

Nanomaterials in Surface Water and Sediments: Fate and Analytical Challenges

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Abstract: Nanomaterials (NMs) present some interesting properties that may be tailored; for this reason, they are being used in different fields, which leads to their entry into the environment, whether by normal use or intentional delivery. Once in water and sediments, they undergo different transformations that might be difficult to predict. NMs are also difficult to characterize because the methods for this are recently developed. Currently, the most plausible approach is to combine separation and measurement techniques; one of the most versatile integrations is field-flow fractionation with inductively coupled plasma mass spectrometry (ICP-MS) or ICP optical emission spectrometry. In the same way, toxicity assays must be adapted to these emerging contaminants because they behave neither as chemical compounds nor their bulk counterparts, which produces different results. Nevertheless, several adverse effects of NMs exposure on organisms have been reported, including DNA damage, mortality, oxidative stress, and growth reduction. However, the majority of these studies utilized acute laboratory exposure, whereas in a real ecosystem, organisms are more likely to experience chronic exposure conditions to numerous NMs and a biomagnification effect should be expected through the trophic chain. Despite the lack of sufficient literature, the present review attempts to link various compartmentalization aspects of NMs, their physical properties, and their toxicity in surface water and sediments. DOI: 10.1061/(ASCE)JHZ.2153-5515.0000264. © 2014 American Society of Civil Engineers.

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Introduction

Nanomaterials (NMs) are defined as materials comprising particles that can be as small as approximately 1 nm and as large as several tens of nanometers in at least one dimension (Council 2001). They have been of particular interest in many fields within the scientific community because many NMs display properties that differ from those of the same material at molecular or macro sizes. These properties can be, for example, electronic, conductive, thermal, thermodynamic, magnetic, mechanical, or optical. NMs have gained wide recognition in a variety of commercial and industrial applications over the years, such as structural performance enhancement, skincare products, information and communication technology, biotechnology, and environmental monitoring instrumentation (Roco 2005; Aitken et al. 2006). NMs that are smaller than 100 nm are important in industrial and environmental applications because of their high specific surface area (SSA) and surface reactivity and their associated properties of adsorbing or binding to organic and trace metal contaminants, especially the surface and interface reactions

of solids, such as catalyzed reactions (Zielinski et al. 1995; Hu et al. 2005); adsorption reactions in liquid (Göppert and Müller 2005; Hu et al. 2005); and gas adsorption on solid surfaces (Schumacher et al. 2004; Leviansky et al. 2006). Anthropogenic NMs (engineered NMs) are increasing in prevalence over natural NMs because of their increasing use in different fields (Roco 2005).

The increasing use of NMs in consumer and industrial products has aroused global concern regarding their fate in biological systems, resulting in a demand for parallel risk assessment. Environmental risk assessment of specially engineered NMs requires thorough characterization of NMs and their aggregates because most are very small in size and with different shapes (Brar et al. 2010). Quantitative analytical methods are required to determine environmental concentrations and enable both effect and exposure assessments, especially for new types of NMs in water and sediment. Technologies based on NMs are developing daily, finding applications as diverse as new sensors for improved monitoring and detection, new medical imaging techniques, novel approaches to the treatment and remediation of contaminated land, and green technologies for chemical production (Howard 2010). However, the efficiency of collecting NMs in large quantities in pure and natural systems is a major challenge in nano-science. This review article focuses on experimental investigation and implications of NMs in surface water and sediment, which is an infrequently explored matrix for these components. It will present a treatise of their presence, fate and transport, toxicological impacts, and characterization.

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Nanomaterials in Environment

The plethora of NMs in the environment is perplexing because they have no defined time frame, nor are they uniform in scale (Dhawan and Sharma 2010). Natural NMs existed in the environment long before the nanotechnology era started, in the forms of soil colloids, airborne nano-crystals of sea salts, fullerenes, carbon

nanotubes, and biogenic magnetite, among others (Buffle 2006; Nowack and Bucheli 2007). Sediment and surface water contain many kinds of inorganic and organic NMs, namely clay minerals, metal oxides and hydroxides, humic substances, allophane, and imogolite (Theng and Yuan 2008). Organic nanoparticles can also be found in natural vegetation (Xia et al. 2010). Anthropogenic NMs can be further divided into two categories: incidental, which are NMs produced unintentionally in synthetic processes such as carbon black, carbon nanotubes and fullerenes, platinum and rhodium containing nanoparticles from combustion by-products (Kiang et al. 1996); and engineered/manufactured, which are NMs that are produced intentionally for to their nano-specific properties.

Engineered nanomaterials (ENMs) enter the environment through accidental release during their life cycle, whether from producing, manufacturing, transporting to consumers, or consumer use or disposal/recycling; or from deliberate release as TiO_2 , which is a photocatalytic treatment in wastewater treatment plants; or $\text{Fe}(0)$, which is for contaminant remediation in polluted ground waters (Kiang et al. 1996; Lin et al. 2010). Many examples illustrate the release of ENMs into the environment. Table 1 lists the nature, chemical classification, and different sources of emission of NMs in the environment and their respective applications. From the table, it is obvious that if sources of emission of NMs are controlled, their release in the environment will be controlled to some extent; thus, control at the source is an important proactive approach. However, after release from the source, they obviously enter the environment.

Behavior in the Environment

Once NMs enter the environment, they infiltrate soils, ground waters, surface waters, and sediments by means of runoff waters (Aschberger et al. 2011; Velzeboer et al. 2011). In these environments, NMs naturally undergo many different transformations; assessing these changes is crucial because they affect the physicochemical properties of NMs, which influence fate, transport, and toxicity (Nowack et al. 2012). However, anticipating which transformation will be effected by a particular NM is difficult because natural systems are complex and dynamic. The type of transformation strongly depends on conditions of the medium and on the physicochemical properties of NMs. Transformations can be irreversible and a given NM can undergo many successive transformations (Lowry et al. 2012). The predominant transformations are degradation, oxido-reduction, binding/adsorption, sulfidation, dissolution, precipitation, aggregation, and biological interactions. To understand their behavior in the environment, it is also necessary to comprehend the associated risks, although studies in this domain are still at their natal stage.

Risk Assessment

In risk assessment, characterization of the NMs, toxicity, and exposure are the keystones. Critical factors to consider when quantifying risk exposure include what is present in the environment and in what form; where the NMs end up; what organisms are the most susceptible and to which extent; the bioavailable concentration of the NMs in the environment; and whether the exposure is acute or chronic (Klaine et al. 2008; Stone et al. 2010). Most of these factors are not well known for NMs. The following sections will skim through known information about characterization and toxicity of NMs, about the problems arising from laboratory exposure tests, and extrapolation of these tests with regard to natural ecosystems.

Characterization

The development of suitable analytical methods is required to determine concentrations and characterization of NMs in complex environmental matrices, such as water, sediments, sewage sludge, and organisms (Hassellöv et al. 2008). The approach for the prediction of environmental concentrations through modeling requires validation by measuring actual environmental concentrations. For ENMs that are only recently being introduced into the environment, extremely sensitive methods are required (Tiede et al. 2009) owing to their low amounts. There are some special challenges for studies of NMs in environmental samples. The first challenge is that, for environmentally relevant concentrations within the range (ng L^{-1} – pg L^{-1}), the detection limits for most methods are not sufficiently low. The second challenge is that, in environmental samples, there is a background presence of natural NMs (Banfield and Zhang 2001; Hochella and Madden 2005; Waychunas et al. 2005; Filella 2007; Wigginton et al. 2007). The third challenge is the presence of several unidentified NMs and the instability of NMs under natural conditions (López-Serrano et al. 2014). There is no single efficient method to analyze all NMs; in fact, a method is chosen to balance the restriction of the type of sample, the information required, time constraints, and the cost of the analysis. Some straightforward techniques may simply detect the presence of NMs, and others may give their quantity, size distribution, or surface area. The measurement techniques used to detect the presence of NMs are different from characterization techniques for assessing the chemical contents of an NM sample, their surface reactions, or interactions with other chemical species.

Among all parameters that should be considered for characterization, size is critical for determining the interactions of NMs in surface water and sediment with living organisms and corresponding toxicities. The smaller the NMs, the greater their interactions with biological cells (Gluga et al. 2014). The particle diameter is probably the most commonly used descriptor of particle size, but a single diameter value is sufficient to describe a perfect spherical particle. However, nonspherical NMs (or colloids) are common in the environment, and it is actually common for NMs to have very large aspect ratios (e.g., clay platelets, rods, or fibrils). Many engineered nanomaterials share these features (e.g., carbon nanotubes, nanowires, nanoclays, and nanorods). Several different diameter measurements correspond to an equivalent size of a specific type, such as hydrodynamic diameter, equivalent spherical volume diameter, buoyant mass, equivalent spherical mass diameter, projected area, equivalent molar mass, equivalent pore size diameter, root mean square radius of gyration, and aspect ratio (Martin et al. 2008). Different particle size analysis methods also yield series of equivalent sizes, which are important to consider when comparing size values obtained by using other methods. Inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), liquid chromatography-mass spectrometry (LC-MS), laser-induced breakdown spectroscopy (LIBS), and graphite furnace atomic absorption spectroscopy (GF-AAS) are important for the quantification of different NMs, such as carbon nanotubes, metallic nanoparticles (NPs), halide salts of different isotopic Cd, CdSe/ZnS, Au, Fe_3O_4 , and fullerenes, among others (Martin et al. 2008).

A variety of methods are available for determining the size of nanomaterials; the most commonly employed techniques are Brunauer-Emmett-Teller (BET), dynamic light scattering (DLS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Each method has its limitations in applicable size and concentration

Table 1. Important NMs in Surface Water and Sediments from Different Sources

Nature of nanomaterials	List of nanomaterials	Applications	Sources of emissions	Chemical classification	References
Engineered nanoparticles	TiO ₂	Self-cleaning, antifouling, and antimicrobial properties, paints and coatings and in cosmetics as UV absorber; waste water treatment	Chemical industry waste; paint industries; municipal waste; cosmetic industries; wastewater treatment plants	Transition metal oxide, inorganic	Biswas and Wu (2005), Mann (2006), and Schmid and Riediker (2008)
	CeO ₂	Catalysts and catalyst support, coatings for infrared filters, buffer layer for superconductors, coloring agents for plastics, infrared absorbents and sintering additives, oxidation-resistant coatings, oxygen pumps and oxygen sensors, heat-resistant alloy coatings, electrolyte and/or electrode materials for solid oxide fuel cells, polishing media for electronic devices, glasses, and bearing balls, UV absorbance (absorption at ~400 nm is the strongest for any oxide)	Smoke from vehicles; industrial waste; municipal waste; chemical lab and industry waste	Transition metal oxides	Dang et al. (2010) and Wang and Feng (2003)
	Quantum dots	Biomarkers, labeling agent in organic dyes, coating agent in solar plate, optical probes, semiconductor devices	Chemical industry waste	Alloy of metal, inorganic	Schirhagl et al. (2012)
	ZnO NiO	Many household products including sunscreens, cosmetics, and bottle coatings, and antifouling paints and construction materials	Waste from chemical and pharmaceutical industries; dye industry waste	Inorganic metal oxide	Biswas and Wu (2005) and Kandavelu et al. (2004)
	CuO			Transition metal oxides	Buffet et al. (2013) and Zhou et al. (2006)
Natural + engineered nano particles	Fe, Fe ₃ O ₄ , Fe ₂ O ₃	Oxidative treatment of soil and water; oxidation of aromatic compounds; chelating agent	Microbial degradation of living beings; chemical industry waste; mine industry waste; municipal waste; natural sources; biogenic magnetite	Metal, inorganic	Mann (2006), Oberförster et al. (2005), Schrick et al. (2004), and Zhang (2003)
	Ag	Antimicrobial, antifungal and partially antiviral properties; paints; coatings; medical uses; food packaging	Pharmaceutical industry waste; hospital waste; paint industry waste; municipal waste; chemical lab waste; natural ores	Metal, inorganic	Blaser et al. (2008) and Choi et al. (2008)
	Au	Diagnostics; contrasting agents for image analysis; therapeutics; catalysis; optical sensing; biomarkers and building blocks in nanotechnology	Pharmaceutical industry waste; hospital waste; chemical lab waste; natural ores	Metal, inorganic	De Jong and Borm (2008)
	Carbon black	Pigmentation; UV stabilization and conductive agents; tires and industrial rubber products; plastics; semiconductors; rubber industry; waste toners; printing inks	Rubber industry waste; natural sources; combustion; paint and plastic industries	C-containing, organic	International Carbon Black Association (ICBA)
	Carbon nanotubes (SWCNTs+MWCNTs)	Solar shells; electronics; synthetic muscles; cell therapy; supercapacitors; water and oil purifiers	Chemical vapor deposition; carbon arc synthesis; industrial waste; natural sources	C-containing, organic	Upadhyayula (2007) and Upadhyayula et al. (2012)
	Fullerenes	Antioxidants; photosensitizers; drug delivery; cosmetics; antiviral activity; catalytic activity with enzyme (HIV protease); cancer treatments	Petroleum and gasoline industries; natural sources	C-containing, organic	Bakry et al. (2007)

Table 1. (Continued.)

Nature of nanomaterials	List of nanomaterials	Applications	Sources of emissions	Chemical classification	References
	Al ₂ O ₃	Usually substrate bound; paintings	Natural ores; paint industries	Amphoteric oxide, inorganic	Biswas and Wu (2005), Schmid and Riediker (2008), and Stenger et al. (2005)
	SnO ₂	Magnetic properties of tin oxide nanoparticles are used in magnetic data storage and magnetic resonance imaging; as catalysts, energy saving and anti-static coatings; electrodes and anti-reflection coatings in solar cells; in the making of gas sensors, optoelectronic devices, and resistors; in the making of liquid crystal displays	Natural ores, industrial waste; hospital waste	Acidic oxide, inorganic	Nowack and Bucheli (2007)
	SiO ₂	Food additives; colored glass	Food industry waste; municipal waste; natural ores	Acidic oxide, inorganic	Mann (2006) and Schmid and Riediker (2008)
Natural nanoparticles	Organic suspension matters, humic substances, allophane, and imogolite DNA	Food additives	Microbial degradation; natural vegetation; all living cells; natural erosion	Mixture of all metals, metal oxides, organic, inorganic	Nowack et al. (2012)

Note: MWCNTs = multi-walled carbon nanotubes; SWCNTs = single-walled carbon nanotubes.

range. According to (Hassellöv et al. 2008), the limitation in concentration range in detection is “the lowest concentration that can be distinguished from the background, typically defined as $3 \times \text{Stdev}$ (blank measurements)” (in this case, “Stdev” refers to standard deviation). Table 2 summarizes the methods used for size analysis and concentration and their corresponding limit of detection. Table 2 indicates that microscopy based particle size analysis techniques are more efficient in size and concentration range detection because they cover long ranges. Unlike filtration or X-ray based techniques, a microscopic technique does not depend on sample type, such as dry powder.

The literature has shown that size is the primary determining factor for toxicity, but shape, physical state of the NMs (crystallinity and amorphicity), and surface functionalization are equally important (Pal et al. 2007; Hassellöv et al. 2008). Some toxicity evidence of these parameters are summarized in Table 3. From the table, it is evident that amorphous SiO₂, surface functionalized Au, and plate shaped Ag NMs are more toxic than those mentioned in different forms in the table, and all smaller NMs are always more toxic.

Concentration of NMs is another very important factor determining their toxic effect in biological systems (Hunt et al. 2013). To determine their concentration, a good extraction, separation, and fractionation method is required (López-Serrano et al. 2014). Extractions, such as cloud point extraction (CPE), filtration like cross flow filtration (CFF) and ultrafiltration, and other methods of quantification, such as field-flow fractionation (FFF), size exclusion chromatography, reversed-phase high-performance liquid chromatography, and capillary electrophoresis (CE), are important for enriching NMs. Nevertheless, a combination of these techniques works effectively for analyzing these NMs.

The primary bottleneck of quantification is the lack of validated analytical methods and standards. Current research focuses on the characterization of NMs, although information on quantification is scarce (López-Serrano et al. 2014). There are different techniques for measuring NMs, but it is not clear which measurement best relates to proper analysis of NMs. Each technique has its own merits and demerits as listed in the Table 4. Nevertheless, combined methods perform better than single techniques. In addition to these analytical challenges, most of the studies conducted so far address laboratory condition tests, which are difficult to scale up to the environmental matrices.

Laboratory Exposure Test Problems

When trying to assess the real impact of NMs on the environment in a laboratory, environmentally relevant concentrations must be used. However, there is currently no way to precisely measure these conditions, thus, model predicted concentrations are the closest existing estimate. These concentrations are in the range of pg L^{-1} to $\mu\text{g L}^{-1}$ in surface water, whereas in sediments, they range from $\mu\text{g kg}^{-1}$ to mg kg^{-1} (Aschberger et al. 2011). Even with relevant concentrations, the laboratory exposure of aquatic organisms is difficult, and most of the NMs are insoluble and tend to precipitate. If they do, there are concentration effects because the quantity of bioavailable NMs will decrease and the full concentration impact will not be observed (Velzeboer et al. 2011). On the other hand, solubilization may lead to modifications of the NMs themselves or changes in their behavior. The most widely used solubilization method is sonication. This can produce good results, depending on the sonication time and does not change the properties of NMs, but over time, NMs aggregate again (Dhawan and Sharma 2010). Another method is stirring, which can be used for a longer time period

Table 2. Specification of Methods for Size Analysis of Nanoparticles and Their Limitation Ranges

Principle technique	Characterization technique	Approximate range (nm)	Limit of detection
Microscopic techniques	AFM	0.5 to >1,000	Ppb–ppm
	SEM	10 to >1,000	
	ESEM	40 to >1,000	
	TEM/HR-TEM	1 to >1,000	
	TEM-SAED	1	
	WetSEM	50 to >1,000	
X-ray based techniques	WetTEM	0.1 to >1,000	Detection dependent
	XRD	0.5 to >1,000	
	XAS	0.6–50	
	XRF	>2,000–5,000	
	XPS	>15,000 – 500,000	
Light scattering	DLS	3 to >1,000	ppm
Spectroscopy techniques	UV-visible	>13	ppb-ppm
	Turbidimetry/ nephelometry	50 to >1,000	
Nanoparticle tracking analysis technique	NTA	30–1,000	
Adsorption technique	BET	1 to >1,000	Detection dependent
Filtration	Dialysis/nanofiltration	0.5–100	Detection dependent
	Ultrafiltration	1–30	
	Microfiltration	100 to >1,000	

Note: ESEM = environmental scanning electron microscope; HR-TEM = high-resolution transmission electron microscope; NTA = nanoparticle tracking analysis; TEM-SAED = transmission electron microscopy with selected area electron diffraction; XAS = X-ray absorption spectroscopy; XPS = X-ray photoelectron spectroscopy; XRD = X-ray diffraction; XRF = X-ray fluorescence; wet-SEM = scanning electron microscopy with wet sample; wet-TEM = transmission electron microscopy with wet sample.

Table 3. Evidence of Parameters in Toxicity

Factors	Parameter	Toxicity	Examples	References
Size	Small	More toxic	Same for all NP _s	Dhawan and Sharma (2010)
Crystallinity and amorphicity	Amorphicity	More toxic	SiO ₂	Zhang et al. (2012)
Surface functionalization	With functional group	More toxic	Au	De Jong and Borm (2008)
Shape	Different	Different effect	Ag (palate)	Singh and Ramarao (2012)

(months). This method has the advantages of being less expensive and not modifying the NMs, but it is not very efficient because NMs aggregate again when stirring stops. To solubilize NMs, one may also add dispersing agents, such as the frequently used tetrahydrofuran (THF). The use of THF, or other chemically strong dispersers, is controversial because they are proven to be toxic (Bringmann and Kühn 1980) and can influence toxicity assay results (Farré et al. 2009). A compromise may be to use a weaker dispersant, such as sodium dodecyl sulfate (Farré et al. 2009). The final method is the modification of NMs by coating them or by adding/removing functionalized groups to make them more polar (Dhawan and Sharma 2010). However, these modifications may alter the toxicity of the original NMs (Handy et al. 2008; Dhawan and Sharma 2010). All cited dispersing methods have a point in common: they tend to uniformize NM concentrations when working with demineralized or tap water. These methods can work from a chemical viewpoint (for example, by understanding the effect of pH on the stability of NMs), but they should not be used in a toxicity assay. For the latter, tests should be conducted in natural or “recomposed like natural” water having similar dynamics to water.

Another problem with NM exposure is that there is no standard, whether for methods or presentation of results (Dhawan and Sharma 2010). All laboratories characterize NMs to different extents (some cannot, and others do not have the facilities for further analyses), thus, it is difficult to link an observed

toxic effect to specific characteristics of NMs. From a toxicological point of view, complete characterization must include size distribution, shape, porosity, agglomeration state, solubility, crystallinity, surface charge, surface area, and chemistry (Dhawan and Sharma 2010).

Many other problems occur in laboratory studies with NMs. First, researchers have to handle NMs potentially contaminated by metals or other toxic components unintentionally added during manufacturing operations (Dhawan and Sharma 2010; Pulskamp et al. 2007). Second, choosing the correct form of NM to study is a problem because NMs are not likely to be found in the environment in the form in which they were produced (Nowack et al. 2012). Finally, a new toxicity assay needs to be developed or the classically used method needs to be adapted because of the specific properties of NMs that occasionally interfere with the assay results, as in a dye based assay (Dhawan and Sharma 2010).

Extrapolation of In Vitro Results to In Vivo

A laboratory, as a controlled environment, is different from natural ecosystems in various ways, and many problems arise while extrapolating laboratory results to occurrences in the field. First, the dynamic aspect of a natural ecosystem cannot be perfectly reproduced in a laboratory. Indeed, NMs undergo different transformations over time and interact with the medium and the organisms,

Table 4. Techniques to Characterize Nanoparticles and Their Merits and Demerits

Technique	Principle	Parameters analyzed	Merits	Demerits
Transmission electron microscopy (TEM)	Electron beam interacts with a sample to form an image on a photographic plate	Size, size distribution, shape, agglomeration, aspect ratio, elemental composition (when combined with energy dispersive X-ray spectroscopy)	<ol style="list-style-type: none"> 1. Provides high resolution, which is beneficial when studying nanoscale samples 2. Directly measures particle properties, including chemical composition 	<ol style="list-style-type: none"> 1. Time consuming 2. Measures samples in dry form, not as a suspension 3. Fails to measure properties of the sample in the form of dispersion 4. Requires a sufficient number of particles containing sample
Scanning electron microscopy (SEM)	High-energy electron beam is used to scan the surface and the backscattering of the electrons is examined	Size, size distribution, shape, aspect ratio, elemental composition	<ol style="list-style-type: none"> 1. Environmental sample can be easily analyzed 2. Best resolution 	<ol style="list-style-type: none"> 1. Sample must be electrically conductive at the surface 2. Electrical coat required for nonconductive sample 3. Time consuming and expensive
Atomic force microscopy (AFM)	Uses a mechanical (cantilever) nanoprobe to feel the surface of a sample	Size, size distribution morphology, surface texture and roughness, agglomeration, aspect ratio	<ol style="list-style-type: none"> 1. AFM is less costly and time consuming than TEM or SEM 2. Visualization in three dimensions 3. Option of multiple scans for greater statistical significance 4. Analysis can be performed in the absence of vacuum 	<ol style="list-style-type: none"> 1. Sample must adhere to a substrate and be rigid and dispersed on it 2. Roughness of the substrate must be less than the size of the nanoparticles being measured
Photon correlation spectroscopy (PCS)	Based on DLS, an extension of the technique is photon cross correlation spectroscopy (PCCS) for high concentration opaque suspensions, providing particle size and stability of nanomaterials	Average particle size and size distribution	<ol style="list-style-type: none"> 1. Sensitive to impurities 2. Can measure liquid, solution, or suspension 	<ol style="list-style-type: none"> 1. Sample must be a very dilute suspension 2. Viscosity of the sample must be known
Nanoparticle tracking analysis (NTA)	Allows nanomaterials to be visualized individually with simultaneous analysis of their Brownian motion	Size, size distribution, agglomeration	<ol style="list-style-type: none"> 1. Wide range of solvents can be used 2. Avoids any intensity bias toward large particles 3. Real-time view of the nanomaterials in the sample is possible 	To increase measurement accuracy, must be used with DLS or PCS
Brunauer–Emmett–Teller (BET)	Examines the surface areas of solids through the physical adsorption of gas molecules onto the solid surface	Size of surface area	Simultaneously provides two parameters: size and surface area	Only provides average size, not size distribution
Dynamic light scattering (DLS)	Measures time-dependent fluctuations in scattering intensity produced by particles in Brownian motion, and yields the size of the particle by applying the Stokes–Einstein relation	Size, size distribution, agglomeration	<ol style="list-style-type: none"> 1. Gives information pertaining to the stability of particles in different media with respect to time 2. Measures hydrodynamic diameter 3. Measures size under conditions that closely resemble exposure conditions 	<ol style="list-style-type: none"> 1. Provides average hydrodynamic size, which is usually greater than the size measured by other characterization techniques 2. Polydispersity of the sample leads to bias toward larger particles

Table 4. (Continued.)

Technique	Principle	Parameters analyzed	Merits	Demerits
Field flow fractionation (FFF); usually combined with other techniques or modified to increase utility: ICPMS-FFF, sedimentation-FFF, flow-FFF	Field is applied perpendicularly to the direction of flow toward the direction of flow in a fluid suspension combined with MS	Size, volume, elemental composition (ICP-MS-FFF)	1. Chromatography-like size fractionating method that does not utilize a stationary phase 2. Characterizes particle size via diffusion coefficients	1. Some nanoparticles tend to stick to the internal membrane of the FFF system, leading to less accurate results
Inductively coupled plasma mass spectrometry (ICP-MS)	MS	Elemental composition	1. High sensitivity 2. Rapid	1. Elements such as Ca and Fe are difficult to determine by conventional Ar ICP-MS because of mass spectral interferences by argides 2. Presence of oxides and doubly charged ions in the plasma deteriorates the quantitative capability of ICP-MS in ultratrace analysis

which change their physicochemical properties. Furthermore, the natural medium is a complex mixture of several NMs and other contaminants (Klaine et al. 2008). With this perspective in mind, one question is what can be learnt from a static laboratory exposure of a single NM. To ensure that studies of combined stressors will be relevant, the effect of each of these parameters must be well known to be able to distinguish the origin of each factor in the combined observed effects. Likewise, one must be aware of exposure conditions to extrapolate the results from in vitro to in vivo studies.

Toxicity

When examining the fate of NMs, it is necessary to address ecotoxicity, because these emerging contaminants interact with organisms. As previously discussed, it is difficult to measure natural concentrations of NMs and to foresee the state in which it will be detected. Consequently, organism exposure to NMs is not very well defined.

Most toxicity studies have been performed in laboratories and the experiments mostly included acute exposure on a single species. In reality, it is more likely that chronic exposure at very low concentration exists on an ecosystem scale (Lowry et al. 2012). NM ecotoxicity literature is not yet exhaustive and much work is still required to understand the direct and indirect impacts of NMs on a natural ecosystem. However, some adverse effects have been observed in bacteria, invertebrates, fishes, and endobenthic species. For bacteria, silver NM and TiO₂ were specifically engineered as antimicrobial agents in medicine and water treatment plants, respectively (Stone et al. 2010). The observed harmful effects of these NMs on bacteria are not surprising. Many toxic effects were observed for bacteria, such as mortality, growth reduction, plasmic membrane direct damage, oxidative stress via reactive oxygen species (ROS), protein dysfunctions, and DNA damage (Klaine et al. 2008; An et al. 2010). For invertebrates, *Daphnia* sp. is the most widely used model species for toxicity tests (Stone et al. 2010) and there is a great difference regarding whether the test is acute or chronic. With acute tests, TiO₂ 48 h LC₅₀ varied from 2 to 20 mg L⁻¹, but with a 21-day chronic assay, there were sublethal effects at concentrations as low as 0.1 mg L⁻¹, highlighting the importance of examining chronic exposure (Aschberger et al. 2011). Concerning fish, for many species and life stages tested, it seemed that gills were the most affected organ, followed by the liver and the digestive system. Carbon based NMs showed no mortality and few sublethal effects (almost always triggered by oxidative stress), and exposure to metal and metal oxide NPs, such as ZnO NPs, Ag NPs, and TiO₂, led to respiratory problems, morphological effects, and even death (Handy et al. 2008; Aschberger et al. 2011). For endobenthic species, toxicological studies are only just arising. Prior to 2012, only a handful studies were completed and few found toxic effects (Aschberger et al. 2011). From current information, it seems that endobenthic species bioaccumulated metal oxide and showed adverse impacts, including DNA damage, oxidative stress, immunomodulation, and even behavioral modifications, such as slower burrowing (Buffet et al. 2013, 2014).

Future Perspectives

The future of NMs must be addressed in a multidisciplinary approach, including the opinions of physicists, chemists, and biologists because it is necessary to improve the knowledge on properties, interactions, and toxicological potential of NMs. Thus, there may be four schools of thought, as discussed henceforth.

According to the chemistry school of thought, the properties that make NMs attractive also have drawbacks. There are many

unknowns about the ENMs lifecycle, including how nanomaterials are present in the environment and how they affect the ecosystem. To protect the environment from the adverse effects of these NMs, sources of nanomaterials should be controlled by adopting a proactive approach. Conventional synthesis of nanoparticles is more dangerous because the final product presents more active vacant sites on the surfaces, leading to a higher probability of reacting with biological systems, and hence, high toxicity. Green synthesis of NMs is an alternative because most of the remaining active sites on the surface are blocked by biodegradable products (plant material, microorganisms) and are expected to be less reactive and toxic for the environment (Das and Brar 2013).

According to the physics school of thought, the major challenges of deciphering the behavior of NMs in the environment include the determination of their extremely small size and proper shape, which are key factors for toxicity. Analytical methods developed for natural NMs are just beginning to be applied to ENMs. The limitation of resolution in terms of quantum mechanics makes these challenges adverse; the minimum size of the exit wave function below the samples is determined from a scattering calculation in which a single atom or a crystal scatters an incident wave function by finite angles (SEM and TEM). High resolution, in situ dynamic, and three-dimensional observations are the most important keywords in the next decade of high-resolution electron microscopy (Tanaka 2008).

According to the biology school of thought, further experiments must include thorough details on the medium (pH and natural organic matter concentration and characteristics) and its handling; additionally, it is necessary to maintain control while adding NMs to solution to achieve particular properties (such as solubility in water) to avoid contradictory and varied results among studies. One challenge to overcome for assessing the toxicological potential of NMs is to develop technology for their simple measurement and tracking in the environment. With proper experimentation and precise characterization, the link between NM characteristics, abiotic actors, and toxicity can be established. Later, there will be a need to examine chronic ecosystem exposure, similar to the environmental conditions faced by the aquatic community.

According to the environmental school of thought, some parallels can be drawn between the behavior of natural colloids and NMs. Nevertheless, it is important to conduct studies in natural waters because orders of magnitude higher concentrations of natural colloids can often have a significant impact. Thus, techniques are needed to distinguish natural from manufactured nanoparticles. Moreover, environmental matrices are loaded with other anthropogenically derived organic and inorganic forms; it is necessary to assess how these NMs interact with these forms. The vital questions are whether these interactions increase their mobility or not because this will have repercussions on the bioavailability of these NMs, and hence, their toxicity.

Conclusions

Currently, extensive attention focusing on the behavior and effects of ENMs, but there remains limited solid information. ENMs are of concern because of their new, specific properties that are being exploited for different applications. NMs have also been added to numerous consumer products such as sunscreens, paints, and clothes. This utilization has made them more likely to be found in the environment through their life cycle or deliberate discharge. Once they reach the environment, they undergo a series of transformations, which makes it even more difficult to predict their behavior or the form in which they will be retrieved.

These transformations can include degradation, oxido-reduction, binding/absorption, sulfidation, dissolution, precipitation, aggregation, and biotransformation, and all depend on the composition and properties of the medium. Precipitation is of particular importance because it links water and sediments. In addition to their movement through the medium, NMs can move along the food chain by adsorbing to organisms or by being ingested. Once ingested, they can be eliminated or distributed in the body, leading to adverse toxicological effects. These include mortality, growth reduction, oxidative stress, and DNA damage. Even if such negative impacts of NMs are found, there is still a lack of information concerning outdoor environments because most of these exposures have been examined in a laboratory and the extrapolation to a natural ecosystem is not difficult. Furthermore, the development of methods to study NMs has just begun, which is a problem in terms of tracking, qualifying, and quantifying NMs *in vivo*. Size may be the most important parameter to measure; the most widely employed methods are BET, DLS, TEM, SEM, and AFM, each method having its limitations. To achieve complete characterization, many methods must be merged. Finally, because in the case of NMs, more factors than the dose determine the toxicity, more attention should be given to simulating natural interactions with the environment when designing experiments, rather than implementing unnatural conditions.

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