Occupational Exposure Science for Nanomaterials
Current State, Challenges, and Future Research

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Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health

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Overview

• Context of Exposure Science
• Application to the Occupational Setting
• Evolution of Workplace Assessment
• Future Work
Responsible development of Nanotechnology has created a high demand for robust exposure science.
Why Exposure Science?

The study of human contact with stressors (for today, Nanomaterials) in their environments (the workplace) and knowledge of the events causing or preventing adverse health outcomes.

Hazard of stressor: toxicology
Anticipate and measure contact: exposure
Risk: predicted, characterized
Prevention: risk management
Why Workplace Exposure Assessment?

- Workers generally the first people in society exposed to a new technology and its materials
- Nanotechnology is no exception
- More than 1,000 nano-enabled products reportedly in commerce
- Workers make and use them; from R&D labs, to concept testing, to manufacturing.
- First opportunity to develop good stewardship practices
Exposure Science: Key Elements
Occupational Focus: Slight Modification
There are many potential sources for initiation of an exposure pathway

Source: Bernd Nowack
Workplace Hazard?

• Dramatic increase in nanomaterial hazard information: Nanotoxicology
• Growing interest in workplace issues
• Small but growing amount of information on actual workplace experience
• Interest and actions by governing bodies
Occupational Exposure Science: Links and Tools

• Toxicology
• Risk Assessment
• Exposure Assessment
  • Strategies
  • Measurement Technology
• Risk Characterization
• Epidemiology
• Predictive Tools
Changing Nanotechnology Workforce

- Trend – from laboratory research to scale-up
- Higher potential exposures

- “Nanotechnology is unquestionably moving toward manufacturing, involving a still very small but increasing component of the labor force.” [Invernizzi N. J Nanopart Res 2011]
Occupational Exposure Assessment

- Critical component of risk management
- Identifies populations at risk
- Characterize the exposure, therefore better understanding of risk
  - Nature of exposure: low vs. high, short vs. long
  - Extent of exposure: few or many
  - Complexity of the exposure
  - Place the exposure on the life cycle
- Verify controls
KEY INDUSTRIES AND WORKER INVOLVEMENT

- Transportation: transportation.ccs.k12.nc.us
- Agriculture: us.123rf.com
- Building Materials: cinorthwest.com
- Cosmetics: dreamtime.com
- Electronics: sathiyan.tv
- Energy: acmworldwide.com
- Food: bubblews.com
- Medical: theavtimes.com
- Paper: openlettersmonthly.com
- Textiles: glogster.com
- Water: dupont.com

Courtesy C. Sayes
Commonly Produced and Used NM
The ENM value chain gets complex quickly and magnifies the challenge

C. Sayes: Contract report to NIOSH
Occupational Exposure Characteristics

• R&D - Basic: Limited to small volumes but the materials are not well characterized
• R&D – Applied: Proof of concept and prototyping. Volumes and characterization increase, still lab scale
• Pilot systems: first processes, high volumes, greatest potential for human exposure to the free, unbound nanomaterial
• Full commercial deployment
A tiny sample of guidance coming out globally
What Does the Nano-EHS Research Tell Us?

Peer Reviewed Nano Environment, Health and Safety Journal Articles

- Exposure
- Hazard
- All
- Environmental
- Worker

http://icon.rice.edu/research.cfm
Meeting the Exposure Science Challenge: An Example from one Agency

The NIOSH Research Program Flow

Follow the Risk Model

1. Hazard Identification
   “Is there reason to believe this could be harmful?”

2. Exposure Assessment
   “Will there be exposure in real-world conditions?”

3. Risk Characterization
   “Is substance hazardous and will there be exposure?”

4. Risk Management
   “Develop procedures to minimize exposures.”

A concurrent approach to match the pace of innovation.

Identify Critical Research Areas

1. Toxicology and internal dose
2. Measurement methods
3. Exposure assessment
4. Epidemiology and surveillance
5. Risk assessment
6. Engineering controls and PPE
7. Fire and explosion safety
8. Recommendations and guidance
9. Communication and information
10. Applications

Contributions to Exposure Science in every area!
“Nanoparticle” Exposure Assessment Challenges

• Definition of nanoparticle or nanomaterial
• Heterogeneity of nanomaterials
• Agreement on the most appropriate metric
• Lack of evaluation criteria: OELs
• Lack of ruggedized methods to measure and characterize
Simple View of a Complex Life Cycle Reality

New ENM → Bigger Batch → Scale Up → Manufacture → Processing, incorporation, weathering

‘New Idea’ → ‘I can make more’ → ‘We have a customer’ → ‘My ENM is a little different, but it works’ → My ENM is in there somewhere...

To measure the presence of this, we have to deal with the realities of change: weathering, transformation, aggregation, etc.
Evaluating the exposure dose

Based on what we know so far, how do we evaluate exposure and risk?

Bulk Material  \[\xrightarrow{\text{Same Mass}}\]  Nano Sized Material

Which metric to use?
Mass, number, size, shape, surface area?
Exposure and Emission Measurements

- Qualitative and Quantitative
  - Confirmation: e.g. TEM with elemental analysis
- Mass concentration
  - Elemental mass, mass by size
- Particle number
  - Total and by size
- Size distribution
  - Count or mass by size
- Surface area
## Occupational Exposures: What metric to use?

<table>
<thead>
<tr>
<th>Metric</th>
<th>Qualification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>Standard (NIOSH CNT and TiO$_2$ CIB)</td>
</tr>
<tr>
<td>Surface Area</td>
<td>Advantage for low solubility particles</td>
</tr>
<tr>
<td>Surface Chemistry</td>
<td>Toxicological studies</td>
</tr>
<tr>
<td>Particle Number</td>
<td>Relevance</td>
</tr>
<tr>
<td>Particle Size</td>
<td>Translocation</td>
</tr>
<tr>
<td>Particle Shape</td>
<td>HAR versus spheres</td>
</tr>
</tbody>
</table>
Harvesting SWCNTs from a Carbon Arc Reactor

Task-based PBZ air sample analyzed via TEM w/ EDS
Initial Focus on ‘First Generation Products’

**Paint containing silver and titanium dioxide acts as a biocide**

**Commercial and Consumer Potential**

**PCI Nanosilent combines leveling, isolating and sound reduction in one step**

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**Examples of consumer products that contain nanomaterials**

1. **K2 CoolCiti, Denver**
   - Company: Eneco
   - Category: Health and Fitness - Cycling

2. **A La Mode Performance Long Biowas Black Work**
   - Company: Dream Tie Apparels
   - Category: Health and Fitness - Cycling

3. **Sural Paint Evolution Black Stuff**
   - Category: Health and Fitness - Cycling

4. **Nano Coated White Paint**
   - Company: ITC
   - Category: Sports and Recreation - Food

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**Nano TiO2 Based Smog Eating Roof Tiles**

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*BASF: “Special polymers and rubber granules”*
Field Challenge: A mix of Simple and Complex Measurements

Electron microscopy

Elemental Analysis

Particle Counters and Size Analyzers
Facing the reality of airborne CNT: A Mini Case Study

Single-walled CNT

MWCNT air samples

Artist’s rendering versus real world
CNT Exposure Metrics

- Mass of CNT
  - Current metric in toxicology
  - Difficult to be specific
  - Markers or surrogates?
  - Sensitive enough?

- Particle number and size
- Fiber or structure count
- Surface area
Variation in elemental carbon exposure by task
(Dahm et al., J Occ Environ Hyg)
Specific Task Evaluation: Dry Powder Handling

**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
Evidence of Activity: OELs for CNT

OSHA Graphite PEL (respirable)

OSHA Carbon black PEL

- SWCNT 1 µg/m³
- CNT & CNF 1 µg/m³
- MWCNTa 2 µg/m³
- CNTb 30 µg/m³
- Baytubes® MWCNT 50 µg/m³

INELa [Aschberger et al 2010]
RELb NIOSH [CITR 2013]
INELa [Aschberger et al 2010]
OEL-PLc,d AIST Japan [Nakanishi 2011]
OELc Bayer [Pauduh 2010]

BSI—0.01 f/ml [benchmark exposure limit; BSI] for high aspect ratio nanomaterials (1/10th asbestos OEL)

*Indicative No-effect Level, **Recommended Exposure Limit, †Occupational Exposure Limit, ‡Period-limited (15-yr)
Exposure Assessment/Tox Challenges

- Two structures measured as EC. Same hazard?

Images from personal breathing zone samples from CNT manufacturing (Dahm et al. 2012)
Connecting the Key Exposure Assessment Elements

Exposure Metrics  
Occupational Exposure Science  
Exposure Assessment  
Toxicology Assessment  
Dose metrics  
Biomarkers  
Epidemiology

Courtesy of M Schubauer-Berigan and M Dahm
## Key Elements of the NIOSH Approach

<table>
<thead>
<tr>
<th>Pre-Assessment Prioritization</th>
<th>Field Measurements</th>
<th>Risk Management</th>
<th>Routine Monitoring</th>
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</thead>
<tbody>
<tr>
<td>Gather Information</td>
<td>• Full-shift and task-based</td>
<td>• Evaluation of data for exposure-informed hazard assessment</td>
<td>• Confirmation of continued risk control</td>
</tr>
<tr>
<td>• Work flows, staffing and tasks</td>
<td>• Integrated filter sampling for elemental mass and microscopy</td>
<td>• Strategies to mitigate hazard and exposure potential based on results and</td>
<td>• May indicate need for additional measurements or controls</td>
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<tr>
<td>• Anticipated and recognized hazards</td>
<td>• Direct reading instruments</td>
<td>utilizing the hierarchy of controls</td>
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<tr>
<td>• Nanomaterials used</td>
<td>• Evaluation of ventilation and engineering controls</td>
<td>• Communications regarding potential occupational risks</td>
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<tr>
<td>• Safety data sheets</td>
<td>• Advanced techniques or developmental methods as needed</td>
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<td></td>
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<tr>
<td>• Literature review</td>
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<td></td>
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<tr>
<td>• Other indicators of potential hazards and</td>
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<tr>
<td>exposure situations</td>
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Exposure Measurements Take a lot of Planning and Effort

Photos courtesy A Eastlake and L Hodson, NIOSH
Exposure Data: Conclusions/Challenges

• New thinking needed
• Exposures do occur in the workplace
• Exposure limits are being developed
• Mass is still the primary metric reported in hazard studies
• Direct-reading approaches have a growing role
• Additional metrics need to be explored: e.g. fiber count for CNT?
• Confirmatory methods are needed
• Controls can be effective
Thank you, and thanks to all of my co-workers!

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www.cdc.gov/niosh/topics/nanotech/

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