Carbon Nanotube Exposure Assessments:
An Evaluation of Workplace Exposures in the U.S.

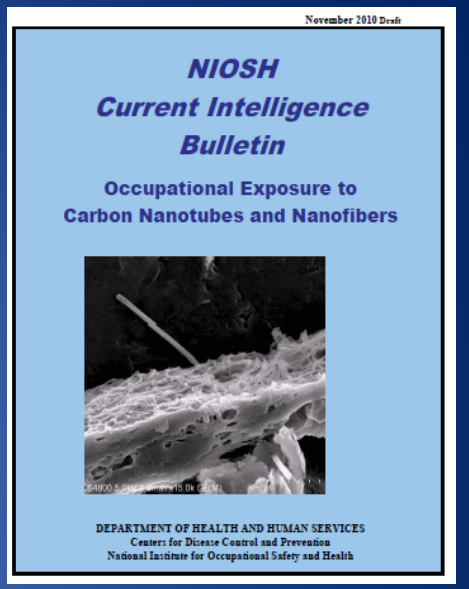
Matthew Dahm, MPH
NIOSH

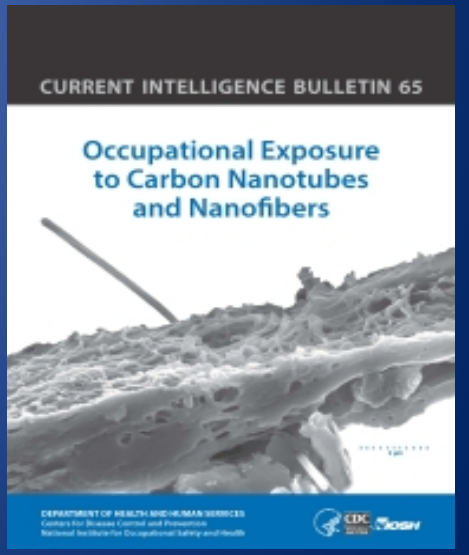
QEEN Workshop – Arlington, VA
July 7, 2015

Disclaimer: The findings and conclusions in this presentation have not been formally disseminated by the National Institute for Occupational Safety and Health and should not be construed to represent any agency determination or policy.

NIOSH Recommended Exposure Limit (REL)

- NIOSH Current Intelligence Bulletin- 2010
  - Fall 2010 for public review
  - Proposed Recommended Exposure Limit
    - 7 µg/m^3 of Elemental Carbon using NMAM 5040
    - Limitations in the sampling methods
- NIOSH Current Intelligence Bulletin- 2013
  - Final version April 2013
  - Final Recommended Exposure Limit
    - 1 µg/m^3 of Elemental Carbon using NMAM 5040
    - Recognize that other metrics may be relevant





Exposure Assessment
2010-2012

- Objectives
  - Characterize task-specific and full-shift exposures in a representative sample of U.S. CNT and CNF workplaces
  - Consider several types of workforces
    - Primary manufacturers
    - Secondary manufacturers (users)
      - Composites
      - Electronics
    - Redistributors

Exposure Assessment

Filter-Based Air Sampling

- Personal Breathing Zone Samples
  - Elemental Carbon (NMAM 5040)
    - Chemical specific mass concentration
    - Size Selective Sampling
      - Respirable
      - Inhalable
    - Anthropogenic sources
      - Background Samples
  - TEM structure counts (NMAM 7402)

Facilities

Demographics

- 14 unique sites (2010-2012)
  - Producers
  - Hybrid- Producer/User
  - Secondary Manufacturer- Electronics
  - Secondary Manufacturer- Composites/Thermo-plastics

	Primary Manufacturer	Hybrid- Producer/User	Secondary Manufacturer- Electronics	Secondary Manufacturer- Composites/Plastics
# of Facilities	4	2	4	4
Average # of employees per company	13	7528	166	1180
Average # of employees exposed	10	32	17	8
Types of Material Produced/Handled	SWCNT; MWCNT	MWCNT	SWCNT	MWCNT; CNF
Max. quantities handled per day (kg)	1.5	1	0.03	2.6
Average reported CNT diameter (nm)	1; 15	50	1.3	54; 140
Average reported CNT length (µm)	500; 70	250	250	279; 100

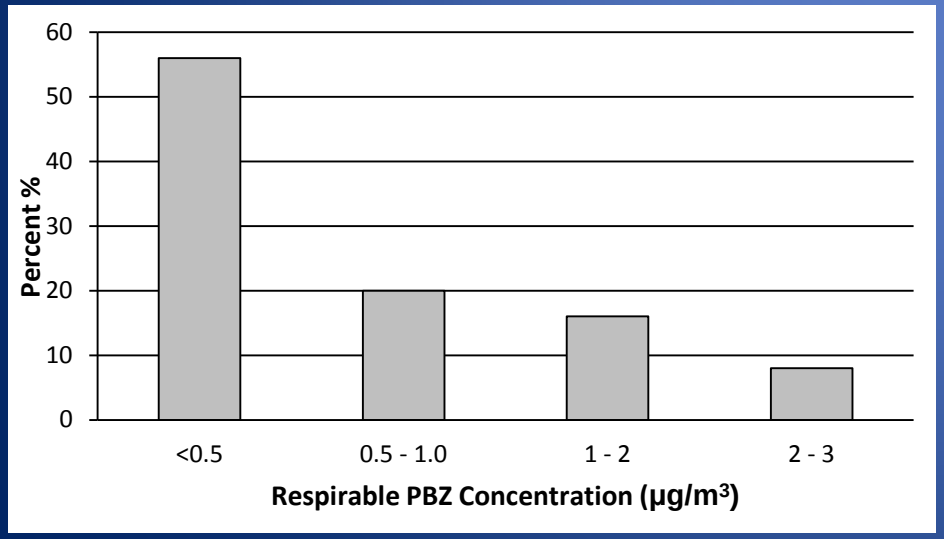
CNT/CNF Products

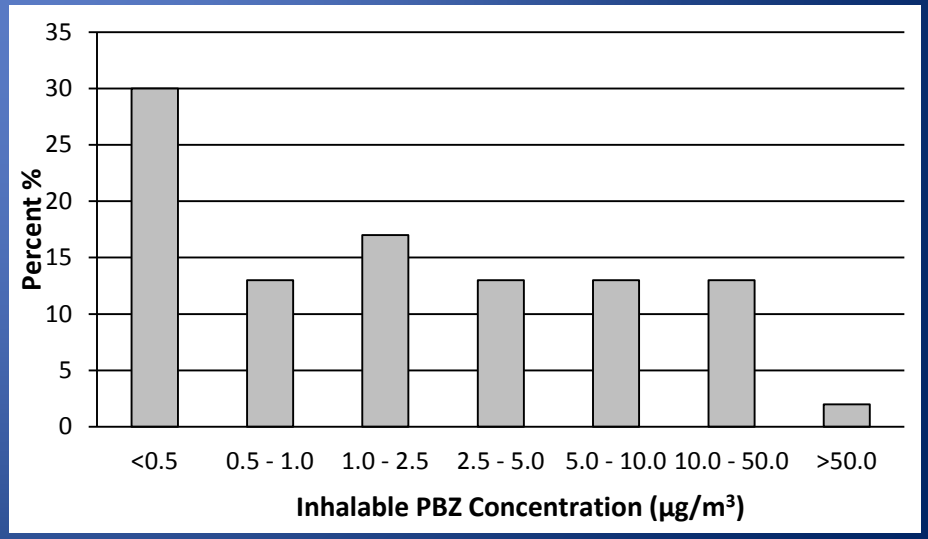
- Solar cells
- Memory devices (MEMS)
- Capacitors
- Printable LED lights
- Body Armor, CNT Yarns
- Baseball bats, bikes, boats
- Drones
- Composites for space crafts and planes

Overall EC PBZ Exposures

Summary of 14 Sites

			EC			
	Sample	n	GM (µg/m³)	Min.	Max.	8-hr TWA GM (µg/m³)
All Sites Combined (n=14)	PBZ Resp.	25	0.34	0.02	2.94	0.16
	PBZ Inhal.	47	1.21	0.01	79.57	0.38





EC Exposures by Group/Material

Summary of 14 Sites

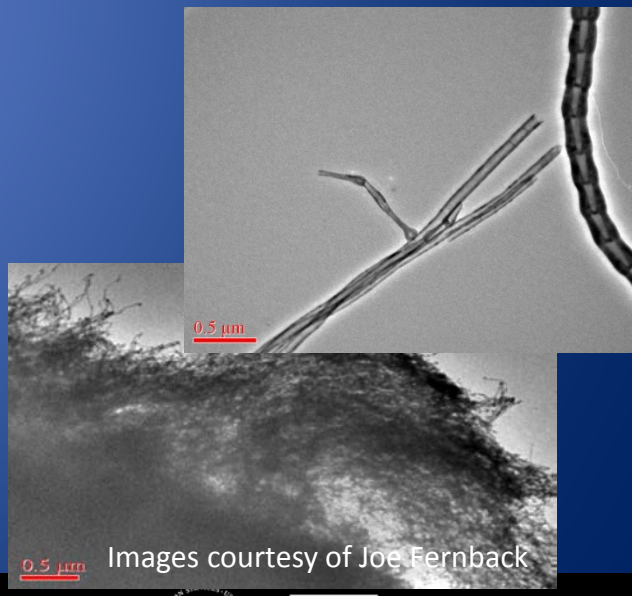
Industry	Sample	n	GM (µg/m³)	8-hr TWA GM (µg/m³)
Primary Manufacturer	PBZ Resp.	7	0.05	0.04
	PBZ Inhal.	11	0.19	0.11
Hybrid- Producer/User	PBZ Resp.	9	0.68	0.41
	PBZ Inhal.	9	13.39	7.93
Secondary Manufacturer- Electronics	PBZ Resp.	5	0.93	0.18
	PBZ Inhal.	18	0.52	0.12
Secondary Manufacturer- Composites/Thermoplastics	PBZ Resp.	4	0.70	0.19
	PBZ Inhal.	9	5.47	0.86

Material	Sample	n	GM (µg/m³)	8-hr TWA GM (µg/m³)
SWCNT	PBZ Resp.	12	0.16	0.08
(n=5)	PBZ Inhal.	22	0.27	0.09
MWCNT	PBZ Resp.	13	0.68	0.33
(n=9)	PBZ Inhal.	25	4.58	1.32

TEM Methodology

- Modified NMAM 7402
  - Three 3 mm, copper TEM grids analyzed by examining appx. 50 grid openings
  - CNT Structures counted
  - Binning- attempt to “approximate aerodynamic (2D) size”

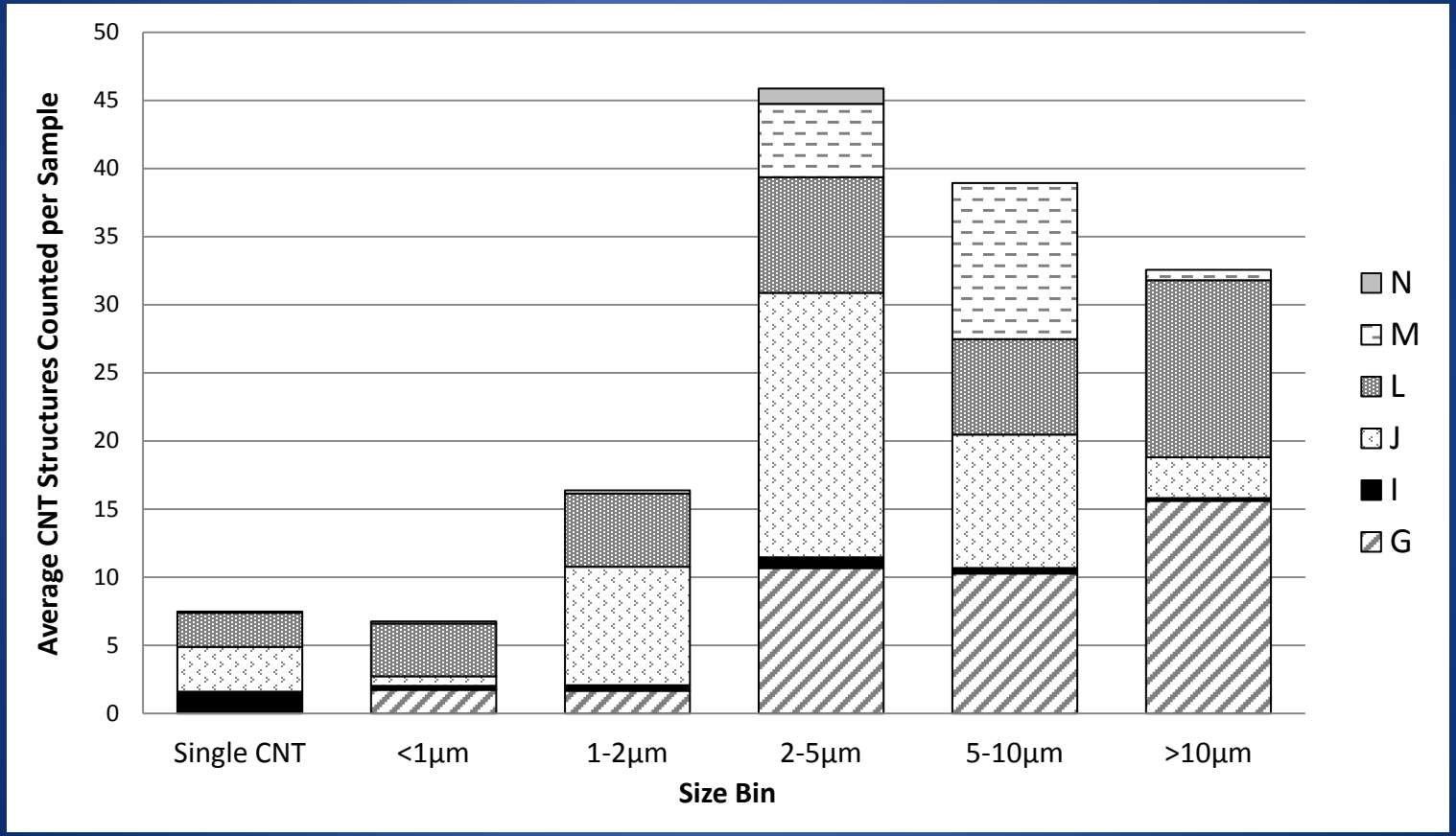
Single CNT	<1µm	1-2µm	2-5µm	5-10µm	>10µm
0.0	1.7	1.7	10.7	10.3	15.6
1.6	0.3	0.4	0.8	0.4	0.2
3.3	0.7	8.7	19.4	9.8	3.0
2.5	3.9	5.4	8.5	7.0	13.0
0.1	0.2	0.2	5.4	11.5	0.8
0.0	0.0	0.0	1.1	0.0	0.0
1.3	**1.1**	**2.7**	**7.7**	**6.5**	**5.4**



Images courtesy of Joe Fernback

Average CNT Structures Size by Bin

6 Sites (FY11 and FY12)



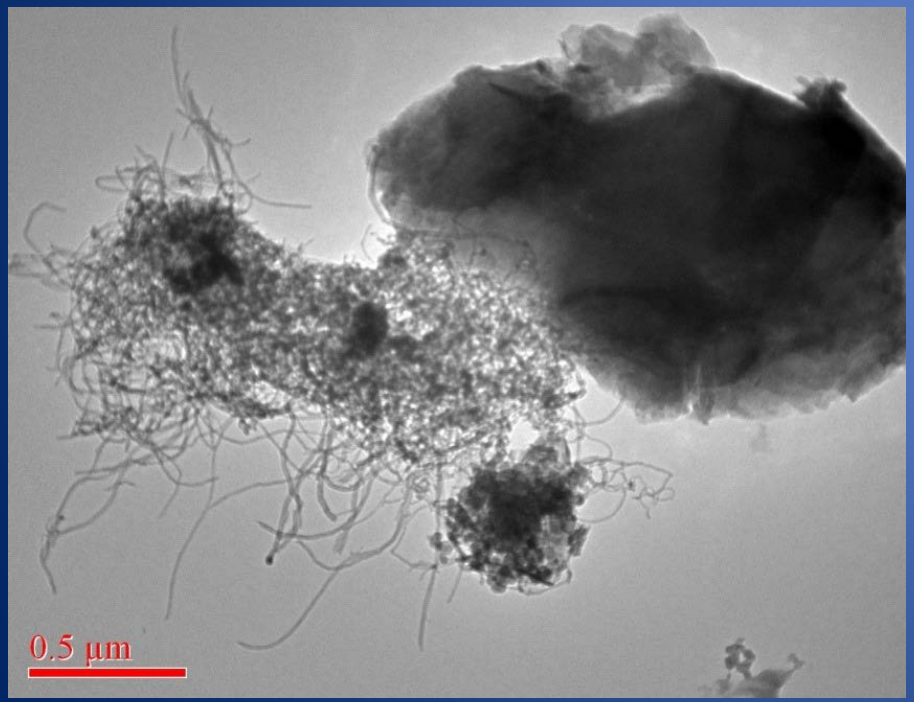
Overall TEM exposures and Exposures by Material

	TEM					
	Sample	n	GM (f/cc)	Min.	Max.	8-hr TWA GM (f/cc)
All Sites Combined (n=14)	**PBZ**	51	0.008	0.0001	1.61	0.003

	TEM			
Material	Sample	n	GM (f/cc)	8-hr TWA GM (f/cc)
SWCNT (n=5)	PBZ Inhal.	22	0.002	0.001
MWCNT (n=9)	PBZ Inhal.	23	0.023	0.007

Exposure Assessment/Tox Challenges

- Do these two structures have the same potential for toxicity?



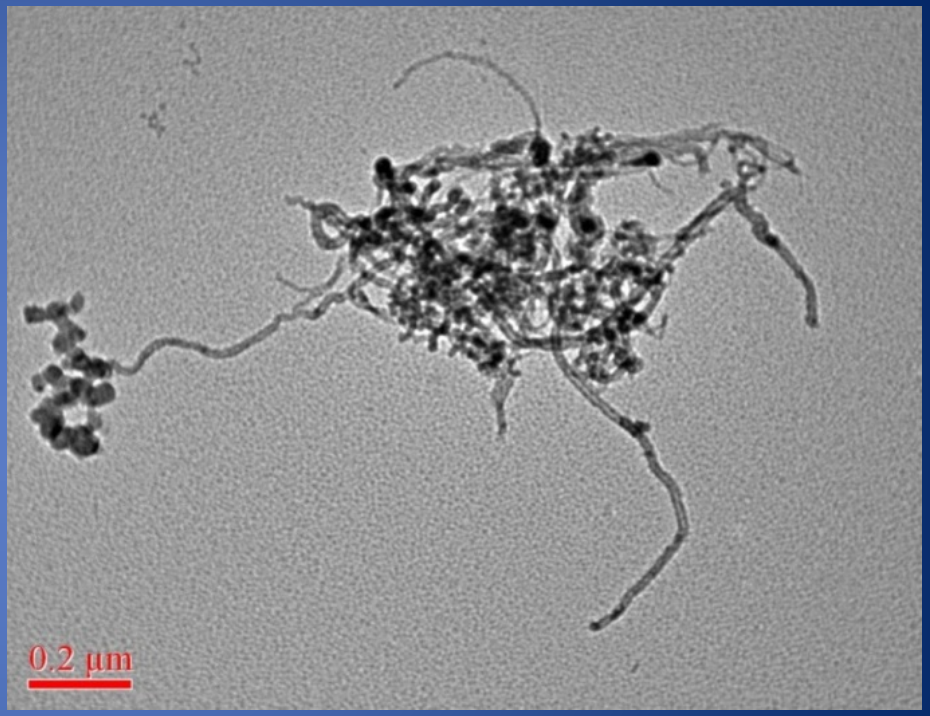


Image from personal breathing zone samples from CNT manufacturing (Dahm et al. 2012)

Exposure Assessment/Tox Challenges

These structures both contribute to measured elemental carbon. Which is more hazardous?

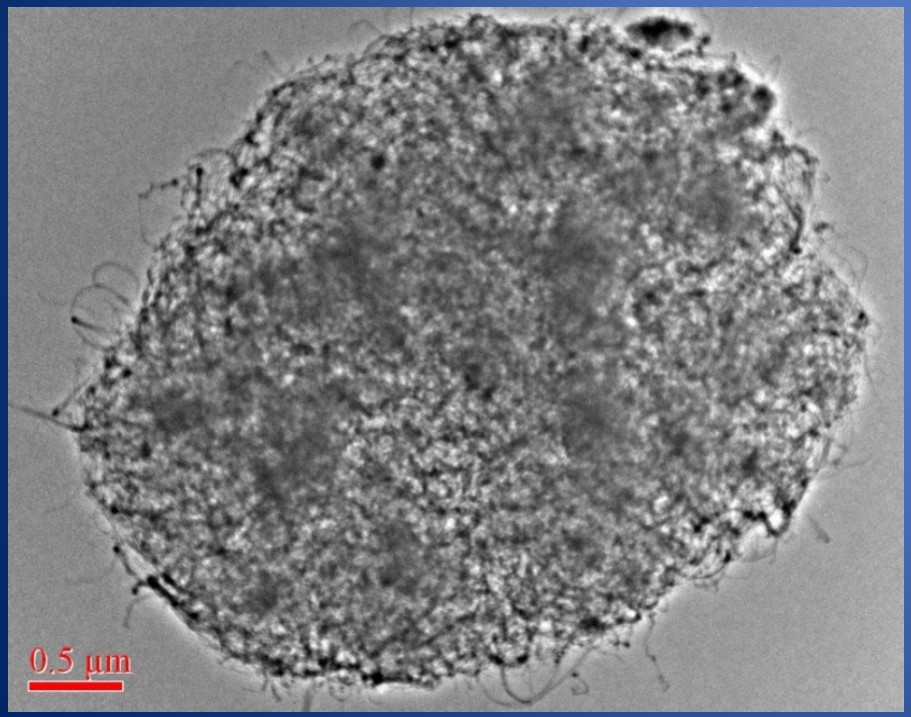
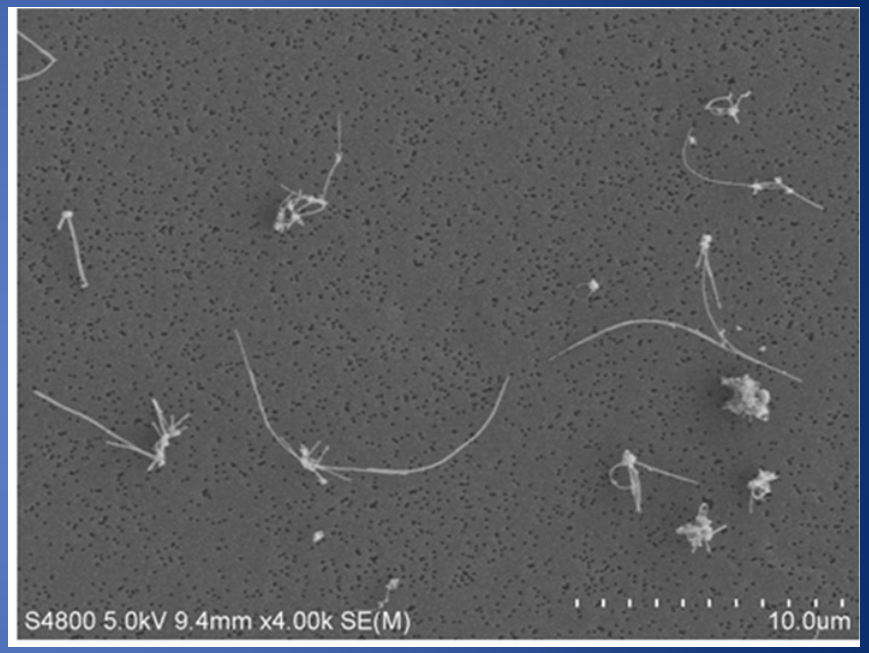


Image courtesy of Joe Fernback, NIOSH



Images from personal breathing zone samples from CNT manufacturing (Dahm et al. 2012; Erdely et al. 2013)

What can we conclude?
2010-2012

- EC Mass exposures are detectable/reliable
  - Respirable samples below NIOSH REL of 1 µg/m^3
    - Inhalable > 1 µg/m^3, no OEL (or thoracic)
    - Health Significance for thoracic/inhalable?
- Number Conc. by TEM
  - Possible metric
    - Need more tox info. on particle sizes of interest

Cross-Sectional Epidemiologic Study

2013-2014

- Medical exams:
  - Basic physical examination
  - Spirometry and cardiovascular function
- Biological sample collection (blood, sputum)
- Collection of information on other influential factors
- Simultaneous measurement of exposure to CNT and CNF using best metrics (elemental carbon, size-specific structure concentrations)

Exposure Assessment Additions

Bulk/Biological Sampling

- Dermal Sampling
  - Qualitative (yes/no)
  - Wrist and palm
- Sputum Analysis
  - Hyperspectral Imaging
  - Qualitative (yes/no)
- Bulk Materials Analysis
  - PAH
  - Residual Metal Content

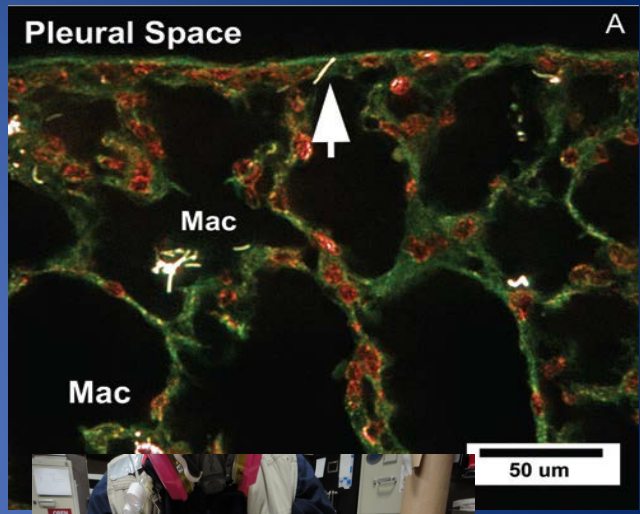
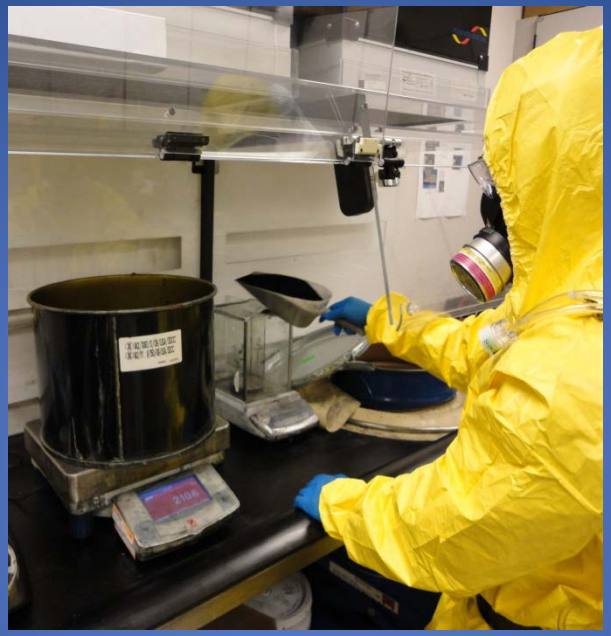


Image A.) Mercer R et al. Pulmonary fibrotic response to aspiration of multi-walled carbon nanotubes. 2011 Particle and Fibre Toxicology

Dry Powder Handling Scenarios

Process: Extrusion
Task: Weighing MWCNT
Volume: 1 kg
Duration of Sample: 112 min
Exposure Concentration=
3.19 µg/m^3



Process: Wet Shipping
Task: Weighing MWCNT
Volume: 7.7 kg
Duration of Sample: 269 min
Exposure Concentration=
0.3 µg/m^3

Process: Resin Formulation
Task: Weighing CNF/MWCNT
Volume: 100-200 g
Duration of Sample: 178 min
Exposure Concentration=
7.54 µg/m^3

Study Collaborators

- Reference
  - Dahm MM, Schubauer-Berigan MK, Evans DE, Birch ME, Fernback JE, Deddens JA. Carbon Nanotube and Nanofiber Exposure Assessments: An Analysis of 14 Site Visits. *Ann. Occup. Hyg.*, 2015, doi:10.1093/annhyg/mev020

- Special Thanks to:
  - Marie De Perio
  - Ken Sparks
  - Donnie Booher

  - Debbie Sammons
  - Chrissy Toennis
  - John Clark

Questions?

For more information contact:

Matthew Dahm
mdahm@cdc.gov
(513) 458-7136

Funded through
The National Institute of Environmental Health Sciences-
National Toxicology Program and
The NIOSH Nanotechnology Research Center