Nanomaterials: New Emerging Contaminants and Their Potential Impact to Water Resources

By William E. Motzer

Introduction

Manufactured nanomaterials (MNMs) are a relatively new class of elemental metals, chemical compounds, and engineered materials with particle sizes in the nanometer (nm) range (1 x 10^{-9} m to 100 x 10^{-9} m). In comparison, a human hair is 80,000 nm in diameter, a red blood cell is about 7,000 nm wide, DNA is about 2 to12 nm in width, and a water molecule is approximately 0.3 nm across. This "nanoworld" now includes several different substance classes, including:

(1) Carbon-based materials and structures such as C_{60} fullerene, which can be formed into carbon nanotubes.

(2) Metal-based substances such as nanogold, nanosilver, and nanometal oxides such as titanium oxide. These also include quantum dots, which are packed semiconductor crystals whose optical properties can change with size; they also have the ability to absorb light and re-emit it in different colors depending on the nanocrystal's size.

(3) Dendrimers are polymers constructed from branched units. A dendrimer's surface has numerous chain ends that can be designed to perform specific chemical functions. Also, dendrimers generally are hollow spheres into which other molecules or atoms can be placed. This makes them useful for drug delivery.

(4) Bio-inorganic composites, such as titanium with attached DNA strands. These can be used to treat disease (Royal Academy, 2004; Elder, 2006; U.S. EPA, 2007).

Several classes of MNMs are now globally manufactured in hundred to thousands of metric tons per year. These include MNMs for structural applications (ceramics, catalysts, films and coatings, and composite metals), skin care products (metal oxides), information and communication technologies (nanoelectronic and optoelectronic materials, organic light emitters, and nanophosphors), biotechnology (drug delivery, diagnostic markers, and biosensors) and environmental technologies (nanofiltration and membranes) (Borm and others, 2006).

Characteristics
The unique size of MNMs means that, in some ways, they will behave as new chemical substances (Borm and others, 2006). Two main factors distinguish MNM properties from ordinary materials (DTSC, 2007; Nel, 2007):

(1) They have relatively large surface areas when compared to the same mass of material produced in larger form. For example, a 1.0 cm cube has a surface area of 6 cm^2. This same cube separated into 1.0 mm cubes now has a surface area of 60 cm^2; but if further divided into 1.0 nm cubes, the total surface area becomes 60 x 10^6 cm^2. This may cause the substance to become more chemically reactive; substances that were inert in large-scale form can become reactive in nanoscale form. Size reduction may also affect the material's strength.

(2) Quantum effects can begin dominating MNMs, particularly at the lower end of the scale, affecting their optical, electrical and magnetic behavior.

Nanoparticles also can quickly change into larger particles by agglomeration processes.

Occurrence in the Environment
Naturally occurring (geogenic) nanomagnetite exists in some bacteria, which use this mineral to sense the Earth's magnetic field (Blakemore, 1975; Colvin, 2003; Faivre and others, 2005). Primary geogenic nanoparticles also occur as aerosols from ocean spray (salts and sulfates), volcanic emissions (sulfate aerosols), forest fires (soot and elemental carbon, and polycyclic aromatic hydrocarbons or PAHs) (Lucas and Akimoto, 2007).

Primary anthropogenic nanoparticles are similar in composition to geogenic nanoparticles, ranging from less than PM$_1$ ($\leq$1,000 nm) to ultrafine particles (UFP) ($\leq$100 nm). Sulfate, hydrogensulfate, and nitrate nanoparticles are emitted to the atmosphere from industrial sources and power plants, and nanocarbons are emitted from internal combustion (primarily diesel) engines. Major MNM sources with potential impacts to air, soil, surface water and groundwater are from industrial production, including amorphous silica, carbon blacks and fullerenes, and titanium and zinc oxides (Borm, 2004,; Lucas and Akimoto, 2007; Mädler, 2007).

Both geogenic and anthropogenic secondary nanoparticles may be formed in the atmosphere from gas-to-particle conversions such as oxidation. Secondary nanoparticles may also "grow" by coagulation and agglomeration to micrometer sizes (Borm and others, 2006). **Table 1** contains a summary of primary nanoparticles produced by anthropogenic and geogenic sources and uses.

Detection and Analysis
Current chemical ("conventional") contaminants require an understanding of their physical properties (molecular mass, boiling and melting points, vapor and water density, water solubility, and volatility from water including Henry's constant, etc.), chemical characteristics (chemical formula, octanol water partition coefficient or K$_{ow}$, soil/water partition coefficient or K$_{oc}$, adsorption coefficient, etc.), and toxicity to determine

transport, fate, and ecological and human health risk. Over the past three decades analytical methodologies for determining such parameters have been carefully developed and perfected using instruments such as atomic absorption spectroscopy (AAS), gas chromatography – mass spectrometry (GC-MS), inductively-coupled mass spectrometry (ICP-MS), etc., and also using parameter estimation methods (Lyman and others, 1990; Harris, 1999; Rouessac and Rouessac, 2000).

An entire analytical industry of commercial environmental and University laboratories has evolved to conduct conventional contaminant analysis with many hundreds of thousands and even multi-million dollar investments in instrumentation. The detection and analysis of MNM will require an understanding of additional parameters and considerable investment by these laboratories in "newer" analytical equipment. Examples (Borm and others, 2006; Scalera, 2006) of some of the parameters required to characterize MNMs are summarized in **Table 2** and include:

(1) *Surface area analysis* can be done using an epiphaniometer, whereby particles are exposed to radiation, passed through capillaries, and collected onto a filter for radiation level analysis. The detected radiation level is proportional to the surface area. Other methods include the Braunauer, Emmet, and Teller (BET) Method, which measures the amount of gas absorbed onto surface areas.

(2) *Surface effects* in which properties like dispersibility, conductivity, catalytic behavior, and optical properties are determined because these will vary with different particle surface properties.

(3) *Particle size distribution* by dynamic light scattering (DLS) or photon correlation spectroscopy (PCS). Nanoparticle sizes from <5 nm to 1,000 nm are analyzed in liquids.

(4) *Zeta potential* is the function of a nanoparticle's surface charge; therefore, it is related to electrostatic repulsion. It gives no data on the nanoparticle's chemical composition, but is important for determining nanoparticle dispersion. Zeta potential can be measured by experiment.

Instrumentation that may be required for MNM analysis (Scalera, 2006) includes:

(1) *Secondary ion mass spectroscopy (SIMS),* which is a destructive method allowing analysis of 1 to 3 nm layers. The analysis provides elemental composition only.

(2) *Atomic force microscopy (AFM)* can be applied in air or liquid media and utilizes the van der Waals forces between the microscopic tip of the AFM and the nanoparticle. Particle size and morphology are determined.

(3) *Scanning electron microscopy (SEM)* and *transmission electron microscopy (TEM),* including energy dispersive X-ray analysis (EDX), wavelength dispersive X-ray analysis (WDX), and electron energy loss spectroscopy (EELS) are used for determining nanoparticle size, morphology, and chemical composition.

Toxicity
The toxic effects to animal and human health by some MNMs are just now being investigated. For most MNMs, no toxicity data are available (Borm and others, 2006). Most current toxicological studies are for the hazards of inhaled nanoparticles produced by industry for several decades in amounts now exceeding many metric tons per year. These bulk-produced nanoparticles include colloidal silica, titanium dioxide, and various iron oxides. Toxicity data indicate that these substances, once considered as nuisance dusts, can, upon prolonged exposure to rats, cause inflammation and lung cancer. Acute effects in human also come from combustion nanoparticles (Borm, 2004).

In the case of potential MNM toxicity from ingested water, C_{60} fullerene water suspensions have been observed as antibacterial agents, antioxidants, and protein stabilizers, whereas metallofullerenes were observed to accumulate in rat livers. Inorganic MNMs such as amorphous silicon dioxide (SiO_2) cause pulmonary inflammation in rats, and anatase (TiO_2) acts as an antibacterial agent also causing rodent pulmonary inflammation. Because many MNMs are smaller than cellular membrane pores, they may have considerable direct impact on animal tissues and DNA. The toxicity of harmful and even relatively nontoxic metals may also be increased upon sorption onto nanoparticles. Leaching of these metals into a cell may occur once such a metal-nanoparticle has penetrated the cell wall (Lubick, 2007; Wiesner and others, 2006).

Transport and Fate
Very little is currently known about MNM's dispersal (transport and fate) in the environment and their impacts, particularly to soil, surface water, and groundwater. Also unknown is individual MNM transformation and degradation products and potential associated toxic impacts. MNM release sources are similar to conventional chemical contaminant release sources, including discharge and leakage from production and storage facilities (e.g. laboratories and factories), transportation (railcars, trucks, and ships, etc.), and applications and disposal of consumer products as waste (landfills and wastewater treatment plants). Environmental transport of some MNMs will result in transformation and diffusion by sunlight, water, and atmospheric oxygen, and dilution from precipitation, surface water runoff and groundwater. Some MNMs will agglomerate into larger particles; these agglomerates may have the potential for blocking porous materials, including wastewater treatment filters and even aquifer materials (Royal Academy, 2004; U.S. EPA, 2007).

Many MNMs have greater environmental mobilities than "ordinary" materials, perhaps resulting in greater exposure potentials because they could be dispersed over much larger distances. An interesting phenomenon is illustrated in multiwalled carbon nanotubes having 1.6 nm inner diameters. Measured velocities of water flowing through these nanotubes exceededby more than three orders of magnitude those calculated by hydrodynamic models (Joseph and Aluru, 2008). Would pollutants entering or leaching from such nanotubes result in their moving faster than groundwater advection rates? As MNMs become more prevalent in commercial products, their adverse effect from manufacturing practices and possible improper disposal may become more widespread.

For example, some MNMs have the potential for easily penetrating sand and commercial filters (>2 μm) used in both wastewater and potable-water treatment systems, and they also may easily penetrate natural porous and permeable media in aquifers and even aquitards (Wiesner and others, 2006).

Regulation

The processing, use and reuse, recycling, transport, and disposal for most MNMs are not currently regulated. However, many current federal regulatory programs probably will be expanded to cover MNMs, including: (1) Federal Insecticide, Fungicide and Rodenticide Act (FIFRA); (2) Occupational Health and Safety Act; (3) Resources Conservation and Recovery Act (RCRA); and (4) the Toxic Substances Control Act (TSCA), the Comprehensive Environmental Response and Liability Act (CERCLA – also known as Superfund), and the Clean Water Act (CWA). Undoubtedly, these will provide some of the legal basis for the future regulation of MNM waste and discharge to the environment. However, many regulatory programs, particularly those on the state level, will have to be amended for MNMs. One example, reported by the U.S. EPA, is for silver ion generating washing machines. These are covered by FIFRA, because the nanosilver generated by such machines is considered a pesticide because it is released into laundry for the purpose of destroying microbial pests (Buckingham, 2007). An excellent review of the current regulatory framework of hazardous materials and wastes and its possible application to MNMs is in Breggin and Pendergrass (2007).

Remediation

Very little has been written concerning remediation of possible MNM environmental contamination. This is because we have not completely determined MNM toxicity and risks, do not have the required regulations governing proper disposal and cleanup of MNM wastes, and have not identified or characterized significant contaminant sites. Possible remediation for some MNM might include methods that would force agglomeration, precipitation, and adsorption onto some type of media.

Conclusions

MNMs and their potential impact to the environment and water resources are becoming a concern to regulatory agencies such as the U.S. EPA, and California EPA (DTSC). Concern is also growing among water treatment facilities and water districts about the potential of MNMs to affect the quality of both surface and underground drinking-water sources. Regulators, research scientists and engineers in academia and industry need to expand our knowledge of the characteristics, environmental effects, and potential toxicity of MNMs. In the next decade, consulting scientists, hydrogeologists, engineers, and analytical chemists (all of whom do the bulk of contaminant investigations) will be challenged to expand their knowledge of MNMs to protect our water resources.

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TABLE 1
Various Sources of Primary Geogenic and Anthropogenic Nanoparticles

Nanoparticle Source	Examples	Application/Main Use(s)
Geogenic:		
Oceanic-derived aerosols	Sea salt (largely halite or NaCl)	Environmental exposure
	Sulfates and nitrates	
Volcanic aerosols	Sulfates (including H_2SO_4) and nitrates	
Forest fire aerosols	Carbon black (soot), PAHs	
Anthropogenic:		
Combustion aerosols	Diesel exhaust	Environmental exposure
	Fly ash	
Bulk synthetics	Amorphous silica (SiO_2)	Paints and fillers, dispersants and flowing agents, toothpaste, tires
	Carbon blacks	Pigments, tires (rubber), toners, inks
	Carbon fullerenes (C_{60})	Medical applications
	Carbon nanotubes	Composite fillers, electronics
	Ceria (cerium oxides)	Catalysts in cars, polishing
	Titanium dioxide (TiO_2) as Titania, anatase, rutile)	Cosmetics, pigments, paints UV-absorber, catalyst
	Zinc oxide (ZnO_2)	Polymer filters, UV-absorber
Engineered (MNM)	*Organic:*	
	Liposomes	Drug delivery
	Polycyanoacrylates	
	Polyethene	Implants
	Inorganic:	
	Gold, dendrimers	Drug delivery
	Quantum dots (cadmium, selenium, indium, gallium, and zinc composites)	Medical imaging
	Zeolites, silver	Antibacterial agents

References: modified from Borm (2004); Lucas and Akimoto (2007); Mädler (2007).

TABLE 2

Comparison of Some Conventional Chemical and Nanomaterial/Nanoparticle Characteristics

Some Conventional Chemical Characteristics			Nanomaterial/Nanoparticle Characteristics		
Parameter	Measured By	Units	Parameter	Measured By	Units
Chemical composition (molecular structure)	Chemical analysis including AAS, GC-MS, ICP-AES and ICP-MS, XRF etc.	Formula and molecular mass	Interactive surface size, shape, and morphology (surface area and porosity), chemical composition	TOD-MS; EM AFM for gases, liquids; SEC for	nm^3 and nm
Melting and boiling points	Thermometry	K, °C	Particle size distribution (dispersion)	Comparative particle size measurements using shear, sonification, and dispersion aids such as surfactants.	nm
Densities of vapors, liquids, and solids	Direct measurements and estimations from chemical composition, boiling points, ideal gas law equation etc.	Vapor density = g/L Liquid density = g/mL	Solubility	Same as conventional methods?	ng/L
Volatilization from water and soil Henry's Constant (H)	Wet chemistry, estimations from solubility and vapor pressure	Solubility in mol/m^3; H = unitless or $atm\text{-}m^3/mole$	Aggregation	Sonication and dispersing agents	nm and μm
pH	pH meter	units	Hydrated surface analysis	Epiphaniometer, BET method, TSI Model 3050.	unitless (ratio)
Solubility (water)	Wet chemistry; estimation methods from Kow	mg/L, μg/L, mol/L	Zeta potential	Experimental	Electrostatic charge
Octanol/Water partition coefficient (K_{ow})	Wet chemistry; estimation methods from solvent regression equations	unitless	Wettability	Capillary penetration, and power tablet methods, microsphere tensiometrery method, gel trapping technique	Contact angle (θ) with water or oil
Adsorption coefficient (K_{oc})	Wet chemistry; estimation methods	unitless	Porosity	Mercury porosimetry; small angle X-ray scattering, electron, Atomic Force and Tunnel Microscopy	Volume in cm^3/g v. log r

References: Lyman and others (1990); Harris (1999); Rouessac and Rouessac (2000); Paunov (2004); Powers (2006), Scalera (2006), Mädler (2007); Volfkovich and Sakars (2005).

Abbreviations: AFM = Atomic Force Microscopy   GC-MS = Gas Chromatography-Mass Spectrometry
AAS = Atomic Absorption Spectroscopy   ICP-AES = Inductively-Coupled Plasma – Atomic Emission Spectroscopy
BET = Braunauer, Emmet, and Teller Method   TOF-MS = Time of Flight Mass Spectrometry
EM = Electron Microscopy   XRF = X-Ray fluorescence

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