Nanomaterials Introduction and Background: Applications, Life-cycle, Toxicity, and Hazardous Waste Management Implications

2014 California CUPA Conference
Burlingame, CA
2/5/14
Background of Nanotechnology

- What is “nanotechnology”? Engineering and manipulation of matter on atomic and molecular scale
- Physical substances with structural dimensions between 1 and 100 nanometers (nm)  
  $1 \text{ nm} = 1 \text{ billionth of a meter}$
- Natural vs. engineered nano-sized particles (NSPs)
Engineered NP’s vs Naturally Occurring NP’s

Figure 1. Diagram indicating relative scale of nanosized objects. (From NNI website, courtesy Office of Basic Energy Sciences, U.S. Department of Energy.)
Name “Nanotechnology” popularized

Eric Drexler popularized the term in mid-1980’s
— In 1986 he wrote the book “Engines of Creation” and subtitled "The Coming Era of Nanotechnology.”
— Predicted “Grey Goo” from unchecked reproduction of nanobots
-Michael Chrichton 2008- “Prey”
Story about nano robots on the loose...
New Imaging Technology Drives Nanotechnology

- TEM resolution improves 20x
- Scanning tunneling microscope-1981
- Atomic force microscope-1986
Nanotechnology Overlaps many Fields
Acheivements for Nanotechnology:

Bible on Head of a Pin, 2007

Iconic IBM Advertisement from 1989
With 35 Xenon atoms using TEM

2 Nobel Prizes for Nanocarbon

• Buckyball: Discovered in 1985 by Robert F. Curl, Harold W. Kroto and Richard E. Smalley.”—1996 Nobel Prize in Chemistry Awarded for this discovery
• Followed by Nobels for graphene (2010)
Types of nanomaterials: Structure + Composition = Functionality

- **Carbon-based materials:**
  - Composed of carbon, taking shape as spheres, cylinders, or tubes: Carbon nanotubes also known as CNTs
  - Large aspect ratio- (1: 132,000)
  - Uses: sports gear, electronics, solar cells, vehicles, medicine, Lightweight batteries, construction

Space Elevator:
SWCNT
100,000 km long
sci-fi or reality?
Metal-based Nanomaterials:

- Quantum dots, nano-gold, nano silver, metal oxides: Titanium Dioxide TiO2, BNPs
- Found in cosmetics, sunscreen, coatings, toothpaste, food additives
- Also utilized in remediation technologies:
  - Contaminant Removal
  - Drinking Water Treatment
Unique Properties of engineered NSPs

- Electrical
- Catalytic
- Magnetic
- Mechanical
- Thermal
- Optical

Engineered NSPs exhibit unique properties as a result of larger surface area, increased reactivity, and quantum effects at the molecular level based on morphology and composition.
Applications for Nanomaterials
What’s in it for me??

Materials Science
- Battery technology, solar cells,
- Sporting goods
- Cosmetics, paints, coatings
- Semiconductors, renewable energy technology
- Military apps, transportation
Consumer Products Inventory- Industry Overview

- 1600+ manufacturer-identified nanotechnology-based consumer products introduced to market to date: [http://www.nanotechproject.org/cpi/](http://www.nanotechproject.org/cpi/)
- As of March 2011 nano-enabled products increased 521% since 2006 (212 products)
- NSF Estimated 1 trillion $ industry by 2015 with 2 million workers.
- Silver, carbon, TiO2 most common-
- 738 products in health & fitness sector
Newest Nano-products on Market

- **Nanoflex® Cotton Suit:** Anti-microbial and hydrophobic
- **NanoChar™**
  - Increased fire protection, hardness
- **Uvex Variomatic Sunglasses**
  - No fog technology and scratch protection
- **MesoSilver® Antifungal Spray**
  - Silver spray kills bacteria and fungal pathogens
Medical Applications:
- Advanced bio-sensors
- Targeted drug delivery systems
- Bone-grafting and tissue repair
Nanomedicine Goals:

- 1) Understand how the biological machinery inside living cells is built and operates at the nanoscale and,
- 2) use this information to re-engineer these structures, develop new technologies that could be applied to treating diseases, and/or leverage the new knowledge to focus work directly on translational studies to treat a disease or repair damaged tissue.
Recent Nanomedical Discoveries:

- **Early lung cancer screening**: Detects early stage via micro RNA sampling
- **Gold nanoparticle flu test**: Test from 2 weeks to instantaneous (gold scatters light)
- **Sandia Cancer hunters**: Protocells seek and destroy cancer cells, no more chemo!
- **Cell feedback**: Makes drugs more effective and speeds up drug trials
- **Spinal cord repair**: Rebuilding spinal cords with CNTs and proteins, success observed in rats, mice.

Environmental Applications

Environmental remediation:
- Toxic spill clean up
- Heavy metals / pesticides
- Soil and groundwater treatment
- Drinking Water treatment using Ti02
In-Situ Nanoremediation

- Potential to reduce costs of clean-up large-scale contaminated sites
- Reduce cleanup time, eliminate the need for treatment and disposal of contaminated soil, and reduce some contaminant concentrations to near zero—all *in situ*.
- More research needed to address adverse environmental effects such as fate and transport and biological uptake.
Nanomaterials Desired Properties for In Situ Remediation

- Nano-size = increased surface area and reactivity + more pervasive > 20 m in GW
- Innovative surface coatings for desired contaminants, effects.
- CNTs, metal oxides, zeolites, TiO2, BNP (bi-metallic nanoscale particulate)
- nZVI (nanoscale zerovalent iron) most common: (10-100 nm diameter)
- Organic solvents, pesticides, PCB’s, metals
- One case study showed 99% reduction of TCE within days of injection (Zhang 2003)
- Thorough site characterization required:
Hazardous Waste Clean-up sites:

EPA estimated haz waste sites in US and cost

Total no. of sites = 294,000

Total = $209 billion
Nanoremediation Applications:

**Type of nanoparticles used**
- Nano-oxide: 2%
- BNP: 29%
- eZVI: 9%
- nZVI: 60%

**Type of media treated**
- Groundwater: 60%
- Soil and groundwater: 16%
- Sands and clayey silts: 2%
- Unknown: 20%
- Soil: 2%
EPA study 2009 “Drinking water treatment and sunscreen case study for Titanium Dioxide (TiO2) NSPs

- EPA case study:
- 2 applications:
- Arsenic removal
- TiO2 in sunscreen
- Comprehensive Environmental Assessment and implications
- 2007 Nanotechnology White Paper:
What are the hazards of NSPs? New field of nanotoxicology:

- Human toxicity and exposure routes- **Inhalation** is primary occupational exposure route. Secondary exposures: Ingestion
- Physico-chemical properties and interactions with ecosystems unknown
- Environmental Fate and Transport Uncertain if materials enter environment at the end of their life. (some intentionally released) e.g. TiO2 in Water treatment or remediation technologies
Common Drivers of “Nanotoxicity”

- **Intrinsic elemental toxicity**
  Individual atoms or ions interfere with biological systems
  (Lead, cadmium, fluoride, etc)
  Usual dose metric is mass

- **Surface area/reactivity driven toxicity**
  Surface catalyzes damaging reactions
  Surface area is likely the most relevant dose metric

- **Morphology-driven toxicity**
  Fiber toxicity
  (Asbestos, fibrous zeolites, MMMF)
  Usual dose metric is particle count
History tends to repeat itself:

- Miracle materials
  - Asbestos
  - Lead
  - PCBs
  - MTBE
  - Nano?
Primary EH&S Issue: *Unbound Engineered Nanoparticles*

- Not firmly attached to a surface
- Not part of a bigger item or (embedded in structure or liquid solution) Can result in exposure via inhalation, skin absorption or ingestion (or other nanospecific routes of exposure!)
- NSPs crossing blood/brain barrier?
  - (Oberdorster 2004)
  - New properties of NSPs
  - *Enhanced* toxicity of materials
  - *New* toxicological properties not seen in bulk material
Respiratory Hazards of NSPs
Size Does Matter!

Nose, throat: Particles < 30 µm

Trachea, bronchi, bronchioli: Particles < 10 µm

Pulmonary alveoli: < 2-3 µm
Carbon Nanotubes already here!

- Sporting goods
- aerospace/defense
- wind turbines
- automobile industry
- batteries, electronics
- filtration

>500 consumer products that contain nanomaterials at last count
Some People Are Showing Their Concern!
Toxicity assessment and exposure routes for CNTs:

- **Inhalation** - (Primary route)
- **Effects**: Carcinogenic - Pulmonary fibrosis, granulomas, mesothelioma, genotoxicity DNA damage (observed in mouse pathology)
- CNTs compared to asbestos exposures by NIOSH: Detection methods inadequate
- High tendency to stick together
Titanium dioxide (TiO2) exposure routes and toxicity

- TiO2 dust or powder - exposures can occur during research and development, manufacture, product use
- Inhalation (Primary route)
  - Carcinogen (IARC) tumors
  - Inflammation
- Ingestion - secondary route
  DNA damage observed in mice
  **Translocation** to Central Nervous System (CNS)
  ENPs can potentially cross the blood brain barrier to CNS as observed in rodent studies and pathology. (Oberdorster 2004)

Potency of nanoparticles vs. larger respirable particles
Managing Occupational Exposures to NSPs

- Administrative Controls
- Mechanical Controls
- Personal Protective Equipment
- Monitoring Equipment
- Medical Monitoring
Best Management Practices, Administrative, Engineering Controls and Exposure Limits

- Preliminary Hazard Assessment
- Chemicals/materials being used in the process
- Production methods used during each stage of production
- Process equipment and engineering controls employed
- Worker’s approach to performing job duties
- 4 Current Strategies for Engineering Controls in Nanomaterial Production and Downstream Handling Processes
- Exposure potential to the nanomaterials from the task/operations
- The facility that houses the operation
Nanomaterial Risk Management Plan

- Automated product transfer between operations—a process that allows for continuous process flow to avoid exposures caused by workers handling powdered or vaporous materials.
- Closed-system handling of powdered or vaporous materials, such as screw feeding or pneumatic conveying.
- Local exhaust ventilation. Steps should be taken to avoid having positive pressure ducts in work spaces because leakage from ducts can cause exposures. Ducts or pipes should be connected using flanges with gaskets that prevent leakage.
- Continuous bagging for the intermediate output from various processes and for final products. A process discharges material into a continuous bag that is sealed to eliminate dust exposures caused by powder handling. Bags are heat sealed after loading.
Nanomaterial Risk Management Plan

- Minimizing the container size for manual material handling. Minimizing the size of the container or using a long-handled tool is recommended so that the worker does not place his breathing zone inside the container.

- NIOSH recommends a maximum container depth of 25 inches [NIOSH 1997]. If large containers are required, engineering controls to provide a barrier between the container and the breathing zone of the worker are recommended.

- Current Strategies for Engineering Controls in Nanomaterial Production and Downstream Handling Processes
Nano Tool-Kit

- GOAL:
  http://www.ehs.ucr.edu/laboratory/nanotoolkit.pdf

- Working Safely with Engineered Nanomaterials in Academic Research Settings

- Developed by University of California Center for Environmental Implications of Nanotechnology UCEIN, and DTSC, as well as other academic institutions: Stanford, UCLA, UCSB, UCI, USC

- Easy to use tool kit to minimize or eliminate exposures and develop SOP’s for specific nanomaterials, and operations.
Occupational Health and Safety Concerns (nano toolkit)

- Routes of Exposure: inhalation, dermal contact, ingestion
- Lack of Information on Full Health Effects: lack of data, apply precautionary principle
- Toxicity: Respiratory tract, cross cell membranes, penetrate skin
- Other: Catalytic effects: Fire or Explosion; can be caused by processes
Occupational Exposure Limits (OEL)

Although there are currently no (legally enforceable) exposure limits in US or Int’l, NIOSH has developed Recommended Exposure Limits (RELS) for CNTS (TWA 7 ug/m3) and nano TiO2 (TWA .3 mg/m3). Some private companies have their own exposure limits.
Risk Level And Controls:

- Category 1: Low exposure potential-bound in substrate, water based suspension. No airborne release potential.
- Category 2: Moderate exposure potential-powders, pellets, or solvent based liquid suspensions. Airborne release potential when handling
- Category 3: High exposure potential: Powders or pellets with extreme potential for release into air, or suspended in gas with high release potential.
Heirarchy of Controls in laboratory: Nano toolkit

- Elimination
- Substitution
- Modification
- Containment
- Ventilation
- Work Practices
- Personal Protection
Engineering Controls: Minimize airborne releases with equipment

- Fume hood or Bio-safety cabinet: (must be ducted if using volatile compounds)
- Glove box or fully enclosed system: Useful for grinding operations or gas phase
- Local capture Exhaust hoods
  Use High-Efficiency Particulate Air (HEPA) system:
  Ensure performance and maintenance: Wet wipes and HEPA vacuums for any maintenance to be performed: complete monitoring, maintenance checks
Acceptable Practice??

Raw single walled carbon nanotube material (HiPCO Process)
BMPs for ENPs in laboratory

- Use solutions or substrates: Prevents airborne releases: liquid solution/ solid matrix
- Keep safety equipment and spill kit
- Use signs and labels: Indicate “ENM work” warning, caution, specific hazard warning
- Clean and maintain: sticky floor mats, absorbent pads, wet wipe and/ or HEPA vacuum work surfaces and equipment after operations
- Personal Hygiene: No eating or drinking
- Store and label properly “indicate nano” + hazard
- Transport in Secondary containment to avoid release:
PPE Selection and Usage:

- Nanomaterial / State
- Glove Type (Recommendation)
- Carbon Nanotubes (CNTs) Nitrile over Latex*, **
- TiO2 Latex**, Nitrile, Neoprene***
- Graphite Latex**, Nitrile, Neoprene, Vinyl
- Consult MSDS, and PPE quick-guide on nano tool kit for specifics.

PPE is always last line of defense:
Respiratory protection will require full RPP program:
Research has shown current PPE does have efficacy:
Proper Disposal: Waste Management

- **General Rule:** Until more information available, assume ENM containing wastes to be hazardous unless they are known to be non-hazardous:
  - Label all nanowaste and specific hazard characteristics include “nano” in name.
  - Keep containers closed at all times!
  - Maintain containers in good condition and free of exterior contamination.
Hazardous Waste Management of Nanomaterials:

- **Waste streams and management methods**
  
  **Solid**
  - Dry ENM product
  - Filter media containing ENMs
  - Debris / dust from ENMs bound in matrix

  2. Collect waste in rigid container with tight fitting lid.

  **Liquid**
  - Suspensions containing ENMs

  2. Indicate both the chemical constituents of the solution and their hazard characteristics, and the identity and approximate percentage of ENMs on container labels.
  3. Use leak proof containers that are compatible with all contents.
  4. Place liquid waste containers in secondary containment and segregate from incompatible chemicals during storage.
Laboratory trash with trace nanomaterials
- PPE
- Tacki mats
- Spill clean-up materials
  2. Dispose of in double clear plastic bags, folded over and taped at the neck.
  3. Avoid rupturing the bags during storage and transport.

**Solid Matrix**
- embedded with nanomaterials
- (intact and in good condition)
- 1. Consult with your EH&S department, as these materials may be non-hazardous
Develop Specific Nanomaterial EHS Program and SOPs for ENPs

Appendix A

Standard Operating Procedures (SOP)

For the Laboratory Use of Engineered Nanomaterials

Instructions: Review the Quick Guide: Risk Levels and Control Measures for Nanomaterials. Use this template to develop a Standard Operating Procedure for your experiment/process.
Nanomaterials and the Environment: Lifecycle Assessments:

There’s a growing recognition that health and safety must be an integral part of nanomaterial design.
Environmental Fate and Transport: Defining Exposure Pathways

- Management and detection of materials from cradle to grave.
- May enter water and food cycles as landfill waste, incineration intentional release as remediation.
- Unknown dangers- Most nanomaterials have not been mass produced until now. (grey goo ...?)
Figure 5. Routes of exposure, uptake, distribution, and degradation of NSPs in the environment. Solid lines indicate routes that have been demonstrated in the laboratory or field or that are currently in use (remediation). Magenta lettering indicates possible degradation routes, and blue lettering indicates possible sinks and sources of NSPs.
LIFECYCLE EXPOSURE ROUTES AND ASSESSMENTS

EPA Nanotechnology White Paper
Nano Products end of life

Number of products based on eol category

- Recycle: 461
- Absorbed by skin/Public sewer: 212
- Landfill: 120
- Ingestion: 75
- Public sewer: 72
- Air release/Public sewer: 35
- Air release: 24
- Burning/Landfill: 12
- Other: 3
While Nano particles differ in particle size and may exhibit different physical and/or chemical properties, EPA considers the two forms to be the “same” chemical substance because they have the same molecular identity.
Berkeley Nano Ordinance

- **Berkeley Manufactured Nanoscale Materials Health and Safety Disclosure Ordinance, December 2006**
- An “add on” to the HMBP process
- Only local nano ordinance, focused on disclosure
- Compels facilities that produce or handle manufactured engineered nanoscale materials to report what they are working with, describe known toxic effects and provide a plan on how the materials are handled safely.
Berkeley Nano Ordinance: Criticism

- No de minimis quantities specified
- “Open” reporting format
- Limited amount of information captured
- Burdensome and may drive out startups
State of California Call-Ins

California Health and Safety
Code 699: Basis for requiring producers of specified nanomaterials to report on nanoparticles—quantity, detection methods, risks, protective steps etc

• Do you consider your waste or material to be hazardous waste?
• Two stages complete
  – Call 1: Carbon nanotubes
  – Call 2: Assortment of metal and metal oxide nanoparticles
California/Federal OSHA

- No specific regulations for new engineered nanomaterials
EPA: TSCA

Prohibit/Regulate introduction of nanoparticles into commerce under TSCA:

— Underway for CNTs and other nanoparticles since 2008

• Regulate as a pesticide (FIFRA):
  — Already underway for nano-silver

• Prohibit releases to air (Clean Air Act) or Water (Clean Water Act, Safe Drinking Water Act)

• Classify as hazardous Waste (RCRA)
EPA: TSCA

Generally, you can only market and use chemicals that are on the EPA Toxic Substances Control Act (TSCA) inventory

- Carbon nanotubes are fundamentally new and are not among the 84,000 chemicals on that inventory...
- Most other “nano materials” are chemically identical to larger materials and thus not subject to regulation as new chemicals, yet
Evolving EPA Rules for CNTs

- EPA receives at least 100 PMNs to import or manufacture nanomaterials, many for CNTs. Eventually the EPA enters into “5(E)” consent decrees with many of these companies, with the following typical requirements:
  - Use the material only for the listed (semi-secret!) purposes
    - Examples: polymer composite materials, electronics, catalyst support
  - Conduct a 90-day rat inhalation toxicity study on their material
  - Require employees who may be exposed to use specified types of personal protective equipment at facilities under its control (fullface respirator/protective coveralls and gloves)
  - Only distribute the material to persons who agree to comply with all of the restrictions of the 5(e) order (except the tox study).
EPA Issues Significant New Use Rules (SNURs) for Multi-Walled Carbon Nanotubes

After signing a Section 5(e) Consent Order, EPA generally promulgates a Significant New Use Rule (SNUR) that mimics the Consent Order to bind all other manufacturers and processors to the terms and conditions contained in the Consent Order for that exact, specific PMN material.

• The SNUR requires that manufacturers, importers and processors of PMN substances notify EPA via a SNUN at least 90 days before beginning any activity that EPA has designated as a "significant new use". These new use designations are typically those activities prohibited by the Section 5(e) Consent Order."

— Significant new uses of multi-walled carbon nanotubes are deemed to occur when employees do not “use gloves impervious to nanoscale particles and chemical protective clothing;” and/or fail to “use a NIOSH approved full-face respirator with an N-100 cartridge while exposed by inhalation in the work area.”

— “Significant new use” applies to the use of a substance outside of the list of approved uses in the PMN (e.g. catalyst support, filler, polymer).
Conclusions and Further Research Needs

- Toxicology
- Regulatory
- Instrumentation
- Lifecycle Management Approach
- Recyclability
- International Collaboration
Nano Resources:

- NIOSH Guide: Current Intelligence Bulletins
- EPA White Paper on Nanotechnology
- ASTM E 2535-07 (10/07) guide for Handling ENPS in occupational setting
- NNI National Nanotechnology Initiative: http://www.nano.gov/
- UC CEIN: University of California Center for Environmental Implications of Nanotechnology http://www.cein.ucla.edu/new/
- PEN; Project on Emerging nanotechnologies
- USEPA: Nanomaterial Remediation Strategy
- Nanosafety at the OECD: http://www.oecd.org/env/ehs/nanosafety/
Questions?

Dan Rompf, M.S.
Hazardous Materials Specialist
(650)372-6201 Office
(650)627-8244 Fax
drompf@smcogov.org
Office Hours: 0700-1800 Tues-Fri
2000 Alameda de Las Pulgas
San Mateo, CA