DANGERS OF NANOTECHNOLOGY: SOLUTION TO POTENTIAL HEALTH AND ENVIRONMENTAL CONCERNS

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Abstract
The benefits of engineering of functional systems at the nanometer-scale as one of the key technologies of the 21st century whether they are being used in medical treatment, as an innovative approach to generating energy, or a smaller data storage device, almost always imply grave risks. Nanomaterials will bring a new range of problems for human health and the environment. Our knowledge of effects nanomaterials on human health and environment is incomplete. In general, potential risks of molecular manufacturing on society are numerous and very real. The greatest potential for exposure over the next few years will be in the workplace, industry and in university labs. This article represents current scientific findings, understandings and identifications of the dangers nanotechnology imposes on the environment and human health with special emphasis on exposure control guidelines and regulatory issues.

Introduction

Over approximately the past 30 years, three different but interdependent technology disciplines have emerged: biotechnology, information technology, and nanotechnology. Today, we are in the middle of a convergence of all three disciplines, and it is still not clear what this might bring about. Nanotechnology is the latest and least understood of these technologies. This emerging family of heterogeneous technologies, which is defined by its scale – the prefix "nano" signifies one billionth (= 0.000000001) of a meter, enables the manipulation of the substance at the atomic level (Drexler et al 1993). Conceptually, nanotechnology refers to the ability to control and take advantage of molecules and atoms, within the range of 1 nm to 100 nm. For comparison, a single human hair is about 80,000nm wide, a red blood cell is approximately 7,000nm wide and the size of an atom is approximately 0.2nm. A landmark report on nanotechnologies, 'Nanoscience and Nanotechnologies: Opportunities and Uncertaintie*s*', published in 2004 by the UK's Royal Society and Royal Academy of Engineering (RS/RAE) makes the distinction between nanoscience and nanotechnology where the former includes 'the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale', and the latter as 'the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the

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nanometre scale'. Nanoscience is often referred to as "horizontal" or "key" since it often brings together different areas of science and benefits from an interdisciplinary or “converging” approach and is expected to lead to innovations that can play a role towards addressing many of the problems facing today’s society and realising sustainable development (Commission of the European Communities, 2001, 2004).

Nanoscience and nanotechnologies are widely seen as having huge potential to bring benefits to existing consumer and industrial products and could have a substantial impact on the development of new applications ranging from disease diagnosis, cosmetics, and fuel cells to environmental remediation (Colvin 2003). To date, over 800 products incorporating nanotechnology (nanoproducts) have already hit the supermarket and pharmacy shelves (Woodrow Wilson International Center for Scholars 2009), with commercially available nanoproducts including compounds and composites for use in foods, pesticides, sunscreens, cosmetics, stain resistant clothing, automotive paints and coatings, sporting goods, and digital cameras. In contrast to these simple nanoproducts, future nanotechnology applications promise significant social benefits, including enhancements in medical diagnosis and health treatments, more efficient energy sources, the potential to benefit the developing world, and lighter, faster, and cheaper materials and electronic products (Perkel 2002; Roco 2003; Royal Society and Royal Academy of Engineering 2004; Mehta 2008). Since its foundation in 2001, the U.S. National Nanotechnology Initiative (NNI) has reached an annual $1.5 billion federal investment in nanotechnology research. Most of this funding is focused on science and engineering that potentially will lead to incredible advances in fields such as healthcare, electronics, aeronautics and energy. By 2014, the nanotechnology consultancy firm Lux Research envisages that $2.6 trillion of manufactured goods will incorporate nanotechnology – about 15 percent of total global output (Lux 2006). If, however, nanotechnology’s potential to improve life is to be realized, one should also understand its harmful potentials.

The paper begins with an introduction that examines the most pressing issues regarding nanotechnology toxicity and the exposure of humans and the environment to nanotechnology. Following that is a brief section on the explosion and fire risks associated with combustible nano-powders. Given the limited amount of information about the possible health or environmental risks associated with nanotechnology at this stage, the paper concludes with a discussion of how exposure control procedures and regulatory issues are understood and followed at the EU level as well as in the United States, and the United Kingdom.

Health and environmental concerns

Current information about the potential adverse health effects of engineered nanomaterials is limited. There are many uncertainties as to whether the unique properties of manufactured nanoparticles pose health or occupational health risks. There is concern that nanoscale particles being exploited in certain applications might penetrate the skin and possibly even to escape the immune system to reach the brain. The most common route of exposure to air-borne particles is by inhalation. So-called 'incidental' nanoparticles (often referred to as ultrafine particulate matter) such as those found in welding fumes, cooking and diesel exhaust have clearly been more extensively studied than engineered nanomaterials, so we have had to rely mainly on analogies with results from studies on exposure to pollutant nanoparticles in urban air. Experimental studies in cell culture and rodents have shown that the toxicity of ultrafine or nanoparticles is greater than that of the same mass of larger particles of similar chemical composition (Oberdöster et al 1994; Barlow et al 2005). Other particle characteristics may also influence the toxicity, including solubility and surface chemistry (Duffin et al 2002; Oberdöster et al 2005; Donaldson et al 2006).

Carbon nanotubes have potential applications in artificial muscles, nanoelectronics, as well as display devices. A study on mouse lungs conducted by Lam et al. (2004, p.133) concludes that 'if nanoparticles reach lungs, they are much more toxic that carbon black and can be more toxic than

quartz which is considered a serious occupational health hazard in chronic inhalation exposures'. Some materials, such as carbon black (used as a filler to reinforce car tyres, pigments in printing inks, photocopier toners, coatings, plastics, fibres, paper and in batteries) or titanium dioxide (currently used in some sunscreens, cosmetics, pigments, toner, coating material etc) are currently in industrial production, but these materials previously regarded as harmless in their larger forms, may exhibit toxicological characteristic in their nanoparticle forms. Nanoparticles of titanium dioxide act as absorbers and reflectors of ultraviolet light. Titanium dioxide is photoactive and it has potential to generate free radicals that are known to cause damage to DNA (RS/RAE 2004).
A 2001 study by Hussain et al demonstrated that research into better formulations for drug delivery has shown that some nanoparticles may permeate gut lymphatic vessels.
Lynch et al (2006) consider that because immune system functions through nanoscale intercellular communications, manufactured nanoparticles can disrupt these processes with harmful results. A 2005 study by Zhao et al demonstrated that DNA repair, another vital biological system that operates at the nanoscale, is also susceptible to modification by nanoparticles.
These unique interactions between nanoparticles and biological systems offer great promise for medicinal applications, but the consequences could be harmful. Natural and unintentionally produced ultrafine particulate matter, which is in the same size range as engineered nanoparticles, can carry a broad range of compounds, including polycyclic aromatic hydrocarbons, metals, and other toxic chemicals. Gutierrez-Castillo et al (2006) found that urban airborne particulate matter with chemicals adsorbed on the surface can damage DNA. These examples suggest that the countless possible interactions between nanoparticles and harmful environmental chemicals may lead to unique exposures and health risks (Balbus et al 2007). All concerns relate to the potential impacts of deliberately manufactured nanoparticles and nanotubes that are free rather than fixed to or within a material (RS/RAE 2004).
From an environmental point of view, as more products containing nanomaterials are developed, there is greater potential for environmental exposure. The White Paper published in 2007 by the U.S. Environmental Protection Agency (EPA) summarises what is recognized about the fate of nanomaterials in the air, in water, and in soil: 1) biodegradation, bioavailability, and bioaccumulation of nanomaterials, 2) the potential for transformation of nanomaterials to more toxic metabolites, 3) possible interactions between nanomaterials and other environmental contaminants; and 4) the applicability of current environmental fate and transport models to nanomaterials. (p. 33)
Potential nanomaterials release to the environment include direct and/or indirect releases from the manufacture and processing of nanomaterials, releases from oil refining processes, chemical and material manufacturing processes, chemical clean up activities including the remediation of contaminated sites. Releases to the environment include nanomaterials incorporated into materials used to fabricate products for consumer use including pharmaceutical products, and releases resulting from the use and disposal of consumer products containing nanoscale materials (NIOSH 2007). Nanotechnology has the potential to substantially benefit environmental quality and sustainability through pollution prevention, wastewater treatment, and remediation. For example, dendrimers can trap metal ions, and therefore could support environmental clean-up. The possible interactions between nanomaterials and the environment are numerous and complex. The handful of studies on the toxicity of fullerenes so far suggested that they are indeed hazardous causing oxidative damage to the brain in the largemouth bass but they can be designed to be less so, by conjugating other chemicals to the surface of buckyballs, thus changing their chemical properties (Oberdörster 2004; Colvin 2003). It is plausible that soil and water organisms could take up manufactured nanoparticles escaping into natural environment and that these particles could, depending on their surface activity interfere with vital functions, i.e. they may inhibit phagocytosis of macrophages (RS/RAE 2004). Organisms may ingest materials that have entered the water system or being deposited on vegetation. Once inhaled or ingested,

nanomaterials may enter the food chain, leading to the possibility of bioaccumulation and ingestion by organisms higher up the chain. Bioaccumulation will depend on the surface activity of nanoparticles. Perhaps the greatest source of concentrated environmental exposure in the near term (less than five years) comes from the application of nanoparticles to soil or waters remediation. Initial studies on their potential for remediation indicate that nanoparticles of iron can travel with the groundwater over the distance of 20 metres and remain reactive for 4-8 weeks (Zhang 2003). Silver, the non-toxic metal has been used for medicines and household appliances because of the recognized sterilisation capabilities. Nanosilver is utilised to kill harmful bacteria in products such as washing machines, but there is concern that silver ions once released into wastewater systems might kill the good bacteria used in biological water treatment facilities.

Risk of explosion and fire

The increased risk of explosion and fire of nano-combustible material is mainly result of its increased surface area. The increased surface area of nanoparticles might indicate that they would be more likely to become self-charged, and be more easily ignited. Any dry, fine and combustible nano-powder poses an explosion or fire risk, either through spontaneous combustion or ignition (RS/RAE 2004; NIOSH 2007).

Safety measures and regulatory issues

The safety measures and risk assessment of manufactured nanomaterials have become the focal point of increasing consideration, mainly related to toxic and explosion hazards associated with nanoparticles and nanotubes. Indeed, a great number of reports have been published discussing the potential environmental and health risks associated with the manufacture, use, distribution and disposal of nanomaterials. Still, there are many unanswered questions. Many scientists are raising questions regarding the manufacturing of nanomaterials and its effect on workforce, researchers and consumers. Research has shown that the properties of manufactured nanoparticles may be different than their larger forms. This is mainly due to the larger surface area per unit mass and probable ability of nanoparticles to penetrate natural tissue barriers and cells more readily. However, manufacturers must take into account the differences in toxic potential between larger and nano-sized particles. At present, the most likely place of exposure to nanoparticles and nanotubes is the workplace, including academic research institutions. Therefore, it is paramount that companies follow the usual methods of industrial hygiene. This involves the specification of personal respiratory protection, along with appropriate procedures for cleaning up accidental emissions within and outside the workplace.

Both the EU and the US established regulatory systems for risk assessment and hazard of nanotechnology. Established in 2007, the new Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as a EU Regulation, REACH is based on the principle that manufacturers, importers and downstream users have to ensure that they manufacture, place on the market or use such substances (nanomaterials are covered by the “substance” definition in REACH) that do not adversely affect human health or the environment (REACH 2008). Substances, including substances at the nanoscale, manufactured or imported in volumes of 1 tonne or more per year have to be registered under REACH. This principle is applicable to substances in whatever size or form and for all their identified uses (the threshold levels do not recognise the fact that substances in nanoparticle form may have different health and environmental impacts per unit mass). Therefore, the RS/RAE recommends in 2004 that chemicals in the form of nanoparticles and nanotubes be treated as new substances. This is currently subject to ongoing debate published in December 2008 (European Commission, 2008).

On May 12 2004, the European Commission's report on 'Towards a European strategy for nanotechnology' in support of a high level of public health, safety, environmental and consumer protection elaborates the need:

> (a) to identify and address safety concerns (real or perceived) at the earliest possible stage;
> (b) to reinforce support for the integration of health, environmental, risk and other related aspects into R&D activities together with specific studies;
> (c) to support the generation of data on toxicology and eco-toxicology (including dose response data) and evaluate potential human and environmental exposure.
> The Commission calls upon the Member States to promote:
> (d) the adjustment, if necessary, of risk assessment procedures to take into account the particular issues associated with nanotechnology applications;
> (e) the integration of assessment of risk to human health, the environment, consumers and workers at all stages of the life cycle of the technology (including conception, R&D, manufacturing, distribution, use, and disposal). (pp. 21-22)

The 2007 Commission Communication 'Nanosciences and nanotechnologies: An action plan for Europe 2005-2009', purports:

> Particular attention must also be given to the various mechanisms that allow authorities and agencies in charge of implementing legislation to intervene, through measures such as safeguard clauses and warning systems, in case risks are identified for products already on the market. Finally, authorities will have to ensure that regulatory priorities are covered by calls for proposals under FP7 and that the outcome of research is scrutinized for its regulatory usefulness. (pp. 8-9)

Legislation dealing with health, safety and environment aspects of nanomaterials can be grouped under chemicals, worker protection, products and environmental protection. The main elements in relation to risks associated with nanomaterials are described in the annexed Commission Staff Working Document (Commission of the European Communities, 2008). The Communication continues with regard to worker and environmental protection:

> Framework Directive 89/391/EEC places a number of obligations on employers to take measures necessary for the safety and health protection of workers. It applies to all substances and work activities including manufacturing and use of chemicals at all levels of the production process, regardless of the number of workers involved and quantities of materials produced or technologies used. This Directive fully applies to nanomaterials. Employers, therefore, must carry out a risk assessment and, where a risk is identified, take measures to eliminate this risk. Relevant directives thus adopted relate to risks related to exposure to carcinogens or mutagens at work, risks related to chemical agents at work, the use of work equipment by workers at work, the use of personal protective equipment at the workplace and safety and health protection of workers potentially at risk from explosive atmospheres. (p. 5)
> Environmental regulation relevant in this context relates in particular to integrated pollution prevention and control (IPPC), the control of major accident hazards involving dangerous substances (Seveso II), the water framework directive and a number of waste directives. Wastes containing nanomaterials could be classified as hazardous, if the nanomaterial displays relevant properties which render the waste hazardous. (p. 7)

The European Commission is making a regulatory inventory, covering EU regulatory frameworks that are applicable to nanomaterials (chemicals, worker protection, environmental legislation, product specific legislation etc.). The European Commission's independent Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) has published its opinion on the most recent developments in the risk assessment of nanomaterials. SCENIHR has advised that, due to unpredictable characteristics of nanomaterials, their hazard assessment should be done on a case-by-case basis (SCENIHR, 2006). SCENIHR has also reviewed the existing data on nanomaterials, data gaps, and issues that are to be considered in conducting risk assessments on nanomaterials.

The UK Royal Society (RS/RAE) published a report in July 2004 and recommended a two to five-year window within which companies and universities are advised to investigate and understand the toxicity before the government should undertake any new regulation in nanotechnology. The RS/RAE proposed the following guidelines: 1) the factories and research laboratories should treat manufactured nanoparticles and nanotubes as if they were hazardous, and seek to reduce or to remove them from waste streams; 2) the use of free (that is, not fixed in a matrix) manufactured nanoparticles in environmental applications such as remediation should be prohibited until appropriate research has been undertaken and it can be demonstrated that the potential benefits outweigh the potential risk; 3) in view of the fact that some chemicals are a much greater hazard in the form of nanoparticles, the Health and Safety Executive (HSE), Environmental Agency (EA) and Department for Environment, Food and Rural Affairs (DEFRA) ought to review their existing procedures for accidental release management within and outside the workplace. On 29 December 2008, the U.S. EPA announces that it is in the process of finalizing a major joint research effort with a number of United Kingdom (UK) agencies regarding the behavior and effects of nanomaterials in the environment. The UK agencies include the Natural Environment Research Council, Engineering and Physical Sciences Research Council, DEFRA, and EA.

In June 2007, The National Institute for Occupational Safety and Health (NIOSH) reported its progress in conducting nanotechnology research and developing recommendations on the safe handling of nanomaterials. NIOSH established the NIOSH Nanotechnology Research Center (NTRC) in 2004 in order to accelerate progress in nanotechnology research. On 26 February, 2008 a report was published by NIOSH on the Strategic Plan for NIOSH Nanotechnology Research and Guidance: Filling the Knowledge Gaps (2008). The NIOSH NTRC research program has identified 10 critical topic areas important for understanding the potential health risks. They are: (1) exposure assessment (2) toxicity and internal dose, (3) epidemiology and surveillance, (4) risk assessment, (5) measurement methods, (6), engineering controls and personal protective equipment (PPE), (7) fire and explosion safety, (8) recommendations and guidance, (9) communication and information, and (10) applications. (p. 6)

Minimizing occupational exposure is the most sensible approach to controlling materials of unknown toxicity such as nanomaterials. In general, these approaches include substituting a toxic material if possible, enclosing the hazardous process, removing workers from exposure by automating the process, isolating workers from the hazard, and/or using local exhaust ventilation where nanomaterials are handled. A concern has been raised that nanoparticles could pass through the protective barrier of PPE (such as respirators, gloves, and protective clothing) at a higher rate than larger particles because of their smaller size and unique properties. NTRC will also continue its research of the potential for nanoparticles to penetrate respirators and other PPE. As a result of the current lack of exposure standards for nanomaterials, improved control methods will become more apparent as the risks of exposure to nanomaterials are better understood.

According to the HSE report (2004, p. 41) strategies to control exposure to nanoparticles may include: (1) total enclosure of the process; (2) partial enclosure with local exhaust ventilation; (3) local exhaust ventilation; (4) general ventilation; (5) limitation of numbers of workers and exclusion of others; (6) reduction in periods of exposure; (7) regular cleaning of wall and other surfaces; (8) use of suitable personal protective equipment; and (9) prohibition of eating and drinking in contaminated areas.

In February 2007, the U.S. Environmental Protection Agency (EPA) published the White Paper with the aim of providing a structured and systematic approach to nanotoxicity risk assessment and research, giving the comprehensive overview of precautionary measures to overcome potential health hazard of the presence of nanomaterials in the air, including properly fitted respirators (HEPA), although due to size and mobility of nanomaterials leakage may occur.

Consequently, nanoparticles should be treated like gases. Nevertheless, PPE may not be as effective at mitigating dermal exposure as a result of touching face with contaminated fingers and PPE infiltration. The use of good practice can help to reduce worker exposures to nanomaterials. Examples of good practices include: cleaning powder or liquid spills of working areas using HEPA-filtered vacuum cleaners, wet wiping methods, isolating individuals, using non-toxic or less toxic substances, and careful disposal of nanomaterials (NIOSH 2006). It would be prudent to base strategies for dealing with spills and contaminated areas on good working practices and as in case of any material spill or cleaning of contaminated surfaces, handling and disposal of the waste material should follow existing national or local regulations.
Evidence shows that combustible nanoparticles might cause an increased risk of explosion because of their increased surface area and potential for enhanced reaction. It is Therefore, it is paramount that combustible nanoparticles are manufactured, handled, and stored in liquid (RS/RAE 2004).
General population exposure may occur from environmental releases from the production and use of nanomaterials and from direct use of products containing nanomaterials. During the production of nanomaterials, there are several potential sources for environmental releases including the evacuation of production chambers, filter residues, losses during spray drying, emissions from filter or scrubber break-through, and wastes from equipment cleaning and product handling (EPA 2007). No data have been identified quantifying the releases of nanomaterials from industrial processes. However, due to the small size of nanomaterials, they will likely stay airborne for a substantially longer time than other types of particulate. The most likely pathway for general population exposure to releases from industrial processes is direct inhalation of materials released into the air during manufacturing (UK Royal Society 2004).

Conclusion

In all cases in which the full extent of risk is unknown but concerns are so high that risk management measures are considered necessary, as is currently the case for nanomaterials, these measures must be based on the precautionary principle. A full estimation of human health risks and the effect of nanoparticles on species other than humans, or of how these particles behave in the air, water or soil, or their ability to accumulate in food chains will require development of satisfactory techniques. Such techniques are required for assessing exposure to nanoparticles in addition to consideration of toxicity. At present, the European Commission has no evidence that these hazards exist outside the workplace or laboratory environment. The US EPA elaborates that occupational exposures demand particular attention because higher concentrations and amounts of nanoscale materials and higher frequencies and exposures are more likely in workplace settings. Workers may be exposed to nanoscale materials during all stages of nanoscale materials manufacturing, beginning from synthesis, formulation, disposal, or recycling of products containing nanoscale materials. However, the most likely pathway for general population exposure to releases from industrial processes is direct inhalation of materials released into the air during manufacturing. Releases from industrial or transportation accidents, natural disasters, or criminal activity such as a terrorist attack may also lead to exposure of workers or the general public. However, this challenge may be faced through international collaboration and research strategy to address these issues and provide comparable and reliable risk assessment data that will lead consequently to successful emergency response planning and recovery activities.

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