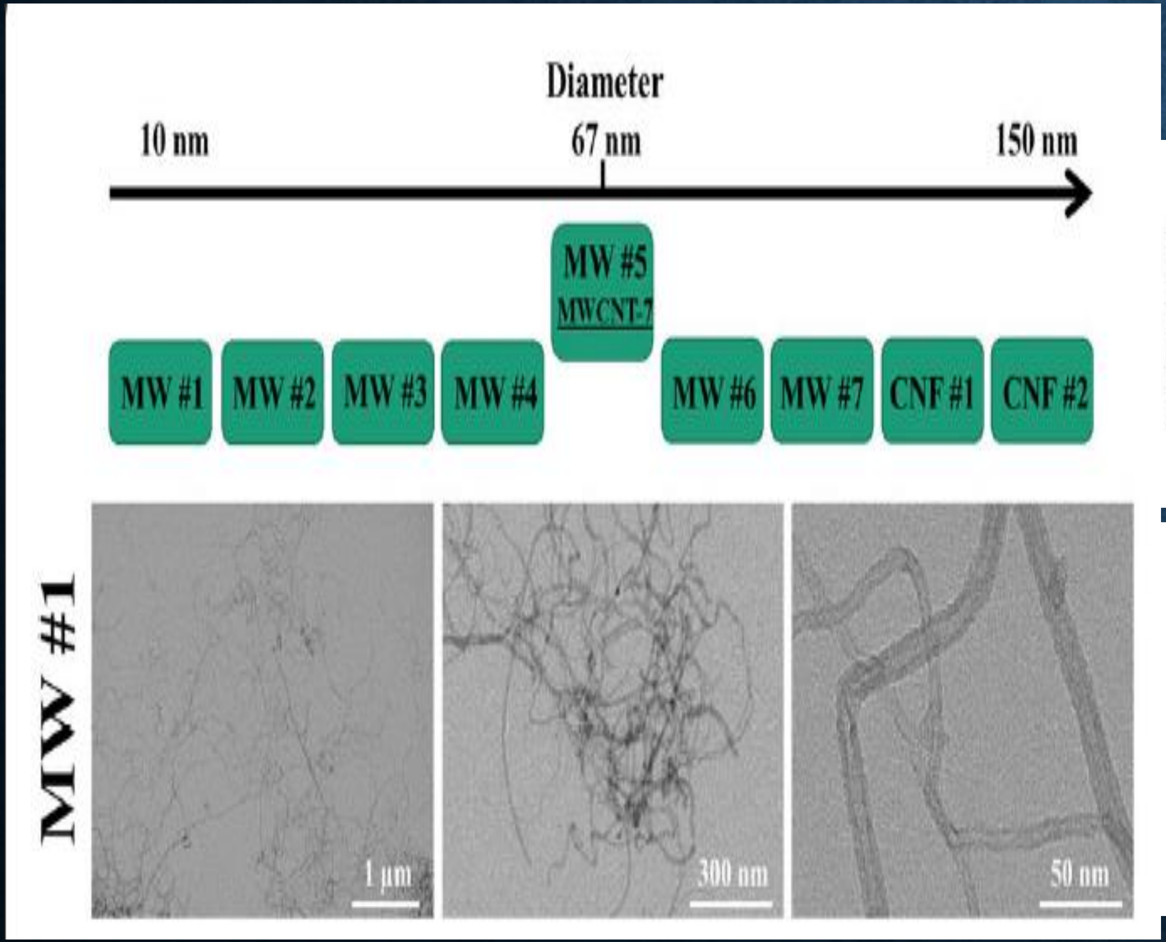
MURRY ET AL, 2012
SWCNT

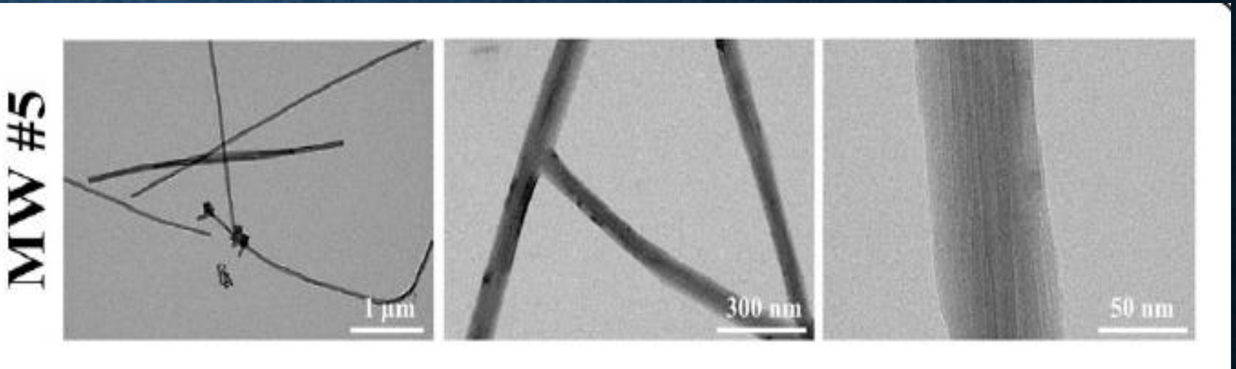


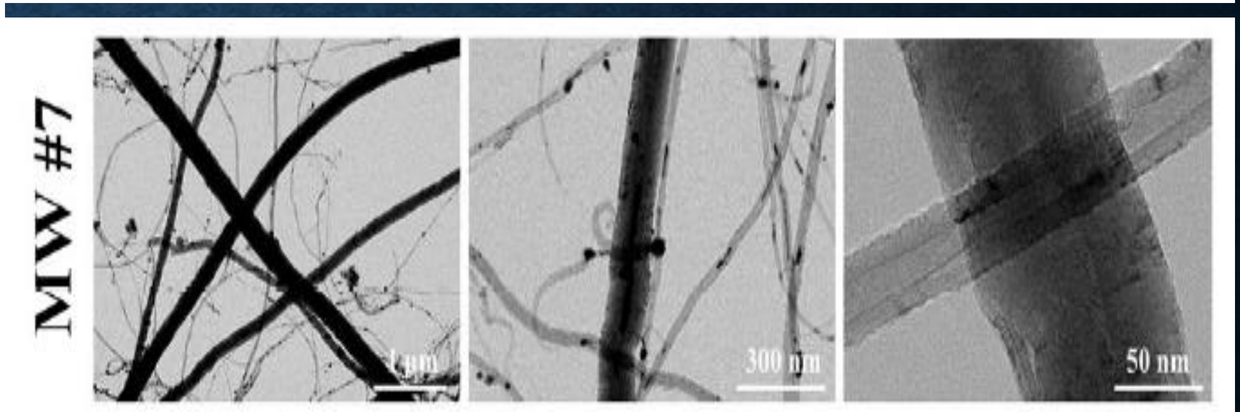
MWCNT AND CNF

- MWCNT - Larger diameters than SWCNT
- MWCNT - Less flexible than SWCNT
- MWCNT - Graphene shell runs parallel to alignment of the fiber
- MWCNT - Very structurally similar to CNF
- CNF – Graphene shell are not exactly parallel to alignment of the fiber
- CNF – cupped like or herringbone shape

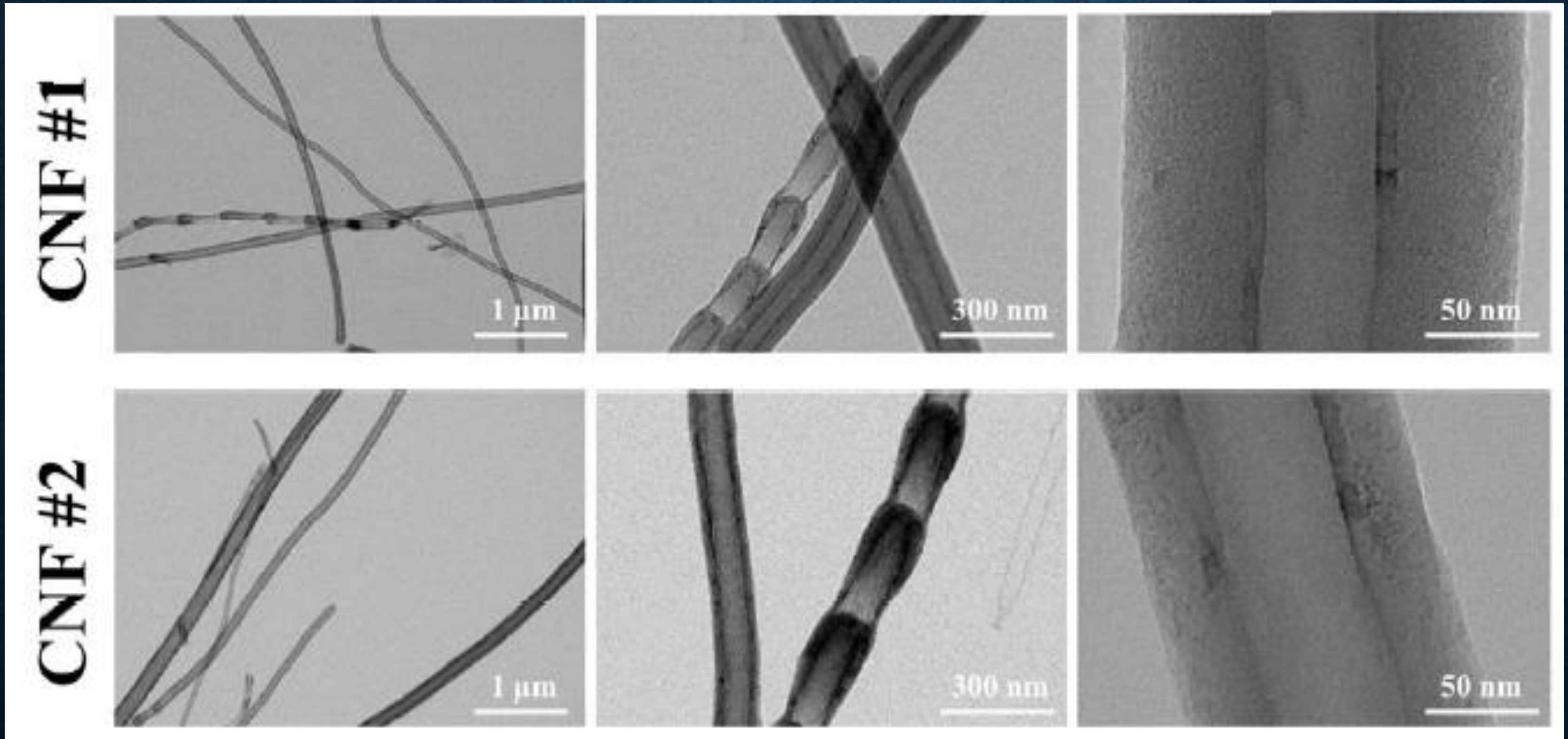
FRASER ET AL, 2020



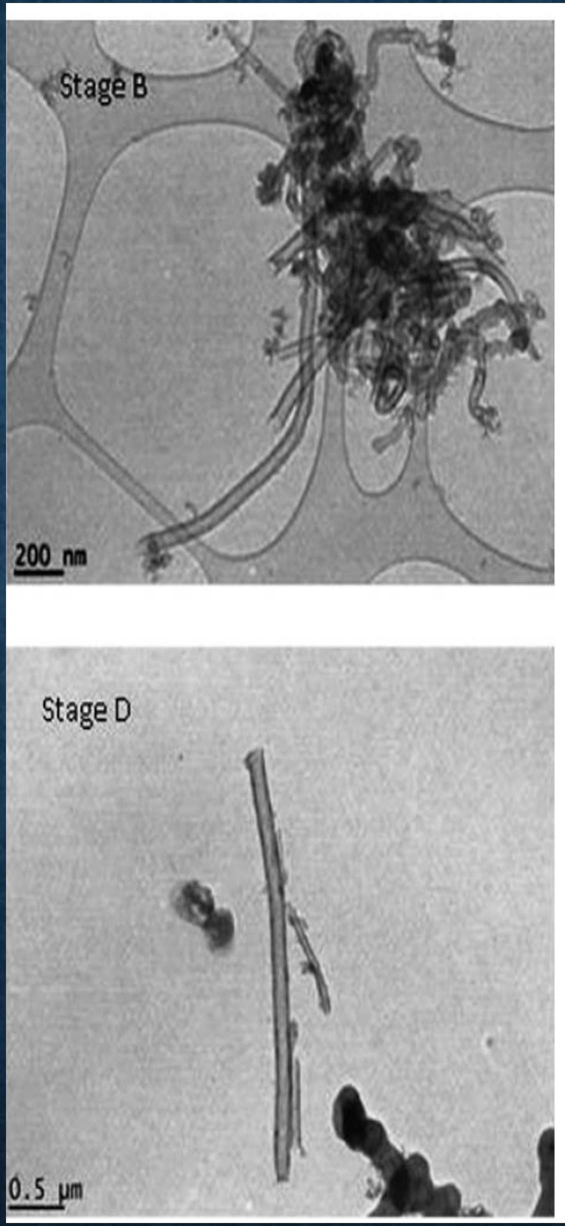




FRASER ET AL, 2020

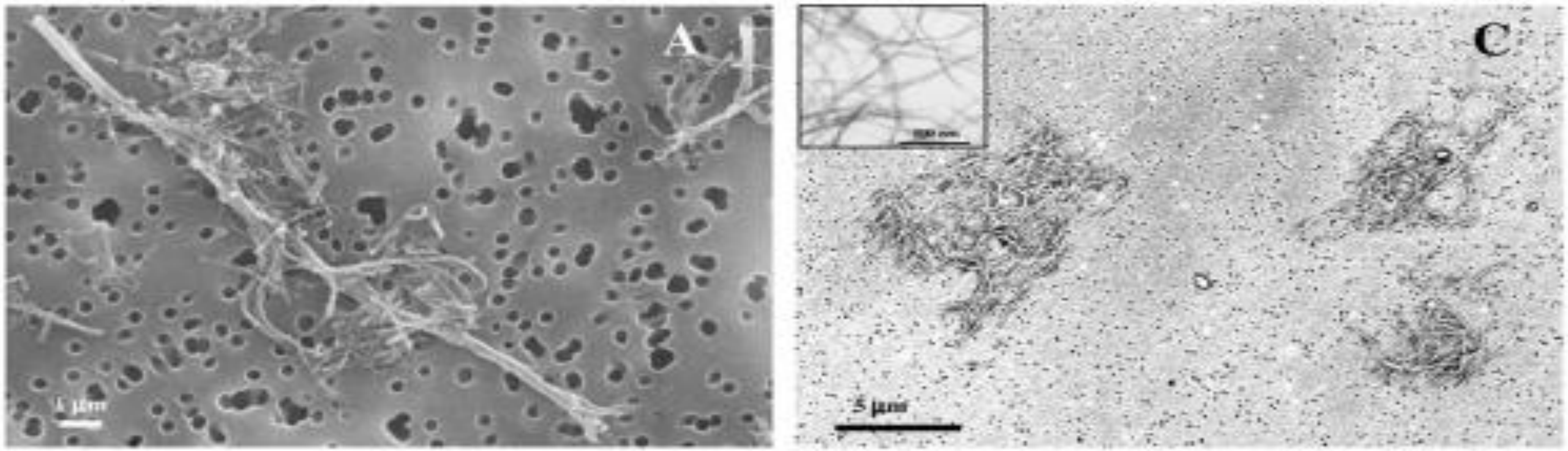


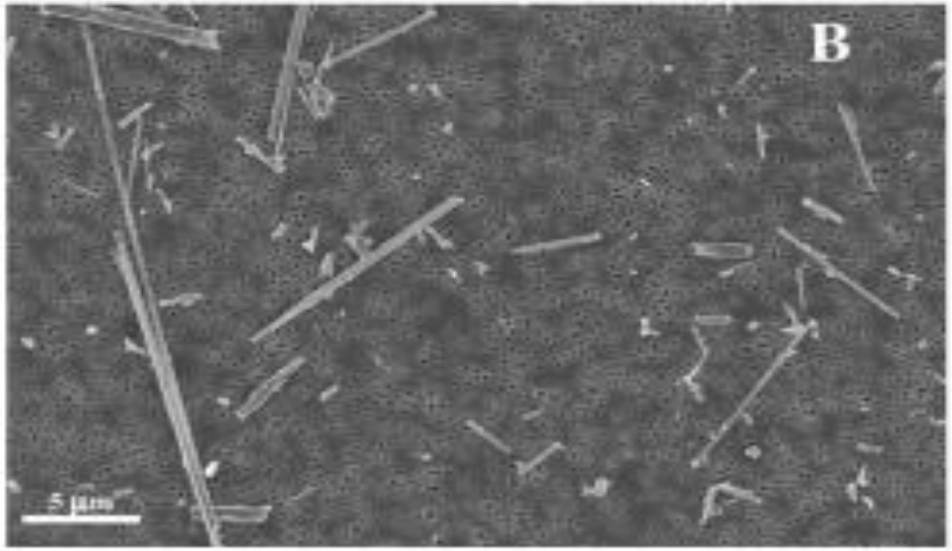
BIRCH ET AL, 2011



CNF in bundle and individual fiber

MURRAY ET AL, 2012 A-CNF, B- ASBESTOS, C-SWCNT





D

	40 µg	120 µg
CNF		$4.14x10^6$
Asbestos		$660x10^6$
SWCNT	$1.84x10^6$	

E

% total/µm	0.1-1.0	1.0-2.0	2.0-5.0	5.0-30.0
CNF	39.47	26.32	25.00	9.21
Asbestos	3.36	21.48	55.70	19.46
SWCNT	0.00	25.00	16.67	58.33

Asbestos fibers, image taken with a scanning electron microscope. Source: http://usgsprobe.cr.usgs.gov/picts2.html.

NIOSH CURRENT INTELLIGENCE BULLETIN 65

CNT	General Measures	
	Diameter	Length
SWCNT	1 to 4 nm	<10,000 nm
MWCNT	2 to 100 nm	<10,000 nm
CNF	40 to 200 nm	10,000 to 1,000,000 nm

FRASER ET AL, 2020; MURRAY ET AL, 2012

Type	Individual		Agglomerated	
	Diameter	**Length**	**Diameter**	**Length**
SWCNT	1 to 10 nm	____________	65 to 150 nm (ropes/bundles)	1,000 to 3,000 nm
MWCNT (not including 7)	13 to 54 nm	800 to 7,640 nm	30 to 9500 nm (bundles/some singles)	1,110 to 49,5500 nm
MWCNT – 7	67 nm	5620 nm	130 nm (bundles/some singles)	6,270 nm
CNF	110 nm	3,200 to 5,200 nm	120 to 210 nm (bundles/some singles)	5,000 nm to 30,000 nm
Asbestos	(by TEM) 160 to 800 nm	(by TEM) 2,000 to 30,000 nm	Only singles	

ASBESTOS and OTHER FIBERS by PCM 7400

FORMULA: Various MW: Various CAS: see Synonyms RTECS: Various

METHOD: 7400, Issue 2	**EVALUATION: FULL**	**Issue 1: Rev. 3 on 15 May 1989** **Issue 2: 15 August 1994**

OSHA: 0.1 asbestos fiber (> 5 µm long)/cc; 1 f/cc, 30 min excursion; carcinogen
MSHA: 2 asbestos fibers/cc
NIOSH: 0.1 f/cc (fibers > 5 µm long), 400 L; carcinogen
ACGIH: 0.2 f/cc crocidolite; 0.5 f/cc amosite; 2 f/cc chrysotile and other asbestos; carcinogen

PROPERTIES: solid, fibrous, crystalline, anisotropic

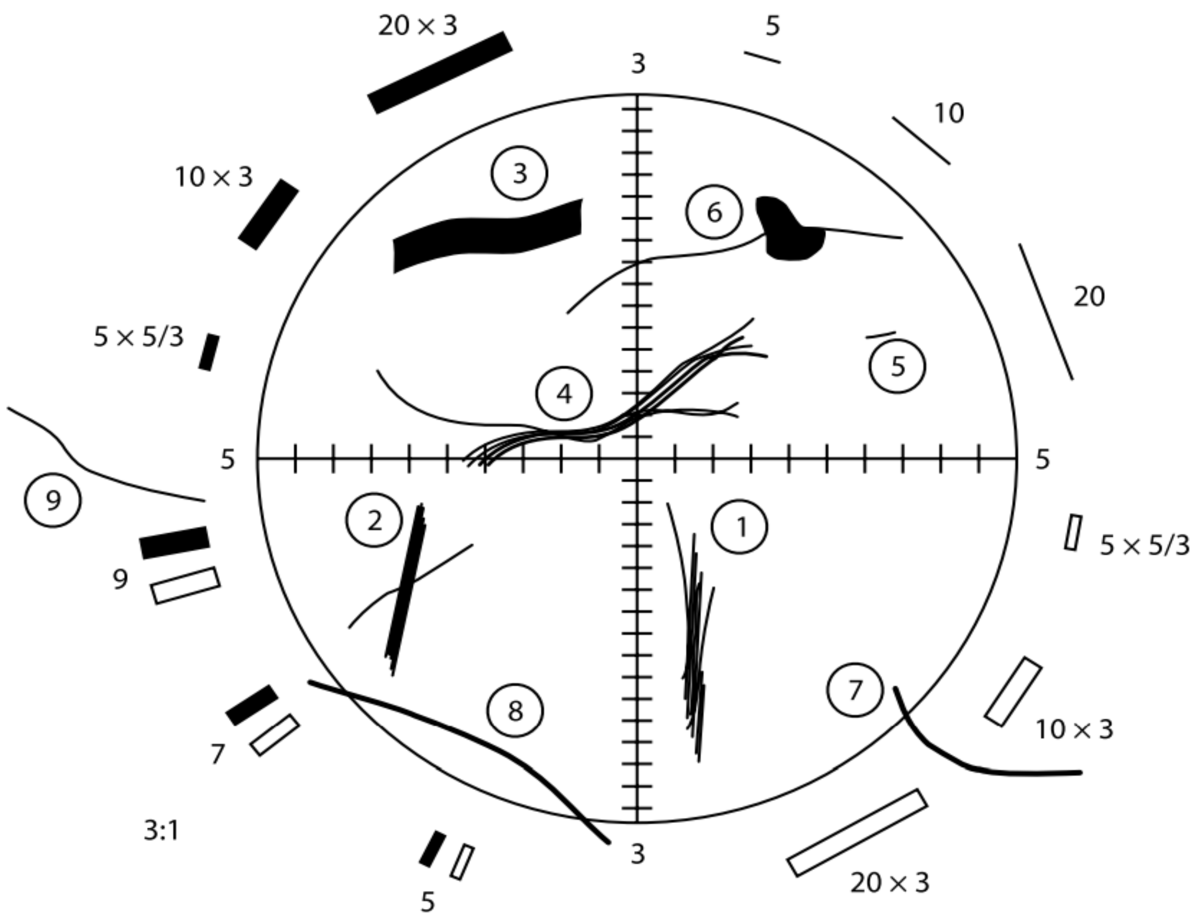
SYNONYMS [CAS #]: actinolite [77536-66-4] or ferroactinolite [15669-07-5]; amosite [12172-73-5]; anthophyllite [77536-67-5]; chrysotile [12001-29-5]; serpentine [18786-24-8]; crocidolite [12001-28-4]; tremolite [77536-68-6]; amphibole asbestos [1332-21-4]; refractory ceramic fibers [142844-00-6]; fibrous glass

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (0.45- to 1.2-µm cellulose ester membrane, 25-mm; conductive cowl on cassette)	**TECHNIQUE:**	LIGHT MICROSCOPY, PHASE CONTRAST
FLOW RATE*:	0.5 to 16 L/min	**ANALYTE:**	fibers (manual count)
VOL-MIN*: **-MAX*:**	400 L @ 0.1 fiber/cc (step 4, sampling)	**SAMPLE PREPARATION:**	acetone - collapse/triacetin - immersion method [2]
	*Adjust to give 100 to 1300 fiber/mm^2	**COUNTING RULES:**	described in previous version of this method as "A" rules [1,3]

ASBESTOS COWL
HTTPS://WWW.ZEFON.COM/CASSETTE-HOUSING-25MM-3PC-ASB-WCOWL-CF-50BX-2

APPENDIX B. COMPARISON OF COUNTING RULES

Figure 2 shows a Walton-Beckett graticule as seen through the microscope. The rules will be discussed as they apply to the labeled objects in the figure.



18. Counting rules: (same as P&CAM 239 rules [1,10,11]: see examples in APPENDIX B).

a. Count any fiber longer than 5 µm which lies entirely within the graticule area.

(1) Count only fibers longer than 5 µm. Measure length of curved fibers along the curve.

(2) Count only fibers with a length-to-width ratio equal to or greater than 3:1.

b. For fibers which cross the boundary of the graticule field:

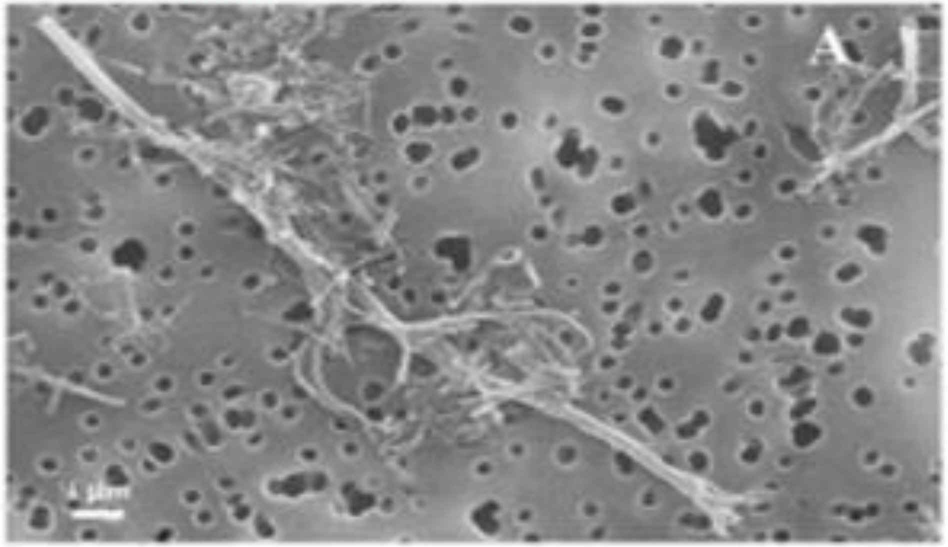
(1) Count as ½ fiber any fiber with only one end lying within the graticule area, provided that the fiber meets the criteria of rule a above.

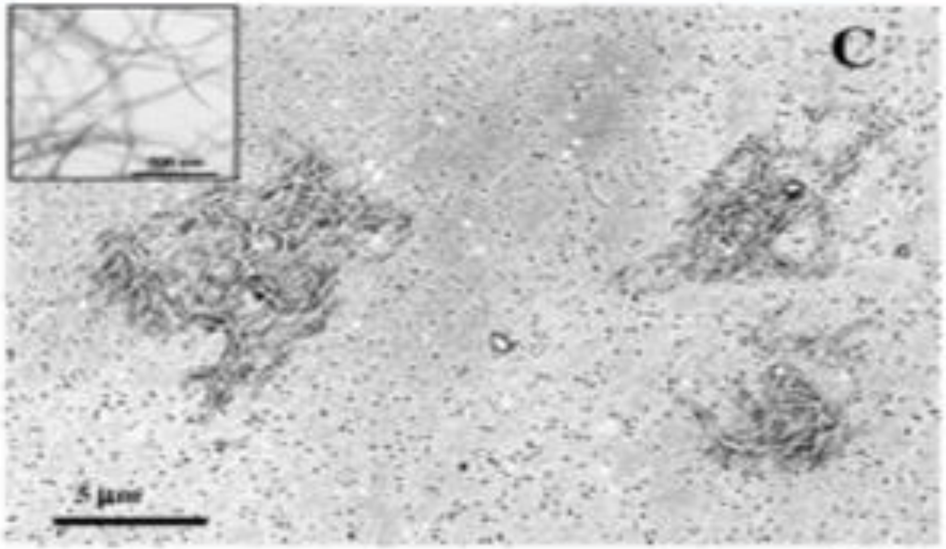
NIOSH Manual of Analytical Methods (NMAM), Fourth Edition

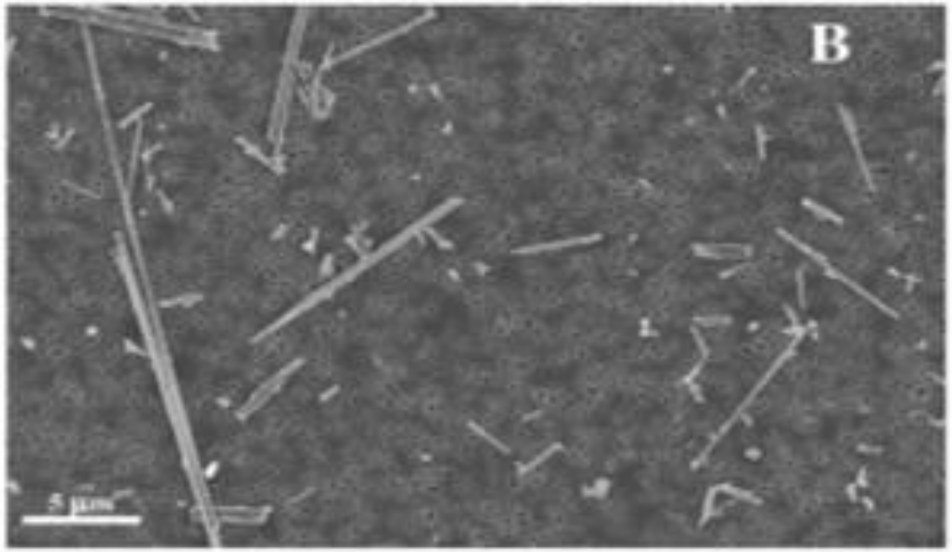
Using this method only asbestos fibers are counted if length is >/= 5 um (5000 nm) and length:width ratio =/> 3:1

Fibers < 0.25 µm (250 nm) diameter will not be detected by this method

MURRAY ET AL, 2012 A-CNF, B-SWCNT, C-ASBESTOS







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CNF	39.47	26.32	25.00	9.21
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DIESEL PARTICULATE MATTER (as Elemental Carbon) 5040

C | AW: 12.01 | CAS: none | RTECS: none

METHOD: 5040: Issue 3	**EVALUATION: FULL**	**Issue 1: 15 May 1996** **Issue 3: 15 March 2003**

OSHA : no PEL
NIOSH: no REL
ACGIH: 20 µg/m³ as elemental carbon (proposed [1])

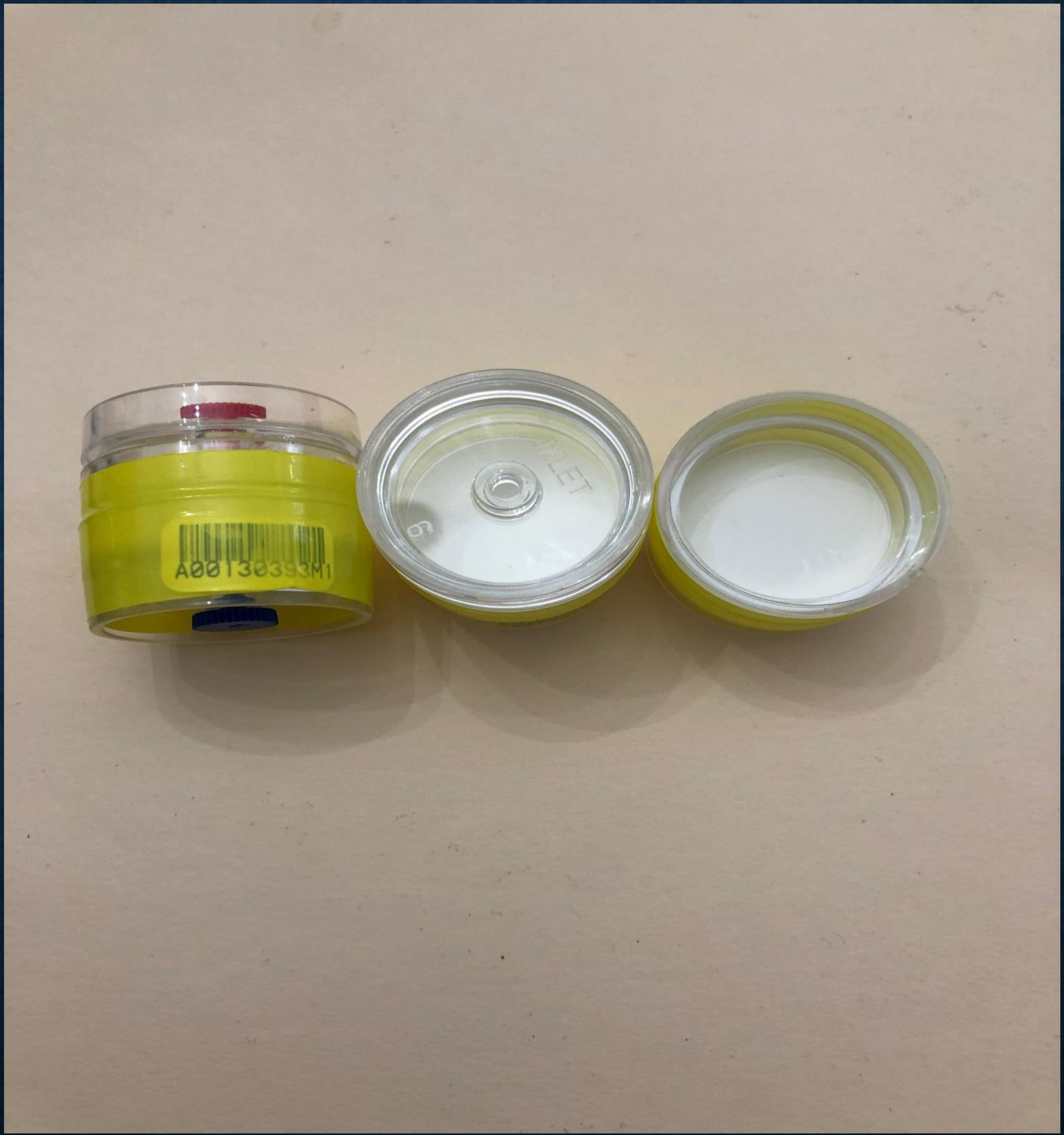
PROPERTIES: nonvolatile solid

SYNONYMS (related terms): diesel particulate matter, diesel exhaust, diesel soot, diesel emissions

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER: quartz-fiber, 37-mm; size-selective sampler may be required [2].	**TECHNIQUE:**	Thermal-optical analysis; flame ionization detector (FID)
FLOW RATE:	2 to 4 L/min (typical)	**ANALYTE:**	Elemental carbon (EC). Total carbon is determined, but an EC exposure marker was proposed. See [2] for details.
VOL-MIN: **-MAX:**	142 L @ 40 µg/m³ 19 m³ (for filter load of ~ 90 µg/cm²)		
SHIPMENT:	Routine	**FILTER PUNCH SIZE:**	1.5 cm² (or other [2])
SAMPLE STABILITY:	Stable	**CALIBRATION:**	Methane injection
BLANKS:	2 to 10 field blanks per set	**RANGE:**	1 to 105 µg per filter portion (See also [2].)

PICTURE OF RESPIRABLE CYCLONE WITH MEDIA

CLOSE-FACED AND OPEN-FACED CASSETTES



AREA AIR SAMPLING

PERSONAL BREATHING ZONE (PBZ) AIR SAMPLING

MAYNARD ET AL, 2004

- Study focus on SWCNT exposure at 4 facilities in US
- Ablation process – very compact vs High Pressure Carbon Monoxide – less dense
- PBZ - 25 mm diameter open-faced filters used – not size selective – not respirable
- Sampled at NASA, Rice University, Carbon Nanotechnology 2x's
- With no agitation particles >/= 0.1 um diameter released, airflow across powder
- With agitation 0.01 um diameter particles released in high numbers
- Estimated SWCNT by % of Ni and Fe found
- 0.7 to 53 ug/m3 PBZ (30 min samples)
- Dermal exposure – on cotton gloves 0.2 to 6 mg per hand

HAN ET AL., 2008

- MWCNT created by CVD – Chemical Vapor Deposition
- Nanotube Research Lab
- Used a cowl sampling device
- Exposure measure was mass concentration, PBZ
  - 210 to 430 ug/m3 over 4 to 6 hours in a blending area
  - No indication of process sampled
  - No EC analysis
  - Not Respirable sampling
- Shows exposure exists

LEE ET AL., 2015

- Large Scale MWCNT manufacturing workplace in Korea
- CVD – chemical vapor deposition process
- Produced 20 kg/day, worked 24/7, 3 shifts
- PBZ samples (n=5) measured Total Suspended Particles (TSP) with closed-face cassette, 25 mm filter
- Analysis for Elemental Carbon (EC) mass concentration
- PBZ range 6.2 to 9.3 ug/m3, mean 8.34 ug/m3 over 8 hr shifts
- Not respirable sampling, can't compare to REL

DAHM ET AL, 2018

Assessed personal respirable exposures for 108 workers at 12 different sites across the US that were primary manufacturers, hybrid produces/users, or secondary manufactures of MWCNT/SWCNT/CNF (Mostly MWCNT but doesn't distinguish difference in PBZ)

PBZ EC Respirable Mean – 1.0 ug/m3

Range – 0.001 to 43.8 ug/m3 (can compare to REL – 1.0 ug/m3) full shift sampling

83 filters collected – highest exposure at extrusion and weighing

7% of average EC mass Respirable Results were found above REL

102 workers – 70% showed CNT/F on wrist (tape method)

- 63% showed CNT/F on hand

90 workers – 18% had CNT/F in sputum

CNF (BIRCH ET AL, 2011)

60 to 250 nm Diameter

Up to 4um (4000 nm) in length

Bundled/discrete

Structurally similar to MWCNT

Graphene plan not parallel to fiber axis

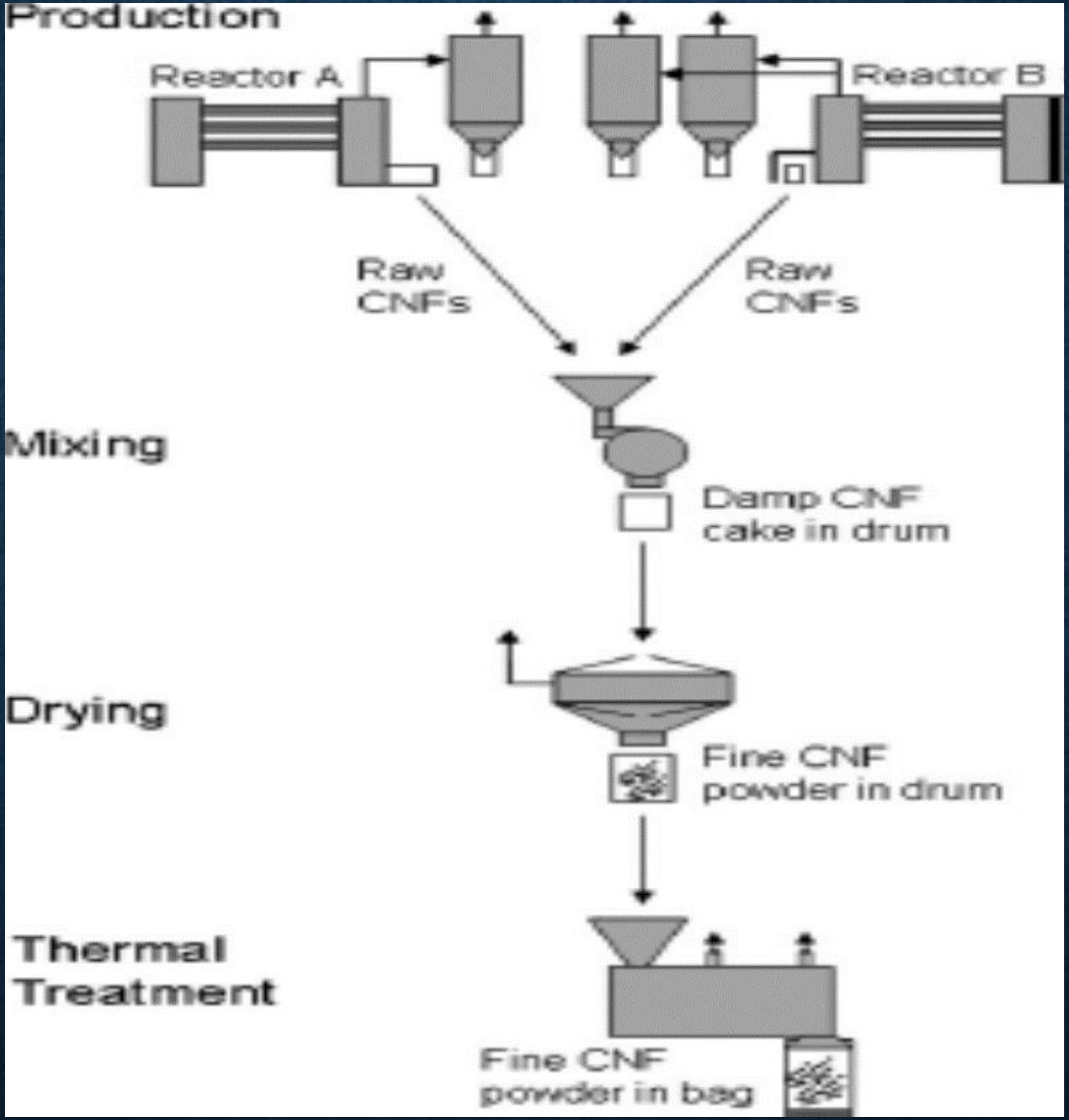
Stacked Cup or Herring- Bone Shape

Highly reactive edges that allow for chemical modifications for max mechanical reinforcement in polymer composites

BIRCH ET AL, 2011

- CNF – exhibit properties between those of CNT and carbon fibers
- CNF – used to improve thermal, electrical, and mechanical properties of a wide variety of polymer-based composite materials
- Used in high performance products, coatings and composites for aerospace, automobiles, sports equipment and construction
- More economical to manufacturer than CNT

EVANS ET AL, 2010



Facility Manufactures Vapor-Grown CNFs

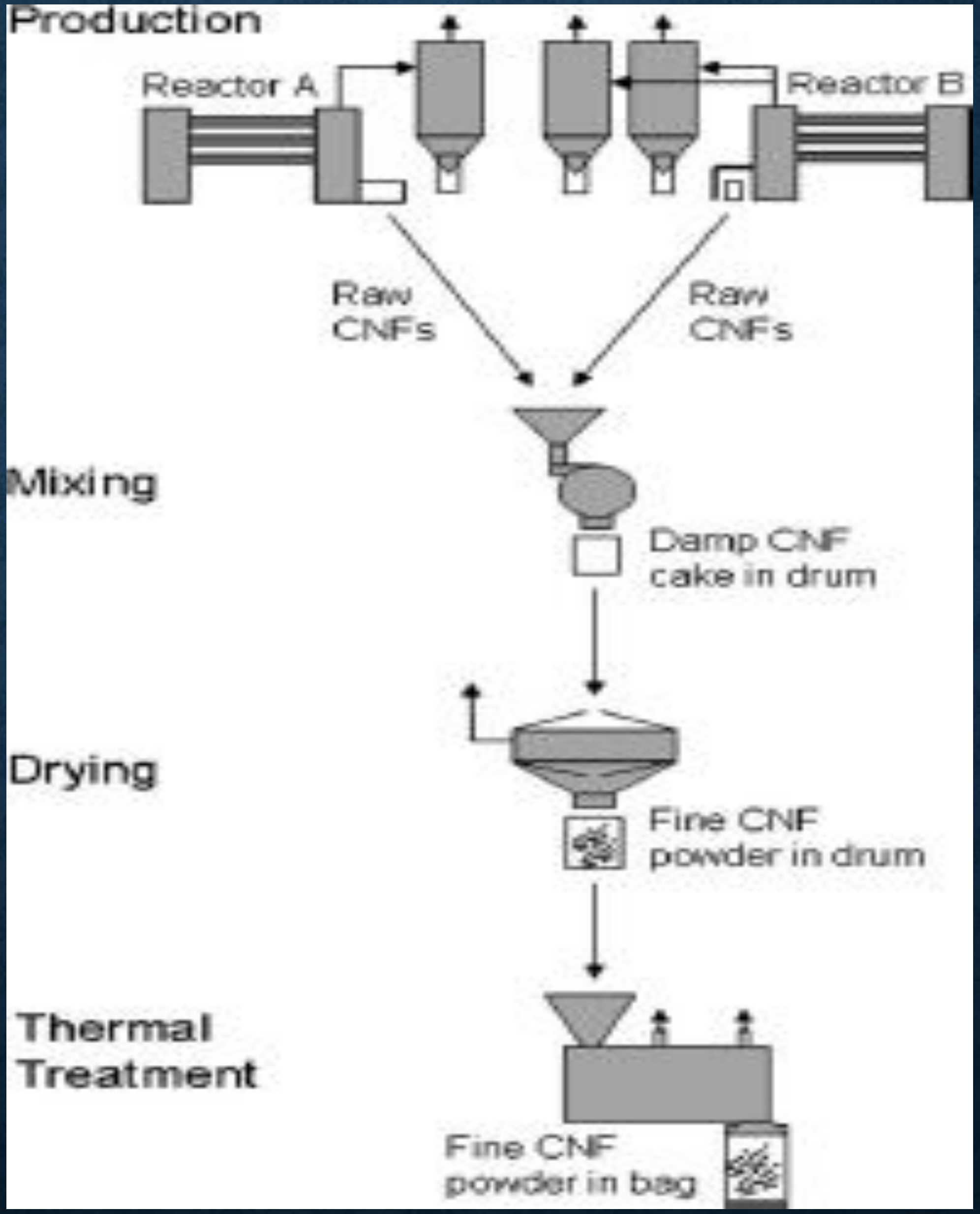
Birch et al, 2011

80 ug/m3 – Resp PBZ EC Reactor A

Resp Particulate Mass Conc. - Manual Change of bags – 0.5 mg/m3 (500 ug/m3) (direct reading)

45 ug/m3 Resp PBZ EC Thermal Treatment

Resp Particulate Mass Conc. - Manual Dumping of fibers into bag - 1.1 mg/m3 (1100 ug/m3) (direct reading)



Tapping of bags to settle material before change out

METHNER ET AL, 2007

- CNF Exposure in a university-based research lab to produce high-performance polymer composite materials
- EC Area sampling using analyzed for TEC using an inhalable sampling device but can't compare to REL (may be slightly overestimated because TC)
- Appears to be task sampling and the length of time sampled isn't given
- Majority of fibers were loosely bundled agglomerates
- Evaluated 5 processes
- Shows exposure exists

TABLE I. Total Carbon Concentrations from Inhalable Dust Samples

Sample No.	Sampling Location and Operation	TC ($\mu g/m^3$)	Multiple of Average Office TC Concentration[A]
1	Weighing out CNF[B] material	64	4
2	Mixing CNF with solvent	93	5
3	General area (on shelf near hood)	55	3
4	Lab bench: handling bulk, partially dry product	221	13
5	Wet saw: cutting CNF composite	1094	64

Methner, Crawford, and Geraci, 2012

FIGURE 1. Photos of workers engaged in some tasks. (a) Weighing CNF's inside lab hood with sash in operating position; (b) Wet saw cutting composite inside canopy ventilated booth; (c) Surface grinding composite containing CNFs with LEV; (d) Table saw with wet diamond blade cutting composite (no controls); (e) Transferring CNF's to tray inside ventilated booth; (f) Hand sanding composite laminate material inside ventilated booth.

METHNER, CRAWFORD, AND GERACI, 2012

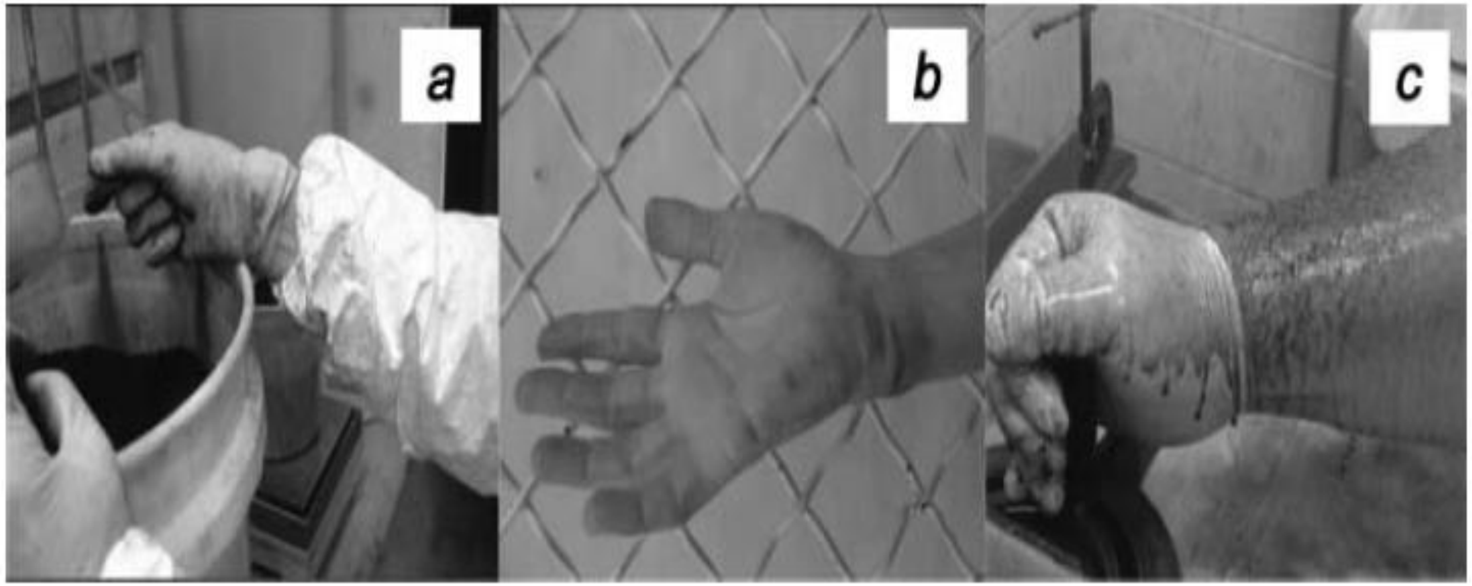


FIGURE 2. Tasks with potential dermal exposure. (a) Glove/elastic wrist closure separation; (b) Dermal exposure due to separation between glove and wrist closure; (c) Aerosol plume deposition onto unprotected skin during cutting of composite (no controls).

During the weighing operation, the sleeve of the PPE garment tended to ride up at the wrist/glove junction, thereby exposing the skin and enabling the deposition of CNFs onto bare skin
(Figures 2a, 2b).

METHNER, CRAWFORD, AND GERACI, 2012

- Facility that researches, develops, and conducts projects on epoxy-based nanocomposite material
- PBZ samples collected using task sampling 21 to 428 mins at 7 l/min
- PBZ were open-faced 37 mm cassettes and calculated for mass concentration of EC using NIOSH 5040
- Side by side samples analyzed by TEM Method 7402 to characterize exposure with respect to bulk sample
- Can't compare to REL because not respirable air sampling
- PBZ samples ranged from ND to 1000 μg/m3, with 90% of the samples having detectable amounts of EC

METHNER, CRAWFORD, AND GERACI, 2012

- The lowest measurable PBZ air sample was collected during the weighing of CNFs inside a laboratory hood (**2 ug/m3**), and highest measured PBZ sample occurred during wet saw cutting of composite without enclosure (**1000 ug/m3**).
- The majority of samples contained mostly non-agglomerated CNFs, but a smaller subset of samples contained a larger amount of loosely agglomerated CNFs.
- CNF material is released to the workplace atmosphere in both bound forms (within or attached to the composite matrix) and unbound forms (free fibers, bundles, or agglomerates).
- Nearly 90% of all samples examined via TEM indicated that releases of CNFs do occur and that the potential for exposure exists.

METHNER, CRAWFORD AND GERACI, 2012

Engineering controls/PPE weren't always effective

- Plume of airborne spray from wet saw cutting without enclosure – analysis indicated that droplets contained structures of nested CNFs – aerosol plume led to contamination of the entire room
- Wet cutting inside a three walled enclosure - area samples inside and outside the booth showed exposure to single and bundled CNFs.
- PBZ analysis showed that an employee weighing CNF inside a laboratory hood was still exposed to a release of CNFs
- Dermal exposure even though wearing latex gloves and Tyvek suit

MURRAY ET AL, 2012

- Oxidation properties in lung - SWCNT>CNF>Asbestos
- Inducing acute pulmonary cell damage – SWCNT>CNF>Asbestos
- Potency of alveolar interstitial fibrosis – SWCNT>CNF=Asbestos
    - Thickness of alveolar connective tissue
- Mice, pharyngeal aspiration

SUMMATION

- CNF – Individual factories made/facilities used
- CNF – Exposures exist at factories/facilities
- CNF – Engineer controls aren't always effective
- CNF – Some measures exceeded the REL
- CNF – Inhalation and dermal exposures exist
- CNF – Structurally similar to MWCNT (Group 2B – possible human carcinogen)
- CNF – May be more reactive than MWCNT on the edges of the cup-liked shapes of the fiber

The End

Questions?

REFERENCES

- Birch, Eileen M. Exposure and emissions monitoring during carbon nanofiber production – Part 1: Elemental carbon and iron-soot aerosols. Ann. Occup. Hyg. (2011) 55:9;1016-1036.
- Dahm, Matthew M. et al. Exposure assessments for a cross-sectional epidemiologic study of US carbon nanotube and nanofiber workers. International Journal of Hygiene and Environmental Health 221 (2018); 429-440.
- Evans, Douglas E. et al. Aerosol monitoring during carbon nanofiber production: Mobile direct-reading sampling. Ann. Occup. Hyg., (2010) 54:5;514-531.
- Fraser, Kelly et al. Physicochemical characterization and genotoxicity of the broad class of carbon nanotubes and nanofibers used or produced in U.S. facilities. Particle and Fibre Toxicology (2020) 17:62.
- Han, Jeong Hee. Monitoring multiwalled carbon nanotube exposure in carbon nanotube research facility. Inhalation Toxicology, 20:741-749, 2008.
- Hinds. William C. Aerosol Technology: Properties, behavior, and measurement of airborne particles. Wiley-Interscience Publication. 1982.
- Lee, Jong Seong et al. Health surveillance study of workers who manufacture multi-walled carbon nanotubes. Nanotoxicology. (2015), 9:6, 802-811.

REFERENCES

- Maynard, Andrew D. Exposure to carbon nanotube material: aerosol release during the handling of unrefined single-walled carbon nanotube material. Journal of Toxicology and Environmental Health, Part A. (2004) 67:1528-7394; 87-107.
- Methner, Crawford, and Geraci, 2012. Evaluation of the potential airborne release of carbon nanofibers during the preparation, grinding, and cutting of epoxy-based nanocomposite material. Journal of Occupational and Environmental Hygiene, 9: 308-318.
- Methner et al., 2007. Identification and characterization of potential sources of worker exposure to carbon nanofibers during polymer composite laboratory operations. Journal of Occupational and Environmental Hygiene, 4: D125-D130.
- Murray et al. Factoring-in agglomeration of carbon nanotubes and nanofibers for better prediction of their toxicity versus asbestos. Particle and Fibre Toxicology 2012; 9:10.
- NIOSH/CDC (2013) Current Intelligence Bulletin 65. Occupational exposure to carbon nanotubes and nanofibers. Department of Health and Human Services.
- NIOSH [1994b]. NIOSH manual of analytical methods (NMAM®). Diesel particulate matter (supplement issued 3/15/03). 4th ed. Schlecht PC, O'Conner PF, eds. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94–113 [www.cdc.gov/niosh/nmam/]. NIOSH method 5040.
- NIOSH (1994). Method 7400: ASBESTOS and OTHER FIBERS by PCM: METHOD 7400, Issue 2, dated 15 August 1994 - Page 4 of 15. NIOSH Manual of Analytical Methods (NMAM), Fourth Edition. https://www.cdc.gov/niosh/docs/2003-154/pdfs/7400.pdf.
- Y. Song, X. Li and X. Du. Exposure to nanoparticles is related to pleural effusion, pulmonary fibrosis and granuloma. Exp Respir J 2009; 34: 559-567.

MURRAY ET AL, 2012

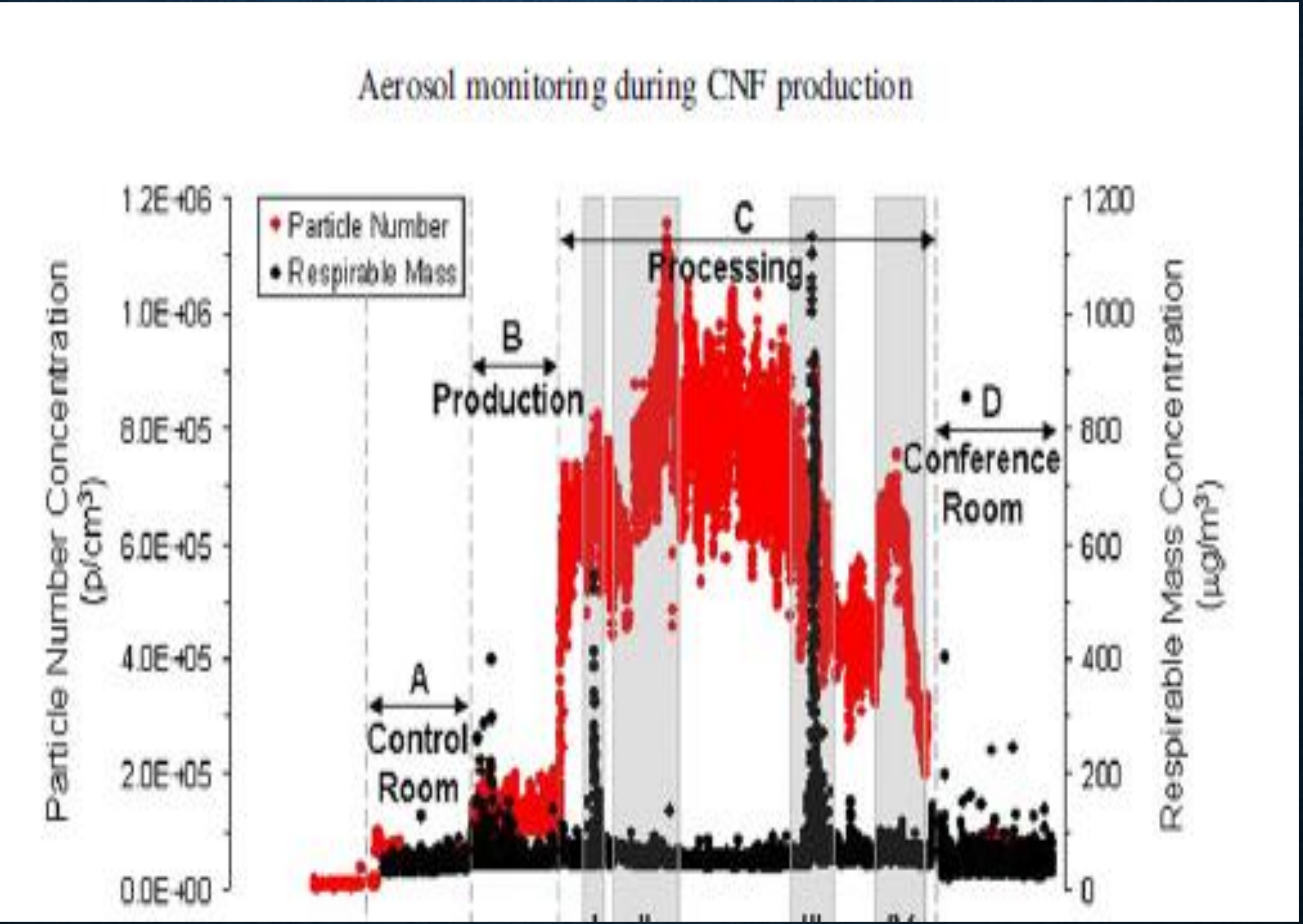
- Pulmonary outcomes assess at 1, 7, 28 days post exposure of pharyngeal aspiration in mice
- CNF exposure – 120 ug/mouse
- SWCNT exposure – 40 ug/mouse
- Asbestos exposue – 120 ug/mouse
- All capable of inducing acute pulmonary cell damage with potency of SWCNT>CNF>Asbestos

BIRCH ET AL, 2011 – PROCESS FLOW

- Raw CNF discharged from Reactor A and B
- Reactor A – compressed raw product was manually pulled from open trough (not B)
- Product broken into small pieces and put in open lined box (picture)
- Large clumps manually broken into smaller pieces
- Raw CNF then loaded into a hopper/mixer with solution
- Placed in ventilated oven to dry and form cakes
- Discharged into drum
- Poured into another hopper for thermal treatment to remove organic and metal impurities
- Final product discharged into plastic bag inside box

EVANS ET AL., 2010

- Measured respirable mass concentration using a real time meter – photometer with attached cyclone
- Compared photometer to BGI cyclone in lab
- Highest exposures in figure.
- First bump – Manual change-out of bags (tapping of bags) – 0.5 mg/m3
- Big bump – Dumping of product into open lined drum after drying - 1.1 mg/m3
- Little last bump – sweeping CNF after a spill
- CNF - 200 to 250 mn diameters
- Clusters of fibers, some single fibers



Evans et al, 2010

PARTICLE NUMBER CONCENTRATION – RED (EVANS ET AL, 2010)

- Red Concentration – due to emission caused by opening and manual redistribution of partially dried CNF product within dryer
  - PAH components and iron rich soot – initially formed during fiber synthesis and volatilized through drying cycle and Thermal treatment area (furnace/stripper: high temperature treatment)
  - Increases in PAH containing particles
  - CO_2 concentrations increased event 3, due to combustion of natural gas from heater and thermal decomposition of carbonyl catalyst precursor during fiber synthesis process
  - Event 4 – Gas fired heater ignited, increase in CO_2 until heater was off
  - Ultrafine particle conc
  - Polycyclic aromatic hydrocarbons

CARBONS

Organic Carbon – carbons from nature, plants, living things and pollution. Includes proteins, lipids, carbohydrates, nucleic acid

Elemental Carbon – carbons from ores and minerals, carbonate minerals