COMMONWEALTH OF MASSACHUSETTS
EXECUTIVE OFFICE OF ENERGY & ENVIRONMENTAL AFFAIRS
DEPARTMENT OF ENVIRONMENTAL PROTECTION
ONE WINTER STREET, BOSTON, MA 02108 617-292-5500

2nd ANNUAL MASSACHUSETTS NANOTECHNOLOGY WORKSHOP

PROCEEDINGS FROM THE JANUARY 29, 2009 WORKSHOP

Promoting the Safe Development of Nanotechnology in Massachusetts

Hosted by:
The Massachusetts Interagency Nanotechnology Committee:

- Department of Environmental Protection
- Department of Public Health
- Division of Occupational Safety
- Executive Office of Housing and Economic Development
- Office of Business Development
- Office of Technical Assistance and Technology
- Toxics Use Reduction Institute

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Acknowledgements

The Massachusetts Interagency Nanotechnology Committee is extremely grateful to a number of individuals who committed their valuable time and expertise to bring this Workshop to fruition.

Facilitators

- Carol Lynn Alpert, Boston Museum of Science
- Dhimiter Bello, University of Massachusetts, Lowell
- Lucy Edmondson, Massachusetts Department of Environmental Protection
- Pam Greenly, Massachusetts Institute of Technology
- Laura Hodson, National Institute for Occupational Safety and Health
- Jackie Isaacs, Center for High-rate Nanomanufacturing, Northeastern University
- Todd Kuiken, Project on Emerging Nanotechnologies, Woodrow Wilson International Center for Scholars
- Sam Lipson, Cambridge Public Health Department
- Elizabeth Mason, Goodwin Procter, LLP
- Jo Anne Shatkin, CLF Ventures

Federal Reserve Bank

- Jenna Labissoniere

Presenters

- Dr. Michael Ellenbecker, Center for High-rate Nanomanufacturing, University of Massachusetts, Lowell, Toxic Use Reduction Institute
- Dr. Charles Geraci, National Institute for Occupational Safety and Health, Ohio
- Laura Hodson, National Institute for Occupational Safety and Health, Ohio
- Dr. Su-Jung (Candace) Tsai, University of Massachusetts, Lowell, Toxic Use Reduction Institute

The University of Massachusetts Donahue Institute

- Leslie Ackles
- Chris Banwarth
- Anne Fitzgerald
- Morgan Mihok, Conference Liaison and Interagency Nanotechnology Committee*
- Susan McAndrew
- Leslie Smythe

The Interagency Nanotechnology Committee also appreciates the efforts of numerous individuals who provided outreach, web and operational support. Lastly, the workshop participants provided lively breakout session discussions with many ideas for promoting protection of workers, public health and the environment.

* Morgan Mihok contributed a huge effort to all aspects of the workshop.

Workshop Proceedings

Promoting the Safe Development of Nanotechnology in Massachusetts
January 29, 2009
Federal Reserve Bank
Boston, Massachusetts

1. Background

In April 2007, the Massachusetts Interagency Nanotechnology Committee was formed to discuss and gain a better understanding of the emerging field of nanotechnology. The collaborating agencies currently include the Massachusetts Department of Environmental Protection (MassDEP), Department of Public Health (MDPH), MA Division of Occupational Safety (DOS), MA Office of Technical Assistance and Technology (OTA), the Toxics Use Reduction Institute (TURI), the Massachusetts Executive Office of Housing and Economic Development (EOHED) and Office of Business Development (MOBD). The collaborating agencies have different authorities and bring diverse interests to Committee forums, allowing for more comprehensive discussions of the nanotechnology sectors in Massachusetts. Appendix A lists the members of the Interagency Committee.

Since the 1st workshop on the "*The Big Picture: Safe Development of Nanotechnology*" in 2007, there have been significant advancements in the emerging field of nanotechnology, from expanded research to new product development. One of the priorities of the Massachusetts Interagency Nanotechnology Committee has been to track these advancements, especially the development of "best practices" to protect workers, the environment and human health.

With that in mind, the Interagency Committee on Nanotechnology decided that best practices should be the focus of the second workshop, "*Promoting the Safe Development of Nanotechnology in Massachusetts,*" which was held on January 29, 2009. The workshop content included a discussion of health and safety practices, breakout sessions on the lifecycle of nanotechnology products and appropriate applications of best practices and good current practices, and a training session on state-of-the-art measurement techniques for nanoparticles.

There were 170 attendees from academia, industry, federal, state and local governments, environmental consultants, law firms, insurance companies and nonprofit groups. The nanotechnology workshop was a success, based upon the evaluation forms. Participants thought the workshop was an excellent platform for everyone to get updated on the new field, provided a chance to learn and exchange ideas and was a great tool for knowledge transfer. Please refer to Appendix B for the list of workshop attendees.

II. Workshop Welcoming Addresses

Commissioner Laurie Burt of the Massachusetts Department of Environmental Protection and Commissioner Laura Marlin of the Massachusetts Division of Occupational Safety provided welcoming remarks, reflecting the complementary roles of their respective agencies to protect the environment, public and occupational health. Appendix C contains a copy of the Welcome letter from the Commissioners to the workshop participants.

The Commissioners highlighted that nanotechnology may usher in the next industrial revolution and replace much of our manufacturing base with new products. Materials and devices at the nanoscale hold a vast promise for innovation in virtually every field, including energy, the environment, medicine, electronics, and transportation. In addition, nanotechnology is an important driver of our local economy. The Commonwealth is a leader in nanotechnology research and technology development, with over 100 self-identified firms, and major research centers at most university campuses. Dollar for dollar Massachusetts attracts more investment in nanotechnology research and development than almost any other state.

The new engineered nanoparticles currently in development and in use have novel biological and chemical properties, and there is insufficient information about their affect on human health and the environment. Sharing information on best practices at the second workshop was a great opportunity for all interested parties to come together – academia and industry, government and law – to share information about preventative steps to safeguard public health and the environment. This approach is consistent with the guiding principle of Massachusetts' collaborative work, to take a proactive approach that is protective of the public and the environment, as well as helping industry avoid unwanted impacts.

The Commissioners acknowledged the workshop's noted plenary guest speakers, Dr. Charles Geraci from the National Institute for Occupational Safety and Health, Dr. Michael Ellenbecker from the Center for High-rate Nanomanufacturing, and the Toxic Use Reduction Institute, University of Massachusetts, Lowell, Laura Hodson, National Institute for Occupational Safety and Health, and Dr. Su-Jung (Candace) Tsai, from the Center for High-rate Nanomanufacturing and the Toxic Use Reduction Institute, University of Massachusetts, Lowell. Appendix D provides biographies of all the speakers at the workshop.

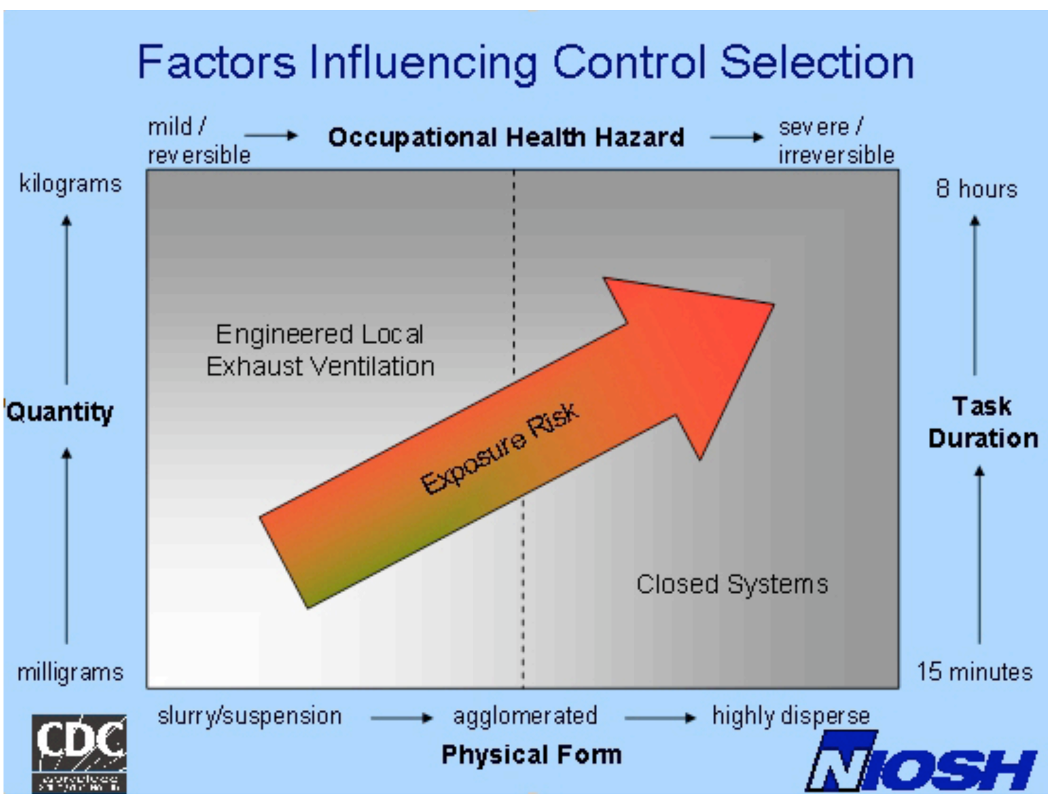
III. Overview of Interim Best Practices and Good Current Practices

a. Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials

Dr. Charles Geraci, CIH, Coordinator, Nanotechnology Research Center and Chief, Document Development Branch, National Institute for Occupational Safety and Health (NIOSH)

Dr. Geraci's presentation slides are located at the following link: http://www.mass.gov/dep/toxics/stypes/geraci_prac.pdf. The presentation began with an introduction covering basic information on nanoparticles, potential health risks, how 'engineered' nanoparticles are distinguished from naturally occurring nanoparticles and manmade nanoparticles that are produced as industrial by-products. Information was then presented on the broad spectrum of current uses and applications of engineered nanoparticles. NIOSH has been working to provide basic health and safety guidance as a starting point for building an effective workplace nanomaterial risk management program. It represents a summary of NIOSH's current thinking and recommendations for occupational safety and health practitioners, researchers, product innovators and manufacturers, employers, workers, interest group members, and the general public to help ensure that no worker suffers impairment of safety or health as nanotechnology develops. The program considers the lifecycle of engineered nanoparticles from laboratory to production settings and the range of possible exposures at each step. The guidance considers hazards, exposures, risk characterization and risk management, which provide a basis for offering selective controls to protect workers. Dr. Geraci provided workshop participants with a compact disc containing an update to NIOSH's *Approaches to Safe Nanotechnolgly: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials*, January 2009 (document available at: http://www.cdc.gov/niosh/docs/2009-125/)

Dr. Geraci's presentation included a slide on the Factors Influencing Control Selection, as shown below. The factors include: the quantity of nanoparticles being handled, their physical form (e.g., dry powder or slurry formulation); duration of the task; and occupational health hazard (e.g., mild or severe irreversible effects). These factors can be used to identify lower and/or higher risk situations, as indicated by the "Exposure risk" arrow, in which different controls can be employed to protect workers. For example, local exhaust ventilation would be an appropriate control for a worker using a small amount of nanoparticles in a slurry for a short period of time whereas exposure risks could be reduced for a worker handling dry or highly dispersible nanoparticles for short time periods by employing a closed system.



Dr. Geraci's presentation covered several examples of small laboratory tasks where work in a ventilated bench top would be preferred over general room ventilation and personal protective equipment. A best practice for mixing carbon nanofibers into a resin would include a closed mixing container for production work. Particle counts can be used to determine where releases may be occurring during production work. Dr. Geraci concluded that 1) nanotechnology is amenable to effective risk management from synthesis to production; 2) many of the controls currently in use for ultrafines and fine particles can be applied to nanoparticle processes; 3) each situation should be evaluated to match the control with the task; and 4) gaps need to be identified as use of the technology continues to expand.

In closing, Dr. Geraci highlighted the NIOSH Nanotechnology Field Research Team which partners with research laboratories and companies working with nanoparticles to assess workplace processes, materials, and control technologies associated with nanotechnologies and conduct on-site assessments of potential occupational exposure to nanomaterials. Through this effort, NIOSH confidentially gathers baseline data to assist in determining potential occupational safety and health implications of exposure to engineered nanomaterials and recommends safe work practices and evaluates exposure control measures. Appendix E contains a copy of the NIOSH Fact Sheet on this opportunity for research laboratories, companies and others working with nanoparticles to partner with NIOSH.

b. Interim Best Practices for Working with Nanoparticles

Dr. Michael Ellenbecker, Toxics Use Reduction Institute and Center for High-rate Nanomanufacturing, University of Massachusetts, Lowell

Dr. Michael Ellenbecker's presentation slides can be found at http://www.mass.gov/dep/toxics/stypes/becker_bp.pdf. Dr. Ellenbecker provided background information on the Center for High-rate Nanomanufacturing (CHN) which is funded by the National Science Foundation and represents a collaborative effort of four Universities: the University of Massachusetts, Lowell, MA; Northeastern University, Boston, MA; the University of New Hampshire, Durham, NH; and, Michigan State University, East Lansing, MI. As a result of actual measures of nanoparticles within CHN laboratories where workers could be exposed, these higher education institutions saw the need to develop best practices for protecting the health and safety of laboratory personnel as well as the outdoor environment. In recognition that other research laboratories could also use guidance and due to a lack of government regulation in this area, Dr. Ellenbecker, Su-Jung (Candace) Tsai, ScD, CHN, and Jacqueline Isaacs, PhD, CHN, Northeastern University, co-authored *Interim Best Practices for Working with Nanoparticles.* This document is available at: http://nsrg.neu.edu/environmental. NIOSH has awarded Drs. Ellenbecker and Tsai with a grant for a new, more comprehensive workplace practices document, "*Safe Practices for Working with Engineered Nanomaterials in Research Laboratories*." It will be available in the fall of 2009.

Dr. Ellenbecker's presentation focused on protecting the health of researchers and the management of nanomaterials to minimize their environmental impact. Regarding worker exposure, he covered four principles to guide best practices for routine research and development (R&D) laboratory operational needs:

- Basic principles: Basic principles should be aimed at minimizing the risk of exposure to nanoparticles. Nanoparticles in a dry form pose the most risk for inhalation exposure whereas nanoparticles suspended in a liquid present less risk from inhalation exposure but may present a greater risk from skin contact
- Control preferences: Control preferences should follow a graded approach where it is preferable to keep particles fixed in a matrix or bound in solution. Use of free nanoparticles should be a last resort.
- Occupational hygiene controls hierarchy: The occupational hygiene hierarchy of controls includes engineering controls (e.g., substitution, isolation and/or ventilation); administrative controls (e.g., worker training, medical monitoring) and personal protective equipment (e.g., respirators, protective clothing, etc.).
- Ventilation design principles: All ventilation systems should be evaluated, approved and maintained by university health and safety officers. Laboratory personnel should never design their own system and/or modify an existing system. Ventilation systems should be maintained on a routine basis by the appropriate university maintenance personnel.

Dr. Ellenbecker stressed the importance of ventilation design principles, described several types of hoods, and discussed information on proper laboratory fume hood performance. The most important variables for proper hood performance are: hood design; face velocity (80 – 100 ft/min); sash position; laboratory conditions; and work practices in the hood.

Dr. Ellenbecker proceeded to provide highlights of CHN's *Interim Best Practices* by discussing that working in enclosures may be a better alternative to using a ventilated hood, for example with dry nanopowders. He discussed the importance of administrative controls such as mandating good housekeeping practices for laboratories where nanomaterials are handled; cleaning all working surfaces potentially contaminated with nanoparticles at the end of each day using a high efficiency particulate air (HEPA) vacuum pickup and/or wet wiping methods; and prohibiting sweeping or using compressed air where nanoparticles may be present. Examples of other good work practices included transferring nanomaterial samples between workstations in closed, labeled containers and using an appropriate hood and respirator or enclosure when nanoparticle powders must be handled. He provided several examples of protective clothing (e.g., gloves) and respirators and described using performance and collection efficiency information for surgical masks and HEPA filters, respectively.

With regard to the environmental impact of nanomaterials, CHN's *Interim Best Practices* also address nanomaterial wastes and specifically promote the management of these wastes as a hazardous waste with proper labeling of containers containing engineered nanomaterials. The *Interim Best Practices* guide also describes the type of waste streams that must be managed in this manner. Dr. Ellenbecker also discussed the proper management of a nanomaterial spill, noting that a HEPA vacuum cleaner has a collection efficiency of >99.97% for 0.2 micrometer diameter particles. Dr. Ellenbecker closed by stating the need for a consensus on best practices for research laboratories, and that the document being prepared under NIOSH funding will provide a step in that direction.

IV. Case Scenarios: Application of Interim Best Practices and Good Current Practices

Four different case scenarios were provided for the breakout sessions, including: paint with silver nanoparticles; groundwater remediation with iron nanoparticles; sunscreen with titanium oxide and zinc oxide nanoparticles; and carbon nanotubes in a research setting. These sessions were designed to provide the participants with an opportunity to apply the best and good current practices to each case scenario, and the goal was for participants to address the following key questions:

-Where can the best and current practices you heard about this morning be applied to the product lifecycle sections you are discussing?
-Are these practices feasible and realistic for nanopractitioners?
-Where are there gaps in the recommended practices? Are there other available practices documents that address those gaps?
-What specific steps can state agencies take to complement the national and international efforts to promote the safe development of nanotechnology? How can state agencies and other stakeholders most effectively work together to bridge the gaps indentified in the breakout session?

The following section briefly describes the scenarios and the discussion of all of the participants in each session. The discussion does not represent Massachusetts state agencies positions. Please refer to Appendix F for a full description of each case scenario and its associated background information.

V. Reports from Breakout Sessions, Next Steps and Concluding Remarks

Following is a summary of the case scenarios and participant feedback.

a. Paint with Silver Nanoparticles Break-Out Session: Occupational exposure, industrial production, application and disposal

This scenario involved a decision to use a new paint containing antimicrobial silver nanoparticles within a school building, because of the manufacturer’s claim that it will be a defense against germs. The contractor sought information about whether he needed to follow any special precautions while applying the paint and cleaning brushes (e.g., rinsing brushes with tap water entering the drain). Several parents learned that the school would be coated this nanoparticle-containing paint and were concerned, because they’d read that the US Environmental Protection Agency (EPA) was regulating silver nanoparticles in washing machines, and it was unclear as to whether the paint would pose a risk to the school population and upset the town’s wastewater treatment system.

1. **Where can the best and current practices you heard about this morning be applied to the product lifecycle sections you are discussing?**
   - During paint manufacturing, the NIOSH’s *Approach to Safe Nanotechnology* provides guidance to protect the worker, especially from dry nanoparticles. This should result in attention to controls when dry ingredients are added to wet ingredients, which is where

the greatest risk for exposure occurs. Enclosures for mixing and ventilation will be applicable.

- EPA Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) will apply to labeling and disposal of paint if it makes anti-microbial claims.

2. Are these practices feasible and realistic for nanopractitioners?

- Yes, for larger manufactures as they already know safe practices from handling ingredients like carbon black.
- It may be difficult in a small manufacturing business to realistically apply those practices. Sometimes the paint application requires adding dry pigments to the wet carrier in the field or in a small shop where engineering controls may be non-existent.
- New consideration: are these practices feasible and realistic for current situations where toxicants other than nanoparticles are being used?

3. Where are there gaps in the recommended practices? Are there other available practices documents that address those gaps?

- Labeling- There are no requirements to list nanoparticle content for the end user either on the label or on the Material Safety Data Sheets (MSDS)
    a. MSDSs are only required to list known hazards, there is no requirement to list these unresolved hazard and exposure questions. There is no requirement to identify nanomaterials.
    b. EPA FIFRA only applies if the nanosilver product makes fungicide claims.
- Toxicological gaps/questions:
    a. Is the dried paint dust harmful?
    b. Is it available for absorption once it has dried?
    c. Can the silver nanoparticles be dermally absorbed?
    d. Do the silver nanoparticles bioaccumulate?
    e. If a painted surface with silver nanoparticles is in a fire, will nanosilver be released to the community?
    f. Do the experiences with titanium dioxide and the enhanced toxicity of ultrafine TiO_2 raise the same concerns regarding nanosilver[1]?
- When and how will longer term lifecycle issues be addressed?
    a. For example, what is the potential for leaching of nanoparticles from paint into groundwater?
    b. What is the mobility of these nanoparticles?
    c. How are they dispersed and deposited after sanding painted surfaces?
    d. What are the environmental fate, potential bioaccumulation, and effects on water treatment plants?
- There is little information regarding the risks of nanoparticles in latex versus oil-based paint, the mobility of the particles from the paint matrix into the air during aerosolized

- [1] Kumazawa, et al. in their study, "Effects of Titanium Ions and Particles on Neutrophil Function and Morphology" concluded that cytotoxicity (danger to the cell) was dependent on the particle size of titanium dioxide. The smaller the particle size, the more toxic it is. Biomaterials 2002 Sep 23 (17): 3757-64.

paint application, while drying, and/or during washing or sanding of dry paint at a later date. This would be important in recommending brush and roller instead of spray paint application, as well as ventilation recommendations and best practices for sanding operations.

- Incomplete information on protective measures regarding gloves and respirators specific to latex and oil paints containing nanosilver. Would the recommendations be any different for nanosilver containing paint versus paint with no added nanoparticles?
- Guidance is needed for disposal and cleanup. This will apply to overspray wherever nanosilver paint is applied, and to cleaning of brushes, materials and protective clothing. FIFRA prohibits disposal of silver, however if the manufacturer makes no fungicide claims then FIFRA may not apply.
- Need for rethinking hazards. Previously, "less is better," has been guidance for reducing exposure. Now, although the total mass quantity of material is reduced, the hazard may be greater.
- There are no worker exposure limits (Recommended Exposure Limits, Permissible Exposure Limits or Threshold Limit Values) specific to nanoparticles.
- Missing guidance/regulation from the U.S. Occupational Safety and Health Administration (OSHA).
- Missing guidance from the Consumer Safety Product Commission (CPSC).
- Will the amount of nanosilver in wastewater, for example, be lower than the analytical technique's limit of detection?

4. What specific steps can state agencies take to complement the national and international efforts to promote the safe development of nanotechnology? How can state agencies and other stakeholders most effectively work together to bridge the gaps indentified in the breakout session?

- Education is an important factor. States can potentially require nanoparticles to be labeled. California is doing this.
- Participate in the National Nanotechnology Initiative looking at life cycle issues.

5. Additional thoughts

- Other technologies may be used for controlling silver nanoparticles. For example, if the dry ingredients could be obtained in gel pacs or other dissolvable packaging, the dry powder would less likely to be released in the manufacturing environment.
- It was suggested that nanosilver paint could be chemically tagged with an identifier so that future generations would know that the paint contained nanosilver. This may be important for anyone sanding or removing the paint in the future.
- Do clothes washed in a washer lined with silver nanoparticles retain silver particles that may be dermally absorbed by the person wearing the clothes?
- Washing machines with silver nanoparticles built in for antibacterial purposes may be contaminating the water supply and killing good bacteria in water treatment plants.
- Controls are available for manufacturing processes, however once paint with silver nanoparticles are regularly available for consumer purchase, what will be the trickle-

down effect to consumers and the environment? Will paint with nanoparticles even be labeled to even allow consumers to take precautionary steps?

b. Groundwater Remediation with Iron Nanoparticles: Use of Nanoparticles (Zero valent iron) for Site Remediation

The subject of this case scenario is a proposal to inject zero-valent iron nanoparticles (nZVI) into the groundwater at a hazardous waste site in Massachusetts in order to cleanup a plume of chlorinated solvents. This is a relatively new technology that has been piloted by the US Environmental Protection Agency (EPA), although non-nano iron has been used for a while. Local officials and other residents in the scenario raise questions about whether or not the nanotechnology under consideration for remediation poses a threat to the environment, especially if nanoparticles migrate to a nearby public drinking water supply, leading to human exposure. To address local concerns, a public meeting was held with an EPA expert on nano-remediation who would explain the technology and answer questions from the public.

1. **Do any of the best practice documents address nanoparticles that will be released into the environment?**
   - Transporting nanoparticles in slurry, rather than as a powder, would help to avoid exposure through inhalation.
   - As a general practice, cleanup programs could require periodic water chemistry testing and evaluation of plume contaminants. This is required by the New Jersey Department of Environmental Protection, which has developed a large data base of water chemistry information.
   - Respirators are effective in the event of a spill.
   - Since the best practices focus on worker protection issues, they don't seem applicable to broader site cleanup environmental issues.

2. **Where are there gaps?**
   - Questions were raised about how these nanoparticles react in the environment: If there is a release of nanoparticles (in air or groundwater), do they travel far? A participant responded that the iron injected into groundwater ultimately adheres to the soil. In addition, when nano-sized calcium peroxide (a different, related technology) is used, it breaks down the contaminants and contaminant constituents become part of the soil environment. In time, the calcium peroxide will begin to release oxygen and becomes calcium oxide, which also becomes part of the soil.
   - To what extent has use of nanoparticles for drinking water remediation been studied? What happens when the particles migrate? Are there unintended consequences from the migration of the nZVI? Do they cause the release of other materials/contaminants? Are the breakdown products also nano size? Are there secondary consequences? Iron occurs naturally and is not a concern, but will "manufactured iron" act and react differently?
   - It was mentioned that studies show that nanoparticles can bind to other particles, such as titanium oxides that mobilize arsenic.

- Most studies show nZVI as not having good enough mobility to keep reacting with contaminants in the groundwater plume, rather than the nZVI migrating far from the injection site.
- Would nZVI interact with biological species? Is there a sense of how iron nanoparticles interact with tissues of humans and nonhumans?
- Are there measurement techniques available, especially for nZVI? What levels would we expect to see in the groundwater post-treatment? What levels are toxic? A participant stated that current monitoring methods are not good for tracking nanoparticles in ground water.
- Is nZVI more or less expensive per unit of cleanup than other alternatives? A participant indicated that EPA and private companies show preliminary significant cost savings, if nZVI is directly injected (i.e., not part of a containment wall), particularly compared to pump and treat systems, which have ongoing energy costs.
- Non-nano particles now are coated with palladium and other metals to make them more mobile and more reactive. Particles are emulsified to get to dense non-aqueous phase liquids (DNAPL) and other non-aqueous phase liquids (NAPL). What is their impact as compared to nanoparticles?
- What is appropriate emergency response for nZVI spills during transportation or explosions? Is it transported in tankers or railroads that go across waterways? Is it classified as hazardous material? Does the material require manifesting?

3. What specific steps can state agencies take to complement the national and international efforts to promote the safe development of nanotechnology? How can state agencies and other stakeholders most effectively work together to bridge the gaps indentified in the breakout session?

- MassDEP could partner with the responsible party and vendor to do research on the effectiveness and impacts of nZVI, rather than put the burden on the responsible party alone. Given MassDEP's privatized cleanup program, research might need to be done at a Federal site or a state-lead site.
- There was sense that this type of innovation comes from the top down. The State could lobby Federal agencies (i.e., Department of Defense remediation sites, US EPA federal Superfund sites) to fill the information gaps.
- DuPont has assessed the use of nZVI and won't use it in the remediation of the company's own sites because there are too many uncertainties. The state should assess and consider DuPont's conclusions.
- There needs to be guidance and background information to MassDEP staff so they can answer questions from the public in communities where nZVI may be used.
- Nano particles may result in better/faster cleanup rates. They allow for *in situ* remediation. The use of long-term pump and treat systems isn't required, energy use is lowered, and you don't have to dispose of the captured/secondary materials. The state could identify opportunities for this application, given the desire to minimize energy use and waste disposal issues. MassDEP could consider providing guidance for when to use nanoparticle remediation.

- Are there any notification requirements? Should there be? Could we utilize the existing federal and state Right-to-Know laws? Is there a potential role for Licensed Site Professionals in notification? Local Boards of Health and the fire and police departments need this information. Is it a concern for first-line responders? Information is needed for planning purposes, making it available before an incident. It's beneficial to have learned from the best practices that respirators could work and we should let responders know that.
- It was suggested that the state could explore the use of MA Toxic Use Reduction Act (TURA) for reporting purposes. The TURA petition process was outlined – it begins with a petition to the TURA Administrative Council to list the chemical; the Science Advisory Board assesses its toxicity and the Toxics Use Reduction Institute (TURI) analyzes its use in Massachusetts in the applicable manufacturing processes; and a recommendation is ultimately made to the Council for its action, i.e., adoption as listed TURA chemical. The use metrics for nano particles would need to be redefined given the nature of nanoparticles. Such modifications have been done in the past to deal with mercury and dioxin for example. In addition, listing as a TURA chemical will only provide use data, if there is a Massachusetts manufacturing company with certain number of employees making nZVI or using it in sufficient quantities.

4. **Additional Thoughts**
   - This scenario is the opposite of the precautionary principle. There are too many uncertainties and gaps that need to be filled.
   - MassDEP has a privatized system and most Responsible Parties and Licensed Site Professionals are hesitant to use a new technology such as nanoparticles and tend to stay with remediation practices that are more familiar and proven. Use of nanoparticles for cleaning up drinking water contaminants could be beneficial, but more certainty is needed.
   - Traditionally, in remediation, the stoichiometric amounts needed for the reactions are known. Is nZVI at that level of knowledge? A participant indicated such information is available, but the potential problem is that there may be incomplete breakdown of the contaminants in the groundwater, with formation of secondary substances that are more problematic (e.g., toxic or mobile).
   - How could nanoparticle remediation work on polychlorinated biphenyls (PCBs) and lead? If the iron is emulsified, it gets to dense nonaqueous phase liquids (DNAPL) sites, but there are times that it "rebounds" if enough iron isn't injected. You can also get secondary pollutants (i.e., vinyl chloride). There is a need for a host of clean up techniques, since nZVI can't remediate lead.
   - Calcium peroxide has been used in remediation of petroleum contaminated groundwater. Use of the 50 nanometer particles in slurry eliminates exposure to applicators. The calcium peroxide is transported and injected as slurry into the contaminated groundwater. A proponent suggested by using this material, you can meet MassDEP cleanup standards in 30 days.

c. Sunscreen with titanium oxide and zinc oxide nanoparticles

This case scenario involved sunscreen being sold at a local pharmacy and a health food store. The pharmacy featured a display of sunscreen with titanium and zinc oxides, which claimed that mineral-based sunscreen reduces concerns about allergic reactions and provides better ultraviolet A protection than traditional sunscreens. On the other hand, the health food store only sold those sunscreens that did not contain nanoparticles and were declared safe in the Friends of the Earth (FoE) Sunscreen Guide[2]. The scenario focuses on consumers' concerns about the safety of sunscreens, particularly their use on children. When it's proposed that information on the sunscreen containing nanoparticles be distributed to parents, there is hesitancy to distribute information that cannot provide clear data upon which to make a choice. How can the public be provided information about the potential risks of products and about uncertainty without causing confusion, panic, commercial problems, and related issues?

Prior to addressing the key questions for the session, the breakout session participants had an initial discussion, including the following points:

- The Friends of the Earth report indicates which sunscreens were known or suspected to have nanoparticles in them, and grades them on a "traffic light" scale with nanoparticle content being "red", no content being "green," and unknown being "orange"; however, the report does not make any specific health claims regarding the nanoparticles. This system presumes nano sunscreens are unsafe and non-nano (e.g., traditional chemical sunscreens or non-nano mineral sunscreens) are safe. This could cause people to change behavior, but does not provide specific guidelines as to why.
- There are potential benefits of having these nanoparticles in the sunscreen, including better performance in the specific ultraviolet (UV) range, avoiding allergic or other sensitivity effects that exist for ingredients of the traditional sunscreens, and ease and acceptance of use of a clear creamy product. Sunscreens can protect against skin cancer and sunburn which are public health issues.
- The U.S. Food and Drug Administration (FDA) has some authority over sunscreens, but have pretty much declined to scrutinize them for 30 years. The FDA is apparently coming out with something on sunscreens; a document for public comment may be available now or soon. FDA is certainly one of the likely regulatory authorities on the subject.
- The group discussed "organic" sunscreens, which are the traditional chemical ones, and "mineral" sunscreens which contain zinc and titanium oxides. The clear "mineral" sunscreens are the ones most likely to contain nanoparticles. A group participant mentioned that she'd heard the traditional types were "four times more likely" to contain a hazardous constituent.

The group then focused on some of the key questions and other relevant issues.

1. What responsibility does the sunscreen manufacturer have for communicating information about ingredients? What information will parents be able to gather from the label?

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[2] http://www.foe.org/nano_sunscreens_guide/Nano_Sunscreens.pdf

- There is no federal law for labeling the nanoparticles now, and none is likely in the near future.
- What is the incentive for voluntary disclosure from the manufacturer's perspective? There only is an incentive if disclosure presents a plus to the product. Some participants thought that disclosure might cause not only a negative initial reaction, but also some continuing liability issues including Resource Conservation and Recovery Act (RCRA).
- Manufacturers should have some sort of profile on the products, but some may not even be able to answer a technical question about it.
- One participant described the label on a soap product, which said something about the presence of the nanoparticles and directed those who wanted more information to a company website. The company website will not be unbiased information, but may provide a starting point for a consumer.
- Is there a role for government, local or otherwise?
- What benefits are there to labeling or other disclosure: perhaps liability protection (i.e., we told you it was there), right-to-know, fostering consumer choice, marketing will exploit positive attributes. One participant mentioned "photo catalysis" of the nanoparticles in sunscreens and said that this might be a reason companies should label products, from a liability standpoint.
- Before a label would help, awareness needs to be raised in consumers so they can understand the information on nanoparticles in general as well as the specific ones added to the product.
- If there's uncertainty, would a label be prudent? Or would it be singling out one aspect that might be risky while another aspect might be even more risky? Is the information even available elsewhere? One participant mentioned the Consumer Reports article where the writers were unable to get an answer about the presence of nanoparticles in many of the products.
- Another point made is that all zinc or titanium oxide based sunscreens have probably contained some nanoparticles, since the sizes would be in a range and some would be small enough. The more modern "nano" sunscreens ones just have a higher proportion of these participles and more consistency in these particles. In this case, how much is enough to cause health and environmental damage?
- What do consumers want versus what the company wants to provide versus what companies even know? This issue is not only complex from that standpoint, but complex from a risk standpoint, since there are many factors there. Is the side of the product (e.g., a label) the best place to try to make this point?
- What is actual risk versus perceived risk? How do you explain a probabilistic risk assessment to a consumer?
- How is this like other products (e.g., cigarettes) that have known risks? How did companies behave regarding that and how does that inform this discussion?
- This is an emerging issue, and nobody has the answers yet. If a company wanted to be responsible, to their customers and also to their shareholders, how should they behave?
- One participant mentioned that her "mother's group" had been talking about nanoparticle sunscreen and were concerned and felt negatively about it . These

mothers think it's risky to their children. "Nano sunscreens go on clear". It's just an aesthetic issue. Information is available but not consistently.
- The simple concept is often wrong. How can "we" communicate clearly about a complicated matter? Clarity of message is often opposed to transparency of operation.

2. Are there any good practices that are applicable during this scenario?
- The group agreed that the good practices discussed earlier weren't very applicable in this case since this is consumer use issue.

3. What is the appropriate way to dispose of unused sunscreens and cosmetics? What information should the manufacturer provide on product use and disposal?

- Given the fact that the health impacts of a nanomaterial can change based on its chemical environment, who is responsible for developing toxicity information? The cosmetics company or the nanoparticle manufacturer?
- End of lifecycle analysis is not often included in product development especially for cosmetics.
- There is little consensus even on how to destroy some nanoparticles – incineration is basically how they are made so it cannot be relied on to degrade them and the metals remain regardless.
- The use of the product involves environmental exposure (surface waters, etc.) and washing it into wastewater plants. Any claimed disposal method that doesn't take this into account will make the message incomplete or inconsistent. This may also scare people from use ("Oh my goodness, I'm putting hazardous waste on my face") and spoil the market.
- Unknowns include: bioavailability in the waste stream under various conditions, its affect on a treatment plant, and particles' behavior. How might this issue relate to the current hot topic of drugs in wastewater?
- Would special instructions unfairly categorize the more "exotic" nanoparticles from all other constituents?
- Can EPA regulate (under FIFRA, RCRA, etc.)? RCRA/Superfund is cradle to grave liability no matter when the hazard is discovered but is likely to be specific to nanoparticle types. What about EPA and the Toxic Substances Control Act (TSCA)? Where does burden of proof rest?
- What about product liability issues, including fraud, failure to warn, end of lifecycle issues? Is this going to be the de facto regulatory mechanism?
- Are there studies that evaluate absorption of nano sunscreen in body? Friends of Earth and the Environmental Working Group have reports on a number of studies. Some studies have found that when nanoparticles permeate cell walls, reactive oxygen species may be created and intracellular components may be affected.
- Should there be authority to include nanoparticles on Material Safety Data Sheets? Also, in Superfund, liability can be retroactive. But that's an incentive for manufacturers who won't advertise pre-acknowledgement.

4. What are other sources of information about cosmetics' ingredients? How should the potential health and environmental risks be communicated to individuals, especially if the results are not conclusive? What do we, as concerned individuals, have control over? Where can we go for data?

- Are there any studies that evaluate the risks? There are some studies showing no absorption through skin of these particles.
- Spraying may be a hazard due to aerosolization of the nanomaterials.
- Other sources of information: cities can help disseminate information, but aren't responsible for a large enough area to make much of an impact. Given the lack of information available, the Interagency Nanotechnology Committee and MDPH should determine the appropriate federal agency to address consumer questions about potential health and environmental risks associated with the use of nanotechnology in cosmetics.
- What about medical offices as another way to get information to people?
- The National Institutes of Health has a database of household products and hazards (see http://hpd.nlm.nih.gov/). Is this something that already does or could eventually include nanomaterials? It provides information for common products with hazards (e.g., cleaners).
- Where do you decide to communicate? Total transparency (which may provide confusion, conflict and complex information) on one end and complete clarity (which may take a lot of time).Where should we aim our information? Is this like the DPH information on fish consumption advisories: benefits versus risks?
- Ingestion is a real pathway for a product like sunscreen – should we be looking for these risks as well as the dermal/inhalation pathway?

5. Additional Thoughts:

- What about ingestion issues and children? Someone suggested looking to Europe (e.g., REACH or Registration, Evaluation, Authorisation and Restriction of Chemical substances) for nano guidance.
- Does it make sense to create a graded scale on relative risk, based on how products are used, and on the toxicity of the product? Yes/no on toxicity doesn't seem to be adequate.
- If you're looking at the risk specific to nanotech you want to consider benefits of sunscreen as well.

d. Carbon Nanotubes in a Research Setting

This case scenario is directed towards a professor's investigative work on the incorporation of carbon nanotubes (CNTs) into resins to give them specific electrical and thermal conductivities.

The researchers are concerned after a spill of some purchased CNTs on the edge of a hood. Although the spill was wiped up with wet towels as recommended by the Environmental Health and Safety (EHS) person, CNTs had dispersed in a fairly large area. The researchers and students were also concerned about an article linking CNTs to similar responses to asbestos in the lung lining. Students were concerned about their exposure and wondered whether the CNTs were released during sawing of the cured resins. The EHS officer was called in to discuss the concerns.

1. Where can the best and current practices you heard about this morning be applied to the product lifecycle sections you are discussing? Are these practices feasible and realistic for nanopracticioners?

- The guidelines presented this morning are reasonable for controlling exposures.
- Enclosure seems to be the preferred method, with glove boxes inside of hoods, ventilated balances for weighing dry powders, etc. These practices are considered effective in controlling exposures.
- Use of glove boxes can also reduce inadvertent loss of product that might otherwise occur with more traditional local exhaust ventilation.
- Concur with goals of containment, entrapment, and disposal.
- Treat waste as hazardous waste until information is available to treat it otherwise.
- It may be difficult to get all people working with nanoparticles to follow the recommended guidelines. There could also be an issue getting maintenance people and outside contractors to follow the guidelines.

2. Where are there gaps in the recommended practices? Are there other available practices documents that address those gaps?

- The lack of good toxicological information for the vast number of nanoparticles with any number of different functional groups attached, each of which may contribute to different health outcomes. Should there be a difference in handling functionalized CNTs and does this require different guidelines for each?
- The lack of good measurement information. We don't know which parameters are most important in terms of possible biological effects. There are also issues in terms of the cost of advanced monitoring equipment, which would make it difficult for smaller employers to self-monitor.
- There is a need to consider the human factor. Even with training, engineering controls, and personal protective equipment, how do you ensure that employees will actually work in an appropriate manner? Many participants had experienced situations where they walked into a lab or other work area and found employees not doing what they were supposed to.
- Can the nanoparticles captured in HEPA filters be released?
- How will the waste handler actually treat the waste?
- Medical monitoring: is baseline testing and periodic retesting for lung capacity a help or a potential liability? Is it necessary? If desired, what should the metrics be?
- How can small companies afford to do monitoring and measurement of nanoparticles?

3. What specific steps can state agencies take to complement the national and international efforts to promote the safe development of nanotechnology? How can state agencies and other stakeholders most effectively work together to bridge the gaps indentified in the breakout session?

- Need a standardized method for measurement.
- Need for a program similar to MassDEP's Environmental Results Program (self certification program) with respect to where and how CNTs are being used, worker protection preferences, disposal, etc.

4. Other Thoughts:

- How to do good risk communication, particularly given the lack of good toxicity information.
- The need to address potentially hazardous byproducts of engineered nanoparticle production, and not to get lost focusing on the nano part of the process to the exclusion of other hazards.
- Hazardous waste- the consensus seemed to be that nano waste should be handled as hazardous, but that labeling it as such then throws you into regulatory compliance issues.
- Facilities staff may be among those with the greatest potential exposure. They may perform tasks that Environmental Health and Safety Personnel should do, like HEPA filter replacement and ventilation system repair that may offer higher potential for exposure, etc.
- There is a need for all parties in the chain, from base material supplier to finished product manufacturer, to provide accurate and comprehensive information (to the best of their ability) on the hazards of the materials they are shipping.

The breakout sessions ended with report-backs from session facilitators moderated by Dr. Jackie Isaacs of Northeastern University. Each group reported back on the top 3-5 key points of each session and other groups were given time to ask questions.

Lucy Edmondson, MassDEP's Deputy Commissioner for Policy and Planning, thanked the participants of the morning session for all of their work, which generated a tremendous amount of information, providing insights about where best and good current practices can be applied, where gaps need to be filled and identifying issues preventing companies from taking steps to implement these recommendations. Ms. Edmondson indicated that information from the workshop would be used to determine the Commonwealth's next steps towards promoting the safe development of nanotechnology and that a proceedings document would be prepared to share the collective learning from the workshop.

VI. Introduction to the Measurement of Nanoparticles

The afternoon workshop session on measurement was the first time this type of training was offered in the East Coast/Mid Atlantic region. The NIOSH and CHN teams demonstrated tools that can be used to measure nanoparticles. The hands on sessions were preceded by an introduction to the measurement of nanoparticles by Dr. Candace Tsai, University of MA, Lowell, MA, TURI and CHN

Dr. Tsai's slides can be found at http://www.mass.gov/dep/toxics/stypes/tsai_meas.pdf. Dr. Tsai provided a comprehensive overview of various measurement methods currently available for evaluating nanoparticle exposures. She mentioned that mass concentration is the simplest property to measure, but that it is usually not appropriate, since mass concentrations of nanoparticles are typically very low, or too low to be measured, and health effects from nanoparticle inhalation may have no direct correlation with the inhaled aerosol mass. Direct-reading instruments include the TSI 8529 DustTrak™ Aerosol Particulate Monitor, which measures real-time mass concentrations of nanoparticles in the range of 0.001 to 100 milligrams/cubic meter. Measurement of the surface area concentration of nanoparticles is of particular interest, since some health effects may be related to particle surface area. The TSI 3550 Nanoparticle Surface Area Monitor can measure total surface area concentration or surface area as a function of particle size, for example measuring total surface area for particles with diameters from 10 to 1000 nanometers. Direct reading instruments that measure total particle number concentration over a certain size range are also available. The TSI 3007 Condensation Particle Counter, for example, is a hand-held, battery-powered instrument that measures total concentration of particles in the size range from 10 nanometers to 1 micrometer. The total particle number concentration instrument has been used for rapid surveys in different areas of a facility – for example, to locate particle release points. Particle size distribution is probably the most useful information for evaluating nanoparticle exposure, but is also the most difficult, expensive and time-consuming information to collect. Available instruments include the TSI 3091 Fast Mobility Particle Sizer™ Spectrometer and the TSI 3936 Scanning Mobility Particle Sizer™ Spectrometer. Information on particle size is not sufficient, however, for characterizing nanoparticle aerosols. Information on particle shape and elemental composition is needed to fully characterize the aerosol. Nanoparticle electron microscopy is required for this type of information.

VII. Demonstration of Advanced Techniques for Nanoparticles Measurement

Dr. Michael Ellenbecker, Director, TURI and Dr. Candace Tsai, TURI and CHN

Equipment and techniques for the session included: Fast Mobility Particle Sizer, Aerodynamic Particle Sizer, a fog machine, methods utilizing transmission electron microscopy (TEM) and scanning electron microscopy (SEM), and data analysis techniques.

Drs. Ellenbecker and Tsai's slides can be found at www.mass.gov/dep/toxics/stypes/tsai_becker.pdf. This presentation focused on airborne nanoparticle measurements, including collecting airborne nanoparticle samples, measuring airborne nanoparticle concentrations and identifying release sources that could be evaluated and controlled to protect laboratory employees. A demonstration of the TSI Fast Mobility Particle

Sizer (FMPS) Spectrometer was provided. This instrument measures airborne particle concentration over time and is capable of measuring nanoparticles in the 5.6 to 560 nanometer range, with a 1-second response time. The presentation included graphics of FMPS-generated-data of actual nanoparticle exposures collected in the field. Nanoparticle concentrations varied over a range of values, with some elevated peaks after three hours of testing, indicating potential source releases. Another graphic of data collected during laboratory fume hood performance tests illustrated variations in operator breathing zone nanoparticle size distribution and airborne concentration, depending on the height of the sash in the hood. This demonstration shows how measurements can be used to identify best practices such as the optimal height of the hood sash to minimize exposure to laboratory personnel.

Drs. Ellenbecker and Tsai also demonstrated the TSI Aerodynamic Particle Sizer (APS) Spectrometer for particle concentration measurements in the 0.5 to 20 micrometer aerodynamic diameter size range. The instrument provides readings on airborne particle number concentration and diameter in 51 size channels.

A description of the mechanics of nanoparticle sampling, followed by scanning or transmission electron microscopy (SEM and TEM, respectively) to examine the size of nanoparticles was also illustrated. This type of protocol is useful for identifying and confirming sources of nanoparticles in laboratories. Laboratory indoor air sampling can be enhanced by using a fog machine which generates a visible indicator to observe airflow patterns to identify representative sampling locations; a fog machine was operated to illustrate this method, and to collect real-time FMPS data.

VIII. Demonstration of the NIOSH Nanoparticle Emission Assessment Technique
Dr. Charles Geraci, CIH, Coordinator, Nanotechnology Research Center and Chief, Document Development Branch, National Institute for Occupational Safety and Health (NIOSH) and Laura Hodson, CIH NIOSH nanotechnology field research team.

Equipment and techniques for the session included: Condensation particle counter, Optical particle counter, Air sampling pumps and Filter cassettes for elemental and TEM analysis, data analysis techniques.

NIOSH created a field research team to assess workplace processes, materials, and control technologies associated with nanotechnology and to conduct on-site assessments of potential occupational exposure to nanoparticles. The purpose and goals of the field research team are to: 1) characterize processes and identify potential nanomaterial emissions that could result in worker exposures, 2) evaluate potential workplace exposures using a variety of measurement techniques, 3) recommend safe work practices, and 4) evaluate exposure control measures. The data collected by the field research team is communicated back to the participant. There are no costs to the participant. This presentation covered the types of measurements NIOSH performs during an on-site visit and can be found at
http://www.mass.gov/dep/toxics/stypes/hodson_dem.pdf

NIOSH's Nanoparticle Emission Assessment Technique (NEAT) uses a semi-quantitative technique, comparing particle number concentrations at suspected emission sources to background concentrations. A condensation particle counter (CPC) and an optical particle counter/sizer (OPC) are used. While any equivalent manufacturers equipment would be appropriate, the CPC used is a TSI 3007 (or TSI P-Trak) instrument that is capable of measuring a particle size range of 10 (or 20) – 1000 nanometers with a concentration range up to 100,000 particles/cubic centimeter (cc). The OPC (ART Instruments, Inc. HHPC-6) measures particles from 300 nanometers to >10 microns. Together, CPC and OPC provide measurement of nanoparticles in the range of 10 nanometers to > 10 microns. In addition, electron microscopy and non-gravimetric, filter-based air samples are collected to identify the nanoparticles. A detailed investigation using more sophisticated particle analyzers may also be undertaken.

During the initial assessment, NIOSH holds discussions with the participant and gets familiar with processes, work practices, existing controls and use of personal protective equipment (PPE). NIOSH measures background particle number concentration with the system/process off and then with the system on to identify potential emission points with the CPC and OPC. When the particle number concentration measured by the particle counters at the potential emission points is higher than background, samples are collected for electron microscopy and analytical analysis at the locations of possible emissions. During on-site visits, if the particle number is not higher at suspected emission points than the background particle number concentrations, then no further testing is conducted.

As an example, NIOSH demonstrated how NEAT could be used to check a reactor vent for emissions/leaks and during packaging of a product. Additionally, NIOSH presented the results of a case study on the effectiveness of local exhaust ventilation (LEV) on nanoscale metal oxides. The facility was producing several nanoscale metal oxides, as 15-50 nm spherical particles, using gas phase condensation reactors and producing 1 kilogram per reactor. NIOSH used the NEAT protocol and determined that nanoparticles were released to the general plant during reactor cleanout. They subsequently suggested the use of a commercially-available, portable, local exhaust ventilation (LEV) system equipped with HEPA filters. The company purchased the LEV and asked the NIOSH field team to determine the effectiveness of the control. NIOSH performed the study and concluded that the LEV effectiveness was approximately 96 +/- 6% based on particle number concentration data and 88 +/- 12% based on air sampling mass concentration data.

The NIOSH Fact Sheet (Appendix E) provides information on how facilities can obtain NIOSH's services such as those above. During NIOSH' measurement session, 2 representatives from 2 different companies provided very favorable comments on the NIOSH on-site visits they experienced and the benefits that ensued.

Appendix A
Members of the MA Interagency Nanotechnology Committee

Massachusetts Department of Environmental Protection, One Winter Street, Boston MA

Phone: 617-292-5500 Fax: 617-556-1049

Carol Rowan West, Director, Office of Research and Standards – Committee Chair
Ed Kunce, Director, Emergency Response and Technical Support
Barbara Kwetz, Director of Planning and Evaluation, Bureau of Waste Prevention
Sharon Weber, Senior Technical Advisor, Commissioner's Office
Suzi Peck, Associate Director of Planning and Evaluation, Bureau of Waste Prevention

Massachusetts Office of Technical Assistance and Technology, Executive Office of Energy & Environmental Affairs 100 Cambridge Street, Suite 900 Boston, MA

Phone: 617-626-1060 Fax: 617-626-1095

Rick Reibstein, Senior Environmental Analyst
Morgan Mihok, Environmental Chemist and Nanotechnology Sector Lead

Massachusetts Department of Public Health, 250 Washington Street Boston, MA

Phone: 617- 624-5757 Fax 617- 624-5777

Ruth Alfasso, Compliance Officer, Bureau of Environmental Health
Frances Medaglia, Clinical Coordinator, Environmental and Public Health Tracking
Roy Petre, Senior Policy Advisor, Bureau of Environmental Health
Kari Sasportas, Environmental Analyst, Bureau of Environmental Health
Elise Pechter, Industrial Hygienist, Occupational Health Surveillance Program

Massachusetts Division Of Occupational Safety, 1001 Watertown Street, W. Newton, MA

Phone: 617-969-7177 Fax: 617-727-4581

Marvin Lewiton, Industrial Hygiene Supervisor
Alexander Murphy, Research Analyst

Toxic Use Reduction Institute, University of Massachusetts, Lowell One University Avenue, Lowell, MA

Phone: 978-934-93275 Fax: 978-934-3050

Gregory Morose, Industry Research Project Manager

Massachusetts Executive Office of Housing and Economic Development, Office of Business Development One Ashburton Place, Room 2101, Boston, MA

Phone: 617-788-3610 Fax: 617-788-3605

April Anderson Lamoureux, Deputy Director, MA Permit Regulatory Office

Appendix B
List of Workshop Participants

First	Last	Affiliation	Email	Phone
Justin	Adams	MIT	jwadams@mit.edu	617-452-3270
Ruth	Alfasso	MA Department of Public Health	ruth.alfasso@state.ma.us	617 624 5757
Carol Lynn	Alpert	Museum of Science, Boston		
Michael	Amster	M.B. Amster & Associates	michael@mbamster.com	
Jessica	Avizinis	Brown University	Jessica_Avizinis@brown.edu	401-863-3353
David	Bachand	MassDEP	david.bachand.jr@state.ma.us	(413) 755-2221
Mark	Banash	Nanocomp Technologies	mbanash@nanocomptech.com	603-442-8992
Matt	Barber	MassDEP		
Daryl	Beardsley	self-employed	darylb@comcast.net	
Dhimiter	Bello	University of Massachusetts, Lowell		
Richard	Bizzozero	Mass OTA	rich.bizzozero@state.ma.us	617-626-1080
Meg	Blanchet	MDPH, Bureau of Environmental Health	meg.blanchet@state.ma.us	617 624 5757
Lawrence	Boise	L.H. Boise, LLC	l.boise@comcast.net	
Mike	Bolko	Entegris	michael_bolko@entegris.com	978-436-6520
Gail	Bowen	Osram Sylvania	gail.bowen@sylvania.com	978-7501565
Grady	Bowen	Advanced MicroSensors	gbowen@advancedmicrosensors.com	508-770-2423
Laurel	Braitman	MIT	lbrait@mit.edu	(202) 549-0939
Deborah	Brown	US EPA		
Robert	Burns	Massachusetts COSH	Robert.Burns@masscosh.org	617-825-7233
Jennifer	Burrill	Mabbett & Associates, Inc.	burrill@mabbett.com	781-276-6050 x311
Laurie	Burt	Commissioner, MassDEP		
Mary	Butow	Toxics Use Reduction Institute	mary@turi.org	978-934-4365
Mario	Cabodi	Boston University Center for Nanoscience	cabodi@bu.edu	617-358-1793
Dede	Cabral	MassDEP		
Jeff	Cantin	Eastern Research Group, Inc.	jeff.cantin@erg.com	
Frank	Carter	F.M. Carter Nanotech & Financial Consult	fmmcarter@cox.net	703 629 1271
David	Collins	Microsemi Corporation	dcollins@microsemi.com	978 442 5662
Tara	Collins	Chubb Insurance	tcollins@chubb.com	617-717-5121
Nancy	Comeau	Ma Division of Occupational Safety	nancy.comeau@state.ma.us	617-969-7177
Janine	Commerford	MassDEP	janine.commerford@state.ma.us	
Mary	Corrigan	Harvard University, EHS	joana_santos@harvard.edu	617-432-1720
George	Courville	Naneum	george@courvilleassociates.com	(617) 320-0385
Elizabeth	Craver	Travelers	ecraver@travelers.com	(860) 687-7407
William	Crouse	Wyeth	crousew1@wyeth.com	518-846-6350
Jim	Curran	Fulcrum Safety Solutions, Inc.	jim@ehs-sos.com	976-649-2756
Lindsay	Dahlben	Northeastern University, CHN	ldahlben@coe.neu.edu	(617) 373-2981
Steven	DeGabriele	Mass. Dept. of Environmental Protection	steven.degabriele@state.ma.us	617-556-1120
Lee	Dillard Adams	MassDEP		
Michael	DiPrima	AVEO Pharmaceuticals	mdiprima@aveopharma.com	617-299-5886
Mary	Dozois	Massachusetts Div of Occupational Safety	mary.dozois@state.ma.us	617-969-7177 x301
Lucy	Edmondson	Deputy Commissioner, MassDEP		

Jon	Eisenberg	Rolf Jensen & Associates	jeisenberg@rjagroup.com	508-620-8900
Scott	Eliasof	Cerulean Pharma Inc	seliasof@ceruleanrx.com	617-551-9607
Pam	Eliason	TURI	pam@turi.org	978-934-3142
Michael	Ellenbecker	Toxics Use Reduction Institute, CHN		
David	Enman	Nantero, Inc	enman@nantero.com	(781) 569-0428
Heidi	Faw	Wyeth	fawh@wyeth.com	617-665-7087
Thomas	Ferraguto	Aegis Lightwave	tferraguto@aegislightwave.com	781-904-4000 x267
James	Field	University of Massachusetts	jmfield@ehs.umass.edu	413 545-5122
Richard	Fil	Robinson & Cole LLP	rfil@rc.com	860-275-8248
Richard	Fink	Wyeth Biotech	rfink@wyeth.com	978-247-2233
Alexander	Fiorentino	Museum of Science, Boston	afiorentino@mos.org	
Kathy	Flannery	MA Dept. of Labor	kathy.flannery@state.ma.us	
Richard	Foote	Triumvirate Environmental	rfoote@triumvirate.com	617-686-6184
James	Freedman	M.I.T.	jrftlo@mit.edu	617-253-6966
Beverly	Gaal	Genzyme Corporation	beverly.gaal @genzyme.com	(508) 270-2102
Millie	Garcia-Serrano	MassDEP		
Mary	Gardner	MassDEP	mary.gardner@state.ma.us	508-767-2820
Jonathan	Gast	Wyeth	gastj@wyeth.com	
Jennifer	Geertsma	UMass Amherst	hill@soc.umass.edu	413-527-3714
Charles	Geraci	NIOSH		
Kathleen	Gilbert	Harvard University, EHS	kathleen_gilbert@harvard.edu	617-432-1720
David	Gillum	University of New Hampshire	david.gillum@unh.edu	603-862-0197
Elizabeth	Gilman Duane	Wyeth	egilman@wyeth.com	
Edward A.	Gomes	Vicor Corporation	egomes@vicr.com	978-749-7730
Charles	Goodhue	Eastern Research Group, Inc.	goodhuec@gmail.com	(781) 249-1692
Michael	Goyetche	Air Motion	mike@airmotion.net	781-598-4900
Pamela	Greenley	MIT	greenley@mit.edu	
Liz	Gross	Safety Partners	lgross@safetypartnersinc.com	
Hamilton	Hackney	Greenberg Traurig	hackneyha@gtlaw.com	617-310-6090
Marilyn	Hallock	MIT	hallock@mit.edu	(617) 253-0344
Valerie	Hatfield	Raytheon		
Mark	Hengen	Johnson and Wales University	mhengen@jwu.edu	401-632-6476
Laura	Hodson	NIOSH		
John	Hovsepian	EBI Consulting	JHovsepian@EBIConsulting.com	781-418-2344
Scott	Ide	Harvard university	scott_ide@harvard.edu	
Jacqueline	Isaacs	Northeastern University		
Amy	Johnson	Harvard University	amy_johnson@harvard.edu	
Dave	Johnston	MassDEP		
William	Judd	Industrial Compliance Group	BJudd@IndCompGroup.com	508-875-1197
Azin	Kavian	MassDEP		
Glenn	Keith	MassDEP		
Robert	King	Capaccio Environmental Engineering, Inc.	bking@capaccio.com	508-970-0033
Patrick	King	GEI Consultants, Inc.	pking@geiconsultants.com	781-721-4071
Jayne	Knott	JFK Environmental Services, LLC	JayneKnott@charter.net	508-344-2831
Todd	Kuiken	Project on Emerging Nanotechnologies	todd.kuiken@wilsoncenter.org	202-691-4398
Kristen	Kulinowski	Rice University	carod@rice.edu	(713) 348-8211
Edward	Kunce	MassDEP	Edward.Kunce@state.ma.us	
Barbara	Kwetz	MassDEP	Barbara.Kwetz@state.ma.us	617-292-5882

Michael	Labosky	Harvard University	michael_labosky@harvard.edu	
Maria	L'Annunziata	MassDEP	Maria.lannunziata@state.ma.us	
Walker	Larsen	CLF Ventures	wlarsen@clf.org	617-850-1709
Del	Leonard	Ransom Environmental Consultants	delano.leonard@ransomenv.com	(207)-318-3901
Marvin	Lewiton	MA Division of Occupational Safety	marvin.lewiton@state.ma.us	617-969-7177 x 314
Sam	Lipson	Cambridge Public Health Dept.		
Wai-Lin	Litzke	Brookhaven National Lab	wlitzke@bnl.gov	631-344-7153
Christopher	Long	Gradient Corporation	clong@gradientcorp.com	617-395-5532
Wendy	Luo	Wyeth	luow@wyeth.com	973-660-6747
Stephen	Mahoney	Turbine Component Services	steve.mahoney@goodrich.com	978-977-6758
Steve	Mahoney	MassDEP		
James	Marcello	Marine Biological Laboratory	jmarcello@mbl.edu	508-289-7424
Elizabeth	Mason	Goodwin Procter, LLP		
Robert	Maxfield	US Environmental Protection Agency	maxfield.robert@epa.gov	617-918-8640
Caitlin	McAllister	Nanotechnology & Society Research Group	mcallister.c@neu.edu	857-334-5151
Tom	McGrath	MassDEP		
Teresa	Medley	Teknor Apex Company	tmedley@teknorapex.com	401-642-3809
Morgan	Mihok	UMass Donahue Institute	morgan.mihok@state.ma.us	617-292-5713
Gary	Moran	MassDEP	Gary.Moran@state.ma.us	617-292-5915
Greg	Morose	TURI	gregory_morose@uml.edu	978-934-2954
Paul	Morse	The New England Consortium / UMass Lowel	paul_morse@uml.edu	978-934-4389
Patrick	Mount	AIG	patrick.mount@aig.com	212-458-6245
Albert	Moussa	BlazeTech Corp	amoussa@blazetech.com	(617) 661-0700
Diane	Mundt	ENVIRON International Corporation	dmundt@environcorp.com	781-346-1697
Alexander	Murphy	MA Div. of Occupational Safety	alex.murphy@state.ma.us	
Ramanathan	Nagarajan	Natick Soldier RDEC	Ramanathan.Nagarajan@us.army.m	508-233-6445
Robert C.	Najjar	Draper Laboratory	rnajjar@draper.com	
J David	Naparstek	Newton Dept. of Health & Human Services	dnaparstek@newtonma.gov	617-796-1420
Robert	Naparstek	Good Samaritan-Occupational Health Servi	gsohs99@aol.com	508 427 3900
Priscilla	Neves	MDPH Bureau of Environmental Health	priscilla.neves@state.ma.us	617-983-6773
Ah-Kau	Ng	University of Southern Maine	ahkaung@maine.edu	207-228-8444
John	Nicholson	UMASS/Amherst	jnicholson@research.umass.edu	413-545-2772
Robert	Nick	QD Vision, Inc.	rnick@qdvision.com	(617) 607-9749
Matthew	Norton	Philotechnics	mdnorton@philotechnics.com	781-222-5050
Peter	Nowak	Tufts University	peter.nowak@tufts.edu	617-627-3246
Augustus	Ogunbameru	MA OTA	augustus.ogunbameru@state.ma.u	
Zeynep	Ok	Northeastern University	zeynep@coe.neu.edu	617-373-2981
Theresa	Park	City of Lowell	tpark@lowellma.gov	978-446-7200
John	Patterson	Continental Remediation LLC	continental.llc@gmail.com	781-891-0431
Dwight	Peavey	US EPA	peavey.dwight@epamail.epa.gov	617-918-1829
Elise	Pechter	Mass. Dept. Public Health	Elise.Pechter@state.ma.us	(617) 624-5681
Matthew	Powers	Colliers Meredith & Grew	matthew.powers@colliersmg.com	(617) 330-8091
David	Querim	U.S. Army Natick R, D & E Center	david.querim@us.army.mil	
Joanne	Regan	USDOL/OSHA	regan.joanne@dol.gov	617-565-9856

Rick	Reibstein	MA OTA	rick.reibstein@state.ma.us	617 626 1062
Diane	Reynolds	Hyperion Catalysis Int,	dreynolds@hyperioncatalysis.co	617 354 9678
Rebecca	Reznik-Zellen	University of Massachusetts Amherst	rreznikz@library.umass.edu	413.577.0912
Paul	Richard	Warner Babcock Institute	danielle.parrott@warnerbabcock	781-937-9000
Paul	Richard	EBI Consulting	prichard@ebiconsulting.com	617-715-1825
Arthur	Robert	MA Office of Business Development		
Buddy	Rocha	MA Office of Business Development		
Craig	Romanowicz	Revere Copper Products, Inc.	cromanowicz@reverecopper.com	774-930-3153
Pam	Rosett	Lockheed Martin Aeronautics	pamela.g.rosett@lmco.com	770-494-7655
Carol	Rowan West	MA DEP	Carol.rowanwest@state.ma.us	617 292-5510
Susan	Ruch	MassDEP		
Brad	Russell	Reed & Barton Corp.	brussell@reedbarton.com	508-977-8474
Hicham	Saade	ITW Devcon	hsaade@devcon.com	978-646-5654
Daniel	Sarachick	Brown University	Daniel@brown.edu	401-863-3353
Kari	Sasportas	MDPH Bureau of Environmental Health	kari.sasportas@state.ma.us	(617) 624-5757
Shaun	Savage	Tufts University	shaun.savage@tufts.edu	(617) 636-0397
Jo Anne	Shatkin	CLF Ventures	jashatkin@clf.org	
Bill	Sirull	Mass. Dept. of Environmental Protection	william.sirull@state,ma.us	617-292-5838
Chris	Stepanian	Unnamed Startup	cstep@sloan.mit.edu	(617) 596-1446
Diane	Stewart	FEI	diane.stewart@fei.com	978-465-1861
Michael	Strem	Strem Chemicals Inc.	mstrem@strem.com	978-499-1600
Linda	Swift	Capaccio Environmental Engineering, Inc.	lswift@capaccio.com	508-970-0033
Julie	Tremblay	Aearo Technologies	julie.tremblay@mmm.com	508-764-5784
Michael	Trevor	Chubb Insurance	mtrevor@chubb.com	617-261-6297
Su-Jung (Candace)	Tsai	University of Massachusetts, TURI	candace.umass@gmail.com	978-934-4366
Edwin	Valis	Cornerstone Environmental Group, LLC	edwin.valis@cornerstoneeg.com	845-695-0221
Helen	VanBenschoten	Warner Babcock Inst. forGreen Chemistry	helen@warnerbabcock.com	
Vesela	Veleva	Boston College	velevav@bc.edu	
Stephen	Venuti	MWRA	stephenvenuti@msn.com	
James	Votaw	Wilmer Cutler Pickering Hale & Dorr LLP	james.votaw@wilmerhale.com	202-663-6244
Winona	Wall	Raytheon	winona_wall@raytheon.com	978-470-6705
Sharon	Weber	MassDEP	sharon.weber@state.ma.us	617-556-1190
Jeff	Welt	LLBean, Inc	jwelt@llbean.com	207-552-6191
Dan	Winslow	Duane Morris LLP	dbwinslow@duanemorris.com	857-488-4200
Sammi	Wyman	MassDEP	swyman@mit.edu	
Bobby	Young	Millipore Corporation	bobby_young@millipore.com	781-533-2832
Margery	Young	Meadowbrook/TPA Associates	myoung@meadowbrook.com	978.886.9233

Appendix C
Welcome Letter from Commissioners

COMMONWEALTH OF MASSACHUSETTS

MASSACHUSETTS
DEPARTMENT OF
ENVIRONMENTAL PROTECTION

MASSACHUSETTS
DIVISION OF
OCCUPATIONAL SAFETY

January 29, 2009

Dear Nanopractitioner:

Since our 1st workshop on the "Safe Development of Nanotechnology" in 2007, there have been significant advancements in the emerging field of nanotechnology, from expanded research to new product development. One of our priorities of the Massachusetts Interagency Nanotechnology Committee has been to track these advancements; especially the development of "best practices" to protect workers, the environment and human health.

With that in mind, best practices will be the focus of our second workshop, "Promoting the Safe Development of Nanotechnology in Massachusetts," on January 29, 2009 at the Federal Reserve Bank in Boston. Workshop content will include a discussion of health and safety practices, breakout sessions on the lifecycle of nanotechnology and appropriate applications of best practices and good current practices, and an afternoon training session on state-of-the-art measurement techniques for nanoparticles.

This workshop will be an excellent opportunity for business, researchers, environmentalists and government to come together to share ideas that will support this emerging industry, learn from best practices, and further the safe development of nanotechnology.

We encourage you to learn, to speak up and to share your experience and opinions. Thank you for attending this event.

Sincerely,

Laurie Burt, Commissioner
Massachusetts Department of
Environmental Protection

Laura M. Marlin, Commissioner
Massachusetts Division of
Occupational Safety

Appendix D
Speaker Biographies

Laurie Burt, Commissioner, Massachusetts Department of Environmental Protection

Laurie Burt has been the Commissioner of the Massachusetts Department of Environmental Protection (MassDEP) since September of 2007 following her appointment by Governor Deval L. Patrick.

Since her appointment, Ms. Burt has championed environmental, energy and public health issues, such as the Regional Greenhouse Gas Initiative (RGGI), a statewide stormwater management plan, the streamlining of environmental permits and wetlands appeals, the protection of drinking water resources through conservation, the use of "Landfills Last" to maximize the recycling and reuse of solid wastes, and Brownfields redevelopment efforts.

Ms. Burt is Co-chairman of the RGGI Strategic Communications Team, and she is Governor Patrick's environmental representative on the board of RGGI, Inc. Ms. Burt is also Secretary-Treasurer of the Ozone Transport Commission, a member of the Air Committee for the Environmental Council of States (ECOS), and a key member of the State Voice group, a coalition of environmental commissioners working to support the development of federal legislation that capitalizes on the experience, success and full potential of state climate change and clean energy programs.

She is also MassDEP's representative on the Energy Facilities Siting Board, and is MassDEP's designee to the Governor's Ocean Management Advisory Commission.

She was formerly a partner at the law firm Foley Hoag, LLP of Boston and Washington, D.C., where she started the firm's Environmental Practice Group. Ms. Burt previously served as a Massachusetts Assistant Attorney General in environmental enforcement, and most recently as Vice President of the Boston Bar Association.

Dr. Michael J. Ellenbecker, CIH, Director, Toxics Use Reduction Institute, and the Center for High-rate Nanomanufacturing, University of Massachusetts, Lowell

Michael J. Ellenbecker is an expert in toxics use reduction and industrial hygiene. Dr. Ellenbecker has been affiliated with TURI from its inception and has been its Director for five years. He manages a staff of twenty and has guided the Institute's research program since 1989. Dr. Ellenbecker is co-author of 'Ventilation for Control of the Work Environment', the standard textbook for the design of industrial exhaust systems. He is also a Professor in the Department of Work Environment at the UMass Lowell, teaching industrial hygiene and cleaner production. Harvard-educated, Dr. Ellenbecker holds Doctoral and Master's degrees in Environmental Health Sciences and Industrial Hygiene and is a Certified Industrial Hygienist.

As Director of TURI, Dr. Ellenbecker is leading efforts to provide health and safety support to the University's NSF-funded Nanoscale Science and Engineering Center for High-Rate Nanomanufacturing (CHN). The CHN, located at UMass Lowell, Northeastern University, and the University of New Hampshire, is committed to developing nano-scale products and materials in a way that is environmentally-appropriate and safe for workers. He and Dr. Su-Jung (Candace)

Tsai are performing research on methods to evaluate and control nanoparticle exposure, and are writing a new textbook for Wiley titled "Health and Safety Considerations for Working with Engineered Nanoparticles in Industry".

Charles Geraci, Ph.D. Coordinator, Nanotechnology Research Center and Chief, Document Development Branch, National Institute of Occupational Safety and Health

Dr. Charles (Chuck) Geraci is overall Coordinator of the NIOSH Nanotechnology Research Center and manages a number of Nanotechnology projects in the Institute, including the development of workplace guidelines contained in "Approaches to Safe Nanotechnology". He also sponsors the NIOSH nanotechnology field team that is conducting visits to nanomaterial producers and users to characterize exposures, evaluate controls, and develop best practices. Dr. Geraci is also Chief of the Document Development Branch where he manages projects dealing with the development of recommendations to address worker health and safety in new or emerging technologies. He has over 32 years of Industrial Hygiene practice experience that has included the federal government, consulting, and private industry, including 10 years at the Procter & Gamble Company where he was an Associate Director of HS&E. Dr. Geraci earned a B.S. in chemistry from the University of Cincinnati and a Ph.D. in chemistry from the Michigan State University. He is Board Certified in both the Comprehensive Practice and the Chemical Aspects of Industrial Hygiene and is a Fellow of the American Industrial Hygiene Association. His research interests include development of exposure monitoring methods, evaluating the effectiveness of training, developing effective methods for risk characterization and management, and assessing the hazards and risks of new technologies. In his spare minutes, Chuck enjoys hiking, backpacking, canoeing, fishing, and completing home improvement tasks assigned by his wife.

Laura Hodson, CIH, National Institute of Occupational Safety and Health

Laura Hodson is a certified industrial hygienist and works for NIOSH in Cincinnati. She is a member of the NIOSH nanotechnology field research team and a document manager in the Education and Information Division. Laura completed her undergraduate studies in chemistry and environmental studies at Wright State University in Dayton, OH and completed a Masters of Science in Public Health at UNC- Chapel Hill, NC. Prior to joining NIOSH, Laura worked as the industrial hygiene program manager and laboratory director at RTI International in Research Triangle Park, NC.

Laura M. Marlin, Commissioner, Department of Labor, Division of Occupational Safety

Laura M. Marlin was appointed Commissioner of the Division of Occupational Safety in May 2007. The Division promotes and protects workers' safety and health, wages and working conditions, and supports the Commonwealth's employers through a combination of workplace consultation and assessment, education and training, and administration and enforcement of applicable laws and regulations. Commissioner Marlin oversees six health and safety programs and three wage-related programs, encompassing more than 50 employees in seven offices across the Commonwealth.

Commissioner Marlin brings to the position more than a decade of leadership in public service and experience in labor and employment law and policy. She came to the Division after spending eight years in the Office of the Attorney General, where she served in the Fair Labor Division on a variety of outreach and educational initiatives, the Executive Bureau as Deputy Chief of Staff and, most recently as an Assistant Attorney General in the Criminal Bureau, prosecuting cases involving computer crimes, fraud, embezzlement and public corruption. In July 2006, Marlin was assigned to the team of state and federal prosecutors, State Police and federal agents investigating potential criminal charges stemming from the collapse of the I-90 Connector Tunnel.

Prior to her service in state government, Commissioner Marlin worked for the Massachusetts AFL-CIO as Director of Workforce Development, and in the Legal Services Division of the Massachusetts Teachers Association. Marlin received her Juris Doctorate from Northeastern University School of Law in 1996.

Dr. Su-Jung (Candace) Tsai, Post-doctoral Fellow, Center for High-rate Nanomanufacturing and the Toxics Use Reduction Institute, University of Massachusetts, Lowell

Su-Jung (Candace) is a post-doctoral researcher in the Department of Work Environment at the University of Massachusetts Lowell. She received both her BS and MS in chemical engineering in Taiwan, and worked for five years as a plant and process engineer at a petrochemical plant in Taiwan. At UMass Lowell she received her MS in management science (manufacturing) and her Doctor of Science in Occupational Hygiene and Cleaner Production.

Dr. Tsai performed her doctoral research as part of the NSF-funded Center for High-rate Manufacturing (CHN), where she did ground-breaking research to evaluate and control occupational exposures to engineered nanoparticles. Her publications presenting the results of her research into the performance of laboratory fume hoods when handling nanopowders and the twin screw extrusion of nanocomposites are the first such papers in the peer-reviewed literature. As a post-doc, she is working with CHN and TURI, where she continues to her research into nanoparticle exposure assessment and control technology. She and Dr. Michael Ellenbecker are writing a new textbook for Wiley titled "Health and Safety Considerations for Working with Engineered Nanoparticles in Industry". In addition, she is leading UMass Lowell's efforts to establish cooperative educational and research efforts with colleagues in Taiwan.

Appendix E

NIOSH Nanotechnology Field Research Effort
Prepared by NIOSH
http://www.cdc.gov/niosh/docs/2008-121/

Background: The National Institute for Occupational Safety and Health (NIOSH), part of the Centers for Disease Control and Prevention (CDC), is the leading federal agency conducting research and providing guidance on the occupational safety and health implications of exposure to engineered nanomaterials. As part of its nanotechnology research agenda, NIOSH created a field research team to assess workplace processes, materials, and control technologies associated with nanotechnology and conduct on-site assessments of potential occupational exposure to a variety of nanomaterials.

Purpose: The purpose and goals of the field research team are to: 1) characterize processes and identify potential nanomaterial emissions that could result in worker exposures, 2) evaluate potential workplace exposures using a variety of measurement techniques, 3) recommend safe work practices, and 4) evaluate exposure control measures. Through this effort, NIOSH will gather baseline data to assist in determining potential occupational safety and health implications of exposure to engineered nanomaterials and developing guidance to ensure safe working conditions.

Who can participate: Research laboratories, producers, and manufacturers working with engineered nanomaterials (1 to 100nm) are invited and encouraged to collaborate with NIOSH. Those who are interested, or unsure of whether they qualify, should contact NIOSH. Contact information is listed at the end of this document.

Benefits: Participants will be able to utilize and have access to the expertise of the field research team. Participants will also receive an unbiased, scientific baseline assessment of the potential sources of workplace exposure to nanomaterials using advanced instrumentation. Participants with a strong occupational safety and health (OSH) program could be used as role models for others in the nanotechnology field. For participants who are not sure about the strength of their OSH program, NIOSH can assist in prioritizing areas of improvement, such as engineering controls, and strengthening the overall program.

Note: *This field research effort is fully funded by NIOSH; therefore, there is no monetary cost to the participant. In addition,* there are federal laws and regulations that provide protection for the proprietary and trade secret information of the participating companies.

What is required of participants: The investment of the participants' time, availability, and access to participating worksites is required. Someone from the field research team will contact those who express interest in participating to determine if they meet the necessary qualifications. For those who qualify, a site visit will be scheduled. If new work practices or engineering control suggestions are implemented, or if modifications of existing practices or controls are made, then a return visit by NIOSH may occur to examine the effectiveness of those changes.

Use of the data: The data collected by the field research team will be communicated back to the participant. It may then be used in a general manner by NIOSH to update its guidance on occupational safety and health implications of exposure to nanomaterials, and made available in technical documents, scientific presentations, or on the NIOSH Web site. Participants will not be identified in any NIOSH documents that are disseminated publicly without their permission.

For more information: To learn more about the NIOSH field research effort, or to express interest in participating, contact Charles Geraci, Ph.D., at (513) 533–8339, cgeraci@cdc.gov, or by mail at 4676 Columbia Parkway, Mail Stop C-32, Cincinnati, OH 45226. For information about other nanotechnology research efforts underway at NIOSH (such as the study of fine [0.1µm to 2.5µm diameter] and ultrafine [<0.1µm diameter] metal oxides), contact NIOSH toll-free at 1–800–CDC–INFO (800–232–46360 [press 1 to speak to an operator]), or visit the NIOSH Web site at www.cdc.gov/niosh.

Nanotechnology has many benefits that could be overshadowed if the risks are ignored. As a non-regulatory research agency, NIOSH focuses on NIOSH monitoring of a worker during a nanomaterial powder production and collection.
effective approaches to reducing occupational health and safety risks from exposure to nanomaterials, as well as conducting research and making recommendations to prevent work-related injury and illness for all workers.

To receive other documents or other information about occupational safety and health topics, contact NIOSH at
Telephone: 1–800–CDC–INFO (1–800–232–4636)
TTY: 1–888–232–6348 ■ E-mail: cdcinfo@cdc.gov
or visit the NIOSH Web site at www.cdc.gov/niosh
For a monthly update on news at NIOSH, subscribe to NIOSH *eNews* by visiting www.cdc.gov/niosh/eNews.

As part of the Centers for Disease Control and Prevention, NIOSH is the Federal agency responsible for conducting research and making recommendations to prevent work-related illnesses and injuries. Fact sheets describe how worker exposures to hazardous agents or activities can be reduced.
Mention of any company or product does not constitute endorsement by NIOSH. In addition, citations to Web sites external to NIOSH do not constitute NIOSH endorsement of the sponsoring organizations or their programs or products. Furthermore, NIOSH is not responsible for the content of these Web sites.
DHHS (NIOSH) Publication No. 2008–121.SAFER • HEALTHIER • PEOPLE™
February 2008.*Cover photo credits :Nanotrees, Ghim Wei Ho and Professor Mark Welland, Nanostructure Center, University of Cambridge* (Not included in Proceedings)
NIOSH Nanotechnology Field Research Effort Fact Sheet
DHHS (NIOSH) Publication No. 2008–121 • February 2008
DEPARTMENT OF HEALTH AND HUMAN SERVICES Centers for Disease Control and Prevention National Institute for Occupational Safety and Health4676 Columbia Parkway Cincinnati, OH 45226–1998

Appendix F

BREAKOUT SESSION CASE SCENARIOS AND BACKGROUND DOCUMENTATION

1. Silver Nanoparticles in Paint

a. Case Scenario: The interior of a public elementary school is in need of a new coat of paint. The facilities manager recently learned of a new paint that contains antimicrobial silver nanoparticles, which the manufacturer claims, will be a "defense against germs." The product literature suggested that it would be good for hospitals and to deal with porous moldy material that cannot be replaced. Because this school housed one of the few remaining pools in the area, the facilities manager thought it might be worth painting not just the classrooms but also the locker rooms and shower areas with this new paint.

The contractor hired by the school had not yet encountered this type of paint, and consulted the supplier to find out whether any special precautions were needed. The supplier checked the technical specifications sheet and the material safety data sheet for warnings, which only included standard recommendations to avoid ingesting the paint. Because the contractor continued to express some concern, the supplier gave the contractor a phone number for the paint manufacturer.

The representative for the paint manufacturer said that employees used dust masks when mixing the silver nanoparticles into the paint base material, but that that was a standard precaution any time a dry material was mixed into a wet base and was not specific to concerns about the silver. The representative also echoed the supplier's statement that there were no special precautions necessary because of the inclusion of silver nanoparticles.

Still slightly uneasy, the contractor decided to contact the local university's EHS department to ask about whether there were any special protective measures he needed to take to ensure safety while applying paint containing nanoparticles. He also asked if it would be safe to wash the paint on the brushes down the drain. The EHS officer he spoke with referred him to a recently revised National Institute of Occupational Safety and Health (NIOSH) Approaches to Safe Nanotechnology.

- From what you heard this morning, how do the NIOSH guidelines for working with engineered nanomaterials recommend handling of nanoparticles:
    - When they are in a liquid matrix (i.e., during paint application)?
    - When the material is embedded in a solid matrix (i.e., if the paint is sanded/stripped in subsequent years, if children are routinely in contact with painted surfaces)?
    - Should the presence of nanomaterials mean that painters should not use spray techniques to apply paint?
- Should there be any nano-specific content on the technical specification sheet or material safety data sheet for the paint when it is sold to professional painters or the public?

Meanwhile, back at the plant, one of the employees approached the company environmental, health and safety manager and asked whether he could expect to turn blue like Stan Jones, a gubernatorial candidate in Montana he had seen on the news recently. Stan Jones had a condition called argyria, in which his skin took on a bluish hue due to the intentional ingestion of silver. While the EHS manager quickly said that the employee would be safe, she realized that she did not know anything about the employee's actual exposure to silver. Upon perusing NIOSH's website, she discovered a document called "Approaches to Safe Nanotechnology." She looked into what the document recommended based on the facility's processes:

- How would the implementation of NIOSH approaches reduce exposure to silver nanoparticles:
    - During the incorporation of silver nanoparticles into the paint (assume mixing dry particles into a liquid for the purposes of this scenario)
    - During subsequent mixing of paint mixture?
    - During transfer of paint mixture to smaller containers for distribution?
    - During cleaning of process vessels that had contained paint with nanoparticles?
- How might worker exposure be monitored?
- Would actions taken to reduce exposure to silver nanoparticles in the facility also serve to reduce exposure to other nanoparticles (i.e., carbon black, pigments)?

A week later… [[If time]]
A parent on the board of the local "Protect our Watershed" group got word that the school was being coated with a paint containing silver nanoparticles. She was concerned because she had read that U.S. Environmental Protection Agency was regulating silver nanoparticles in washing machines, and was unclear as to whether the paint, in the locker rooms especially, would pose a risk to the town's wastewater treatment system. She knew that other heavy metals in paints had posed serious environmental threats (such as tri-butyl tin in anti-fouling paint), and was wondering what research had been done about the long term effects of silver nanoparticles.

- How do the NIOSH good practices recommend considering long-term effects of exposure to nanomaterials?
- Should the paint manufacturer be required to provide information as to what extent the chemicals in the paint stay fixed or leach out? Are the silver nanoparticles the only material with long-term concerns here?
- Who is responsible for this part of the product lifecycle? The consumer? The manufacturer?

b. Background Document: Germ-Free Paint: Paint Containing Silver Nanoparticles
Type of Nanotechnology/Nanoparticles (NP): Paint embedded with silver nanoparticles, known for their antimicrobial effect.

Purpose of the NP: Silver has antimicrobial properties and in nanoparticle form, is suggested to be especially potent at killing microorganisms. This type of paint is being produced to provide antibacterial protection for hospitals, schools, homes, restaurants and other facilities. The paint would be used on walls, countertops and other surfaces. This paint has been tested on different types of pathogens including salmonella, E. coli and staphylococcus, etc.

Level of development and availability: Paints with silver nanoparticles are currently available on the market. One major producer of the paint has a contract with a company that controls an estimated 25% of the market for external architectural paints. However, this contract is not an exclusive agreement, leaving the company free to sign additional agreements with rival paint firms.

Production of silver nanoparticles for paint: Silver nanoparticles can be formed through gas phase deposition of silver vapor and also through solution chemistry. Techniques to produce particles with a narrow size distribution are largely proprietary.

Potential benefits of the NP or nanotechnology in the product: The use of this paint holds promise for use on interior surfaces in hospitals and other health care settings to control mildew and where risks of infections are important. It is intended that the use of this paint on walls and countertops will reduce surface fungal and bacterial contamination. The mechanism of action is that the silver nanoparticles interact with the bacteria and rupture the cell wall. As a result, it is claimed by some that antimicrobial resistance may not be issue; however, potential for damage to protective bacteria may remain an issue.

Potential detriments of the NP or nanotechnology in the product: Little research has been done on the health and environmental effects of silver nanoparticles. Silver nanoparticles will kill good microorganisms along with the bad. There are no restrictions on the use of silver nanoparticles, which are being added to a huge range of consumer products (sheets, socks, stuffed animals, silverware, door knobs, faucets, cosmetics, refrigerators, water filters, spa and pool sanitizers, etc.). The cumulative exposure of humans and ecosystems to silver nanoparticles has not been studied.

The high surface area of nanoparticles also raises concerns about the potential for explosions.

Other considerations: There is no information regarding whether silver nanoparticles are available for dermal exposures when people touch dried paint. There are no specific regulations covering paint with silver nanoparticles.

Major potential exposure opportunities

Receptor	**Ingestion**	**Inhalation**	**Dermal**
Paint Manufacturer (mixing, processing, etc.)	Accidental	Potential if dry silver NPs can be dispersed in air.	Spillage, splashing during mixing, processing, etc.
Painters and home remodelers (commercial, home owners, etc.)	Accidental, hand to mouth contact with paint dust	Via spray gun, aerosolized particles, vapor, paint dust	Spillage, splashing, washing brushes, paint cans, vapor or dust deposition from aerosolized vapor or

			dust, etc.
Children	Paint chips	Unlikely	Touching wet paint
General Public	Potential drinking water if unused paint poured down drains enters drinking water supply.	Unlikely	Touching wet paint
Patients in health care facilities	Accidental contact with dust during remodeling	Remodeling while facility is occupied	
Health care workers and custodial staff	Accidental contact with dust during remodeling	Remodeling while facility is occupied. Released from cleaning painted surfaces	
Building fires – firefighters and general public	Unlikely	Possible	Unlikely
Aquatic Life/Microorganisms at treatment plants or in septic systems – unused paint poured down drains or landfill leachate is treated at POTWs not removing silver NP	Likely	Likely via gills	Likely
People handling disposal of leftover paint at collection sites, incinerators or landfills.	Unlikely	Possible, via incineration.	Likely from spillage.

2. Groundwater Remediation with Nanoscale Zero Valent Iron

a. Case Scenario: Sal's Solvents, of Seaside, MA needs to remediate a large area contaminated with chlorinated solvents. In the course of its research, the company learned about the use of nanoscale zero-valent iron (nZVI) for remediation, a relatively new technique that has been piloted by EPA. The technology involves the direct injection of nanoparticles into groundwater to affect remediation.

The mayor of Seaside has taken an interest in the project because Sal's land, once sufficiently remediated, is scheduled to be the site of a new sports and entertainment complex. However, she knows that Cambridge just finalized some report about "nanotechnology" and is concerned about whether or not the nanotechnology under consideration for remediation poses a threat to the environment, or the town's residents through air or the drinking water supply. She asked Sal's to explain the project in more detail.

The contractor for Sal's Solvents reassured the mayor that EPA has been using the direct injection method to remediate other sites with a higher success rate than traditional technologies. Furthermore, he said that some of EPA's leading experts on the technology would be in New England evaluating Sal's as a potential nZVI pilot site. The contractor suggested that it would be reasonable to have a town meeting where an EPA official could explain the nZVI technology to concerned residents of Seaside.

The mayor thought the contractor's suggestion was a good one, and agreed to hold the public meeting with an EPA official. She also asked Seaside's health agent to look into the toxicity of nZVI and also into whether any special security or handling measures would be needed by the town if the technology was implemented.

The health agent had time to briefly review three documents: National Institute of Occupational Safety and Health's Approaches to Safe Nanotechnology, the Interim Best Practices for Working with Nanoparticles by the Center for High-rate Nanomanufacturing, and a case study on nZVI by DuPont that the company produced using their "Nano Risk Framework."

At the town meeting, the mayor introduced the EPA official, who briefed the group on the data available to date. The health agent then presented some of the concerns raised by DuPont in their analysis of the technology through the Nano Risk Framework (*document is available in folders for session participants*). The following questions were then raised for discussion:

- Do any of the best practices documents address nanoparticles that will be released into the environment?
    - If so, how? What are the recommended precautions?
    - If not, what would be helpful to have included?
        - How is this similar to or different from other products, such as road salt, that have substantial benefits as well as some environmental concerns?
- If nZVI was clearly demonstrated to be more effective at remediation than other remediation approaches, does that change your expectations for the use of the technology? What concerns should the cost/benefit analysis include?
- What questions would you like the company to answer prior to Seaside's decision to use this technology?
    - Immediate concerns (i.e. worker handling, storage of nanoparticles prior to injection, potential for air release during injection, handling of spills)
        - *Worker for Contractor: "Will I need special equipment to handle this method? I did a similar project for another company in Seaside and we didn't use any personal protective gear."*

        - *Worker for Contractor: "Plus, if this stuff is in a slurry and it spills, what do we need to do about it? Is it OK if it the nanoparticles are on the surface instead of in the groundwater?"*
    - Long term concerns (i.e., fate and transport, what are final products of reaction – salts, insoluble nanoparticles, etc., bioaccumulation/other toxicological problems for soil biota)
        - *Town citizen: "Can these particles get into the surface water?" "Will they be a problem for fish or other wildlife?" "Are they around forever?"*
        - *Town citizen: "Will these get into our drinking water?"*

b. Background Document: Use of Nanoparticles for Site Remediation

Type of Nanotechnology/Nanoparticles (NP): NPs such as zero-valent iron, bi-metallic nanoscale particles and emulsified zero-valent iron hold promise for remediating chemical contaminants at sites. Researchers are also investigating the use of other NPs such as dendrimers, carbon nanotubes, and metalloporphyrinogens for full scale remediation.

Purpose of the NP: Recent research indicates that nanoscale zero-valent iron (nZVI) may prove more effective and less costly than macroscale ZVI under similar environmental conditions. nZVI particles degrade trichloroethylene, tetrachloroethylene, 1,2-dichloroethylene, vinyl chloride, PCBs, halogenated aromatics, and nitroaromatics and can reduce the oxidation states of metals such as arsenic or chromium.

Production of nZVI: The generation of nZVI by reduction of ferric or ferrous salts with sodium borohydride has been used by many research groups. A major advantage of this method is its simplicity; the two reagents are common and there is no need for special equipment or instrumentation. Nevertheless, there are important health and safety considerations associated with the borohydride reduction approach. The synthesis needs to be conducted in a fume hood as the chemical reactions produce hydrogen gas as a byproduct. Moreover, explosion resistant mixers should be used to minimize the production of sparks. Nanoparticle aggregates can be collected by vacuum filtration.

Level of development and availability: Since the early 1990s, nanomaterials, primarily nZVI and related products, have been used to remediate contaminated groundwater and subsurface source areas of contamination at hazardous waste sites. As part of EPA's draft Nanomaterial Research Strategy, EPA is assessing the performance of using or testing NPs for remediation at 26 sites.

Potential benefits of the NP or nanotechnology in the product: The use of nanomaterials may result in faster, more effective and less costly cleanups of chlorinated hydrocarbon contamination at sites. nZVI can be injected directly into a contaminated aquifer, eliminating the need to dig a trench, install a permeable reactive barrier, and dispose of soil off-site. Researchers are developing a variety of nanomaterials for potential future use to adsorb or destroy a wide range of contaminants, including radioactive and mercury wastes.

Potential detriments of the NP or nanotechnology in the product: Knowledge is limited on the fate and transport of NPs in the environment and little research has been done on the potential toxicological effects NP might pose. NP may migrate beyond the contaminated plume area, seeping into drinking water aquifers or wells, or discharging into surface water during the remediation process. The increased surface area and larger number of reactive sites of nanomaterials may equate to greater biological activity per unit of mass than larger particles of the same composition; therefore if exposure occurs, effects could differ from that of larger particles. It is unknown whether nZVI will prove to be an improvement over macroscale ZVI.

The high surface area of CNTs also raises concerns about the potential for explosions.

Major potential exposure opportunities

Receptor	Ingestion	Inhalation	Dermal
Researcher	Accidental/splash	If synthesis process is in powder, gas phase or vapor deposition	Processing of dry NPs, cleaning equipment.
Site worker applying NPs	Accidental/splash	Unlikely, but possible if slurry is allowed to dry (i.e. during cleanup, spill)	Contact with liquid containing NP.
General public	Drinking water, if NPs migrate to supplies.	Inhalation of NPs while showering, if NPs migrate to water supply	Skin contact while washing, if NPs migrate to water supply
Aquatic life	Direct	Via gills	Direct
Microbial life at treatment plant/septic system	Direct	-	-

Other considerations: Concern about the toxicity of using NPs for remediation has limited its use by some companies. For example, DuPont has ruled out the use of nZVI for site remediation at any of its sites until issues concerning fate and transport have been more thoroughly researched (http://www.edf.org/documents/6554_nZVI_Summary.pdf). Meanwhile, EPA Office of Solid Waste and Emergency Response (OSWER) has numerous sites across the U.S. testing NP for site remediation, many associated with Department of Defense sites (http://clu-in.org/products/nanozvi).

3. Titanium Oxide and Zinc Oxide Nanoparticles in Sunscreen

a. Case Scenario: With summer fast approaching, store owners are moving sunscreens into the spotlight. The manager of a chain pharmacy received orders from company headquarters to put the new mineral-based sunscreens in a prominent position at the end of an aisle, because the producers of those sunscreens were running television and magazine ads that claimed the products reduced concerns about allergic reactions and provided better ultraviolet A (UVA) protection. Across the street, however, the owner of a local health food store was stocking only those sunscreens declared safe in the Friends of the Earth (FoE) Sunscreen Guide[3]. The owner provided customers a copy of the guide, which only listed sunscreens that did not contain nanomaterials as safe.

Mrs. River went into the pharmacy and bought a mineral-based sunscreen, and then headed across the street to do some grocery shopping at the health food store. The health food store's sunscreen display caught her eye, and she saw that the sunscreen she had just purchased was on FoE's red flag list as one that contained nanomaterials.

After completing her purchases, she returned to the pharmacy to ask the pharmacist some questions about the sunscreen. The pharmacist, Mr. Pill, was also a frequent customer of the health food store, and had similar concerns after seeing the sunscreen display there. He had done some research and come across the Environmental Working Group's (EWG) report on the topic[4]. The EWG report indicated that, while there were still many uncertainties about the use of nanoparticles in sunscreen, the zinc and titanium oxide-based formulations provided better UVA protection and reduced exposure to harmful chemicals or breakdown products of traditional organic UV-blockers. Furthermore, it noted that almost no UV blockers, organic or mineral, had been tested for penetration of damaged skin. Due to Mr. Pill's family history of skin cancer, he had opted for the mineral-based formulations, though not without reservations.

As Mr. Pill and Mrs. River continued their conversation, they learned that their children were on the same swim team at the local pool. Guessing that their sunscreen concerns were not unique, they decided to compile some of the available resources, including the FoE and EWG guides, to distribute to parents at the next swim meet.

Mrs. River and Mr. Pill told the pool manager their plans. Much to their surprise, the pool manager was hesitant to distribute information that did not provide clear data about which choice to make. She did not want to have some parents worried about their children's exposure to nanoparticles, especially because she did not have a way to know whether or not sunscreens with nanoparticles were being released into her pool. She asked Mrs. River and Mr. Pill to hold off on presenting any information until there was guidance from a governmental agency.

The town's health agent, whose child was also on the swim team, happened to overhear the conversation and offered that he might be able to help develop a balanced information sheet, but noted that it might be some time before he could find a chance to get to it. Mrs. River, Mr. Pill, and the health agent agreed to sit down and talk in the next week to identify what questions should be addressed in the health agent's educational materials. They decided to invite the health food store manager to the meeting as well. The outline of initial questions included the following:

- What responsibility does the sunscreen manufacturer have for communicating information about ingredients? What information will parents be able to gather from the label?
- Are there any good practices that are applicable during this scenario?

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3 http://www.foe.org/nano_sunscreens_guide/Nano_Sunscreens.pdf
4 http://www.cosmeticsdatabase.com/special/sunscreens2008/report_nanotechnology.php

- What is the appropriate way to dispose of unused sunscreens and cosmetics?
- What information should the manufacturer provide on product use and disposal?
  - Given the fact that the health impacts of a nanomaterial can change based on its chemical environment, who is responsible for developing toxicity information? The cosmetics compounder? The nanoparticle manufacturer?
- What are other sources of information about cosmetics ingredients? Who supports these efforts? How should the results of these efforts be communicated to citizens, especially if the results are not conclusive?
- What do we, as concerned citizens, have control over? Where can we go for data?
- Do consumers need to be informed about the size of the ingredients?
- How should consumer education be approached given uncertainty of risk?
  - What are some other situations in which uncertainty has been a concern for consumers? How has it been handled?
- We are learning of environmental problems associated with organic UV blockers – should we be considering those issues described in the background document for TiO_2 and ZnO nanoparticles?
- What about any nano-specific environmental concerns, such as the used sunscreen being washed off into the swimming pool, environment, septic tanks, or public wastewater treatment systems?

b. Background Document: Use of Nanoparticles in Sunscreen

Type of Nanotechnology/Nanoparticles (NP): Particles of various sizes and shapes composed of zinc oxides and titanium oxides. These are mixed into a liquid base composed of a variety of organic and inorganic compounds such as lipids, water, alcohols, proteins, fragrances, colorants and other ingredients.

Purpose of the NP: Non-nanosized zinc and titanium oxides are already used in sunscreens to block UV rays. Use of nanosized versions are designed to make the product appear visibly clear (e.g., no chalky streaks) and to improve the UV blocking ability or "fine tune" the wavelengths that are blocked by the products. These oxides are also used, in nano- and non-nanosized formulations, to create the colorant and reflectance properties of other cosmetics.

Level of development and availability: Sunscreen and cosmetic products with nanoscale particles are on the market today. Many brands of sunscreen contain nanoscale zinc and titanium oxides already. According to the cosmetics industry (http://www.cosmeticsdesign.com/), the proportion of products using these particles is expected to increase. The Environmental Working Group (http://www.cosmeticsdatabase.com/special/sunscreens2008/report_nanotechnology.php) and Friends of the Earth (http://www.foe.org/nano_sunscreens_guide/Nano_Sunscreens.pdf) have published reports on the use of nanoparticles in sunscreens.

Potential benefits of the nanotechnology in this product: NP use may result in improved performance and consumer acceptance, possibly leading to prevention of UV exposures that might lead to health effects such as skin cancer. The NP-containing product is a replacement for organic UV blocking compounds that may have adverse health and environmental impacts such as free-radical generation, hormone mimicking, and coral reef damage. The NP-containing products may have improved sales and market share.

Potential detriments of the nanotechnology in this product:
There are significant unknowns as to potential health impacts of nanoscale particles of these types in general. The product is applied directly to the skin. Studies show that damaged skin, including UV damaged (sunburned) skin, may be more easily penetrated by nanoscale particles. Other routes of exposure to users (ingestion, mucous membranes, etc.) are possible. Once absorbed through the skin, particles may distribute throughout the body. Product is released to the environment during use. Product and NP in product have unknown effects on aquatic, sewage treatment or other environmental micro and macro-organisms.

Major potential exposure opportunities

Receptor	Ingestion	Inhalation	Dermal
Researcher	Accidental	If synthesis process is in powder, gas phase or vapor deposition	Processing of dry NPs, cleaning equipment.
Manufacturing worker	Accidental	If NP in free powder form when added to product	Contact with dry NP or liquids containing NP.
General public	Incidental during use on face and hand-mouth contact. Possible ingestion from pool water. Drinking water, if NPs migrate to supplies.	Possible if NPs are incorporated into spray-on product. Also possible following disposal and incineration.	Direct contact, commercial product is meant to be used on skin.
Aquatic life	Product meant to be used during water contact, and is likely to wash off and be accessible for contact with aquatic life.		
Microbial life at treatment plant/septic system	Product will be washed off into wastewater. Spent product/container may leach NP into landfill leachate	-	-

Other considerations: Some products describe the use of nanoscale titanium dioxide as "natural," "mineral," "chemical free," or "hypoallergenic," which may encourage use by children and other sensitive populations. The Woodrow Wilson nanotech project database points out cosmetic products do not have to be labeled as containing nano particles. Products may claim to contain them that potentially do not, while others may not claim to but contain them. Other components of product may impact the penetration, toxicity, environmental transport of the particles in unpredictable ways. The most obvious difference from non-nanoscale titanium and zinc oxides is visual.

4. Carbon Nanotubes (CNTs) in a Research Setting

a. Case Scenario: Professor Cienty's (pronounced C-N-T) work focuses on the incorporation of carbon nanotubes into resins to give them specific electrical and thermal conductivities. The end-use for these materials is still uncertain; rather, Dr. Cienty's work focuses on how the use of different kinds of nanotubes (single walled vs. multi-walled, longer vs. shorter, etc.) affects the desired properties. She is also investigating how different methods of synthesizing CNTs affect the desired properties, and therefore has her students work with CNTs synthesized in the lab and those purchased from a large chemical supplier.

To incorporate CNTs into the resin, dry CNTs are dispersed in a liquid polymer, which is then mixed with another chemical to form the resin. Once cured, the pieces of resin are sawed into pieces appropriately sized for various analyses. The mixing of the dry CNTs into the liquid polymer is done in the hood, but the sawing of the cured resin is conducted on a lab bench without local exhaust ventilation.

Upon starting their graduate work, all of Dr. Cienty's students had to attend a session in lab safety protocol. They handle free and unbound nanotubes in the hood, and have requested that a high efficiency particulate air filter be installed in the ventilation duct for the hood in which they conduct their CNT syntheses and mixing processes. At the recommendation of the university EHS representative, all CNT-containing wastes, including gloves, wipes, and air filters, are labeled as such when they are picked up, and are segregated from other solid waste.

Recent events, though, have the researchers a bit on edge. In May, one of the graduate students spilled some purchased CNTs on the edge of the hood. Though he wiped the spill up with wet towels as recommended by the EHS person, he observed that the black CNTs had dispersed in a fairly large area. When he returned to his desk to browse the latest issue of *Nature Nanotechnology*, he saw an article linking CNTs to similar responses to asbestos in the lung lining. Slightly rattled, the student wondered whether he had been exposed to more than just a few CNTs, given that he knew his hood was not always at the optimum working height marked on the side of the hood. Furthermore, he wondered whether the CNTs were released when he sawed the cured resins – he could see the resin dust but was unsure about free nanotubes. He called the EHS officer to discuss the following questions:

- Upon reviewing the appropriate sections of the Interim Best Practices, what controls should be in place to ensure that the graduate student's exposure to CNTs is minimized during the following stages of use:
    - when CNTs are free and unbound?
    - while CNTs are being incorporated into the liquid polymer?
    - while the cured resin containing CNTs is being cut or otherwise processed?

  If not specified in the Interim Best Practices, what further guidance is needed?

- Who should be responsible for training the graduate student about nano-specific control techniques? Can/should this just be incorporated into standard good chemical hygiene training?

- How should nanospecific concerns be communicated to lab workers – through material safety data sheets (MSDS), EHS training, and other routes?
- Are there other concerns for the safety of the graduate student that have not been addressed?

A visit by a facilities engineer to change the high efficiency particulate air (HEPA) filter in the hood also triggered some concern. As he watched the engineer remove the filter, the graduate student noted that the engineer wasn't wearing any personal protective equipment. The graduate student asked the facilities engineer whether he was worried about being exposed to the materials the filter was in place to collect, and asked whether he was going to bag the filter before any collected materials were released into the lab.

- What would you recommend the facility do to prevent exposure to the engineer? To others?
- What should be done with the filter upon removal?
- What is recommended in the Interim Best Practices?
- Who should be responsible for communicating these concerns to the engineer? Is this covered by a Hazard Communication program or Right to Know?
- Are there other concerns you would have for facilities' engineers that have not been addressed?
- Would these concerns be addressed the same way in small start-ups as they would be at a university or larger company research facility? If not, what would differ?

Finally, the head of EHS at the university got a query from the hazardous waste hauler regarding waste labeled "contains nanomaterials." The hauler had not received materials before labeled this way, and was unclear as to how to dispose of them properly. To the best of the hauler's knowledge, there were no regulations specific for these materials.

- How do the Interim Best Practices recommend disposing of nanoparticles? What about materials used to cleanup spills? The HEPA filters on the ventilation system?
- Do the Interim Best Practices give instructions for those responsible for the materials after they leave the lab?
- Are there other sources of guidance on disposal? (DoE labs, British Standards)
- What types of guidance would be helpful to researchers/nanopractitioners?
- What are the concerns here? How might they be addressed?

b. Background Document: Lab Synthesis of Carbon Nanotubes

Type of Nanotechnology/Nanoparticles (NP): Single- and multi-walled carbon nanotubes are used in a variety of applications.

Purpose of the NP: CNTs are of broad interest for their strength and interesting thermal, kinetic, and electrical properties, among others. Single-walled carbon nanotubes (SWCNTs, OD ~ 1nm) are of interest particularly for electronics, while multi-walled carbon nanotubes

(MWCNTs) are used in composites to improve the thermal, electrical, and mechanical properties. For example, CNTs are incorporated into plastic used for car parts to dissipate static build up.

Level of development and availability: Several companies around the world manufacture and sell CNTs. Some sell only CNTs embedded in a solid matrix, while others sell unbound CNTs with or without functional groups. A variety of grades, purities, widths, and lengths can be purchased. CNTs are also frequently synthesized and/or modified within a research laboratory setting for further use.

Production of CNTs: There are four primary methods of synthesizing CNTs:

- Arc discharge – single and multiwalled nanotubes are produced in the carbon soot of graphite electrodes following an arc discharge
- Laser ablation – carbon is vaporized from a graphite target with a pulsed laser; nanotubes form as the vaporized carbon condenses
- Chemical vapor deposition (CVD) – nanotubes are grown from a metal nanoparticle catalyst that is heated in the presence of a process gas and a carbon-containing gas
- High-pressure carbon monoxide process (CVD variation) – nanotubes are grown from a gas-phase reaction of iron carbonyl and carbon monoxide.

The latter two methods are the most economically viable and widely used in industry; all four are used in laboratory settings. All methods require some sort of metal catalyst (Fe, Co, Ni, and Mo are common), which can be removed from the CNTs in some cases. Residual catalyst may constitute up to 40% by mass of the CNTs.

Potential benefits of the NP or nanotechnology in the product: CNTs can be used to make stronger, lighter materials, thus requiring less energy to move the material (i.e. less car fuel). They are also being investigated for high-speed electronics, as detection devices, and for drug delivery. CNTs have been incorporated into antifouling paint for boats to prevent barnacle growth. They are also being investigated for waste site cleanup.

Potential detriments of the NP or nanotechnology in the product: Limited research has been done on the health effects of CNTs, and even less has been done to evaluate environmental effects. Within the body of data, effects vary by size, extent of agglomeration and entanglement of nanotubes, whether the nanotubes are single- or multi-walled, the presence of residual catalyst, and the surface functionality of the nanotubes. Primary concerns about CNTs relate to pulmonary inflammation, oxidative stress, fibrosis and the formation of granulomas. Because some nanotubes are similar in structure to asbestos, specific concerns have been raised about mesothelioma; a study published in 2008 demonstrated that once inserted into the pleural lining, some CNTs cause reactions similar to those leading to mesothelioma. It has yet to be demonstrated whether CNTs in ambient air can be inhaled and transported to the pleura. CNTs can present difficulties for the body's defense mechanisms when they are present as single, extended tubes because individual cells cannot process the tubes.

Similar concerns exist for animals and for other microorganisms, though little research has been done on the environmental fate of CNTs. It is also not clear to what extent CNTs are contained by a laboratory hood, contained or disseminated by the facility's ventilation system or released into the atmosphere.

The high surface area of CNTs also raises concerns about the potential for explosions.

Other considerations: EPA has recently declared carbon nanotubes a new material under the Toxic Substances Control Act, and European Commission removed carbon and graphite from the substances exempted from REACH due to the fact that nanoscale forms of these materials do not meet the criteria for exemption. The vast majority of CNTs available in consumer products are found embedded in composites.

Major potential exposure opportunities (laboratory use)

Receptor	Ingestion	Inhalation	Dermal
Research scientist	Accidental spill	Potential if free and unbound CNTs are handled outside an enclosed area during synthesis, cleanup, or processing. Also potential for exposure during processing and grinding of CNT-containing polymers.	Potential during equipment maintenance, cleanup or spillage.
University environmental health and safety personnel	Accidental spill	Possible, during material transfer	Possible, during material transfer
People handling disposal of CNT-containing waste.	Accidental spill	Possible, during material transfer or incineration.	Possible, during material transfer.