Emerging Contaminants – Nanomaterials

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FACT SHEET

At a Glance

- Diverse class of small-scale substances that have structural components smaller than 1 micrometer (1000 nanometers (nm)) in at least one dimension (Luoma 2008). NMs include nanoparticles (NPs) which are particles with at least two dimensions between approximately 1 and 100 nm in the nanoscale.
- Can be categorized into three types: natural, incidental, and engineered.
- Engineered NMs are being used in a wide variety of applications including environmental remediation, pollution sensors, photovoltaics, medical imaging, and drug delivery.
- May be released through point and nonpoint sources, or introduced directly to the environment when used for remediation purposes.
- May be readily transported through media usually over much greater distances than larger particles of the same composition. The mobility of NMs depends on their surface chemistry and particle size, among other factors, and also on biological and abiotic processes in the media
- May stay in suspension as individual particles, aggregate, dissolve, or react with natural materials.
- Characterization and detection technologies include differential mobility analyzers, mass spectrometry, and scanning electron microscopy.
- Can be removed from air using air filters and respirators, and from water by flocculation, sedimentation, and filtration.

Introduction

An "emerging contaminant" is a chemical or material that is characterized by a perceived, potential, or real threat to human health or the environment or a lack of published health standards. A contaminant may also be "emerging" because a new source or a new pathway to humans has been discovered or a new detection method or treatment technology has been developed (DoD 2010). This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a brief summary of nanomaterials (NMs) as emerging contaminants, including their physical and chemical properties; potential environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information.

Because of their unique properties, NMs are increasingly being used in a wide range of scientific, environmental, industrial, and medicinal applications. However, there is a growing concern about the lack of environmental health and safety data. This fact sheet is intended for use by site managers and other field personnel who may need to address or use NMs at cleanup sites or in drinking water supplies.

What are nanomaterials?

- NMs are a diverse class of small-scale substances that have structural components smaller than 1 micrometer (1000 nanometers (nm)) in at least one dimension. NMs include nanoparticles (NPs) which are particles with at least two dimensions between approximately 1 and 100 nm in the nanoscale (EPA 2008a; Luoma 2008).
- NMs can be categorized into three types according to their source: natural, incidental, and engineered. See Exhibit 1 for examples.
- Engineered NMs, designed with very specific properties, are intentionally produced through certain chemical processes, physical processes, or both, such as self-assembly (from atoms and molecules) or milling (from their macro-scale counterparts), and may be released into the environment primarily through industrial and environmental applications or improper handling of NMs (DHHS 2009; EPA 2007).
- Due to their novel nanoscale size, NMs may possess unique chemical, biological, and physical properties as compared to larger particles of the same material (Keiner 2008).
- The unique properties of NMs allow them to be used for various applications as shown in Exhibit 1.
- More than 1,000 consumer products that contain NMs are on the market today (WWIC 2010).

Exhibit 1: Properties and Common Uses of NMs

Types of NMs (Occurrence)	Example	Physical Properties	Chemical Properties	Uses
Carbon-based (Natural or Engineered) (EPA 2007; Klaine et al 2008)	Fullerenes/Buckyballs (Carbon 60, Carbon 20, Carbon 70); carbon nanotubes; nanodiamonds; nanowires.	They exist as hollow spheres (buckyballs), ellipsoids, tubes (nanotubes); 1nm wires (nanowires) or hexagonal structures (nanodiamonds). Excellent thermal and electrical conductivity;	Carbon-based NMs are stable, have limited reactivity, are composed entirely of carbon, and are strong antioxidants.	Biomedical applications, super-capacitors, sensors, and photovoltaics.
Metal Oxides (Natural or Engineered) (Klaine et al 2008)	Titanium dioxide (TiO_2); zinc oxide (ZnO); cerium oxide (CeO_2).	Some have photocatalytic properties, and some have ultraviolet (UV) blocking ability. When used in sunscreen, nano-TiO_2 and nano-ZnO appear transparent when applied on skin.	High reactivity; photolytic properties.	Photocatalysts, pigments, drug release, medical diagnostics, UV blockers in sunscreen, diesel fuel additive, and remediation.
Zero-Valent Metals (Engineered) (EPA 2008a, Klaine et al 2008)	Nanoscale zero-valent iron (nZVI), emulsified zero-valent iron (EZVI), and bimetallic nanoscale particles (BNPs). BNPs include elemental iron and a metal catalyst (such as gold, nickel, palladium, or platinum)	Between 1 to 100 nm or greater, depending on the NM-type containing the zero-valent metal. Properties can be controlled by varying the reductant type and the reduction conditions.	High surface reactivity. Popular starting materials used in production include: ferric (Fe [III]) or ferrous (Fe [II]) salts with sodium borohydride.	Remediation of waters, sediments, and soils to reduce contaminants such as nitrates, trichloroethene, and tetrachloroethene.
Quantum Dots (Engineered) (Klaine et al 2008)	Quantum dots made from cadmium selenide (CdSe), cadmium telluride (CdTe), and zinc selenide (ZnSe).	Size: 10 to 50 nm. Reactive core controls the material's optical properties. The larger the dot, the redder (lower energy) its fluorescence spectrum.	Closely packed semiconductor whose excitons (bound electron-hole pairs) are confined in all three spatial dimensions. Possible metal structures include: CdSe, CdTe, CdSeTe, ZnSe, InAs, or PbSe, for the core; CdS or ZnS for the shell.	Medical imaging, photovoltaics, telecommunication, and sensors.
Dendrimers (Engineered) (EPA 2007, Watlington 2005)	Hyperbranched polymers, dendrigraft polymers, and dendrons.	Size: 2 to 20 nm. Highly branched polymers. Common shapes include cones, spheres, and disc-like structures.	Highly branched; multi-functional polymers.	Drug delivery, chemical sensors, modified electrodes, and DNA transferring agents.
Composite NMs (Engineered) (EPA 2007, Gil & Parak 2008)	Made with two different NMs or NMs combined with nanosized clay. They can also be made with NMs combined with synthetic polymers or resins.	Composite NMs have novel electrical, magnetic, mechanical, thermal, or imaging features.	Multifunctional components; catalytic features.	Potential applications in drug delivery and cancer detection. Also used in auto parts and packaging materials to enhance mechanical and flame-retardant properties.
Nanosilver (Engineered) (Klaine et al 2008; Luoma 2008)	Forms include colloidal silver, spun silver, nanosilver powder, and polymeric silver.	Size: 10 to 200 nm. Made up of many atoms of silver in the form of silver ions.	High surface reactivity; strong antimicrobial properties.	Medicine applications, water purification, and antimicrobial uses. They are used for a wide variety of commercial products.

How can nanomaterials impact the environment?

- NMs in solid wastes, wastewater effluents, direct discharges, or accidental spillages may be transported to aquatic systems by wind or rainwater runoff (Klaine et al. 2008).
- NPs fate and transport in the environment are largely dependent on material properties such as surface chemistry, particle size, and biological and abiotic processes in environmental media. Depending on these properties, NPs may stay in suspension as individual particles, aggregate forming larger sized NMs, dissolve, or react with natural materials (Luoma 2008).
- Because of their small size and slower rate of gravitational settling, some NMs may remain suspended in air and water for longer periods and may be readily transported over much greater distances than larger particles of the same material (EPA 2007; 2009).
- The mobility of NMs in porous media is influenced by their ability to attach to mineral surfaces to form aggregates. For example, NMs that readily attach to mineral surfaces may be less mobile in ground water aquifers (Wiesner et al. 2006); smaller NMs that can fit into the interlayer spaces between soil particles may travel longer distances before becoming trapped in the soil matrix (EPA 2007); and soils with high clay content tend to stabilize NMs and allow greater dispersal (EPA 2008a).
- The surface chemistry and therefore the mobility of NMs in porous media may be affected through the addition of surface coatings. For example, TiO_2 can be harmless in soil, but could be problematic in water once a surface coating is added (Lubick 2008).
- Research is still being conducted on the effects of NMs on wildlife species. Some studies have reported oxidative stress and pathological changes in aquatic species, specifically trout, after exposure to nano-TiO_2 (Federici et al. 2007).
- Some NMs are reported to be photoactive, but their susceptibility to photodegradation in the atmosphere has not been studied (EPA 2007).
- The potential mechanisms of biodegradation of NMs are the subject of current investigation. Some fullerenes such as C60 and C70 have been found to biodegrade after several months. Many NMs containing inherently non-biodegradable inorganic chemicals like metals and metal oxides may not biodegrade as readily (EPA 2007).
- Although nanoscale zero-valent iron (nZVI) is widely used in site remediation, information is limited on its fate and transport in the environment. While increased mobility due to the smaller size may allow for efficient remediation, there are insufficient data regarding whether such NMs could migrate beyond the contaminated plume area and persist in drinking water aquifers or surface water (EPA 2008a).

What are the routes of exposure to nanomaterials?

- Human exposure to NMs may occur through ingestion, inhalation, injection, and dermal exposure depending on the source and activities of the person. In the workplace, inhalation is a widely recognized route of human exposure (EPA 2007; Watlington 2005).
- The small size, solubility, and large surface area of NMs may enable them to translocate from their deposition site (typically in the lungs) and interact with biological systems. Circulation time increases drastically when the NMs are water-soluble. With smaller NM sizes, the likelihood of greater pulmonary deposition and potential toxicity exists (DHHS 2009; SCENIHR 2009).
- Studies have shown that NMs, due to their small size, have the potential to pass through both the blood-brain barrier (BBB) and the placenta. For example, a recent study showed that nano-anatase TiO_2 may pass the BBB of mice when injected with high doses (Liu et al. 2009).
- Some types of NMs that translocate into systematic circulation may reach the liver and spleen, the two major organs for detoxification and further circulatory distribution. Various cardiovascular and other extra pulmonary effects may occur (Nel et al. 2006). In humans, although most inhaled carbon NMs remain in the lung, less than 1 percent of the inhaled dose may reach the circulatory system (SCENIHR, 2009).
- Use of sunscreen products may lead to dermal exposure of NMs (TiO2 and ZnO) depending on the properties of the sunscreen and the condition of the skin. In healthy skin, the epidermis may prevent NM migration to the dermis. However, damaged skin may allow NMs to penetrate the dermis and access regional lymph nodes, as suggested by quantum dots and nanosilver (Nel et al. 2006; Mortensen et al. 2008).
- Ingestion exposure may occur from consuming NMs contained in drinking water or food (for example, fish) (Wiesner 2006).

What are the health effects to nanomaterials?

- There are insufficient scientific data to determine whether NMs, under realistic exposure scenarios, may present adverse health effects to humans.
- The health effects of NMs are variable depending on their characteristics. Depending on their charge and particle size, NMs can induce different levels of cell injury and oxidative stress. In addition, particle coatings, size, charge, surface treatments, and surface excitation by UV radiation can modify surface properties and thus the aggregation and biological effects of NMs (Nel et al. 2006; Stone & Donaldson 2006).
- Some NPs may generate reactive oxygen species (ROS), which can lead to membrane damage, including increases in membrane permeability and fluidity. Cells may become more susceptible to osmotic stress or impaired nutrient uptake (Klaine et al. 2008).
- When cultured cells are exposed to NMs of various metals (such as NMs containing titanium and iron), NMs may be absorbed and gain access to tissues that the metals alone cannot normally reach. The uptake-and-damage mechanism is frequently called the “Trojan Horse effect,” where the NPs appear to “trick” the cells to let them in, and once inside, the toxic metals can significantly increase the damaging action of such materials (Limbach et al. 2007).
- Metal-containing NMs may cause toxicity to cells by releasing harmful trace elements or chemical ions. For example, silver NMs may release silver ions that can interact with proteins and inactivate vital enzymes. The lead and cadmium used in quantum dots are known reproductive and developmental toxins (Powell & Kanarek 2006). However, estimates of releases of these metals from NMs are very crude because of varying factors such as the concentration of metal in the source (Klaine et al. 2008; Luoma 2008).
- Research has shown that NMs may stimulate or suppress immune responses (or both) by binding to proteins in the blood (Dobrovolskaia & McNeil 2007).

Are there any federal and state guidelines or health standards for nanomaterials?

- Currently there are no specific federal standards that regulate NMs based solely on their size. However, depending on the specific media of application or release certain federal statutes apply to NMs. These are presented below:
  - Many currently available nano-products fall under the Food and Drug Administration’s (FDA) regulation, such as cosmetics, drugs, and sunscreen products. FDA regulates these products based on a safety assessment of the bulk material ingredients or product (Kimbrell 2006).
  - The presence of a NP in a pesticide may affect EPA’s assessment under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of whether the product causes unreasonable adverse effects on the environment (EPA 2009).
  - Many nanomaterials are regarded as "chemical substances" under the Toxic Substances Control Act (TSCA) and therefore subject to the requirements of the act. EPA has already determined that carbon nanotubes are subject to reporting under section 5 of TSCA. Under TSCA, EPA may also regulate nanomaterials considered to be existing chemicals. (EPA 2008b; 2010).
  - EPA is developing a Significant New Use Rule (SNUR) that would require persons who intend to manufacture, import, or process new nanoscale materials based on chemical substances listed on the TSCA Inventory to submit a Significant New Use Notice (SNUN) to EPA at least 90 days before commencing that activity (EPA 2010).
  - If NMs enter drinking water or are injected into a well, they may be subject to the Safe Drinking Water Act (EPA 2009). However, currently no Maximum Contaminant Level Goals (MCLGs) and Maximum Contaminant Levels (MCLs) have been established for NMs based solely on their size. MCLGs and MCLs are established for the macro-sized forms of NMs.
  - Risks from NMs in waste sites may be evaluated and addressed under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Resource Conservation and Recovery Act (RCRA) (EPA 2009).

Are there any federal and state guidelines or health standards for nanomaterials? (continued)

- Discharges containing NMs to waters of the United States may require authorization under a Clean Water Act (CWA) permit pursuant to Section 402 of the CWA. EPA can establish compound-specific effluent limits in permits under the CWA (EPA 2009).
- NMs may also be regulated under the Clean Air Act if it is determined that their presence in the air would endanger public health and welfare (EPA 2009).
- The Occupational Health and Safety Administration (OSHA) has approved plans for 21 states that enable them to adopt federal safety standards for workers in private industry. This allows states to adopt guidelines to manage the risks of NMs in the workplace (Keiner 2008).
- The National Institute for Occupational Safety and Health (NIOSH) has developed interim guidance on the occupational safety and health implications and applications of NMs, including the use of effective control technologies, work practices, and personal protective equipment (NIOSH 2010).

❖ State and local standards and guidelines:
  - In 2006, Berkeley, California, adopted the first local regulation specifically for NMs requiring all facilities manufacturing or using manufactured NMs to disclose current toxicology information, as available (Keiner 2008).
  - In January 2009, the California Department of Toxic Substances Control (CA DTSC) requested information regarding analytical test methods, fate and transport in the environment, and other relevant information from manufacturers of nanomaterials (CA DTSC 2009).
  - Several other states may have community right-to-know laws that authorize reporting or disclosures broader than the federal law; this may provide authority to require reporting when facilities use or produce NMs (Keiner 2008).

What detection and characterization methods are available for nanomaterials?

❖ The detection, extraction, and analysis of NMs are challenging due to their small size, unique structure, physical and chemical characteristics, surface coatings and interactions in the environment, including agglomeration and sequestration (EPA 2007). The analysis of NMs in environmental samples often requires the use of multiple technologies in tandem. This can include the use of size separation technologies combined with particle counting systems, morphological analysis and /or chemical analysis technologies

❖ Aerosol fractionation technologies (differential mobility analyzers and scanning mobility particle sizers) use the mobility properties of charged NMs in an electrical field to obtain size fractions for subsequent analysis. Multi-stage impactor samplers separate NM fractions based upon the aerodynamic mobility properties of the NMs (Grassian et al. 2007; EPA 2007).

❖ Aerosol mass spectrometer provides chemical analysis of NMs suspended in gases and liquids by vaporizing them and analyzing the resulting ions in a mass spectrometer (SCENIHR 2009).

❖ Expansion Condensation Nucleus Counters measure and derive NM density in gas suspension through adiabatic expansion followed by optical measurement. Currently available instruments can detect NPs as small as 3 nm (Saghafifar et al. 2007).

❖ Size-exclusion chromatography, ultrafiltration, and field flow fractionation can be used for size fractionation and collection of NM fractions in liquid media. NM fractions may be further analyzed using dynamic light scattering for size analysis and mass spectrometry for chemical characterization (EPA 2007).

❖ One of the main methods of analyzing NM characteristics is electron microscopy. Scanning Electron Microscopy and Transmission Electron Microscopy can be used to determine the size, shape, and aggregation state of NMs below 10 nm (SCENIHR 2006). Atomic Force Microscopy, a more recently developed technology, has the ability to provide single particle size and morphological information at the nanometer level in air and liquid media (Colton, 2004).

What detection and characterization methods are available for nanomaterials? (continued)

- Other analytical techniques include X-ray diffraction to measure the crystalline phase and X-ray photoelectron spectroscopy to determine the surface chemical composition and functionality of NMs (Grassian et al. 2007).
- Additional research is needed to determine methods to detect and quantify engineered NMs in environmental media.

What technologies are being used to control nanomaterials?

- Limited information is available about which technologies can be used to control NMs in water and wastewater streams.
- Air filters and respirators are used to filter and remove NMs from air (Wiesner et al. 2006).
- NMs in ground water, surface water, and drinking water may be removed using flocculation, sedimentation, and sand or membrane filtration (Wiesner et al. 2006).

Where can I find more information about nanomaterials?

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Where can I find more information about nanomaterials? (continued)

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