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

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NIOSH Recommended Exposure Limit (REL)

• NIOSH Current Intelligence Bulletin- 2010
  – Fall 2010 for public review
  – Proposed Recommended Exposure Limit
    • 7 µg/m³ 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/m³ 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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>n</th>
<th>GM (μg/m³)</th>
<th>Min.</th>
<th>Max.</th>
<th>8-hr TWA GM (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Sites PBZ Resp.</td>
<td>25</td>
<td>0.34</td>
<td>0.02</td>
<td>2.94</td>
<td>0.16</td>
</tr>
<tr>
<td>Combined PBZ Inhal.</td>
<td>47</td>
<td>1.21</td>
<td>0.01</td>
<td>79.57</td>
<td>0.38</td>
</tr>
</tbody>
</table>

![Graph of Respirable PBZ Concentration](image)

![Graph of Inhalable PBZ Concentration](image)
## EC Exposures by Group/Material

### Summary of 14 Sites

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample</th>
<th>n</th>
<th>GM (μg/m³)</th>
<th>8-hr TWA GM (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT (n=5)</td>
<td>PBZ Resp.</td>
<td>12</td>
<td>0.16</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>PBZ Inhal.</td>
<td>22</td>
<td>0.27</td>
<td>0.09</td>
</tr>
<tr>
<td>MWCNT (n=9)</td>
<td>PBZ Resp.</td>
<td>13</td>
<td>0.68</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>PBZ Inhal.</td>
<td>25</td>
<td>4.58</td>
<td>1.32</td>
</tr>
</tbody>
</table>
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”

<table>
<thead>
<tr>
<th>Single CNT</th>
<th>&lt;1μm</th>
<th>1-2μm</th>
<th>2-5μm</th>
<th>5-10μm</th>
<th>&gt;10μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.7</td>
<td>1.7</td>
<td>10.7</td>
<td>10.3</td>
<td>15.6</td>
</tr>
<tr>
<td>1.6</td>
<td>0.3</td>
<td>0.4</td>
<td>0.8</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>3.3</td>
<td>0.7</td>
<td>8.7</td>
<td>19.4</td>
<td>9.8</td>
<td>3.0</td>
</tr>
<tr>
<td>2.5</td>
<td>3.9</td>
<td>5.4</td>
<td>8.5</td>
<td>7.0</td>
<td>13.0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>5.4</td>
<td>11.5</td>
<td>0.8</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.3</td>
<td>1.1</td>
<td>2.7</td>
<td>7.7</td>
<td>6.5</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Images courtesy of Joe Fernback
Average CNT Structures Size by Bin
6 Sites (FY11 and FY12)

![Bar Chart]

- **Single CNT**: <1μm
- **1-2μm**: 1-2μm
- **2-5μm**: 2-5μm
- **5-10μm**: 5-10μm
- **>10μm**: >10μm

Legend:
- N
- M
- L
- J
- I
- G

Horizontal axis: Size Bin
Vertical axis: Average CNT Structures Counted per Sample
### Overall TEM exposures and Exposures by Material

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample</th>
<th>n</th>
<th>GM (f/cc)</th>
<th>Min.</th>
<th>Max.</th>
<th>8-hr TWA GM (f/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>PBZ</td>
<td>22</td>
<td>0.002</td>
<td></td>
<td></td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>Inhal.</td>
<td>23</td>
<td>0.023</td>
<td></td>
<td></td>
<td>0.007</td>
</tr>
<tr>
<td>MWCNT</td>
<td>PBZ</td>
<td>51</td>
<td>0.008</td>
<td>0.0001</td>
<td>1.61</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>Inhal.</td>
<td>23</td>
<td>0.023</td>
<td></td>
<td></td>
<td>0.007</td>
</tr>
<tr>
<td>All Sites Combined (n=14)</td>
<td>PBZ</td>
<td>51</td>
<td>0.008</td>
<td>0.0001</td>
<td>1.61</td>
<td>0.003</td>
</tr>
</tbody>
</table>

**Note:** TEM exposures are presented as geometric mean (GM) values with minimum and maximum values. 8-hour time-weighted average (TWA) GM values are also provided.
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)
These structures both contribute to measured elemental carbon. Which is more hazardous?

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

Image courtesy of Joe Fernback, NIOSH
What can we conclude?
2010-2012

- EC Mass exposures are detectable/reliable
  - Respirable samples below NIOSH REL of $1 \mu g/m^3$
    - Inhalable $> 1 \mu g/m^3$, 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/m³

**Process:** Wet Shipping  
**Task:** Weighing MWCNT  
**Volume:** 7.7 kg  
**Duration of Sample:** 269 min  
**Exposure Concentration:** 0.3 μg/m³

**Process:** Resin Formulation  
**Task:** Weighing CNF/MWCNT  
**Volume:** 100-200 g  
**Duration of Sample:** 178 min  
**Exposure Concentration:** 7.54 μg/m³
Study Collaborators

• Reference

• Special Thanks to:
  – Marie De Perio
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  – Donnie Booher
  – Debbie Sammons
  – Chrissy Toennis
  – John Clark
Questions?

For more information contact:

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