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Use of Nanomaterials for Environmental Remediation of Hazardous Waste Sites: The Role of Nanoinformatics in Support of State Agencies' Health and Safety Oversight Actions

Sponsored by: U.S. EPA, Office of Superfund Remediation and Technology Innovation

Delivered: May 21, 2012, 2:00 PM - 3:30 PM, EDT (18:00-19:30 GMT)

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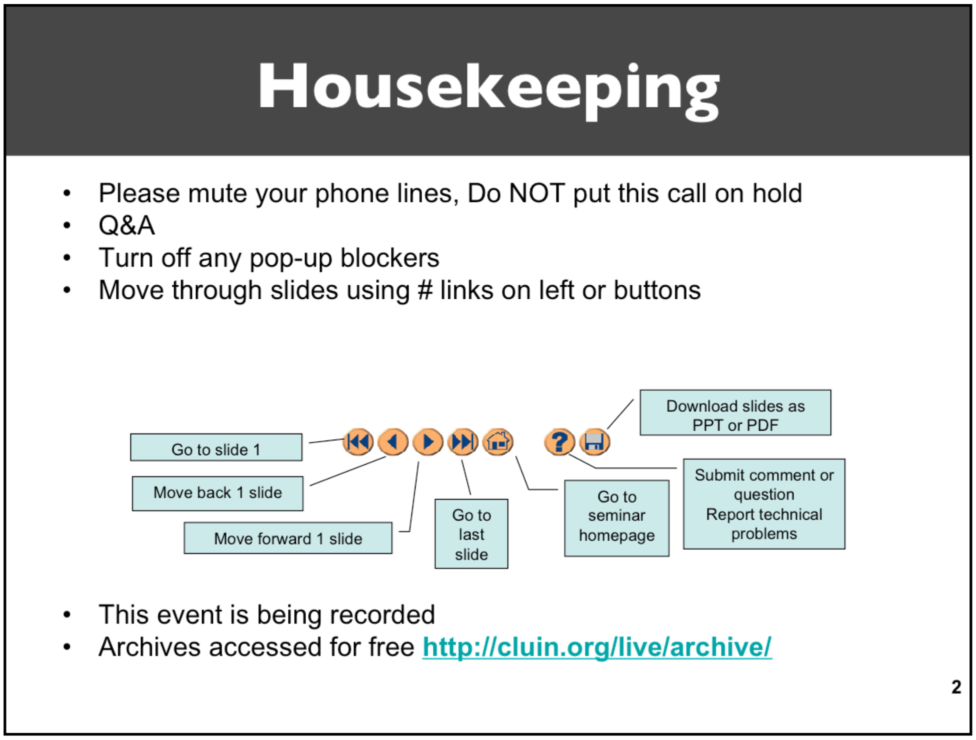

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With that, please move to slide 3.

Use of Nanomaterials for Environmental Remediation of Hazardous Waste Sites: The Role of Nanoinformatics in Support of State Agencies' Health and Safety Oversight Actions

Presented at the U.S. Environmental Protection Agency
Contaminated Site
Clean-Up Information Seminar - CLUIN

May 21st, 2012

Dr. Ephraim Massawe
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Nanoremediation or nano-enhanced environmental remediation defined

- Nanoremediation (nano-enhanced remediation) defined:
  - A method or technique employing nanomaterials to:
    - Decontaminate or detoxify contaminants
    - Reinstate land or ecosystem to original state

Examples of environmental and other related applications of nanomaterials

TiO_2	Pigments, UV-absorber, catalyst
ZnO	Polymer filler, UV-absorber
Au, Fe, Ag	Remediation, clothing
CeO_2 / $Ce2O_3$	Catalyst (cars), fuel additive
ZrO_2	Ceramic, catalyst support
Quantum dots; CdSe/ ZnS/ InAs/ InP/ InGaP	Medical imaging, drug delivery

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Specific application of nanomaterials in remediation

Nanomaterials	Examples	Remediation Uses
BNPs and Zero-valent Iron	Ni; gold; Pd or Pt; BNPs - Bimetallic Nano Particles; nZVI	Remediation of •waters, •sediments or •Soils •(hydrocarbons)
Metal oxide ENPs	TiO_2; ZnO; and Cerium Oxide (CeO)	
Nano Metals	Engineered Nanosilver (Ag)	
Carbonaceous ENPs	Multiwalled Carbon Nanotubes – MWCNTs-much better than activated C	Sorption of metals e.g. Cd; Pb; Cu etc.
	Nanoporous Activated C Fibers (ACFs)	Sorption of BTEX compounds
Nano Clays/ Zeolites	$Na_6Al_6.Si_{10}.12H_2O$	Sorption/Ion Exchange for metals
Carbon-based Dendrimers	Hyper-branched polymers (1-20 nm)	PAHs; Ultra-filtration of heavy metals

Nanoparticles - Definition

- According to the American Society for Testing Materials (ASTM) standard definition nanoparticles includes:
  - A nanoparticle is one whose length is measured in nanometers (10^{-9} m); and
  - Range from 1 to 100 nm in two or three dimensions
  - At this size nanomaterials poses properties including large surface area, and other novel chemical, physical, and biological properties which are distinctly different from larger (bulk) particles of similar chemical composition.

Source: ASTM International (2006) Terminology for Nanotechnology, ASTM E 2456-06.

Various Types of Nanomaterials!

Anthropogenic or Engineered NPs	Incidental Particles from:	Natural Particles from:
•Carbon-based •Nanotubes, •Fullerenes •Metal Oxides •Quantum Dots •Nanotubes •Nanowires •Dendrimers	•Combustion products •Industrial Processes •Vehicles emissions •Construction	•Plants, Trees •Oceans, other •water bodies •Erosion •Dust

Why this project: Introduction

- Thousands of hazardous waste sites in the country are known as "superfund sites", regulated by the U.S. EPA
- Some of the hazardous wastes deposited in the Superfund sites can be persistent, bioaccumulative and toxic (PBT)
- Traditional remediation techniques can be costly, and may take a very a long time
- Nano-enhanced remediation is fast, cost-effective and a promising technique of conducting clean-up operations

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What is a Superfund Site?

- A Superfund site is an uncontrolled or abandoned place where hazardous waste is located
  - **Contaminants from the sites can affect remediation workers, nearby community, general public and environment.**

- Superfund is a federal program
  - **Implemented under the Comprehensive Environmental Response, Contamination and Liability Act (CERCLA-1980).**
  - **Nearly 1200 superfund sites require immediate clean up.**

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Superfund sites are the "high risk" part of a larger problem

Site "Owner"	# of Sites	%age
National Priority List (NPL) *superfund sites*	740	<1
Other *superfund sites*	500	<1
States and private companies	150,000	51
Civilian agencies	3,000	1
Department of Energy / DOD	12,000	4
Underground Storage Tanks (UST) contaminated sites	125,000	43
Resource Conservation and Recovery Act (RCRA)	3,800	1
Total # Sites	~ 295,000	100%

Chemistry or Process Governing Nano-enhanced Environmental Remediation

Process Exploited	Nanomaterials used	Target compounds
Photocatalysis	TiO_2	Organic pollutants
Adsorption	Iron oxides, dendrimers	Metals, organic compounds, arsenic
Redox reactions	Nanoscale zero-valent iron (nZVI), nanoscale calcium peroxide	Halogenated organic compounds, metals, nitrate, arsenate, oil

Ref: Mueller, N.C. and Nowack, B (Elements, Vol. 6, pp. 395–400

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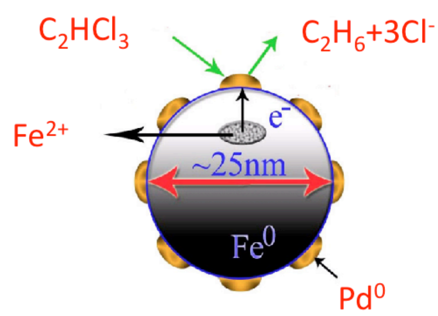
Chemistry of Nanoremediation of TCE with nZVI

- Reactive surface coatings (e.g. Pd; Pt; Cu; Ni; or Ag doping)
- High surface areas (e.g., 150 m^2/gm)
- nZVI Redox is 25-30 x faster than bulk iron



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Economic Incentives for Nano-enhanced Remediation (Cost Comparison Per Site) - reference

Remediation Technology	Cost of Remediation ($)
Traditional remediation methods using **pump and treat (without nano-enhancement)**	**5,000, 000**
Traditional remediation methods e.g. **permeable reactive barriers (PRBs)**	**3,400,000**
Nano-enhanced remediation methods **using nano-zero valent iron (nZVI)**	**600,000**

Traditional remediation methods or technologies are costly and may take as many as 40 years to clean up all sites across the United States

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Nano-Informatics Project Background

- Nanotechnology and nanomaterials research and development have reached an advanced stage of commercializing, and various applications are currently documented
- Nanomaterials use for environmental remediation applications has been successfully reported by the U.S. EPA in their superfund sites
- Exposures to engineered nanoparticles have the potential to cause significant ecological and safety impacts as well health effects in laboratory animals and cells
- Scientific community is concerned about environmental, health, and safety risks associated with the handling of nanomaterials

Nano-Informatics Project Background (continued)

- Past examples of materials that emerged as "good" for various applications such as DDT and PCBs, were confirmed to be deadly. This precedent cannot be repeated for nanomaterials!

- Since nanomaterials in workplace in particular and in the environmental in particular remains largely unregulated, a precautionary approach based on information available

- A precautionary approach is voluntary, and nano-specific EHS oversight mechanisms would be prudent to account for the unique characteristics of the materials.

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Nano-Informatics Project Background

Why nanoinformatics project?

- Collect and collate information and technological relevant to nanomaterials to enhance the capability of state agencies and programs to better anticipate, recognize, evaluate, control, and confirm * potential EHS hazards associated with nanomaterial in all applications, including environmental remediation

*Hoover, M.D., T. Armstrong, T. Blodgett, A.K. Fleeger, P.W. Logan, B. McArthur, and P.J. Middendorf: Confirming Our IH Decision-Making Framework, The Synergist, 22(1): 10, 2011.

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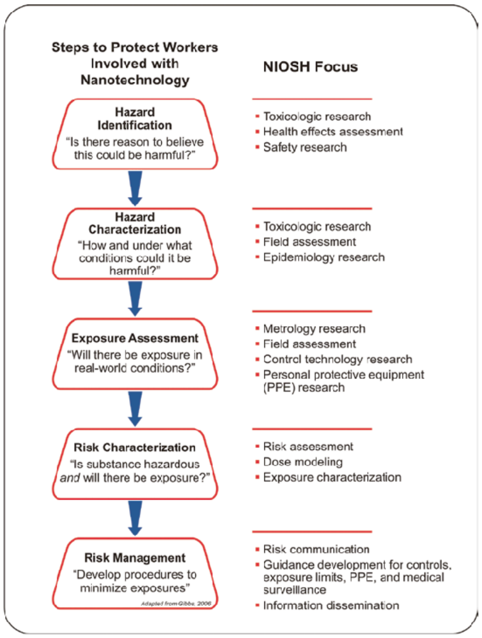

Information related issues for consideration

Progress Toward Safe Nanotechnology in the Workplace

A Report from the NIOSH Nanotechnology Research Center

http://www.cdc.gov/niosh/docs/2010-104/pdfs/2010-104.pdf (04-16-2012)

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Working hypotheses to evaluate information needs for EHS professional work and oversight

Information Needs → / Technological Needs ↓	Existing Information and Scientific Knowledge Sufficient	New Information and Scientific Knowledge Is Perhaps Needed
Traditional Remediation	?	???
Nano-enhanced Remediation	?	???
Output Product	A Compendium of Information Relevant to Various Professions Working with Nanomaterials	

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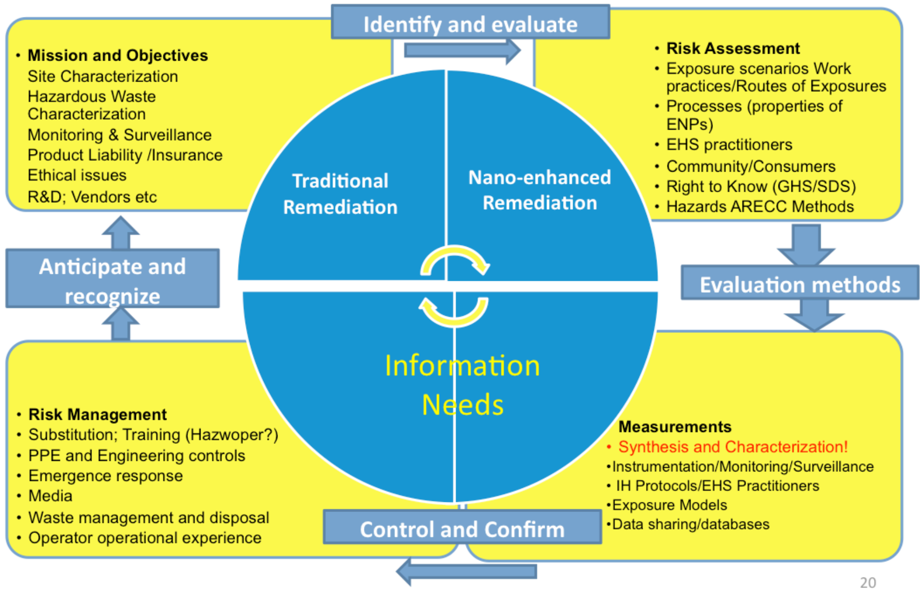
A framework for understanding information needs for regulatory and oversight actions during nanoremediation



Nano-information related issues of consideration

Safety issues

Fig 1.0 Nanoscale zero-valent iron may ignite spontaneously when it comes into contact with air.

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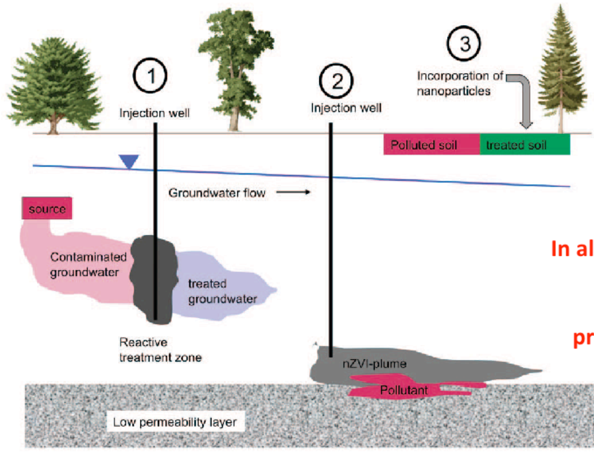
Information on physicochemical properties and other concerns in nano-enhanced remediation



In all the three treatment methods Described how do physicochemical properties being transformed?

Fig 2.0 In situ technologies used to treat polluted groundwater and soils: (1) injection of nZVI to form a reactive barrier; (2) injection of mobile nZVI to form an nZVI plume; (3) incorporation of NP into topsoil to adsorb or degrade pollutants

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Information on physicochemical properties and other concerns in nano-enhanced remediation

Fig 3.0 Mixing station where the iron particles in the slurry are re-suspended before injection.

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Information on physicochemical properties and other concerns in nano-enhanced remediation

Fig 4.0 nZVI slurry being poured into a well.

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Nanoremediation: the roles of EHS professionals

- There has been a great interest of the scientific community in nano-enhanced remediation
- A large amount of information related to environmental remediation case studies has been generated.
- Not so well structured to help with the IH work of exposure or risk assessment studies; or epidemiology etc…
- There is need for structuring the available documents and tools and organize the information

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Communication and Education Message and Audience Planning Tool for Understanding Information Needs of Various Professionals , Regulators for Safety and Health Protection of Nano-Remediation Workforce

Focus → / Information ↓	Workers	Health and Safety Practitioners	Management	Policy Makers and Regulators	Insurance/Lenders	Raw Material' R&D ; Manufacturing	Liability	Education and Training	Students	Media	Consumers	Society/Ethical Issues	Emergency Response (Police/ Fire)
Literacy/Critical Thinking													
Real-Life Examples													
Understanding practices													
Continuous Improvement													
Modeling/Sharing													
Assessment													

Information required or provided by various stakeholders - Nanoinformatics 2020 Roadmap, Hoover, M.D, 2011.

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Information availability and accessibility at the federal level

- Currently limited or no nano specific standards exist
  - NIOSH's REL TiO_2 (Ultrafine 0.3 mg/m^3) (fine 2.4 µg/m^3).

- *ENPs are "chemical substances" under TSCA (Statute)
  - Premanufacture Notifications (100 PRN received by EPA for various ENPs
- *Significant New Use Rule (SNUR) – §5(a)(2) TSCA – appropriate reviews needed by EPA for any manufacture, import or processing (Significant New Use Notice – SNUN to be submitted 90 days before activity begins)

- *Information gathering rule - §8 TSCA – production volume, methods of manufacture and processing, exposure and release information, and available health and safety data. - http://www.epa.gov/opptintr/chemtest/pubs/sect8a.html

  - * http://www.epa.gov/oppt/nano/

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Nano-related information for EHS oversight: availability and accessibility at the federal level

- Test rule – TSCA §4 – ENPs on the market to be tested - http://www.epa.gov/oppt/chemtest/pubs/sct4rule.html

- ENPs may be regulated under CAA (statute) – or U.S.EPA *40 CFR part 50 (National Ambient Air Quality Standards)* if they endanger workers and public health.
  - In this case, the role of the state governments will be to develop and implement SIPs, if the sites are close to urban centers or large cities

Nano-related information for EHS oversight: availability and accessibility at the federal level

- EHS (occupational and non-occupational) risks:
  - Nanomaterials be wastes in water effluents; or discharges; air contaminants or water run off
    - Currently, no Maximum Contaminant Levels (MCL) for ENPS
  - If airborne, ENPs may cover large areas and impact public health
- Discharge of the ENPs into water bodies may require special permits under CWA. States enforce regulations
  - Health effects (reproductive, developmental etc.)

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Concerns for state government agencies and programs in nano-enhanced remediation

– States may need to issue permits/licenses to contractors; vendors or transporters of ENPs; inspect or audit and enforce S&H plans or programs

– OSHA has approved S&H plans for 21 states to enable them enforce standards e.g. HAZWOPER

– State governments will play a key role to protect EHS across R&D; manufacture; transport; use and disposal of the ENPs, the need for relevant information is important!

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Readiness of state agencies to regulate synthesis, transportation, use and disposal of ENPs

- Although not closely related to nano-enhanced remediation, the city of Cambridge, MA requires:
  - Inventories of ENPs manufacturing or handling facilities;
  - Share technical advise with other stakeholders;
  - Share EHS updates with workers and communities;
  - Track R&D activities;
  - Track status of regulations and best work practices; and
  - Review changes in regulatory landscape every 2 years

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Nanoinformatics and EHS oversight
What are the relevant metrics of exposure?

1. Sampling and measurements of ENPs - too small to sample or measure?
    1. Do state have the capability?
    2. Exposure and health risk measurements and estimations?
2. Detection of contamination levels as airborne or waterborne
    1. Standardized operating protocols – OSHE, NIOSH, EPA etc.
3. Control of contamination to acceptable levels – airborne or waterborne
    1. ENPs better –substitutes – based on technical efficiency? Time? Cost?
    2. Engineering control? - Glove box? Conventional hoods? LEVs? GEV?
    3. Administrative control?
    4. Selection of PPE's – if we cant measure, we cant manage - how do we promote proper selection if without sampling or measurements?

Nanoinformatics and EHS oversight
What are the relevant metrics of exposure?

4. Metrics to evaluate biological effects – what would these be?
    1. Particle size?
    2. Particle shape?
    3. Oxidant generation?
    4. Surface functionality?
    5. Rate of dissolution?

These five parameters are believed to important determinant of exposure vs. biological response

5. Other physical and chemical properties of the ENPs – solubility, pH etc -

6. What is the dominating chemistry? And the dose response relationship?

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Exposure and Health Risks Assessments

- **Risk = Hazard x Concentration (Exposure)**
  - Do we need to redefine hazards of nanomaterials in the absence of exposure measurements
  - Chemical properties to be taken into account
    - Surface area
    - size, shape, solubility, brittleness, aspect ratio
  - Toxicity Info: short-and long-term cumulative effects
  - Genetic Changes [up or down regulation]
- **Mass or concentration or c**omputational models – to predict distribution of particles within each biological compartment; or use of the Monte-Carlo simulation models

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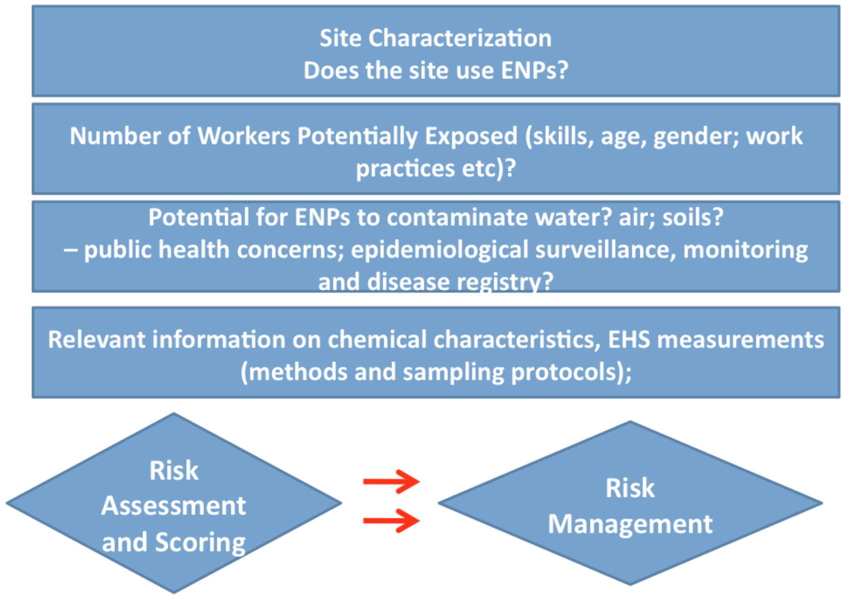
Flow diagram for a framework to understand the information needs of the state agencies



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Conclusion

- Health and safety of workers handling ENPs can be enhanced by accessing relevant information
- Researchers, scientists, manufacturers, vendors can provide the 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

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Conclusion

- Availability, access and sharing of information will lead to enhanced technical capability of all states in addressing EHS issues of ENPs!

- Survey questions to state agencies were based on this framework.

- Preliminary analysis of the responses received from agencies and programs across the country indicate that there is urgent need of information related to nanomaterials
  - Information on EHS,
  - Toxicity measurements and evaluation, and
  - EHS regulatory framework, including exposure standards.

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Conclusion

- Public health and workers' safety and health can be protected by limiting exposures to ENPs and other nanoparticles through precautionary approach and oversight mechanisms
  - This can be done by generating information necessary to set up standards and regulatory framework - based on science and relevant information
- At federal level a lot of work has been done, standards described – non-legally binding; some states have on-going activities; other states do not.
- Set up of Site Exposure Matrix (SEM) similar to the DOE's and DOL for Radiation Sites: ENPs/Health effects/Job Categories/Exposure/Risks

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United States Environmental Protection Agency

Thank You!

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Acknowledgement: LA-Board of Regent, Grant # LEQSF(2011) -Pfund-256 – NSF - Experimental Program to Stimulate Competitive Research (EPSCoR)

Q & A

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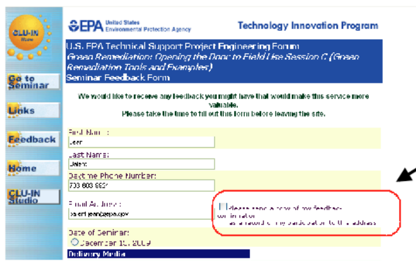

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