Training Workers on Risks of Nanotechnology

By: Kristen Kulinowski, Ph.D. and Bruce Lippy, Ph.D.

Photos courtesy of NIOSH.

February 2011

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
National Institutes of Health

NIEHS
National Institute of Environmental Health Sciences

This paper is a product of the National Clearinghouse for Worker Safety and Health Training. Following the 2009 workshop entitled, *Global Safety and Health Issues and their Impact on Worker Training*, Drs. Kulinowski and Lippy were contracted by the Clearinghouse to write this paper. The National Clearinghouse for Worker Safety and Health Training is the national resource for hazardous waste worker curricula <http://tools.niehs.nih.gov/wetp/index.cfm?id=603> , technical reports, and weekly news <http://tools.niehs.nih.gov/wetp/newsbrief/currentissue.cfm> on hazardous materials, waste operations and emergency response. Funded by the National Institute of Environmental Health Sciences' Worker Education and Training Program (NIEHS WETP <http://www.niehs.nih.gov/careers/hazmat/index.cfm>), the Clearinghouse provides assistance for NIEHS WETP staff, program grantees, and the general public.

The National Clearinghouse's services include disseminating technical information related to safety and health training development, organizing and documenting NIEHS WETP meetings and workshops <http://tools.niehs.nih.gov/wetp/index.cfm?id=2460> , and analyzing research products to enhance and support on-going and new initiatives. The Clearinghouse is operated by MDB, Inc.

Bios for the Authors

Dr. Kristen Kulinowski is a Senior Faculty Fellow in the Department of Chemistry at Rice University, Executive Director for Policy for the Center for Biological and Environmental Nanotechnology (CBEN) and the Director of the International Council on Nanotechnology (ICON). ICON is an international, multi-stakeholder organization whose mission is to develop and communicate information regarding potential environmental and health risks of nanotechnology thereby fostering risk reduction while maximizing societal benefit. She has experience as a chemical researcher, educator, curriculum developer, administrator, outreach coordinator and policy fellow.

Since 2004, Dr. Kulinowski has been actively engaged in developing and promoting the International Council on Nanotechnology (ICON) which provides a neutral forum in which experts from academia, governments, industry and nonprofit organizations can explore questions of nanotechnology's impact on environment, health and safety (EHS). She directed an effort that resulted in the web publication of the first publicly available database of citations to peer-reviewed papers on nano EHS. Other activities of ICON include a survey of best practices for nanomaterial handling in the workplace, a public portal of information on nanotechnology EHS and the GoodNanoGuide, an interactive forum for sharing information about nanomaterial handling practices.

Dr. Kulinowski has extensive experience in science education, particularly in developing innovative curricula at the undergraduate level, and developed Rice's first introductory undergraduate course on nanotechnology. From 2002-2004 Dr. Kulinowski served as CBEN Executive Director for Education, developing and managing an educational outreach portfolio of programs for audiences that range from middle school children to adults. During this time, the center established itself as a national leader in nanotechnology educational outreach. She is principal investigator on a Susan Harwood Targeted Topics training grant from the Occupational Safety and Health Administration to develop instructional materials to assist small-to-medium sized nanomaterial companies in creating and sustaining safer workplaces.

Dr. Kulinowski has been invited to speak on issues of nanotechnology environmental health and safety and science policy throughout the US, Europe, Asia and the Middle East. She has consulted with governments and governmental advisory bodies regarding responsible nanotechnology, and served as chair of the ASTM International Subcommittee E56.03 on Environment, Health and Safety. Dr. Kulinowski earned a B.S. in chemistry at Canisius College and her M.S. and Ph.D. in chemistry at the University of Rochester. She blogs at http://nanorisk.net and Tweets at http://www.twitter.com/Kulinowski.

Dr. Bruce Lippy has a Ph.D. in policy from the University of Maryland, with coursework concentrated in regulatory economics and quantitative measures of management. His doctoral research was on communicating the hazards of operating and maintaining innovative environmental technologies for cleaning up the Department of Energy's nuclear weapons complex. His work led to the development of over 150 Technology Safety Data Sheets for the Department of Energy. His undergraduate degree is a B.A. summa cum laude in biology from Western Maryland College. He is a Certified Industrial Hygienist and Certified Safety Professional. While with the University of Maryland School of Medicine, he co-authored an extensive review of the hazard communication literature on MSDSs, labels and warnings. Dr. Lippy, while serving as the Director of the National Clearinghouse for Worker Safety and Health Training, developed guidance on training mold remediation workers.

He has participated in the White House Office of Science and Technology Policy's Nanoscale Environment and Health Initiative. Dr. Lippy has spoken on the worker health and safety issues of nanotechnologies at the Mount Sinai School of Medicine, the University of Massachusetts at Lowell, the Society for Chemical Hazard Communication, the American Society of Safety Engineers and at the EPA's international conference in Chicago, October 2008.

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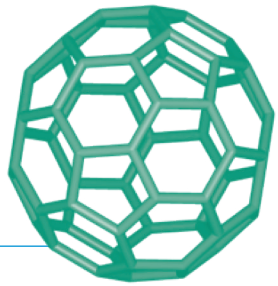


Introduction

Joseph "Chip" Hughes, Director of the Worker Education and Training Program of the National Institute of Environmental Health Sciences

Since 1987, the Worker Education and Training Program has been a major national force for developing effective occupational safety and health training. The program has generated guidance on training hazardous waste workers under OSHA's 1910.120 Hazardous Waste Operations and Emergency Response (HAZWOPER) Standard, on using advanced training technologies to train workers, and on training workers exposed to mold. These guidance documents advocate peer training of workers and good use of adult learning techniques.

In the Fall of 2009, the program held a technical meeting entitled, *Global Safety and Health Issues and their Impact on Worker Training*. A panel that included Drs. Kristen Kulinowski from Rice University, Richard Niemeier from the National Institute for Occupational Safety and Health, and Sam Paik from Lawrence Livermore National Lab addressed nanotechnology and control banding and the implication for worker training. The panel was moderated by Dr. Bruce Lippy.

This paper is a direct result of the conference. Rather than produce our customary conference report, we felt the subject of training workers about the risks and benefits of nanomaterials was so important and unexamined that we should explore it in-depth in a discussion paper that can hopefully lead to a guidance document with broad value to workers and employers. To that end, we welcome your comments. Unfortunately, the history of introducing new materials like asbestos, lead, acrylonitrile and polychlorinated biphenyls has been a legacy of government actions *after* disease has been discovered in a worker population. The U.S. government has learned from history and has been much more proactive in identifying the hazards of nanomaterials. The efforts to collect and disseminate nano-related information through outlets like Rice University's International Council on Nanotechnology, the National Nanotechnology Initiative of the federal government that coordinates the activities of 25 Federal agencies, and the Woodrow Wilson International Center for Scholars, has been unprecedented.

The growth of nanotechnologies is so explosive, however, that regulatory agencies are having difficulties keeping up. As the Government Accountability Office (GAO) starkly noted in its May 2010 report on nanotechnology, "Although the body of research related to nanomaterials is growing, the current understanding of the risks posed by these materials is limited." The area that has received the least amount of attention is the training of the nanotechnology workforce. Hopefully, this document will begin to redress that deficit.

1. Purpose and overview

1.1. Purpose of this document

Among the thousands of papers published on nanotechnology, this is one of the first to address the critical issue of how workers who are creating and handling nanomaterials should be trained about the hazards they face – in laboratories, manufacturing facilities, at hazardous waste cleanup sites and during emergency responses. Given the limits in the current understanding of nanotoxicology, workplace exposures and effectiveness of control strategies, defining effective training is particularly problematic. But workers clearly have the potential to be exposed and are guaranteed the right to know about the risks they face, under international hazard communication standards that are being harmonized across the globe.

The purposes of this document are to:

1. Provide a broad overview of the key issues that workers and instructors should understand about nanotechnology, particularly the occupational health and safety issues;
2. Define current knowledge on worker protection through work practices, engineering controls and personal protective equipment;
3. Review the applicability of current U.S. regulations to nanomaterials with a focus on the OSHA Hazardous Waste Operations and Emergency Response standard (HAZWOPER);
4. Provide a suggested outline for an 8-hour awareness course that would prove beneficial to most workers handling nanomaterials and may satisfy OSHA's requirement for HAZWOPER refresher training; and
5. Provide a framework that will eventually enable the hundreds of instructors funded by the National Institute of Environmental Health Sciences' Worker Education and Training Program (WETP) to train their constituents about the hazards of and controls for specific nanomaterials in their workplaces. Nearly two million workers have received NIEHS WETP-supported safety and health training since the inception of the program in 1987. The primary objective of the program is to fund non-profit organizations to provide high quality occupational safety and health training to workers who are involved in handling hazardous materials or in responding to emergency releases of hazardous materials. These are covered by OSHA's Hazardous Waste Operations and Emergency Response (HAZWOPER) standard, 29 CFR 1910.120, which arguably covers nanoparticles.

The term nanotechnology describes a wide range of technologies, materials and applications that are affecting or will affect every sector of commerce including medicine, energy, construction, environmental remediation, automotive and aerospace. Examples that exist today include photocatalytic particles that break down organic pollutants in contaminated groundwater, novel medical devices that demonstrate greater specificity for cancer cells, and fibers that improve mechanical strength while reducing mass in automobile parts. The aspects of nanotechnology that merit the attention of the worker training community are its impact across sectors, its novelty and its potential for growth.

Not a single technology itself, nanotechnology has enjoyed widespread support from the federal government and large investments by industry because it offers a platform for improving existing materials, devices and drugs by exploiting the novel properties that emerge when matter is taken down (or up) to the nanoscale. These new modes of action can significantly enhance the properties of the products in which they are used, leading to materials that are stronger, multifunctional or more energy efficient. But novelty is a double-edged sword; i.e., the same unique properties that benefit a particular application could result in new risks to people or the environment. Concerns about health and safety are being addressed in research laboratories around the world but the application of this risk-relevant research to worker safety is still in the early stages. In science fiction, depictions of

nanotechnology abound, making it seem like something from the future; however, there are over a thousand products already on the market today and many more in the pipeline. If the scale of the potentially affected workforce tracks the rapid growth of nanotechnology research and product development, the implications for worker training should be clear: many workers should already be trained in safe handling of nanomaterials and many more will need training in the near future, particularly the secondary and tertiary users.

1.2. Outline

This paper will provide a basic understanding of nanotechnology and its implications for worker training. Section 1 introduces essential concepts of nanotechnology, presents the major areas of its application and identifies unresolved issues around workforce identification. Section 2 reviews the relevant environmental, health and safety literature and what this means for worker training. Section 3 assesses the strengths and weaknesses of applying traditional risk management approaches to the nanotechnology workplace. Regulatory and voluntary approaches developed specifically for use with nanoparticles are described in Section 4. Freely available resources that will help trainers stay up to date on new developments in nanotechnology and worker training are catalogued in Section 5. The paper concludes in Section 6 with concrete suggestions for implementing a nanotechnology-specific training program.

2. Introduction to nanotechnology and nanoparticles

2.1. Definitions

Nanotechnology is an emerging area of technology development involving structures that measure between 1–100 nanometers (nm) in one or more dimensions. While precise definitions are still somewhat variable, most standard definitions recognize that nanotechnology involves science and engineering of matter at the nanoscale where properties may change with size or new properties may emerge. Nanotechnology can be further subdivided into nanomaterials and nanostructured materials. These terms are often used interchangeably but have subtly different meanings depending on whether it is an external dimension or merely a component, internal feature that falls within the nanoscale size range of about 1-100 nm. According to some definitions, **nanomaterials** are small pieces of matter with one or more **external** dimensions on the nanoscale. If the object has two or three external dimensions on the nanoscale it may be referred to as a **nanoparticle**. Quantum dots that measure 4 nm in diameter are nanoparticles. If it has two or three external dimensions on the nanoscale AND has a length-to-width aspect ratio of 3:1 or greater it may be referred to as a **nanofiber**. Nanofibers include carbon nanotubes and nanorods. **Nanostructured materials** have internal features that fall within the nanoscale but may be larger than 100 nm as a whole. Examples of nanostructured materials that are larger than 100 nm include a microscale particle that has nanoscopic internal pores or a 300-nm aggregate of 20-nm primary particles. Nanoparticles are a subset of nanomaterials. For the most part, this paper will focus on nanomaterials but not nanostructured materials.

Nanoparticles are a subset of nanomaterials.

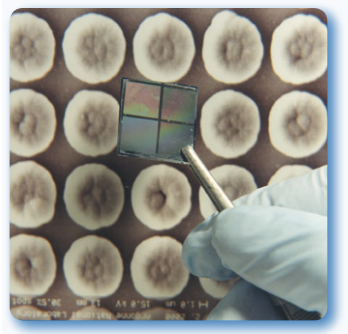
Smaller than microscale particles, yet larger than atoms and all but the largest molecules, nanoparticles occupy a transitional regime between classical and quantum physics where physical and chemical properties may depend on the nanoparticle's size, structure, composition, surface structure or surface composition. Classical physics governs the behavior of objects in our everyday experience and thus is more intuitively familiar to us. We know, for example, to duck (or put our glove up) when we see a baseball flying toward our head. The ball's trajectory, which is governed by the forces of gravity and friction, is easily predicted and can even be precisely calculated using the principles of classical physics. If that baseball were an object about 10 trillion times smaller, its behavior would be governed by quantum physics and we would lose our ability to predict its location and path. We wouldn't know when to duck. Nanoparticles behave more like quantum objects than like baseballs, especially

at the lower end of their size scale. This means that our prior knowledge and experience with a substance may not always predict how that substance will behave when it is made at the nanoscale. As the nanoparticle's size increases, it acts more and more like a baseball, which is why there is an upper boundary on most definitions of the size scale.

Gold affords a great example of the striking differences of materials at the nanoscale. Everyone is aware of the shiny orange-yellow color of gold in coins and jewelry. That is a feature of the macroscale world. Between 100 and about 30 nanometers, gold is purple and at 30 nm in size, a gold particle is bright red. Smaller particles become brownish in color.[1] Macroscale gold is prized for its chemical inertness as well as its luster. But nanoscale gold can be highly reactive, even being used as a catalyst in some chemical reactions. Color, magnetism, electrical conductivity and chemical reactivity are just some of the properties that can change at and throughout the nanoscale.

Dust plume from the Icelandic volcano, April 17, 2010.

Nanoparticles can be intentionally designed for a purpose (engineered or manufactured), unintentionally produced as part of another industrial or anthropogenic process (incidental) or produced naturally. Incidental nanoparticles may also be referred to as ultrafine particles. (See Table 1.) To meet the definition of "nanotechnology" the particles must have been engineered; e.g., a microscale titanium dioxide particle may be reduced to the nanoscale to prevent it from appearing white in a sunscreen formulation. In contrast, the nanoparticles that may compose a fraction of diesel exhaust are not intentionally designed to exploit special properties that occur at the nanoscale. Rather they are an accidental by-product of incomplete combustion and therefore are not considered to meet the definition of nanotechnology. Practically speaking the distinction in the mode of production between incidental and intentional nanoparticles may have little bearing on the worker if an exposure leads to unwanted outcomes. However, for the sake of clarity this paper will assume the nanoparticles are engineered.



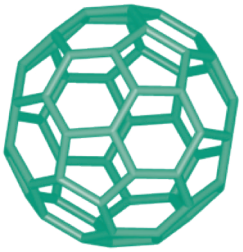
Silicon plate holding 40,000 diamond film dots for microelectronics.
Image courtesy of Lawrence Berkeley Laboratory

Table 1: Distinguishing nanoparticle types by their mode of production

Nanoparticle Type	Examples
Naturally occurring	Volcanic ash, sea spray, combustion by-product
Incidental (Ultrafine)	Fresh welding fume, freshly generated diesel exhaust
Engineered (Manufactured)	Nanotube, nanoscale titanium dioxide

Engineered nanoparticles can be made from many different chemical substances. The types of nanoparticles in use today can be broadly classified into five categories: metals, metal oxides (ceramics), carbon-based, semiconducting (quantum dots) and organics. (See Table 2). Within these broad classifications, there may be several subcategories, each of which has its own set of properties. A nanoscale metal may be prized for its unique optical, electrical or catalytic properties or, in the case of silver, its antimicrobial activity. Metal oxides may have interesting magnetic, mechanical or catalytic behavior.

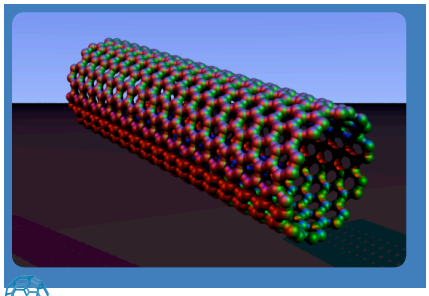
Carbon-based nanoparticles may impart mechanical strength and can be made to conduct electricity. Quantum dots have useful optical properties. Organic nanoparticles are especially useful in medical applications.



Buckminsterfullerene (Buckyball) composed of 60 carbon atoms.
Courtesy Rice University

Table 2: Broad categories of nanoparticles

Broad category	Examples
Metals	Silver, Gold, Copper
Metal oxides (ceramics)	Titanium dioxide, Zinc oxide, Cerium oxide
Carbon-based	Fullerenes, Nanotubes
Semiconducting (quantum dots)	Cadmium selenide, Cadmium sulfide, Zinc sulfide
Organic	Polymer beads, Dendrimers



Computer simulation of a nanotube.
Courtesy Wikimedia Commons

Multiwalled carbon nanotubes as a black clumpy powder. 10 gram container, scale in centimeters.
Courtesy Shaddack, Wikimedia Commons

Nanotech for environmental remediation

As of February 2009, the EPA's National Priorities List contained 1,255 Superfund hazardous waste sites that are estimated to take up to 35 years and cost up to $250 billion to remediate. Federal agencies looking for ways to do cleanup "quicker, cheaper and better" are investigating catalytic nanoparticles as an attractive alternate to expensive pump-and-treat technologies. Magnetic iron oxide nanoparticles have been shown to bind arsenic irreversibly up to 10 times more effectively than micrometer-sized particles. These particles can be separated from water with magnetic fields, yielding a 99 percent cleanup in laboratory and field tests.

A case study at a manufacturing site in New Jersey where the primary contaminants of concern in ground water were trichloroethylene (TCE) and perchloroethylene (PCE) found that using iron oxide nanoparticles would reduce costs 80 to 90 percent and cut the required time even more dramatically, from an average of 18 years for pump-and-treat on EPA sites to – in one study – a 99% reduction in TCE levels within days of injection.

2.2. Quantifying the size of the industry and affected workforce

Because nanotechnology is a set of technology platforms that are applied across multiple sectors, it is difficult to quantify the nanotechnology "industry." No North American Industry Classification System (NAICS) code for nanotechnology exists and a company may choose whether or not to disclose that it is engaged in commercial nanotechnology research, manufacture or use at its discretion. Nonetheless there have been some attempts to estimate nanotechnology's impact on the marketplace today, as well as to project how much it is expected to grow. A 2008 report by Lux Research estimated that nanotechnology was used in $147 billion worth of products in 2007 and will impact $2.5 trillion of products by 2015. [The Recession's Ripple Effect on Nanotech] Another analysis puts these same figures at $2.3 billion in 2007 and only $81 billion in 2015. [Nanoscale Materials and Markets 2008-2015] Since there are no standard industry codes or even well established standard definitions for nanotechnology, these analyses may better serve as measures of the potential future growth of nanotechnology than as actual market values.

If the size and scope of the industries involved in nanoparticle production or use are difficult to quantify, it is even harder to collect demographic information on the worker population. Such information would be invaluable in the development of a nanotechnology worker registry that would enable medical surveillance to identify potential problems early. The prospect of identifying the nanotech workforce is less daunting when considering a small-to-medium nanotechnology enterprise, as its core business most likely involves the manufacture or use of engineered nanoparticles. But for many large companies, nanoparticle production or use may constitute a small fraction of the total business and the employees who handle nanoparticles may not be distinguished from workers in other parts of the company. For this class of companies the nanotechnology workforce may not differ substantially in key demographic categories from workers in the chemicals industry. NIOSH, in particular, is interested in gaining a greater understanding of the potentially affected workforce though it asserts, "there is insufficient scientific and medical evidence to recommend the specific medical screening of workers potentially exposed to engineered nanoparticles."[2] NIOSH, however, also recommends the continued use of established medical surveillance approaches and the conduct of hazard surveillance. The European Agency for Safety and Health at Work unambiguously noted that, "At present, there is insufficient information on the number of workers exposed to nanomaterials in the work place or the effects on human health of such exposure."[3]

Recent studies indicated that the current number of workers who are directly involved with nanoparticles is probably relatively low. Although there is limited information about the size and scope of the U.S. worker population, studies done on other industrialized nations with strong nanotechnology research and development programs reveal small percentages of workers engaged in handling nanoparticles. Research published in 2010 indicated that only 0.6% of manufacturing companies in Switzerland used nanomaterials, which led to an estimation of only 1,309 workers across the entire country, an average of 2.5 workers per company handling nanomaterials. An earlier study in England estimated 2,000 workers handling nanomaterials in that country, although the researcher's definition of a "nano" company was quite proscribed.[4] One market analysis estimates that the global workforce in nanotechnology industries will reach 2 million by the year 2018.[5] A better accounting of the potentially exposed workforce is needed to guide risk management and worker training programs.

As manufacture and use constitute only part of the lifecycle of an engineered nanoparticle, chemical industry workers are only a part of the potentially affected workforce. In addition to production line workers, maintenance and housekeeping staff must be considered. Moreover, smaller pockets of workers will also be found throughout the scores of institutes and universities performing research on novel nanoparticles. These workers may not account for a significant population in any given workplace, but in the aggregate may account for a substantial number of people.

Except at the point of original manufacture, most workers will not encounter nanoparticles in their native form. Instead the worker may encounter a nanoparticle that has been physically or chemically modified for use in an end-product. As an example, carbon nanofibers may be manufactured by one company, sold in their native form to another company, incorporated by that second company into a car bumper, sold in the car bumpers to an auto manufacturer which then sells the car to the final consumer. To measure the full impact of engineered nanoparticles, the entire lifecycle must be assessed, from production through formulation and use to disposal or recycling. The maintenance and custodial workers at these locations may be exposed during their work on labs and systems. Health and safety of workers handling nano-enabled products or materials at their end-of-life must also be considered. The majority of nanomaterials encountered will be various products that are improved or "nano-enabled" by having engineered nanomaterials in them. In some cases, the nanoparticle will persist largely unchanged, whereas in others it will change drastically or even dissolve altogether. Once in the natural environment a nanoparticle may be transported beyond the point of release through waters or soils in unexpected ways, be broken down by microbes or be chemically transformed by oxygen and sunlight. At this point, few complete assessments have been attempted and there is not enough information to predict how a given nanoparticle in a specific application will behave throughout its lifecycle. This results in significant knowledge gaps that can impact the training of workers who handle nano-enabled products in the waste and recycling industries.

It is clear, however, that nanoparticles will figure much more prominently in the cleanup of hazardous waste sites into the future. The NIEHS Worker Education and Training Program was created under the Superfund Amendments and Reauthorization Act of 1986 to train workers to safely remediate the hundreds of thousands of hazardous waste sites in this country. The work continues. The EPA has been allocated nearly a billion dollars for remediation projects under the American Recovery and Reinvestment Act of 2009.[6] Greater than 80 percent of NPL sites have contaminated groundwater. Nanoparticles, like nano zero-valent iron (nZVI), have been shown to be particularly effective in groundwater remediation, which has a direct impact on greater than half of the U.S. population relying on groundwater for drinking. Polluted groundwater cleanup, even though the trend is moving from pump-and-treat to *in situ* methods, has proven to be "protracted, costly, and sometimes infeasible."[7] Nanomaterials like zeolites, metal oxides, carbon nanotubes, bimetallic nanoparticles (BNPs) and titanium dioxide have been successfully applied in remediation, but the use of nZVI dominates and is "increasingly rapidly."[8] See figure 1.

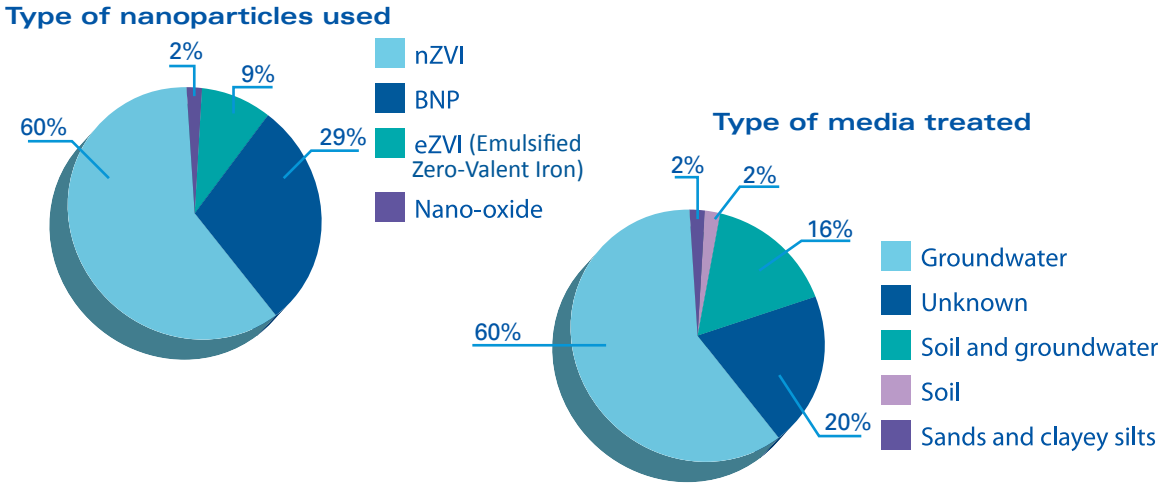


Figure 1: Type of nanoparticles used (A) and type of media treated (B) at 44 international sites.
From Karn et al. 2009

Based on findings of 80 to 90 percent cost reductions using nZVI rather than pump-and-treat for removing chemicals from groundwater noted previously, the EPA projects that using nanoremediation could potentially save this nation $87 to $98 billion on remediating hazardous waste sites over the next 30 years.[9] Consequently, the exposure of hazardous waste workers to nanoparticles will increase. There is, unfortunately, much greater agreement on the effectiveness of treatment than the risk posed by release of particles in the environment. As the Royal Commission on Environmental Pollution noted in 2008:

> *"While there have been no significant events that would lead us to suppose that the contemporary introduction of novel materials is a source of environmental hazard, we are acutely aware of past instances where new chemicals and products, originally thought to be entirely benign, turned out to have very high environmental and public health costs."*[10]

The Royal Commission primarily addressed acute exposures and release events, which doesn't consider the potential for chronic effects.

2.3. Nanoparticles' environmental, health and safety impacts

Nanotechnology environmental, health and safety (nano-EHS) research is still in an early phase with published findings scattered across dozens of different journals. Publications of relevance to this topic are collected, catalogued and indexed within the ICON Virtual Journal of Nano-EHS, an open web-based resource that contains citations to more than 4,600 papers. [http://icon.rice.edu/virtualjournal.cfm] The Nano-EHS Database Analysis Tool permits users to sort this comprehensive resource by particle type, exposure target population, exposure pathway and other criteria. A search on all papers reveals a rapid acceleration in the pace of knowledge generation in the fields of toxicology and environmental impact within the last decade. (See Figure 2.) Reports of direct relevance to worker health, such as research findings on the ability of respirators or gloves to filter out nanoparticles, the ability of local exhaust ventilation to control the flow of nanoparticles or the proper methods of exposure monitoring in the workplace, constitute a very small fraction of this literature.

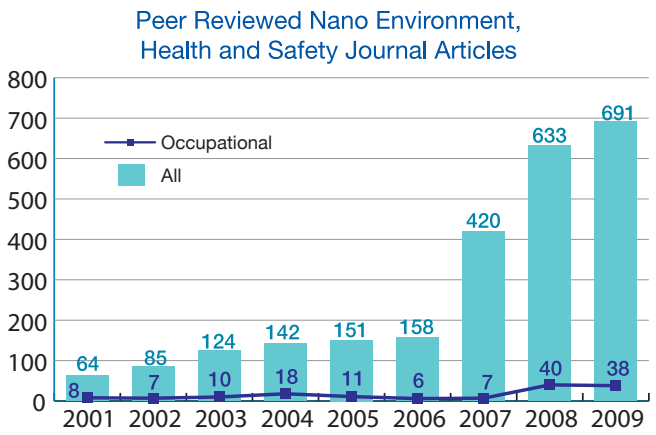


Figure 2: Occupationally Relevant Research. Results from a search of the ICON Virtual Journal on Nanotechnology Environment, Health and Safety for all peer-reviewed nano-EHS papers published between 2000-2009 (green) and those papers that address some aspect of worker safety (purple). *SOURCE: http://icon.rice.edu/report.cfm.*

Despite the large number of papers on the general subject of nano-EHS, it is difficult to draw robust conclusions about the risks engineered nanoparticles might pose to workers or the environment. The reasons for this are myriad, and include a lack of validated protocols for performing toxicology tests on nanoparticles, questions about the appropriate metric for measuring dose, lack of models for how nanoparticles are transformed in the body or the natural environment and the role of surface area and surface chemistry in controlling bio-interactions.[11] Despite these challenges, the large body of work does permit some general conclusions of relevance to worker safety to be drawn.

Because of their small size and active surface chemistry, nanoparticles may behave in different ways in the body than their non-nanoscale analogs. The majority of nano-EHS papers address some aspect of hazard, mostly acute toxicity tests done in cell culture.[12] Certain nanoparticles have been shown in animal studies to translocate along the olfactory nerve into the brain, cross the placenta and penetrate damaged or diseased skin. Once inside the body, certain nanoparticles have induced inflammatory responses, cardiovascular effects, pulmonary fibrosis and genotoxicity. Certain carbon nanotubes, one of the most widely researched class of nanoparticles from both a technological and toxicological perspective, have even been shown to induce asbestos-like effects in rodents which raises concerns among occupational safety professionals.[13] It must be emphasized, however, that effects demonstrated by one type of nanoparticle in one laboratory study cannot be generalized to other nanoparticles.

In one highly publicized carbon nanotube study, for example, only the long, straight, multiwalled forms acted in a manner similar to asbestos fibers when injected into the rodents' bodies. Other nanotube forms that were shorter and more flexible did not induce the harmful response, nor have other types of non-carbon-based nanotubes been shown to mimic toxic asbestos fibers.[14] The most recent draft guidance from NIOSH, their Current Intelligence Bulletin, "Occupational Exposure to Carbon Nanotubes and Nanofibers," indicates that mesothelioma has been produced in a strain of mice with multiwalled nanotubes.[15] Examples such as these serve to illustrate not that "nanoparticles are toxic" but that hazard is related to specific material properties such as composition, form, dimension and specific use scenarios.

The research community is working to develop a better understanding of how nanoparticles' physical and chemical characteristics can be correlated to their biological interactions. Without predictive models for linking measurable properties such as size, shape and surface area to biological interactions such as the production of reactive oxygen species, protein misfolding, cell death (apoptosis) and mutagenicity, the number of individual nanoparticle variants that would have to be tested is practically infinite. Experts recently concluded that predictive models are an important long-term goal requiring ten years of work or more.[16]

The relevance of the nano-EHS hazard studies to real-life working conditions is unclear. Risk assessment relies upon an understanding of both hazard and exposure; when one is absent, the assessment is incomplete. Exposure studies that measure the likelihood that one would come in contact with a toxicant in a high enough dose to cause the unwanted outcome lag far behind the hazard studies as demonstrated in Figure 3. In the absence of nano-specific exposure studies, the likelihood of exposure may be able to be estimated using surrogates, predictors, or historical experience.

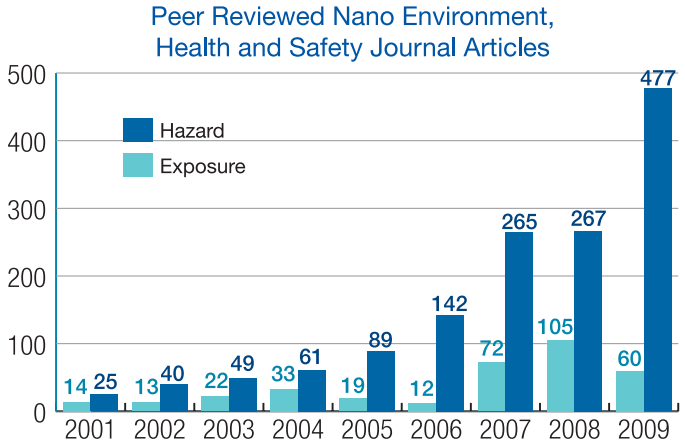


Figure 3: Hazard vs. Exposure. Results from a search of the ICON Virtual Journal on Nanotechnology Environment, Health and Safety for all peer-reviewed nano-EHS papers published between 2000-2009 that address nanomaterial hazards and those papers that address nanomaterial exposure. *SOURCE: http://icon.rice.edu/report.cfm.*

3. Application of traditional risk management approaches to protect workers handling nanoparticles

Nanoparticles may be new but hazardous substances are not. We need not assume a risk management program has to be constructed from scratch. What is important, however, is to carefully examine our assumptions and validate our existing tools when applying them to situations where nanoparticles are present. Many of the existing frameworks for dealing with toxic substances may be able to be applied to nanoparticles with little revision. Others may need to be scrapped altogether. As always, the first steps are to understand the specific tasks that could bring a worker into contact with a nanoparticle and then identify how best to control that exposure. What follows here is a review of the applicability of existing tools for measuring and controlling exposure to nanoparticles.

3.1. Most likely exposures among NIEHS representative groups

NIOSH, working with the private sector, has attempted to identify the tasks that are most likely to generate worker exposures to nanoparticles. The following have been specifically noted:

- Generating nanoparticles in the gas phase in non-enclosed facilities;
- Handling nanostructured powders;
- Working with nanoparticles in liquid media without adequate protection, particularly gloves;
- Working with nanoparticles in liquid during pouring or mixing operations or where a high degree of agitation is involved;
- Conducting maintenance on equipment and processes used to produce or fabricate nanoparticles; and
- Cleaning up spills or waste materials.[17]

Sampling during handling of carbon nanotubes
Courtesy of NIOSH.

As noted earlier, the NIEHS Worker Education and Training Program has been funding training for high-risk populations of hazardous waste workers and emergency responders since 1987 under the Superfund Amendment and Reauthorization Act. The organizations that provide this training serve distinct populations that may benefit from training in the identification and control of nanomaterials hazards. Table 3 is the result of an informal survey of principal investigators from the NIEHS-funded programs.

Table 3: Potential exposures among NIEHS-supported worker populations

NIEHS WETP awardee	Worker population	Types of nanomaterials	Tasks
(CPWR) The Center for Construction Research and Training	Workers involved in construction, demolition and remediation	nano-scale zero-valent iron; photocatalytic concrete (which uses nano-scale TiO2 as an additive); nano-enabled construction materials	Using nano-scale iron to treat soil contaminated with chlorinated solvents; demolishing structures containing photocatalytic concrete
International Association of Fire Fighters	Firefighters	Wide range of nanomaterials	Responding to fires, explosions or leaks at firms producing carbon nanotubes
Teamsters	Truck drivers	Solutions of nanoparticle such as multiwalled carbon nanotubes and packaged dry nanoparticles	Driving trucks carrying packaged nanoparticles that may be involved in a spill on the highway
International Union of Chemical Workers	Chemical plant industrial workers	Wide range of nanoparticles	Producing batches of nanoparticles in chemical plants
International Union of Operating Engineers	Stationary engineers	Nanosilver biocides	Adding biocides to cooling tower water and HVAC drip pans
Laborers International Union of North America	Cleanup workers	Nanoparticles in hazardous waste	Performing cleanup of waste sites
Midwest Consortium	Industrial emergency responders	Wide range used in production of personal care products, paints and new ones daily	Spill cleanup and response

NIEHS WETP awardee	Worker population	Types of nanomaterials	Tasks
Midwest Consortium	Municipal first-on-scene	Wide range of materials that may be spilled during transport	Spill cleanup and response
Midwest Consortium	Treatment, Storage and Disposal Facilities (TSDF)	Wide range	Transfer, repackaging and disposal
Service Employees International Union	Nurses and physicians; facility maintenance workers, janitorial services	Nanoparticles used in medicines; nano-enabled cleaners and disinfectants	Preparing intravenous liquids
Dillard University	Cleanup workers	Nanomaterials in hazardous waste	Performing cleanup of waste sites
United Steelworkers	DOE cleanup site workers	Nanoremediation agents like Nano iron oxide	Performing in situ injection of agents
United Auto Workers		Nanomaterials in autoparts	Assembling cars

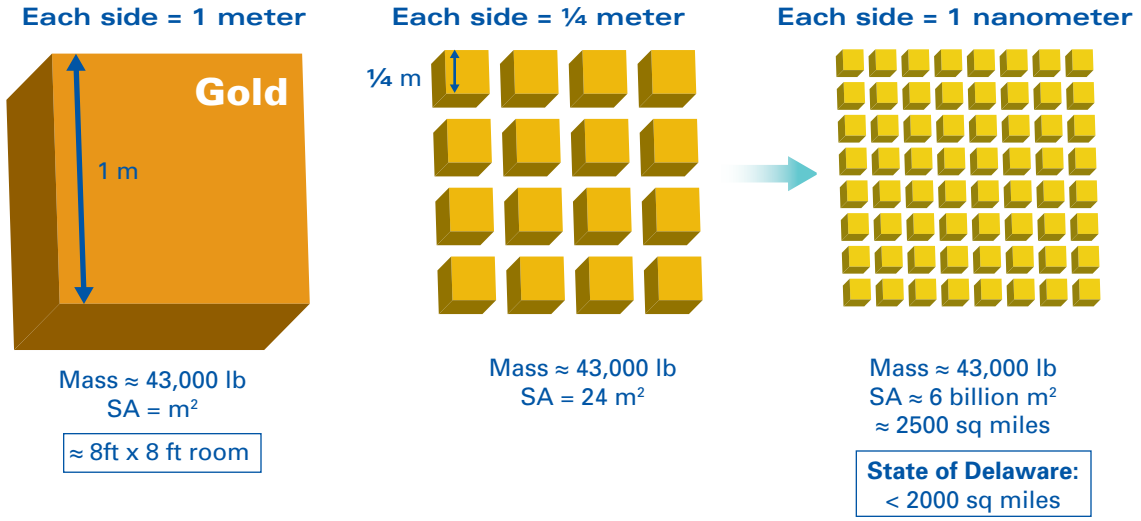
3.2. Assessing exposures

3.2.1. Difficulty with the standard IH paradigm

The standard model of industrial hygiene that has underpinned the profession as well as the OSHA regulatory approach since 1970 has been the measurement of exposures in the personal breathing zone of workers for comparison against established occupational exposure limits. These limits were established based on animal tests and, too often, upon human epidemiology; but given the decades of use of standard industrial solvents like toluene, the accumulated data were often impressive and persuasive for setting a limit that would arguably allow a working career of exposure without permanent, deleterious health effects. These numbers were generally set to be an 8-hour time-weighted average. For dust exposures, the unit of measurement has historically been milligrams (or micrograms) per cubic meter of air.

Given the extraordinarily small size and weight of nanoparticles, however, these mass-based measurements are of limited value. The majority of animal toxicology studies have used mass as the exposure dose for evaluating adverse health outcomes. Until improved sampling and analytical methods can be developed, and until data become available to determine if alternative exposure metric to mass may be more biologically relevant, mass-based measurements may have to be applied along with other exposure metrics for evaluating worker exposures. One critical feature of nanoparticles is the tremendous surface area that is created for the same amount of mass. A thought experiment can illustrate how significant this can be for determining the nanomaterial's behavior. Consider that we have a large block of pure, solid gold that measures 1 meter on each side. This makes a surface area of 6 m^2. Now imagine that we cut that block of gold into pieces that each measure ¼ m on a side; the surface area is now 24 m^2. Taking this thought experiment to the extreme, if we divide the same mass of gold into particles measuring 1 nm on each side, the surface area exceeds 6 billion m^2. That is more than enough to cover the surface of the entire state of Delaware.

Figure 4: Dividing a solid into nanometer-sized particles exposes a high fraction of the interior atoms to the surroundings making surface area a critical metric for measuring exposure.



This is also of concern for health effects: the same reactive surfaces that are prized in creating unique properties in new products appear to be implicated in much of the unwanted health effects. As the British Standards Institute correctly noted, "Altered chemical and/or physical properties might be expected to be accompanied by altered biological properties, some of which could imply increased toxicity."[18]

Making risk comparisons solely based on weight ignores the importance of surface area and, consequently, may greatly underestimate the health hazards posed by nanoparticles. Referencing 40 year old "nuisance dust" standards, as most current Material Safety Data Sheets for carbon nanotubes do, is essentially saying that normal use of these carbon nanotubes should generate less dust than a sawmill. Almost no other risk conclusion can be drawn from the use of old, mass-based standards. Even if the engineered nanoparticles are delivered suspended in solution, recent studies indicate that workers can be exposed to water droplets containing the particles during standard laboratory practices like sonicating the liquid to break up agglomeration, which is a common occurrence.[19]

3.2.2. Absence of a Permissible Exposure Limit

Currently, there are no accepted occupational exposure limits for any nanoparticles; however, there have been 16 Occupational Exposure Limits offered for consideration by various organizations and companies.[20]

NIOSH is about to complete a Current Intelligence Bulletin on titanium dioxide (TiO_2) that will provide Recommended Exposure Limits (RELs) for two size ranges of TiO_2: one for particles in the micrometer-diameter range and one for particles in the diameter range below 100 nanometers. NIOSH will be providing Recommended Exposure Limits (RELs) for ultrafine (including nanoscale TiO_2) and fine TiO_2. The RELs will be 8-hour TWAs in the range of 0.3 mg/m^3 for ultrafine TiO_2 and 2.4 mg/m^3 for fine TiO_2. Nevertheless, NIOSH admits, that questions remain about specifying the sampling and analytical methods for the nanoscale TiO_2, the extent of workplace exposures, and the ability to control exposures at or below the REL."[21]

NIOSH has announced its intention to create one or more Recommended Exposure Limits (RELs) for nanoparticles likely to be commercially available. This may have to be set by broad category of nanoparticles based on physicochemical similarities. There may be, for instance, more than 10,000 combinations of carbon nanotubes possible.[22]

NIOSH, in its draft Current Intelligence Bulletin on carbon nanotubes is recommending an REL of 7 ug/m3 as an 8-hour time weighted average. This is roughly 3 orders of magnitude lower than the levels found in section 2 of many MSDSs for carbon nanotubes now on the market.

Given the tentative nature of governmental action thus far, private companies have begun to set exposure limits for their products. In November 2009, Bayer Material Science (BMS) announced an occupational exposure limit of 0.05 mg/m^3 for Baytubes, a multi-wall carbon nanotube product. The company has incorporated this OEL in their Material Safety Data Sheets, which is an enlightened policy compared to the standard practice of referencing Threshold Limit Values for graphite.

Given the lack of benchmarks for sampling, very few private organizations have reported monitoring their workplace for nanoparticles, although those that handle larger volumes of nanomaterials are more likely to do so.[23]

3.2.3. Approaches used by NIOSH to count particles and measure surface area

NIOSH has examined the following innovative approaches in its 2009 guidance document, "*Approaches to Safe Nanotechnology*."[24]

The first is counting particles. Fortunately, the industrial hygiene field has had access to affordable real-time instruments that count particles for a considerable time. The best known use of these instruments is for quantitative fit-testing of respirators with instruments like the TSI Portacount. NIOSH researchers have used handheld **condensation particle counters (CPC)** to count nanoparticles; these instruments use isopropyl alcohol to coat particles so they are large enough to be counted with a laser beam. The CPC report the total number of particles counted per cubic centimeter of air without identifying the chemical makeup. The CPC measures particles in the size range of 10 or 20 nanometers (nm) up to 1,000 nm.

A slight variation on this technique, optical particle counters (OPC), use laser light scattering to provide the total number of particles per liter of air without providing any chemical identification. The OPC measures the total number of particles per liter within 6 specific size cut points: 300 nm; 500nm; 1,000 nm; 3,000 nm; 5,000 nm and 10,000 nm.

NIOSH conducted field studies at 12 sites including research and development laboratories, pilot plants, and manufacturing facilities using a new approach involving a battery of measurements that it called Nanoparticle Emission Assessment Technique (NEAT). The results demonstrated the success of the sampling strategy, using cost-effective portable methods and equipment available to the average industrial hygienist.[25]

A more complex and expensive instrument is the **Particle Surface-Area Analyzer**. Instruments like the TSI Aerotrak™ 9000 Nanoparticle Aerosol Monitor do not measure total active surface area, but indicate the surface area of particles which may be deposited in the lung in units of square micrometers per cubic centimeter, corresponding to either the tracheobronchial or alveolar regions of the lung. The Ecochem DC 2000-CE measures the total particle surface area. These devices are being evaluated by NIOSH for usefulness in conducting initial assessments.

Scanning Mobility Particle Sizers report particle diameter sizes and numbers, which can significantly enhance the capacity to identify releases of engineered nanoparticles, rather than naturally-occurring ultrafines. The SMPS is widely used as a research tool for characterizing airborne nanoparticles, but won't be widely used to measure worker exposures because it is much more expensive and physically larger than other instruments. It also contains an internal radioactive source, which further complicates its use.
The cutting edge of sampling may be represented by the **Fast Integrated Mobility**

Spectrometer (FIMS), which has been developed for rapid aerosol size distribution measurements including those aerosols with low particle number concentrations. Results from this instrument compared well with those measured by a scanning mobility particle sizer (SMPS) and total particle concentration measured by the FIMS agreed well with simultaneous measurements by a condensation particle counter (CPC).This device is also able to capture the size distribution of rapidly changing aerosol populations.[26]

3.2.4. Results from limited sampling

The results from the NIOSH field survey of 12 facilities reviewed earlier is the most comprehensive look at potential worker exposure published thus far.

An important case study measured very fine particle number and mass concentrations in an engine machining and assembly facility. A condensation particle counter (CPC) and an optical particle counter (OPC) were used to measure particle number concentrations over a broad range. The OPC measurements were used to estimate the respirable mass concentration. The study demonstrated the importance of considering all sources of very fine particles. The authors reported that, "In summer, the very fine particles present in the outdoor air may have substantially contributed to very fine particle number concentration observed inside the plant." In winter the main source of very fine particles was not plant operations but gas-fired heaters.[27]

A NIOSH case study that examined potential emission sources of engineered nanoparticles (ENM) during a variety of operations showed that reactor cleanout was an uncontrolled source of emissions, apparently due to technicians brushing and scraping unwanted buildup from the inside of the reactor. This prompted an effort to minimize potential worker exposure, mainly through the use of PPE as well as consideration of other measures such as local exhaust ventilation systems (LEVs).

Sampling at this site showed that reductions of 96 percent with particle counters and 88 percent with filter-based methods led researchers to report "properly maintained LEV can be highly effective in controlling ENM emissions. This finding, coupled with the current use of PPE, appears to be an acceptable method of reducing the potential for worker exposure."[28]

NIOSH received a request to evaluate a university-based lab that used carbon nanofibers (CNFs) to produce polymer composite materials. NIOSH researchers used various methods to measure exposures during tasks such as transferring CNFs into a lab hood, mixing CNFs with acetone in a vessel and cutting composite with a wet saw. Measurements of total airborne carbon were significantly elevated over background during handling of bulk materials and cutting composite. Surface sampling also suggested CNFs were being transported into adjacent areas, probably on soles of shoes. The authors concluded that the potential for release of engineered nanoparticles does exist during various processes.[29]

Sampling in an automotive grey iron foundry by NIOSH researchers demonstrated the importance of particle concentration mapping because concentrations differed greatly over time and by location, elevating considerably during melting and pouring operations.[30] A separate study in an automotive engine manufacturing plant looked at the relationship among particle number, surface area and respirable mass, and recommended "simultaneous measurements of particle number, active surface area and mass concentrations."[31] If this combination of measurements really is the minimum required to clearly determine worker exposures, then adequate monitoring will not be practicable in many workplaces producing nanoparticles for the foreseeable future, which points out the need for alternative approaches like such as control banding. Fortunately, technology for measuring nanoparticles is constantly improving and advancing, including the development of sensors. (See Section 5.3.5)

3.3. Controlling exposures

3.3.1. Hierarchy of controls

Any discussion of training must start with the clear acknowledgment that in the hierarchy of controls, training is an administrative control that is below elimination, substitution and engineering controls in the hierarchy.

The hierarchy has served the industrial hygiene profession well for decades and works well in considering nanoparticles, as indicated in the diagram from NIOSH researchers in Figure 5. NIOSH guidance on applying the hierarchy to nanotechnology can be found in "Approaches to Safe Nanotechnology."

Detailed guidance on applying the hierarchy of controls can be found in the Canadian document, *Best Practices Guide to Synthetic Nanoparticle Risk Management* (IRSST Report 599). The guide recommends that high-risk operations be isolated in separate rooms, ventilated and equipped with independent ventilation systems to avoid the possibility of workstation contamination and worker exposure. A closed circuit process was recommended as the main production method capable of effectively controlling emissions. Carbon black, silica fumes, nanoscaled TiO_2, metals and metal oxides are normally synthesized in closed circuit, according to the Canadian guidance.[32]

An international survey by the International Council on Nanotechnology (ICON) of manufacturing firms and research labs found that the principal means of controlling exposure are:

- 43% laboratory hoods,
- 32% glove boxes,
- 23% vacuum systems,
- 23% white rooms, clean rooms
- 20% closed circuits,
- 15% laminar flow ventilation tables,
- 12% biosafety cabinets and
- 12% glove bag.

Most companies or laboratories use more than one means of emission control so the percent sums to greater than 100. The primary finding of the survey was that "actual reported EHS practices… do not significantly depart from conventional safety practices for handling chemicals."[33]

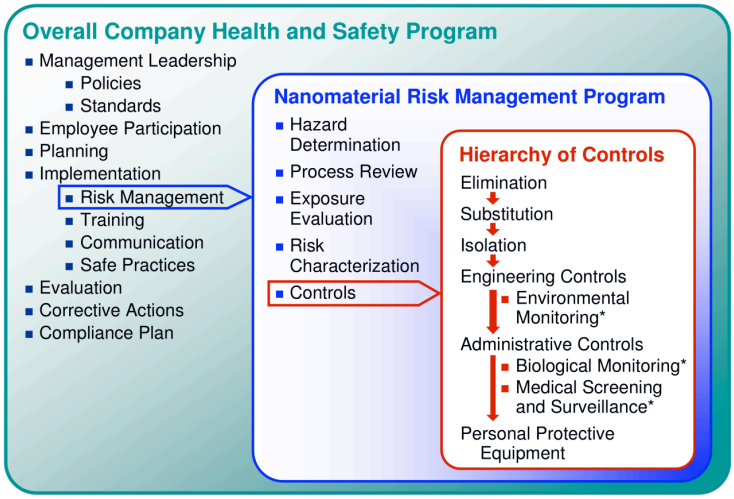


Figure 5: Management system for nanotechnology. *Schulte et al., 2008*

3.3.2. Ventilation

Standard industrial ventilation approaches must be carefully considered because of the buoyancy of nanoparticles. Even when the ventilation is a laboratory fume hood, totally enclosed on three sides, the universal recommendation of a face velocity at the sash of 100 feet per minute will generate too much turbulence inside, possibly releasing particles.

Field studies have shown that handling dry nanoparticles inside laboratory fume hoods can cause a significant release from the hood. Hood design affects the magnitude of release. With traditionally designed fume hoods, the airflow moves horizontally toward the hood, but becomes turbulent in the worker's wake, which can cause nanoparticles to be carried out with the circulating airflow.

> Airborne particle concentrations were measured for three hood designs (constant-flow, constant-velocity, and air-curtain hoods) using manual handling of nanoalumina particles. The hood operator's airborne nanoparticle breathing zone exposure showed high variability for the constant-flow hood while the constant-velocity hood showed some variability, but was usually very low. The performance of the air-curtain hood, a new design with significantly different airflow pattern from traditional hoods, was consistent under all operating conditions and release was barely detected. Fog tests showed more intense turbulent airflow in traditional hoods, but not in the air-curtain hood.[34]

NIOSH, based on field sampling, considers engineering controls that most employers have readily available useful in minimizing nanoparticle emissions.[35]

Manufacturers are now making hoods recommended for use with nanoparticles, but a worldwide survey of laboratories conducting nano-related research found that only 10 percent of researchers reported using nano-enabled hoods, and one in four did not use any type of general laboratory protection.[36]

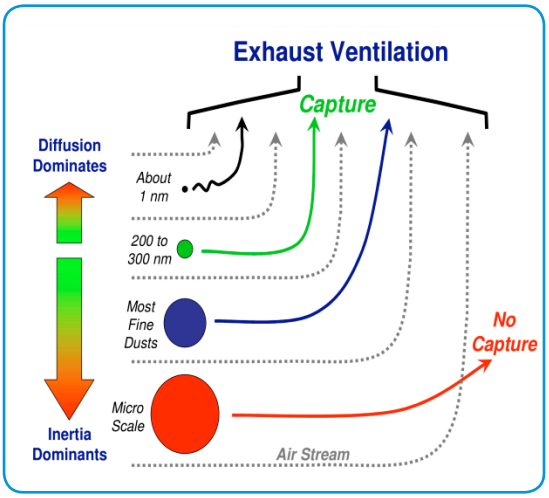
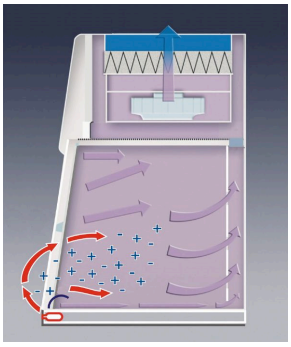


Figure 6: Exhaust ventilation and particle size. *Schulte et al. 2007*



Xpert Nano Enclosure. Room air is pulled into the enclosure through the front, flows to the baffle and finally passes through a 99.999% ULPA exhaust filter before returning to the laboratory or cleanroom. *Images courtesy of Labconco*

3.3.3. HEPA filtration

Given the extremely small size of nanoparticles there has been understandable concern that they might be able to slip through even the highest efficiency filters. All indications thus far show that this is not the case.

It is important that trainers provide students with a clear understanding of the principles of HEPA filtration. High Efficiency Particulate Air filters are tested and shown to be at least 99.97% efficient against monodispersed aerosols of 0.3 microns in aerodynamic diameter. This does not mean that particles smaller than that size – including all nanoparticles – will pass through the filter, like dust through a screen door. HEPA filter material does not resemble most regular filters, rather forcing the air to follow a "torturous path." The 0.3 micron diameter was chosen because it is the most difficult size to capture, i.e. larger particles will be captured more easily through impaction and smaller ones through electrostatic charges.

NIOSH has concluded that "a well-designed exhaust system with a high-efficiency particulate air (HEPA) filter should effectively remove nanoparticles."[37]

3.3.4. Personal Protective Equipment (PPE)

Despite occupying the bottom rung on the hierarchy of controls, PPE against nanoparticles seems prudent even as other risk management strategies are put in place. Unfortunately, there is little guidance on selecting PPE against nanoparticles. NIOSH researchers have identified that large uncertainties remain, particularly the possibility of a thermal rebound effect for particles as large as 20 nm, as well as the high potential of inward leaks at interfaces. In terms of protective clothing and gloves, the paucity of information available is troubling because the commonly held belief that the skin serves as a barrier to nanoparticles has been thrown into doubt by recent research.[38]

Studies on the filtration performance of N-95 filtering-facepiece respirators have found that the mean penetration levels for 40 nm particles range from 1.4% to 5.2%, indicating that 95 and higher performing respirator filters would be effective at capturing airborne nanoparticles.[39,40,41] A NIOSH approved filtering-facepiece respirator or elastomeric half-face respirator equipped with a 95 or 100 series filter, should provide adequate protection when properly fit-tested on the worker.[42] However, selection of the appropriate respirator type should be based on knowledge of the hazard, the airborne exposure concentration, and whether an exposure limit exists for the engineered nanoparticle. Some trainers associated with the NIEHS WETP program have expressed concerns about the actual protection afforded in the field by disposable filtering-facepiece respirators, compared with more substantial, elastomeric, dual-cartridge respirators. This is a subject for additional research – and meaningful class discussion.

> "It is likely that NIOSH-certified respirators will be useful for protecting workers from nanoparticle inhalation when properly selected and fit-tested as part of a complete respiratory protection program."

N-95 respirator. *Image courtesy of 3-M Corporation*

One positive sign is that some clothing standards incorporate testing with nanoscale particles and therefore provide some indication of the effectiveness of protective clothing with regard to nanoparticles.[43] One governmental body recommended that outerwear be modified to reduce the production of static electricity, which increases the attraction of nanoparticles. They also recommended the use of disposable protective clothing because cleaning of garments to remove nanoparticles has not been sufficiently evaluated.[44]
The ICON 2006 survey of international firms and labs found that:

- 41 percent of the organizations said they used lab coats (7 percent of which were disposable);
- 26 percent used more protective coveralls (7% of them disposable),
- 11% used shoes reserved for the laboratory,
- 9% have their own laundry service, and
- The most common gloves were nitrile, latex and rubber.

As all trainers know, the efficiency of the respirator can approach zero if the device isn't conscientiously worn. An international survey of nano-related laboratories found that nearly half of the researchers reported not using any type of respiratory protection.[45] Hopefully, the prevalence of respirator use is higher in industry.

3.3.5. Controlling safety hazards like fire potential

While most attention has rightly been given to the potential health effects of nanoparticles, there is clearly a need to focus on the safety issues as well. OSHA has begun the process of holding hearings on a combustible dust standard, because more than 130 workers have been killed and more than 780 injured in combustible dust explosions since 1980.[46]

It is common knowledge that explosive dust clouds can be created from most organic materials, many metals and even some non-metallic inorganic materials. The main element affecting the ease of ignition and explosive violence of airborne dust is the particle size and surface area, which are inversely related (i.e. for the same mass, as the particle size decreases, the surface area increases). The violence of the explosion and the ease of ignition generally increase as the particle size decreases. Consequently, many nanoparticle types have the potential to cause explosions, yet data on fire and explosion hazards of nanoparticles is almost nonexistent.[47]

Despite the cutting edge nature of producing nanoparticles and nanomaterials, these workplaces can be susceptible to the same ubiquitous hazards as plants making brooms. Slips, trips, equipment entanglement and other safety hazards will need to be constantly evaluated and controlled.

3.3.6. Hazard communication for nanoparticles

In the United States, the Occupational Safety and Health Administration's Hazard Communication Standard (29 CFR 1910.1200) requires that employers inform their workers of the chemical hazards to which they are exposed and how they should protect themselves. In Canada, the Workplace Hazardous Materials Information System (WHMIS) has the same requirement. The 2006 European REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) initiative on chemical hazard communication is more comprehensive and ambitious than the OSHA requirements and requires chemical manufacturers to follow how their products are used by purchasers. THE EU REACH recently announced (Sept 15, 2010) that it is proposing a specific register for nanomaterials.[48]

The most significant development in hazard communication in decades has been the international effort to create a harmonized system. In 2003, the United Nations adopted the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), which includes criteria for classifying health, physical and environmental hazards; GHS also specifies what information should be included on labels of hazardous chemicals and on safety data sheets. OSHA published a proposed rulemaking on September 30, 2009 to align OSHA's Hazard Communication standard (HCS) with the GHS.

The GHS provides consistency in format. Under the GHS, labels would include signal words, pictograms and precautionary statements. Safety data sheets would have a standardized format of 16 sections based on the ANSI Z400.1 consensus standard. It is valuable to ask if it the ANSI standard really is appropriate for nanomaterials. The last section of the GHS (and ANSI) format is called "other information" and is the only section that is not tightly prescribed and could, therefore, contain specific cautionary language about the nano-sized component in the product. One Hazcom expert offered an example of a warning he created: "Established exposure values do not address the small size of particles found in this product and may not provide adequate protection against occupational exposures."[49]

Material Safety Data Sheets (MSDSs) are required for nanoparticles that meet the definitions of hazardous chemicals under OSHA's Hazard Communication standard. According to a survey of firms in Massachusetts, MSDSs from suppliers are the preferred source of risk information for nanotechnology firms.[50] ANSI has recently published a new combined standard that covers MSDSs (ANSI Z400.1) and Precautionary Labeling (ANSI Z129.1).

Unfortunately, industry hasn't done a good job of communicating the hazards of standard industrial chemicals despite having two and a half decades since the promulgation of OSHA's Hazard Communication standard in 1983 to perfect it. An OSHA-funded 1997 study of the peer-reviewed hazard communication literature indicated broad shortcomings with MSDSs, labels and warnings.[51] Three separate studies found that literate workers only comprehended roughly 60 percent of the health and safety information on sample MSDSs.[52,53,54]

A recent review of more current literature regarding the accuracy, comprehensibility and use of MSDSs unfortunately did not show improvements over the 1997 review. Accuracy and completeness were found to be relatively poor: the majority of studies showed that the MSDSs did not contain information on all the chemicals present and workers showed low comprehensibility because of overly complex language.[55]

NIOSH appears to maintain the most complete collection of MSDSs for engineered nanoparticles and recently analyzed 60 of them from 33 different manufacturers for technical sufficiency.[56] The researchers only rated 5 percent as "good" while 55 percent were rated as "in need of serious improvement." Over half contained Occupational Exposure Limits (OELs) for the bulk material without providing guidance that the OEL may not be protective for the nanoscale material. Eighty percent "failed to recognize the material as being nano in size or list a particle size distribution showing the nano size range" and a higher percentage "lacked toxicologic data specific to the nanoparticles." Eight percent failed to "suggest any type of engineering controls or mechanical ventilation."

These findings corroborated a similar analysis of a subset of the same MSDSs presented at an international conference sponsored by the EPA in October 2008.[57] The earlier analysis also noted that of those MSDSs that recommended local exhaust ventilation, 25 percent recommended a face velocity greater than 100 feet per minute even though, as noted

earlier, NIOSH has specifically warned against operating fume hoods at that rate because the turbulence can release nanoparticles. Additionally, not one of the MSDSs reported that nanoparticles pose a much greater flammability risk despite warnings from authoritative sources that "an increasing range of materials that are capable of producing explosive dust clouds are being produced as nanopowders."[58]

4. Regulatory and voluntary approaches specific to nanoparticles

Given the many unknowns regarding nanoparticles, a wide range of risk assessment approaches has been suggested for nanotechnology, from recommendations for a total moratorium on any development and use of nanoparticles if and until they are proven to be safe to humans and the environment, to recommendations for relying on existing occupational safety and health laws and regulations.[59]

It is useful to review approaches that are being taken by government as well as new initiatives or paradigms being developed outside a strict regulatory framework.

4.1. Pro-active efforts of the federal government compared to past

Most HAZWOPER trainers cover in their courses, however briefly, the sad and repeated history of occupational diseases killing hundreds or thousands of workers before the federal government acted to eliminate or curtail exposures. Asbestos is the most notorious example, but the list includes acrylonitrile, benzene, acetyl and lead. The latter is painfully illustrative. Austria, France and Belgium phased out lead in household paint in 1909. In this country, the trade association for lead paint agreed to remove it from paint used on children's toys in 1936, but it wasn't phased out completely until 1977. These additional 68 years of exposure from all sources, including leaded gas and house paint, have been credited with causing a population-wide IQ drop.[60] Even with the bans and existing regulations, products containing lead-based paint still surreptitiously enter the country.

The federal government has acknowledged this sorry history and publicly vowed to avoid a similar path with nanotechnology. The results thus far have been encouraging. Under the National Nanotechnology Initiative, all of the key agencies – NIOSH, EPA, OSHA, DOE, DoD, CPSC, FDA – and the White House have been working together in the Nanotechnology Environmental and Health Implications (NEHI) working group to identify the key research that should be conducted to protect workers and the environment.

Government must be constantly on guard, however, for what Princeton historian Ed Tenner called the "tendency of advanced technologies to promote self-deception." According to David Rejeski, Director of the Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars,"Nanotech is riding the hype wave like a happy surfer at Waikiki," which increases the chance of self-deception because nanotechnology has turned into a "surrogate indicator of U.S. technological leadership in the global economy."[61] He concluded that "Even if some governmental official believed that our existing set of safeguards and statutes would likely fail if applied to nanotechnologies, the probability that they would publicly state such a propostion is infinitesimally small." He also warned that "Dealing with safety issues around nanotechnology at this point in time is a piece of cake compared to what is coming."[62]

> "When the science is just developing – as it is for nanotechnology and its human health effects - it is a difficult call to know when to take action to protect or at least monitor workers. I think we learned from the impacts of asbestos exposure that if there is a technical uncertainty then precaution is well advised. We need to ensure that we make efforts to protect worker health and make sure all employers do so."
>
> *–Bill Kojola, Industrial Hygienist for the AFL-CIO Health and Safety Department*

4.2. Review of government regulatory actions

4.2.1. Overview

As a set of technologies, materials and devices, "nanotechnology" has been or will be determined to fall within several different regulatory frameworks. Each agency with regulatory authority over some form of nanotechnology has taken concrete steps to understand how best to apply its statutes to this new class of technologies. The actions taken by the key regulatory agencies are summarized in Table 4.

Table 4: Actions on nanotechnology by key federal regulatory agencies

Agency	Primary Statutes	Actions
EPA	Toxic Substances Control Act (TSCA)	» Implemented voluntary reporting program (TSCA) » Published white paper (TSCA) » Issued rules specific to nanoparticles (TSCA) » Issued fines for noncompliance (FIFRA) » Funded intramural and extramural research
	Federal Insecticide, Fungicide and Rodenticide Act (FIFRA)	
	CERCLA (Superfund)	
	Clean Air Act	
	Resource Conservation and Recovery Act	
FDA	Federal Food, Drug and Cosmetic Act	» Created topics page at website » Commenced internal research program » Formed Task Force » Issued white paper » Published monograph on nanoscale sunscreen ingredients
OSHA	Occupational Safety and Health Act	» Created topics page at website » Funded development of worker training materials
CPSC	Consumer Product Safety Act	» Published white paper » Commenced internal research program
	Federal Hazardous Substances Act	

For nanoparticles, the two federal statutes that have the most relevance today are the Toxic Substances Control Act (TSCA) and the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), both enforced by the Environmental Protection Agency (EPA).

4.2.2. Nanoparticles as toxic substances

Nanoparticles meet the definition of chemical substances under TSCA.[63] At issue is whether they are considered new forms of existing chemicals, which would lower the burden on the manufacturer bringing that substance to market, or whether they are "new chemicals", which imposes greater reporting requirements. EPA's initial position that a nanoscale form of a chemical substance is not new solely by virtue of its size has garnered significant criticism. There are indications that EPA may be rethinking this, which could lead to big changes in how the agency regulates nanoparticles. If EPA were to deem nanoparticle forms new chemicals, the nanoparticles could be subject to reporting and testing that are not required for most nanoparticles being sold today.

Meanwhile, EPA is exercising its authority to regulate some nanoparticles using the significant new use rules (SNUR) under Section 5(a)(2) of the Toxic Substances Control Act (TSCA). SNURs have already been issued on certain carbon nanotubes and siloxane nanoparticles, largely based on the nanoscale form and influenced by publicly available toxicity data. The (siloxane) SNURs require manufacturers to notify EPA 90 days prior to sale and describe specific worker protection measures that must be taken when handling the materials.[64] EPA must consider nanoparticles in media other than air; those in liquids will enter the body by different routes and at different rates.

4.2.3. Nanoparticles as pesticides

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) provides EPA the authority to control the distribution, sale and use of pesticides and pest control devices. Under FIFRA, EPA may determine the risks and benefits of pesticidal products incorporating nanotechnology ("nanopesticides") and may impose restrictions to limit potential risks. Some nanoscale materials such as titanium dioxide and nanoscale silver exhibit potent antimicrobial effects, which have been exploited in a growing number of consumer products. EPA has taken note of several products making antimicrobial claims on the label and leveled fines against the manufacturers for failing to register the products as pesticides or pest control devices as required by FIFRA. Examples of these include a $208,000 fine imposed on ATEN Technology, Inc. for the failure of its subsidiary IOGEAR to register several antimicrobial computer mouse and mouse/keyboard combination products and for making "unverified claims that coatings on keyboard and mouse accessories would eliminate pathogens and kill bacteria,"[65] and a fine of nearly $1 million against VF Corporation for failure to register 70 styles of footwear sold under the North Face brand that contain an AgION silver treated foot bed that claim to "inhibit the growth of disease-causing bacteria," "prevent bacterial and fungal growth" and continuously release antimicrobial agents.[66] In each case a nanoscale ingredient is believed to be the active antimicrobial agent. Partly in response to criticism that EPA was not doing enough to scrutinize and regulate nanosilver pesticides,[67] the agency convened a special meeting of its Scientific Advisory Panel (SAP) in November 2009 to get advice on the science behind its regulatory decision making with regard to nanoparticle-based pesticides. As the market for these products continues to grow, the evolution of EPA's thinking on these issues is worth watching.

Their thinking may be prodded by the Government Accountability Office's recent and formal recommendations to the agency to:

1. Complete its plan to issue a Significant New Use rule for nanomaterials.
2. Modify FIFRA pesticide registration guidelines to require applicants to identify nanomaterial ingredients in pesticides.
3. Complete its plan to clarify that nanoscale ingredients in already registered pesticides, as well as in those products for which registration is being sought, are to be reported to EPA and that EPA will consider nanoscale ingredients to be new.[68]

How a washing machine became a pesticide

In everyday language, a pesticide is something that kills cockroaches, ants, mosquitoes and other nuisance pests. In addition to insects, the word 'pest' in EPA jargon includes another class of 'bugs': microbes. Therefore, any product that claims to kill bacteria, viruses, fungi or other unwanted microbes, is classified as a pesticide or pest control device by the EPA. A product that uses physical or mechanical means to control a pest is a pest control device (e.g., untreated flypaper and UV light disinfection systems) and does not require registration under FIFRA, but if it uses a substance to control pests, then it is a pesticide and must be registered if it makes a pesticidal claim.

In 2005, EPA advised a washing machine manufacturer (presumably Samsung) that its product (presumably the Silver Nano™ Silver Wash) would be classified as a pest control device. The Samsung Silver Wash product claims to kill odor-causing bacteria on fabrics by using electrolysis of a silver electrode to release silver ions into the wash water. Moreover, the product's marketing claims that the silver ions permeate the fabrics, providing anti-bacterial protection for up to one month.[69] Shortly after its decision became public, EPA received letters from waste water treatment facility operators urging it to reconsider its decision and classify the Samsung washing machine as a pesticide because it uses a substance (silver ions) to kill bacteria.[70] The basis for their concern was the inevitable release of silver ion-containing water into sanitary sewer systems which could hamper efforts by plant operators to keep their effluents in compliance with federal limits on silver. Classification of the machine as a pesticide would permit EPA to request data on the potential impact of the machine on silver levels in the waste treatment system and open the door for mandatory restrictions on the sale of the product to avoid further bioaccumulation of silver in the environment. In 2007, EPA revised its ruling "because these items incorporate a substance or substances that accomplish their pesticidal function."[71] And that is how a washing machine became a pesticide.

(L) Samsung's patented Silver Nano™ Silver Wash machine as marketed by Samsung Electronics Australia Pty Ltd. (R) Samsung claims the product "protects sensitive skin and help prevent dermatitis." *SOURCE: http://www.samsung.com/au/silvernano/site.html*

4.2.4. Nanoparticles as workplace toxicants

Worker exposures have not been directly addressed in regulations, nor does OSHA have any plans to regulate nanoparticles. NIOSH has taken the lead by examining the measurement and control of exposures, but has not yet exercised their powers under the OSHAct to create a recommended standard. When examining the regulatory tools available to OSHA, their 29 CFR 1910.120 HAZWOPER standard must be seen as extremely durable in its applicability over the 20 years of its history - being applied to cleanup of drums of waste in the 90s and the response to terrorist attacks involving anthrax in 2001.

The Hazardous Waste Operation and Emergency Response (HAZWOPER) standard, which went into effect in 1990, protects the safety and health of employees involved in cleanup operations at hazardous waste sites; operations at hazardous waste treatment, storage and disposal facilities; and emergency responses to releases or potential releases of hazardous substances. Although created to protect workers dealing with uncontrolled industrial chemicals at that time, it takes little imagination to see the HAZWOPER connection to nanoparticles. Workers may encounter nanoparticles in the course of handling hazardous waste from a research lab or industrial operation or when cleaning up a large-scale spill in a factory or by the roadside. In addition to these more predictable scenarios for encountering nanoparticles, hazardous waste workers may find themselves purposefully introducing nanoparticles as part of an EPA Superfund cleanup: nanoremediation is projected to be a major part of the overall cleanup strategy on governmental sites over the next 30 years, estimated to be between $87 and $98 billion in scope. The U.S. GAO has recently reviewed the EPA's regulatory options under CERCLA (Superfund) for regulating nanoparticles and noted that the EPA has the statutory authority to designate additional substances as hazardous under CERCLA if their release may present substantial danger to the public health or welfare or to the environment.[72] It may be more a matter of agency commitment and philosophy than regulatory authority.

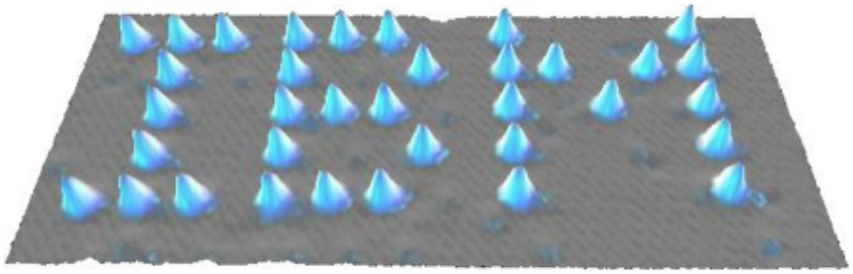
HAZWOPER trainers may want to visit the EPA's searchable database called Nanotechnology Project Profiles that can be found on its CLU-IN website.[73]

If HAZWOPER coverage involves some ambiguity, OSHA's Hazard Communication standard, 29 CFR 1910.1200, applies completely and importantly. It is hard to envision any population that has a more compelling issue of hazard communication than workers creating nanoparticles or adding them to the broad array of products currently on the market.

Going back to the earliest, contentious debates over the OSHAct, labor and management leaders at least agreed that occupational diseases presented the most serious case for government action.[74] With nanoparticles there are clear safety issues, particularly the risk of fire and explosions from reducing materials to extraordinarily small particle sizes that take exponentially less energy to ignite.[75] But the unknown health risks posed by nanoparticles are an even more stark argument for government involvement.

Properly informing workers about the risks of nanoparticles requires a frank appraisal of the history and current state of industrial chemical regulation. OSHA has regulatory standards, called Permissible Exposure Limits (PELs), for approximately 600 chemical substances; the majority of these PELs are based on consensus standards set at least 40 years ago by volunteer members of the American Conference of Governmental Industrial Hygienists (ACGIH), many of whom were from the industries that produced the chemicals. During the past 40 years, the ACGIH has lowered many of their recommended exposures limits based on continuing research, but OSHA continues to use the levels from 1969, despite an updating of the PELs in 1989 that the courts threw out in 1992.

The age of the OSHA PELs is a minor issue compared to the dearth of information on the overwhelming majority of chemicals in production. There is no definitive count of the number of chemicals in regular use today, but the EPA maintains a list of 83,000 chemicals under the Toxic Substances Control Act.[76] The Chemical Abstract Service had registered 52,122,026 organic and inorganic substances developed by industry as of February 12, 2010.[77]



Manipulation at the atomic level by IBM researcher Donald Mark Eigler. In 1989 he spelled IBM with individual xenon atoms using the Scanning Tunneling Electron Microscope. *Image courtesy of Wikimedia*

Given the 118 elements available for combination, a mind-numbing range of between 10^{200} to 10^{900} distinct nanoscale creations has been estimated as plausible; these are truly awe-inspiring numbers for regulators.[78] While federal regulators grapple with these large issues, local and state regulators are dealing with the direct impact of nanomaterials in their jurisdictions.

4.2.5. Regulations at the local level

In California, the city of Berkeley amended its hazardous-material reporting requirement in December 2006 to include a notification requirement regarding manufactured nanoparticles.[79] In 2009, the California Department of Toxic Substances Control (DTSC) exercised its authority under the Health and Safety Code, Chapter 699, to request information regarding analytical test methods, fate and transport in the environment, and other relevant information from manufacturers of carbon nanotubes.[80] DTSC has indicated its interest in expanding the data call-ins to other types of nanoparticles. These are the only concrete steps taken by a local or State government but there is active interest in nanoparticles in others, including Massachusetts and Wisconsin, that could result in more actions in the future.

4.3. Voluntary approaches

There is still a perception among many that guidance and existing regulation are not enough to address the knowledge gaps. In response, established international and intergovernmental bodies and corporations are engaging in their own processes to fill the gaps, often with extensive participation from governments that recognize voluntary processes take less time than regulations. Additionally, grassroots groups and consortia are developing interim strategies for managing risk while governments and other established bodies continue to do their work. Several of these organizations have created guidance documents and consensus standards that trainers can use as resources. One key advantage of voluntary efforts is that guidance can be issued much more rapidly than regulatory rule making. The importance of voluntary guidance is underscored by the international survey of research laboratories referenced previously that found nearly half of the labs had no internal rules on handling nanomaterials and another quarter of the respondents weren't aware of any internal regulations.[81]

4.3.1. Organization for Economic Co-operation and Development (OECD)

The OECD is an intergovernmental organization in which representatives of 30 industrialized countries in North America, Europe and the Asian and Pacific regions, as well as the European Commission, meet to co-ordinate and harmonize policies and work together to respond to international problems through more than 200 specialized committees and working groups.

The Working Party on Manufactured Nanomaterials was established in 2006 to help member countries address the safety challenges of nanomaterials by bringing together more than 100 experts from governments and other stakeholders. The Working Party is tackling the following important issues:

- Developing a database on human health and environmental safety (EHS) research;
- Establishing EHS research strategies for manufactured nanomaterials;
- Testing the safety of a representative set of nanomaterials; and
- Cooperating on exposure measurement and exposure mitigation.[82]

4.3.2. International Organization for Standardization (ISO)

The International Organization for Standardization (ISO) is a non-governmental organization that develops and publishes voluntary consensus standards via a network of national standards institutes of 161 countries. ISO Technical Committee 229 Nanotechnologies (ISO/TC 229) was formed to develop consensus standards in nanotechnology and currently has four working groups. Working Group 3 is dedicated to developing standards in the health, safety and environmental aspects of nanotechnologies. ISO/TC 229 recently published a Technical Report, ISO/TR 12885:2008, *Health and safety practices in occupational settings relevant to nanotechnologies*, which focuses on the manufacture and use of engineered nanomaterials. This report was produced in conjunction with the American National Standards Institute and "provides advice for companies, researchers, workers and other people to prevent adverse health and safety consequences during the production, handling, use and disposal of manufactured nanomaterials."[83] NIOSH personnel were heavily involved in creating this Technical Report, which was based on key NIOSH guidance documents, including Approaches to Safe Nanotechnology.

4.3.3. ASTM International

ASTM International (ASTM) is another international non-governmental organization that develops and publishes voluntary consensus standards. Its Committee E56 on Nanotechnology produced an occupational health standard in 2007 titled, Standard Guide for Handling Unbound Engineered Nanoscale Particles in Occupational Settings.[84] The guide outlines six elements for establishing a program to minimize exposures:

1. Establishing management commitment to the control principle;
2. Identifying and communicating potential hazards;
3. Assessing potential unbound, engineered nanoparticle exposures within the worksite;
4. Identifying and implementing engineering and administrative controls for all relevant operations and activities;
5. Establishing documentation; and
6. Periodically reviewing its adequacy.

ASTM premised exposure control in their Guide on the principle "that, as a cautionary measure, occupational exposures to unbound nanoscale particles should be minimized to levels that are as low as is reasonably practicable." The ALARA principle, As Low As Reasonably Achievable, is the foundation for radiation control and very familiar to trainers who provide radiation worker training.

4.3.4. Nano Risk Framework

One of the most widely recognized voluntary approaches came from the unusual partnership of the DuPont company and the Environmental Defense Fund. In June 2007, they jointly launched the Nano Risk Framework as a comprehensive, practical and flexible system to address the potential risks of nanoscale materials. The Framework has been widely cited as best practice for industry and valuable input for government policy. The framework has six basic steps (as indicated in the diagram):

1. Describe Material and Its Applications
2. Profile Lifecycles
3. Evaluate Risk
4. Assess Risk Management
5. Decide, Document, and Act
6. Review and Adapt

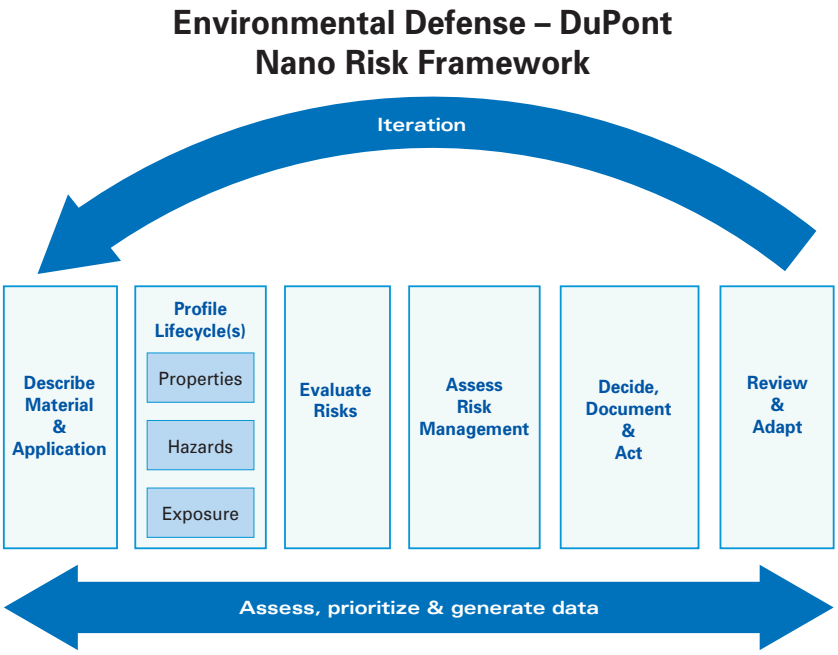


Figure 7: The framework includes a detailed output worksheet that companies can use to document each step of this process.

4.3.5. Control banding

Given the difficulties, expense and lack of acceptable reference standards for air sampling, as detailed in section 4, another approach is certainly worth pursuing. Control banding has been suggested as a viable option, particularly given its success controlling worker exposures in the absence of complete toxicological and exposure information in the pharmaceutical industry over the last 20 years.

Control banding, unlike air sampling, is a qualitative technique that uses categories or bands of health hazards that are combined with exposure potentials to determine desired levels of control.

A conceptual model was created by Andrew Maynard in 2007 using "impact" and "exposure" indices to combine elements like shape, size and surface area on the nanoparticles with their exposure availability (dustiness and amount in use.) This led to four control strategies:

1. General ventilation,
2. Fume hoods or local exhaust ventilation,
3. Containment, and
4. Seek specialist advice.[85]

A team of experts from Lawrence Livermore National Laboratory elaborated on that design to create a "CB Nanotool" that incorporates a Risk Level (RL) that is a combination of a

severity score and a probability score in a standard 4 x 4 risk matrix. The model uses the same four control categories as the Maynard model.

Unlike the Maynard model, however, the CB Nanotool has been validated against the recommendations of independent industrial hygiene experts. The CB Nanotool was demonstrated to have a high level of consistency and tended towards over-control rather than under-control, which is preferable.[86] The tool, which is an Excel spreadsheet, has now been used internationally with good results. It represents an excellent teaching tool, as well. Hazmat instructors should consider having students, preferably working in groups, rate a nanomaterial with which they are familiar using either the electronic CB Nanotool or a paper copy.

The model requires assigning numerical weights to specific severity and probability factors. For instance, surface chemistry must be considered as a severity factor and assigned a score based on whether the surface activity is high (10 points), medium (5) or low (0). Similarly, points are assigned to particle shape, with fibrous forms getting the highest score.

The following severity factors are also scored for the nanoparticles:

- Particle diameter,
- Solubility,
- Carcinogenicity,
- Reproductive toxicity,
- Mutagenicity,
- Dermal toxicity, and
- Asthmagenicity.

The probability factors that are weighted and must be reviewed include:

- Estimated amount used during the operation,
- Dustiness of the operation,
- Number of employees with similar exposure,
- Frequency of the operation, and
- Duration of the operation.

Total scores are calculated for severity and probability and the following 4 x 4 matrix is used to determine the Risk Level (RL), which defines the appropriate control strategy. As the Risk Level increases, the control methods similarly increase in protectiveness from general ventilation (RL1), to fume hood or local exhaust ventilation (RL2), to containment (RL3), to seeking the advice of a specialist (RL4).[87]

Severity	Probability: Extremely Unlikely (0-25)	Probability: Less Likely (26-50)	Probability: Likely (51-75)	Probability: Probable (76-100)
Very High (76-100)	RL 3	RL 3	RL 4	RL 4
High (51-75)	RL 2	RL 2	RL 3	RL 4
Medium (26-50)	RL 1	RL 1	RL 2	RL 3
Low (0-25)	RL 1	RL 1	RL 1	RL 2

Figure 8: RL 1: General Ventilation, RL 2: Fume hoods or local exhaust ventilation, RL 3: Containment, RL 4: Seek specialist advice

5. Resources

5.1. Online nanotechnology resources for workers and trainers

There are many free informational resources on nanotechnology and its potential impacts on human health and the environment. Given the growth of the field of nanotechnology in general and the explosion of information on nano-EHS issues, it is not practical to create an exhaustive list of web-based resources. Instead, the following sites either are themselves essential for all nanotechnology workers and worker trainers or aggregate relevant information from a broad set of sources.

Governmental

- **Environmental Protection Agency (EPA):**
  - National Center For Environmental Research; *http://www.epa.gov/ncer/nano/index.html*
  - Office of Pollution Prevention and Toxics: *http://www.epa.gov/oppt/nano/*
  - Office of Pesticide Programs: *http://www.epa.gov/pesticides/about/intheworks/nanotechnology.htm*
- **Lawrence Livermore National Laboratory:** Control banding tool; *http://controlbanding.net/Services.html*
- **National Institute for Environmental Health Sciences (NIEHS):**
  - Clearinghouse for Worker Safety and Health Training page on nanotechnology; *http://tools.niehs.nih.gov/wetp/index.cfm?id=537*
  - National Toxicology Program Nanotechnology Safety Initiative; *http://ntp.niehs.nih.gov/?objectid=7E6B19D0-BDB5-82F8-FAE73011304F542A*
- **National Institute for Occupational Safety and Health (NIOSH):** Guidance, field studies, research, Nanoparticle Information Library; *http://www.cdc.gov/niosh/topics/nanotech/*
- **National Nanotechnology Initiative (NNI):** US Government's nanotechnology portal; *http://nano.gov*
- **Oak Ridge Institute for Science and Education (ORISE):** Industrial Hygiene/Occupational Safety Special Interest Group; *http://orise.orau.gov/ihos/Nanotechnology/nanotech_safetyTraining.html*
- **Occupational Safety and Health Administration (OSHA):** Standards for occupational practice; *http://www.osha.gov/dsg/nanotechnology/nanotechnology.html*

Nongovernmental

- **GoodNanoGuide:** Information and protocols for safe handling; *http://goodnanoguide.org*
- **International Council on Nanotechnology:** Aggregator of nano-EHS news, research, policy reports, industry survey, backgrounders
  - Homepage: *http://icon.rice.edu*
  - Database to research paper citations: *http://icon.rice.edu/virtualjournal.cfm*
  - Survey of handling practices in the nanotech workforce: *http://tinyurl.com/iconsurvey*
- **Project on Emerging Nanotechnologies:** Policy analysis and Consumer Product Inventory: *http://www.nanotechproject.org/*
- **Standards**
  - ASTM International Technical Committee E56 on Nanotechnology: *http://www.astm.org/COMMIT/COMMITTEE/E56.htm*

- International Organization for Standardization (ISO) Technical Committee 229 Nanotechnologies: *http://www.iso.org/iso/iso_technical_committee?commid=381983*

» **1.4. Educational Repositories**

- *http://www.NanoEd.org* (basic to intermediate)
- *http://NanoHub.org* (intermediate to advanced)

6. Suggested training program

6.1. Limited literature

Despite the abundance of literature on nanomaterials, only one article on training workers potentially exposed to nanoparticles was identified. The researchers distributed questionnaires and conducted focus groups to assess the training needs of safety and health personnel in nanotechnology industries in Taiwan.[88] They divided training courses into three levels: 1) introductory, which was aimed at providing a basic, awareness level of knowledge for reducing the incidence of occupational illness in nanotechnology industries; 2) advanced, which was aimed at individuals responsible for organizing and conducting occupational illness control programs in nanotechnology industries; and 3) professional, which was aimed at training experts to serve as consultants to reduce incidence of occupational illness in industry. For teaching purposes, these categories correspond roughly to the HAZWOPER categories of first responder awareness, operations level and hazardous materials technician level under 1910.120 (q)(6).

The Taiwanese researchers identified the following training needs based on the level of the individuals:

I. Hazard Recognition		
Introductory Level	Advanced	Professional
Introduction to nanoparticle health-hazards	Nanoparticle health-hazards of different exposure routes	Health-hazards for nanoparticle inhalatory exposures
	Nanoparticle toxicities and their evaluation techniques	Health-hazards for nanoparticle dermal exposures Nanoparticle toxicities and metabolisms
		Nanoparticle toxicities evaluation techniques

II. Hazard Evaluation		
Introductory Level	Advanced	Professional
Introduction to nanoparticle exposure assessments	Inhalation exposure assessment for nanoparticles	Techniques for assessing nanoparticle inhalation exposures
	Dermal exposure assessment	Instrumentation for assessing inhalation exposures
	Biological monitoring for nanoparticles	Principles and techniques used in biological monitoring for nanoparticles
	Sampling strategy for assessing nanoparticle exposure	Sampling strategy for assessing nanoparticle exposure
		Data analysis techniques for assessing nanoparticle exposures

III Hazard Control		
Introductory Level	Advanced	Professional
Introduction to the management and control of nanoparticle health hazards	Control of nanoparticle health hazards	Enclosure and isolation techniques for control of nanoparticles
	Management of nanoparticle health hazards	Ventilation techniques for controlling nanoparticle exposures
		Selection of PPE for protection from nanoparticles
		Hazard communication techniques
		Self-auditing techniques for nano-workplaces
		Creation of standard operating procedures for nanoparticle operations
		Medical surveillance concepts for nanoparticle exposures
		Emergency response planning for nanoparticle operations

Suggested learning objectives for a nanomaterials course for workers

6.1.1. Module 1: Introduction to nanotechnology and nanoparticles

At the end of this module the students will be able to:

- Define nanoparticles and nanomaterials.
- Differentiate among nanoparticles, ultrafines, and engineered nanoparticles.
- Explain the main classes of nanoparticles.
- Describe carbon nanotubes and list some of their valuable properties.
- Explain quantum dots and describe their properties.
- Explain Dendrites and give examples of their properties.
- Analyze the arguments raised about the risks versus the benefits of nanomaterials.
- Describe the main difficulties with characterizing the exposed populations.
- Analyze the importance of considering the life cycle of nanomaterials.

6.1.2. Module 2: Environmental, health and safety impacts of nanoparticles

At the end of this module the students will be able to:

- Describe the difference between the amount of research on developing nanotechnologies and the amount on the health, safety and environmental impacts of nanotechnologies.
- Describe the routes of entry for nanoparticles into the body.
- Describe several of the health effects caused when nanoparticles enter the body.

6.1.3. Module 3: Application of traditional risk management approaches to protect workers handling nanoparticles

At the end of this module the students will be able to:

- List tasks that are most likely to generate worker exposures to nanoparticles.
- Explain why the standard model of industrial hygiene sampling is of questionable value for airborne nanoparticles.
- Explain the importance of the surface area of nanoparticles for biological activity.
- Describe the specific needs for working with nanoparticles under local exhaust contamination.
- Explain the current status of governmental and private efforts to develop occupational exposures limits and analyze the difficulties surrounding those efforts.
- Review the hierarchy of controls and apply it to the management of risk associated with nanomaterials.
- Define High Efficiency Particle Air (HEPA) filtration and describe the current understanding of the effectiveness of HEPA for capturing nanoparticles.
- Discuss the current information available on the protection afforded by NIOSH-certified respirators against nanoparticles, including the use of N-95 filtering facepiece respirators.
- Formulate a message on the effectiveness of protective garments against nanoparticles based on the current findings.
- Describe safety hazards associated with nanomaterial production.

» Characterize the international developments in hazard communication and their impact on informing workers about the risks of nanomaterials.

» List several shortcomings of MSDSs for nanomaterials.

6.1.4. Module 4: Regulatory and voluntary approaches specific to nanoparticles.

At the end of this module the students will be able to:

» Take an informed stance on whether the federal government is being sufficiently proactive managing the risks of nanotechnologies.

» List several regulatory initiatives underway by federal agencies.

» Discuss the difficulties faced by the EPA in regulating nanomaterials that enter the ecosystem.

» Provide an overview of the scope of chemicals in use compared to the number regulated by OSHA and the potential number of chemicals that could be created at the nanoscale.

» Describe several of the international voluntary guidance efforts underway.

» Explain the steps of the Nano Risk Framework for identifying risks of nanoscale materials.

» Explain the principles of control banding and why this approach is receiving serious consideration for assessing the risks of nanomaterials.

6.2. Outline for 8-hour HAZWOPER refresher

6.2.1. Purpose

Worker training must be preceded by a needs assessment that allows the training organization to tailor the course as tightly as possible, using workplace examples that are meaningful to the workers being trained. The generic outline provided here should only serve as a template to facilitate adding information needed for protecting the specific worker population. The training should include good adult education techniques, as recommended in the NIEHS Minimum Criteria document (see Section 6.3).

6.2.2. Module 1: Introduction

During this module, the instructor should:

» Review the essential concepts of nanotechnology, particularly the classes of nanomaterials and concepts of relative size.

» Discuss the major areas of application.

» Identify unresolved issues around workforce identification.

» Prompt a discussion about what products the class has observed that contain nanoparticles.

» Ask questions like, “You have been appointed to the worker S&H committee at this carbon nanotube plant, what questions do you ask?” to promote discussions.

6.2.3. Module 2: Environmental, health and safety impacts

During this module, the instructor should:

» Review the major known health effects caused by nanoparticles.

» Describe the limitations to the toxicology information.

» Review the health and safety issues by working through the recognition, evaluation and control of exposures.

» Explain the process of control banding and lead a discussion on why it may be a better approach to controlling exposures to nanoparticles than traditional industrial hygiene.

» Describe the issues around conducting effective hazard communication with limited information.

» Consider disseminating several MSDSs for nanomaterials to facilitate discussions about improving hazard communication to workers.

6.2.4. Module 3: Application of traditional risk management approaches to protect workers handling nanoparticles

During this module, the instructor should:

» Facilitate a discussion of possible exposures among the worker populations in class.

» Prompt the class to describe the standard industrial hygiene practice of personal monitoring and why it has serious shortcomings when applied to nanotechnologies.

» Demonstrate the critical importance of surface area in understanding the uniqueness of nanoparticles.

» Compare and contrast the use of local exhaust ventilation for working with standard lab chemicals and nanoparticles.

» Explain the concept of HEPA filtration and engage the class to describe the value of HEPA for nanoparticles.

» Review the current governmental guidance on the protectiveness of N-95 filtering facepiece respirators against nanoparticles and allow the class to debate the use of N-95s.

» Facilitate a discussion on the efforts to develop standards for nanoparticles.

» Challenge the class to think of potential safety hazards associated with nanoparticles and appropriate controls.

6.2.5. Module 4: Regulatory and voluntary approaches specific to nanoparticles

During this module, the instructor should:

» Describe the efforts of the federal government to identify risk to workers exposed to nanomaterials, and then facilitate a discussion on how those efforts compare with the government's past handling of asbestos, lead, acrylonitrile and other major workplace toxins.

» Review the specific roles of the U.S. agencies responsible for safeguarding workers, the public and the environment from negative effects of nanomaterials.

» Use case studies to illustrate the difficulties faced by EPA in preventing release of nanoparticles into the environment.

» Discuss risks during the life cycle of nanoparticles, from raw materials to inclusion in products to use and to disposal.

» Consider using the internet to show the current number of chemicals assigned a Chemical Asbstract Services number (CAS) and compare that to the number of chemicals in regular use, the number regulated by OSHA and EPA, and to the possible number of nanoparticles that could be generated.

» Proceed systematically through the Nano Risk Framework by Dupont and the Environmental Defense Fund.

» Describe the basic principles of control banding and facilitate a discussion on why this may be the best way to approach controlling nanomaterials. Consider having the students do a group exercise of applying control banding to a chemical with which they are familiar.

Summary of the 2-hour Training Modules

Module	Topic	Description	Adult learning techniques
1	Introduction to nanotech-nology and nanoparticles	An overview of the definition of nanoparticles, classs of nanomaterials with an explanation of engineered versus naturally occurring and a discussion of the benefits, risks and life cycle of nanomaterials.	» Demonstration of commercially available models of nanoparticles; » Group discussions on whether the benefits exceed the risks and who bears the risks; » Class exercise of handling actual products (some nano and some not) and trying to determine if they contain nanoparticles; » Class discussion of operations in student workplaces where nanoparticles or nanomaterials are handled.
2	Environmental, health and safety impacts of nanoparticles	A facilitated discussion of routes of entry, known health effects, the value of control banding and areas where research is still needed.	» Group exercises analyzing historical occupational health problems in the workplace and their applicability to nanoparticles; » Demonstration using the Livermore Control Banding Nanotool
3	Application of traditional risk management approaches to protect workers handling nanoparticles	Discussion of limitations of standard industrial hygiene approach to airborne measurement, status of development of occupational exposure limits, current understanding of ventilation effectiveness handling nanoparticles and respiratory protection recommendations by NIOSH. Review of hazcom issues.	» Facilitated discussion of the hierarchy of controls and its applicability to nanoparticles; » Group exercise reviewing actual MSDSs for nanomaterials; » Hands-on exercises with N-95 filtering facepiece respirators; » Hands-on exercises with industrial hygiene sampling equipment.
4	Regulatory and voluntary approaches	Review of regulatory efforts across the federal government and internationally to protect workers from exposure to nanomaterials.	» Class internet exercise putting number of chemicals in perspective by checking current CAS numbers and potential number of nanoparticles versus EPA and OSHA regulated chemicals; » Group exercise applying Dupont/EDF NanoRisk Framework; » Group exercise applying control banding to a specific chemical familiar to the class; » Class discussion on the steps OSHA should be taking; » Class discussion on the value of the Precautionary Priniciple.

6.3. Value of NIEHS Minimum Criteria in structuring nanoparticles training for workers

There are many good sources available for creating effective training materials for workers. Arguably the guidance with the most substantial results to corroborate its value is the "Minimum Criteria" guidance of the National Institute of Environmental Health Sciences' Worker Education and Training Program. This guidance, which was updated in 2006, has provided the underlying principles for the creation, delivery and evaluation of training for over two million workers since the beginning of the program in 1987.

The initial quality control for the program was developed through a participatory national technical workshop in 1990 and issued by the Program in 1991. This original "Minimum Criteria" was updated in 1994 as the "Interpretive Guidance" to the "Minimum Criteria." The guidance has served as the quality control basis for the WETP training grants program to the present time. It was also adopted by OSHA as a non-mandatory appendix to the HAZWOPER standard.

The following Minimum Criteria recommendations should be applied as much as practicable to any training program created to deal with nanoparticles:

- Provide peer-to-peer training with hands-on activities whenever possible.
- Fill at least one-third of the training program hours with hands-on training.
- Avoid making computer-based training methods the sole form of training, although they can greatly augment the effectiveness and reduce the cost of hazardous waste worker training.
- Make sure proven adult-learning techniques are the core of all worker training.
- Precede all worker safety and health training with a needs analysis to ensure the appropriate knowledge, skills and attitudes are being transmitted.
- Follow all training with a proper evaluation to document that the knowledge, skills or attitudes were acceptably transmitted and that the worker possesses the necessary abilities to perform the tasks.[89]

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This publication was made possible by contract number 273-05-C-0017 from the National Institute of Environmental Health Sciences (NIEHS), NIH.

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