Nanotechnology for environmental remediation: Empowering state agencies with information for health and safety oversight of nanomaterials

June 5-7th, 2013

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Southeastern Louisiana University
Outline of Presentation

• (A) What is happening at Southeastern Louisiana University?
  – The genesis of the **Nano-4-Rem AnsseRs Initiative**

• (B) Why focus on nanotechnology?
  • Definitions; Nanoinformatics (2020); NNCO Signature initiatives and the Nano-4-Rem AnsseRs Initiative
  • Areas where engineered nanoparticles (ENPs) are being used
    – Why nano-enhanced remediation?
    – Benefits and costs?

• (C) Where do we go from here? A case study: survey of local and state agencies – nanoinformatics and empowerment
What is happening at Southeastern Louisiana University: A Nano-Informatics Case Study

- Overall goal and mission of the grant which is supported by Louisiana Board of Regent for Higher Education and NIOSH:
  - To understand the scientific and technological information needs relevant to nanotechnology physico-chemical behavior and characteristics throughout the life cycle (synthesis, characterization, manufacture and handling) to support local and state agencies and programs in the regulatory and oversight functions of engineered nanoparticles; and to help scientists to estimate health risks
What is happening at Southeastern Louisiana University
Nanoinformatics case study in nano-remediation

• Nanoinformatics: “Science and practice to determine relevant information to nano-scale science, and to use it to develop and implement effective mechanism to collect, validate, store, share, analyze, and apply that information to prevent human health risks”

• Current nanoinformatics projects include: Nanomedicine; Nanoparticle Information Library; Nanomaterial – Biological Interaction Database; ICON’s GoodNano Guide; Nanomaterials Registry (web-based for inf. on the biological and environmental interactions of nanomaterials).

• And now a case study on nano-enhanced remediation – at Southeastern!
Genesis of the project:
Funds from the Board of Regent Support/NIOSH-UTHealth

• Use information to model exposure scenarios to estimate health risks.

  – Information to support local and state government agencies’ oversight
    • Understand work practices at Superfund sites that use ENPs
    • Use the knowledge to develop guidelines for best work practices, including training manuals

  – Use the information to estimate exposures to ENPs and health risks
Genesis of the nano-informatics project: Funds from the Board of Regent and support from NIOSH-UTHealth

- Objective 1: Review the properties and characteristics of ENPs which have been used and continue to be used at various superfund sites – To investigate the nature, characteristics and properties of ENP that have been used or continue to be used at the U.S. Superfund sites across the United States. This effort will allow effective risk assessment models to be developed.

- Objective 2: Investigate and document work practices associated with the handling of ENPs by major vendors, laboratories who synthesize and characterize ENPs and workers at the remediation sites. This approach is based on a life-cycle management of occupational exposure to ENPs.

- Objective 3: Develop risk assessment models for estimating occupational exposures to ENPs at the superfund sites – The PI will use the work practices derived from the preceding objectives as tools to develop risk assessment models and to establish best practices for handling ENPs at superfund sites to minimize or prevent worker exposures.

- Objective 4: Develop tool kits and templates for training and educational modules for safe handling of ENPs throughout their life cycle in the environmental remediation sector – Training modules will be developed that are easy to comprehend and understand for vendors, laboratory technicians and operators or site project managers of the superfund sites that may want to use or handle ENP for their operations, including those in the state of Louisiana.

Applications of Nanotechnology for Safe and Sustainable Environmental Remediations

Inaugural Workshop
Understanding and meeting information and technology needs to prevent exposures to engineered nanoparticles

Southeastern Louisiana University
Hammond, Louisiana
June 6-7, 2013
Nanotechnology: How big is nano (nm); how small is small, and does it matter?

• The size of a human hair divided by 100,000X
• Perhaps the thickness of a sheet of paper ~ 10 x10^5 nm.
• Diameter of a strand human hair 15 x10^3 – 180 x10^3 nm!
• A length of 1” (inch) is approximately (~) equal to 25.4 x10^6 nm!!
• A nanometer is a millionth of a millimeter (10^-9)

• Definition: Nanotechnology is the science and technology of manipulating matter at the atomic and molecular level for specific functionality – the level of greatest concerns in terms of the EHS impacts!
The definition of nanotechnology (cont’d)

– Is a term encompassing science, engineering, and technology focusing on understanding, controlling and managing atoms and molecules (matter) at the dimensions ranging from 1 and 100 nm.

– The intention of this manipulation is to produce unique properties (phenomena) of matter – properties which are distinct or different from bulk materials of same characteristics.

– Some of these properties of matter at the nano-scale (size; high-surface area-to-volume ratio) create an environment to enable novel applications of matter – what are these applications?
Evolution of nanotechnology and the role of chemistry and physics: The 1959 igniting talk by Richard Feyman

There's Plenty of Room at the Bottom

An Invitation to Enter a New Field of Physics

by Richard P. Feynman

Richard P. Feynman presentation made on 12-29-1959 (American Physical Society Annual Meeting at the California Institute of Technology)

Published in Caltech Engineering and Science, Vol. 23:5 February 1960; pp 22-36

“....What I want to talk about is the problem of manipulating and controlling things on a small scale.....

“......Why cannot we write the entire 24 volumes of the Encyclopaedia Brittanica on the head of a pin? .......

“.......The theory of chemical processes today is based on theoretical physics. In this sense, physics supplies the foundation of chemistry....”

“...chemistry and chemical processes be described by the physicist...”

Applications of Nanotechnology for Safe and Sustainable Environmental Remediations

Inaugural Workshop
Understanding and meeting information and technology needs to prevent exposure to engineered nanoparticles

Southeastern Louisiana University
Hattiesburg, Louisiana
July 1-4, 2014
Physico-chemical properties of matter impacting nano: During and after use of nano-scale materials

- A partial list of physical and chemical properties that can change at the nanoscale, each has own set of properties.
  - Color
  - Melting temperature
  - Crystal structure
  - Chemical reactivity
  - Electrical conductivity
  - Magnetism
  - Mechanical strength
  - Surface area
The color of bulk and macroscopic Gold – that we LOVE suddenly changes to GOLD at the nano-scale

Bulk Gold (Au) = Yellow
Conductive
Nonmagnetic
Chemically inert

Nano Gold = Red
Loses conductivity at ~ 1-3 nm
Becomes magnetic ~ 3 nm
Explosive and catalytic!
Gold – nano-GOLD and the implications to employees

Bulk Gold (Au) = Yellow
Conductive
Nonmagnetic
Chemically inert

Nano Gold = Red
Loses conductivity at ~ 1-3 nm
Becomes magnetic ~ 3 nm
Explosive and catalytic!

Much of the conventional understanding knowledge about the physico-chemical properties of the atomic or molecular and macroscopic gold tend to disappear at the nano-scale gold
# Nanotechnology and various types of nanomaterials

<table>
<thead>
<tr>
<th>Naturally Occurring</th>
<th>Human Origin (Incidental)</th>
<th>Human Origin (Engineered)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest fires</td>
<td>Cooking smoke</td>
<td>Metals oxides</td>
</tr>
<tr>
<td>Sea spray</td>
<td>Diesel exhaust and related by-products</td>
<td>Quantum dots</td>
</tr>
<tr>
<td>Mineral composites</td>
<td>Welding fumes</td>
<td>Buckyballs (Fullerenes60)</td>
</tr>
<tr>
<td>Volcanic ash</td>
<td>Industrial effluents</td>
<td>Nanotubes (SWCNTs &amp; MWCNTs)</td>
</tr>
<tr>
<td>Viruses</td>
<td>Sandblasting, construction and related by-products</td>
<td>Sunscreen pigments</td>
</tr>
</tbody>
</table>

**Dendrimers**

*Nanotechnology*

*Dendrimers*: polymers made from two monomers: acrylic acid and a diamine. Dendrimers, like plastics, are polymerized products of two or more monomers.
Nanoscale chemistry and ENPs: the tree and branches of the areas of application of various nanomaterials
Other applications of engineered nanoparticles

<table>
<thead>
<tr>
<th>Areas</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive</td>
<td>Lightweight construction; Catalysts; Painting; Tires; Sensors; Windshield</td>
</tr>
<tr>
<td></td>
<td>and body coatings</td>
</tr>
<tr>
<td>Construction</td>
<td>Materials; Insulation; Flame retardants; Surface coatings; Mortar</td>
</tr>
<tr>
<td>Electronics</td>
<td>Displays; Data memory; Laser diodes; Fiber optics; Optical switches; Filters;</td>
</tr>
<tr>
<td></td>
<td>Conductive coatings; Antistatic coatings; Transistors</td>
</tr>
<tr>
<td>Engineering</td>
<td>Protective coatings for tools, machines; Lubricant-free bearings</td>
</tr>
<tr>
<td>Food and Drink</td>
<td>Packaging; Storage life sensors; Additives; Juice clarifiers</td>
</tr>
<tr>
<td>Medicine</td>
<td>Drug delivery systems; Contrast medium; Rapid testing systems; Prostheses</td>
</tr>
<tr>
<td></td>
<td>and implants; Antimicrobial agents; In-body diagnostic systems</td>
</tr>
<tr>
<td>Textiles</td>
<td>Surface coatings; “Smart” clothes (anti-wrinkle, stain resistant, temperature</td>
</tr>
<tr>
<td></td>
<td>controlled)</td>
</tr>
<tr>
<td>Chemical</td>
<td>Fillers for paints; Composite materials; Impregnation of papers; Adhesives;</td>
</tr>
<tr>
<td></td>
<td>Magnetic fluids</td>
</tr>
<tr>
<td>Cosmetics</td>
<td>Sunscreen; Lipsticks; Skin creams; Toothpaste</td>
</tr>
<tr>
<td>Energy</td>
<td>Lighting; Fuel cells; Solar cells; Batteries; Capacitors</td>
</tr>
<tr>
<td>Environmental</td>
<td>Environmental monitoring; Soil and groundwater remediation; Toxic exposure</td>
</tr>
<tr>
<td></td>
<td>sensors; Fuel changing catalysts; Green chemistry</td>
</tr>
<tr>
<td>Household</td>
<td>Ceramic coatings for irons; Odor removers; Cleaners for glass, ceramics,</td>
</tr>
<tr>
<td></td>
<td>metals</td>
</tr>
<tr>
<td>Sports</td>
<td>Ski wax; Tennis rackets; Golf clubs; Tennis balls; Antifouling coatings for</td>
</tr>
<tr>
<td></td>
<td>boats; Antifogging coatings for glasses, goggles</td>
</tr>
<tr>
<td>Military</td>
<td>Neutralization materials for chemical weapons, bullet-proof protection</td>
</tr>
</tbody>
</table>

Promises and perils of nanotechnology in various applications

- Clean, secure affordable energy? Provide clean portable water. Detect impurities (heavy metals, organic pollutants, microbes, etc). Nano-remediation: fast, cost-effective for conducting clean-up operations

- By 2010, a report to Congress estimated that there were more than 1,000 ENPs are available commercially [Lux Research, 2010]

- NSF estimates the number of workers ~ 2 million worldwide; about 800,000 in the U.S. alone by 2015. These workers will be in direct support of nanotechnology and nanotechnology-related activities.

- Potential health and safety impacts on a significant number of workers.

Source: http://www.nanotechproject.org/inventories/consumer (5-2-2013)
Nano-4-Rem AnnseRs: 
The application of ENPs on the U.S. EPA Superfund Sites

• Thousands of hazardous waste sites in the country are known as “superfund sites”, regulated by the U.S. EPA

• Persistent, bioaccumulative and toxic (PBT) wastes are on the sites.

• Traditional remediation techniques are costly, take a long time

• Nano-enhanced remediation seems to be a fast, cost-effective and a promising technique of conducting clean-up operations
Common chemical wastes at the Superfund sites that require clean up operations

- DDT
- Aldrin & Dieldrin
- Chlordane
- PCB’s; PERC; TCEs
- Heptachlor

Clean-up operations, in particular for persistence, bio-accumulative and toxic (PBT) hazardous wastes may be costly and take a long time to accomplish.
## Nanomaterials Used for Remediation

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>Examples</th>
<th>Remediation Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>BNPs and Zero-valent Iron</td>
<td>Ni; gold; Pd or Pt; BNPs - Bimetallic Nano Particles; nZVI</td>
<td>Remediation of • waters, • sediments or • Soils • (hydrocarbons)</td>
</tr>
<tr>
<td>Metal oxide ENPs</td>
<td>TiO$_2$; ZnO; and Cerium Oxide (CeO)</td>
<td></td>
</tr>
<tr>
<td>Nano Metals</td>
<td>Engineered Nanosilver (Ag)</td>
<td></td>
</tr>
<tr>
<td>Carbonaceous ENPs</td>
<td>Multiwalled Carbon Nanotubes – MWCNTs-<em>much better than activated C</em></td>
<td>Sorption of metals e.g. Cd; Pb; Cu etc.</td>
</tr>
<tr>
<td></td>
<td>Nanoporous Activated C Fibers (ACFs)</td>
<td>Sorption of BTEX compounds</td>
</tr>
<tr>
<td>Nano Clays/ Zeolites</td>
<td>Na$_6$Al$<em>6$Si$</em>{10}$.12H$_2$O</td>
<td>Sorption/Ion Exchange for metals</td>
</tr>
<tr>
<td>Carbon-based Dendrimers</td>
<td>Hyper-branched polymers (1-20 nm)</td>
<td>PAHs; Ultra-filtration of heavy metals</td>
</tr>
</tbody>
</table>
## Typical examples of ENPs used for environmental applications

<table>
<thead>
<tr>
<th>ENP</th>
<th>Application</th>
<th>Target Pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Pigments, UV-absorber, photo-catalysts</td>
<td>Organic pollutants</td>
</tr>
<tr>
<td>ZnO</td>
<td>Polymer filler, UV-absorber</td>
<td></td>
</tr>
<tr>
<td>Au, Fe, Ag</td>
<td>Remediation, clothing</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Ceramic, catalyst support</td>
<td></td>
</tr>
<tr>
<td>nZVI (Redox reactions/Adsorption)</td>
<td>Metals, organic compounds, arsenic (Halogenated organic compounds, metals, nitrate, arsenate, oil)</td>
<td></td>
</tr>
</tbody>
</table>
U.S. EPA Superfund sites; RCRA; Brown fields; Urban sanitary landfills

<table>
<thead>
<tr>
<th>Site “Owner”</th>
<th># of Sites</th>
<th>%age</th>
</tr>
</thead>
<tbody>
<tr>
<td>National Priority List superfund sites</td>
<td>740</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Other superfund sites</td>
<td>500</td>
<td>&lt;1</td>
</tr>
<tr>
<td>States and private companies</td>
<td>150,000</td>
<td>51</td>
</tr>
<tr>
<td>Civilian agencies</td>
<td>3,000</td>
<td>1</td>
</tr>
<tr>
<td>Department of Energy / DOD</td>
<td>12,000</td>
<td>4</td>
</tr>
<tr>
<td>Underground Storage Tanks (UST) contaminated sites</td>
<td>125,000</td>
<td>43</td>
</tr>
<tr>
<td>Resource Conservation and Recovery Act (RCRA)</td>
<td>3,800</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total # sites known to-date</strong></td>
<td>~ 295,000</td>
<td>100%</td>
</tr>
</tbody>
</table>
Costs vs. time of the clean-up operations  
nano-enhanced remediation vs. traditional remediation

- Traditional remediation methods  
  e.g. pump and treat ~ 5,000,000

- Traditional remediation methods (PRBs) - 3,400,000

- Nano-enhanced remediation methods
  - e.g. nano-zero valent iron (nZVI) - 600,000

- Traditional methods are costly. It is estimated that it many take as many as (40) years to clean-up all sites across America!
What if……? Benefits/opportunities and challenges

• Do the properties of ENPs that bring about their benefits, also inherently responsible for their shortcomings?

• At the launching of the NNI in the early 2000’s, it was recognized that the EHS impacts of nanotechnology (nano-remediation) were uncertain.

• Regulatory/oversight of nanotechnology is a challenge to both the U.S. OSHA and U.S. EPA, and by extension to the local and state government officials
  – This is attributed to the lack of relevant information on
    • who; where; how; when nanomaterials (ENPs) are being used
    • Requirements for the synthesis, characterization, transportation, use, disposal and interaction of ENPs with people
What is needed for occupational environment?

The term "hazard" has many definitions. This paper uses the definition of the United States Environmental Protection Agency (EPA) which defines "hazard" as the "inherent toxicity of a compound" [5]. According to this definition, if a chemical substance has the property of being toxic, it is therefore hazardous. Any exposure to a hazardous substance may lead to adverse health effects in individuals or even death.

Progress Toward Safe Nanotechnology in the Workplace
A Report from the NIOSH Nanotechnology Research Center

Standard and regulatory framework to protect workers against exposure to hazards

Steps to Protect Workers Involved with Nanotechnology

<table>
<thead>
<tr>
<th>NIOSH Focus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toxicologic research</td>
</tr>
<tr>
<td>Health effects assessment</td>
</tr>
<tr>
<td>Safety research</td>
</tr>
</tbody>
</table>

Hazard Identification
"Is there reason to believe this could be harmful?"

Hazard Characterization
"How and under what conditions could it be harmful?"

Exposure Assessment
"Will there be exposure in real-world conditions?"

Risk Characterization
"Is substance hazardous and will there be exposure?"

Risk Management
"Develop procedures to minimize exposures"

Adapted from Gibb, 2006

A framework for conducting exposure evaluations as part of a process to estimate human health and safety risks

Exposure Assessment Approaches

Direct Methods

Biological Monitoring

Modeling

Personal Monitoring

Dose-Response

Indirect Methods

Environmental Monitoring

Questionnaires and Diary of Activities

Human Health Risk Estimates

What information goes into each of these steps? ______________________________?
What did we find out at the state level

• Age Group Responding:
  • 2.9% ~ <20 yrs
  • 31.4% (40-50 yrs)
  • 31.4% (60-70 yrs)

• Numbers of years working as a regulatory professional
  20 yrs = 34.4% (highest)

• Monitoring and Surveillance Needed? y/n

• Technological shift
• Emerging technology (information)
What did we find out at the state level

• U.S. EPA responses
  • Region 3/8: least 2.8% responding
  • Region 6: highest with 25.7% response rates

• Budget allocation for information and technological needs
  0$ = 80.8%
  <$10,000 =

• Region 3: Delaware; Maryland; PA; Virginia; D.C.

• Region 8: Colorado, Montana; ND; SD; UT
  Region 8: LA; AR; NM; TX; OK

•? = how do we provide information here?
A snapshot of the responses from the survey of the U.S. agencies and programs

| Willingness to provide input in the study and to have contact information in final report | 207 (34.3) | 346 (57.1) | 52 (8.6) |
| Willingness to review the first draft of the report | 295 (48.6) | 277 (45.7) | 34 (5.7) |
| Region | 34 (5.7) | 34 (5.7) | 121 (20.0) |
| U.S. EPA, Region 1 Connecticut, Massachusetts, Maine, New Hampshire, Rhode Island, and Vermont | 34 (5.7) | 34 (5.7) | 121 (20.0) |
| U.S. EPA, Region 2 New Jersey, New York, the Commonwealth of Puerto Rico, and the Virgin Islands | 34 (5.7) | 34 (5.7) | 121 (20.0) |
| U.S. EPA, Region 3 Delaware, Maryland, Pennsylvania, Virginia, West Virginia, plus the District of Columbia | 34 (5.7) | 34 (5.7) | 121 (20.0) |
| U.S. EPA, Region 4 Alabama, Florida, Georgia, Kentucky, Mississippi, N Carolina, S Carolina, and Tennessee | 34 (5.7) | 34 (5.7) | 121 (20.0) |
| U.S. EPA, Region 5 Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin | 34 (5.7) | 34 (5.7) | 121 (20.0) |
| U.S. EPA, Region 6 Arkansas, Louisiana, New Mexico, Oklahoma, and Texas | 34 (5.7) | 34 (5.7) | 121 (20.0) |
| U.S. EPA, Region 7 Iowa, Kansas, Missouri, and Nebraska | 34 (5.7) | 34 (5.7) | 121 (20.0) |
| U.S. EPA, Region 8 Colorado, Montana, North Dakota, South Dakota, Utah | 34 (5.7) | 34 (5.7) | 121 (20.0) |
| U.S. EPA, Region 9 AR, CA, Hawaii, and NV, American Samoa, Guam, and Commonwealth of N. Mariana Is. | 69 (11.4) | 69 (11.4) | 69 (11.4) |
| U.S. EPA, Region 10 Alaska, Idaho, Oregon, and Washington | 69 (11.4) | 69 (11.4) | 69 (11.4) |
| Budget for information gathering, analysis and sharing | 489 (80.8) | 101 (16.7) | 16 (2.5) |
| $0 | 489 (80.8) | 101 (16.7) | 16 (2.5) |
| <$10,000 | 101 (16.7) | 101 (16.7) | 101 (16.7) |
| No response | 16 (2.5) | 16 (2.5) | 16 (2.5) |
Fig 3
Questions and Responses from the State Agencies and Programs

Information and technical needs assessment at the local level

- Strengthening agencies’ capability
- Communication and sharing
- Public and private partnerships
- Public health and safety impacts
- Collection of relevant information
- Interagency cooperation
- Dissemination of information

Examples
- Health and safety oversight
- Various applications
- Contractors, insurance liability, and vendors
- Site characteristics
- Toxicology, epidemiology, monitoring, surveillance
- Workshops
- Consumers
Evolution of nanotechnology and the role of chemistry and physics: Molecular nanotechnology and the IBM

- 1977 - Molecular nanotechnology concept by Drexler of MIT.
- In 1979, Drexler paper on molecular nanotechnology was followed by a book Engines of Creation: The Coming Era of Nanotechnology.
- 1981 - IBM scientists invent the Scanning Tunneling Microscope, giving ready access for the first time to the nanoscale world of individual atoms and molecules on electrically conducting substrates.
- 1986 - The Atomic Force Microscope is invented by IBM and Stanford University scientists, quickly becoming the workhorse of nanoscience, providing general purpose imaging and manipulation in the nanometer realm.
- 1989 - IBM Fellow Don Eigler is the first to controllably manipulate individual atoms on a surface, using the STM to spell out "I-B-M" by positioning 35 xenon atoms, and in the process, perhaps creating the world’s smallest corporate logo.
The magic of organic carbon:
Properties of organic carbon also change at the nanoscale

- Small dimensions of nano-scale
  - Carbon nanotubes (CNTs) are chemically stable
  - Carbon nanotubes are mechanically robust
  - Carbon nanotubes have high thermal conductivity
  - High specific surface area & good adsorbents
  - Low resistivity and so high electrical conductivity

- Potential uses: materials, batteries, memory devices, electronic displays, conductors, sensors, medical imaging**.

Understanding information needs to support regulatory functions

Where in ENPs being used?

Number of people potentially exposed (workers: skills, age, gender; work practices etc; community settings)?

Potential for ENPs to contaminate water? air; soils?

Preliminary chemical and physical properties and other EHS measurements (methods and sampling protocols)

Risk Assessment and Scoring

Risk Management
Risks of handling of engineered nanoparticles

- Risk Sources
  - Laboratories
  - Vendors
  - Packages

- Risk Release Processes
  - Mixing
  - Injection

- Exposure Processes
  - Number of people
  - What applications
  - Disposal

- Human health consequences
  - Health effects
  - Ecosystems effects
  - Organisms and human interactions

- Monitoring

- Surveillance
Conclusion and recommendations

• Health and safety of workers when handling ENPs can be enhanced by accessing and making relevant information available to employees; regulatory agencies and other stakeholders.

• Researchers, scientists, manufacturers, vendors can provide such information if the needs are known.

• Some states are doing something; other states may not. Many professionals need to work together to capture the information necessary to protect public and workers’ health and safety.

• Availability, access and sharing of information will lead to enhanced technical and regulatory capabilities of state and local governments!
Thank You!

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