



Review

Nanomaterials and the environment: A review for the biennium 2008–2010

Jose R. Peralta-Videa^a, Lijuan Zhao^a, Martha L. Lopez-Moreno^c,
Guadalupe de la Rosa^d, Jie Hong^b, Jorge L. Gardea-Torresdey^{a,b,*}

^a Department of Chemistry, The University of Texas at El Paso; 500 West University Ave., El Paso, TX 79968, United States

^b Environmental Science and Engineering PhD program, The University of Texas at El Paso; 500 West University Ave., El Paso, TX 79968, United States

^c Department of Chemistry, University of Puerto Rico at Mayagüez, PO Box 9000, Mayagüez, PR 00681, USA

^d División de Ciencias e Ingeniería, Campus León, Universidad de Guanajuato, Loma del Bosque 103, C.P. 37150, León, Gto., Mexico

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ABSTRACT

Applications of nanotechnology are touching almost every aspect of modern life. The increased use of engineered nanomaterials (ENMs) in consumer products, chemical and medical equipment, information technology, and energy, among others, has increased the number of publications (informative and scientific) on ENMs. By the 1950s, very few papers were committed to nanomaterials (NMs), but in 2009, more than 80,000 journal articles included the concept nanotechnology. The objective of this review is to compile and analyze publications on NMs in the biennium 2008–2010. This review includes the most recent publications in risk assessment/toxicity, characterization and stability, toxicity, fate and transport of NMs in terrestrial ecosystems, and new ENMs. Carbon nanotubes, metallic, metal oxides and hydroxides nanoparticles, quantum dots, and polystyrene NPs are included.

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Contents

1. Introduction	2
2. Engineered nanomaterials: composition, characterization, and stability	3
2.1. Engineered nanomaterials composition	3
2.2. Characterization of engineered nanomaterials	5
2.3. Engineered nanomaterials stability	6
3. Toxicity of nanomaterials	6
3.1. Nanocotoxicity	6
3.2. Bacteria	7
3.3. Aquatic nanotoxicology: the importance of testing aquatic invertebrates	7
3.4. Nanotoxicity studies in terrestrial organisms	7
3.5. Testing nanotoxicity in human and other mammalian cells	8
3.6. Studies in higher plants	8
3.7. Evidence of biotransformations	9
4. Fate and transport of NPs in terrestrial ecosystems	9
4.1. Sources and environmental amounts of NP in terrestrial ecosystems	9
4.2. Possible behavior of NP in soil media	9
4.3. Behavior and transport of NPs in soil solution	9
4.4. Interactions of NPs with soil organic matter	10
4.5. Interactions of NPs with soil minerals	10
4.6. Interaction with existing soil contaminants	10
4.7. Transport of NP in soil columns	10

* Corresponding author at: University of Texas at El Paso, Chemistry and Environmental Science & Engineering PhD program, 500 W. University Avenue, Physical Science Bldg., Room 201, El Paso, TX 79968-0513, United States. Tel.: +1 915 747 5359; fax: +1 915 747 5748.

E-mail address: jgardea@utep.edu (J.L. Gardea-Torresdey).

4.8. Transport by terrestrial organisms	10
5. New nanoproducts	12
Acknowledgements	12
References	12

1. Introduction

As time passes, the debate concerning the nomenclature linked to nanoscience and nanotechnology is becoming less and less voiced. Conversely, day after day it is becoming popular that the term nanomaterials (NMs) includes natural or manmade particles with at least one dimension of 100 nm or less, while nanoparticles (NPs) include those with at least two dimensions between 1 and 100 nm [1].

Nanotechnology has advanced in all fronts: instruments, goods, literature, and profits. According to the Project on Engineering Nanotechnologies [2], since March 2006–August 2009, 212 new nanotechnology-based products (increase of 379%) have been added to the consumer products list, totaling 1025 items produced by 485 companies situated in 24 countries. Pertaining to the literature, an analysis of publications available in electronic data bases indicates that the number of articles on NMs has increased from a very few papers at the beginning of the NM studies in the 1950s, to more than 80,000 journal articles in 2009 that include the con-

cept nanotechnology. Likewise, revenues for nanotechnology and nanomaterials in consumer products were approximately US\$1545 million in 2009 [3]. This is expected to increase to \$5335million by 2015, driven by the demand for consumer electronics and household cleaning products segments [3].

A search using as engines Sciencedirect.com, Google, and Scifinder has shown that in the biennium 2008–2010, 15 outstanding articles reviewing risk assessment, safety surveys, and NMs toxicity were published (Table 1). As seen in this table, most of the articles refer to uncertainties on NMs toxicity and the needs for more information on NMs handling to prevent environmental and human health effects after long exposure. Pertaining to risk assessment, a study including 40 industries from Switzerland and Germany showed that 26 companies (65.0%) did not perform any risk assessments and 13 (32.5%) performed risk assessments 'sometimes' or 'always' [4]. In addition, Conti et al. [5] surveyed the safety practices at 82 organizations that either manufacture, handle, research, or use NMs in North America, Asia, Europe, and Australia. Results showed that almost 75% of the organizations

Table 1
Review papers published in the biennium 2008–2010 describing nanoparticle toxicity and risk assessment.

Nanomaterial	Risk assessment/Toxicity	Major findings/Contents	Reference
Manufactured nanomaterials	Toxic effects of NMs in aquatic and soil systems	Review of the existing NMs research in freshwater, marine and soil environments. Discuss the risk assessment and the effect of NMs to the environment	[1]
Engineered nanomaterials	Risk assessment on 40 companies working with NMs in Germany and Switzerland	Twenty-six companies (65%) indicated that they did not perform any risk assessment of their NMs and 13 companies (32.5%) performed risk assessments sometimes or always	[4]
Nanomaterials	Health and safety practices in the NMs workplace worldwide	Findings of an international survey of NMs firms and laboratories about what they have done about health and safety. Risk communication is required to further the implementation of environmental health and safety programs	[5]
Nanoparticles	Health risk for humans	Personal protection equipment is needed to work with NMs. Specific medical evaluation protocols must be designed for exposure to NPs	[6]
Engineered nanoparticles	Toxicological effects on animals and how to work safety with NMs	Discuss some practices in universities to prevent exposure, such as using exhaust ventilation and gloves. Specific toxic effect of some NPs	[7]
Nanoparticles	Exploiting methods and tools to figure out adverse effects of manufactured NPs in the environment	A center has been created to study the implications of nanotechnology in the environment	[8]
Metallic nanoparticles	Relationship between chemical stability and vitro toxicity	Chemically stable metallic NPs have no significant cellular toxicity. Unstable NPs are cytotoxic and even genotoxic for cellular organisms	[10]
Nanoparticles	New technology and more effort are needed in order to know exactly the risks of NPs	Current literature does not provide clear information about ecotoxicology and environmental risk assessment of NMs	[11]
Waste containing nanomaterials	Toxicity to organisms and risk assessment to environment	Toxicity of NMs, risk assessment for NPs in the environment and remediation of NPs. There is a lack of information about the treatment of nanowaste	[13]
Engineered nanoparticles	Life-cycle concepts provide a means for identification of priorities for risk assessment	Studying the whole life cycle of NPs can help us to discover the possible impacts of NPs to environment and people	[14]
Nanomaterials	Potential risks of NMs towards human health	NM can be used in tissue engineering. There is still to clear information about NMs toxicity to humans	[15]
Engineered nanoparticles	Stages and methods of risk assessment of engineered NP	Specific information on how to do risk assessment of engineered NPs is needed	[16]
Engineered nanoparticles	Interactions with organisms and ecotoxicity of engineered NPs	The bioavailability of NPs, their uptake by algae, plants, and fungi and the toxicity mechanisms are still not well understood	[17]
Nanoparticles	NPs cause serious health effects on the cardiovascular and respiratory system	NPs cause serious health effects on the cardiovascular and respiratory system. Combustion in motor traffic and tobacco smoke are the main sources of exposure to NPs	[18]
Nanomaterials	Persistence, bioaccumulation, toxicity of NMs in environment	NanoImpactNet provides a discussion forum for the impact of NMs on human health. The physicochemical characterization of NMs is important for environmental studies and there is a need to have test materials for ecotoxicology	[19]

did not have a nanospecific health and safety program but most of them (89%) implemented a general environmental health and safety program. Also, a high percentage of the organizations with more than 1000 employees did not provide safe use guidance for the nanoproducts [5]. A feature article by Hoyt and Manson [6] has described the advantages and risk associated to nanotechnology, pinpointing people at risk due to their connection to NMs. At first level are researchers and workers – and their family members – in NM-connected industries, followed by consumers and the general public. Hoyt and Manson [6] have stated that despite the rapid pace of nanotechnology related research, development, and commercial exploitation, by the end of 2006, there were no standards or regulations to govern these activities. This gives an idea of the risk perception at the NM-related organizations and the risks the environment would be exposed to in case of an accidental or intentional NPs spill. Another feature article [7] describes the best practices used at universities and other enterprises to prevent exposure to NMs. The authors remark that academic researchers manage NMs as dangerous substances. For personal protection, they work in the fume hood not in lab benches, transport NMs in sealed containers, and use personal protection equipment (gloves, lab coats, goggles). To prevent lab contamination, wipe hood and other possible contact sources and have spill kit on hand to prevent exposure on spill. They manage NMs and NM-contaminated lab materials as hazardous waste until specific regulations appear. In this way, academic institutions contribute to a better handling of nanomaterials.

Governmental agencies in the United States are taking actions to decrease uncertainties in assessing the exposure and risks derived from nanotechnology. The National Science Foundation jointly with the Environmental Protection Agency created two centers to determine the fate and interactions of NMs in complex environments. These two centers, the Center for the Environmental Implications of Nanotechnology (CEIN) at the University of California – Los Angeles (The University of Texas at El Paso is part of the CEIN) and the Center for the Environmental Implications of NanoTechnology (CEINT) at Duke University were established to generate basic knowledge on NPs toxicity at organismal and community levels and to generate models to predict the NP effects in ecosystems [8]. CEINT is specifically focused on the determination of properties and conditions influencing the distribution of nanoparticles in the environment, the differences between natural and fabricated NMs, possible “nano” effects beyond the surface area effect, and the way we can do risk assessments on an emerging technology.

According to the Nanotechnology Law Report [9], the United States Government Accountability Office (GAO-10-549, June 27, 2010) has stated: “Nanomaterials are widely used in commerce, but EPA faces challenges in regulating risk.” The Law Report [9] highlighted that one of the handicaps is that EPA lacks the technology to monitor and characterize these materials.

A worthwhile reading review on the chemical stability of metallic nanoparticles appeared in 2009 [10]. In that review, Auffan et al. [10] have pointed out that the fate of NMs in the environment and within organisms may be dissolution dependent. The authors gathered information about the comparative toxicity of ZnO and TiO₂ NPs to *in vitro*-cultured mammalian cells. Higher toxicity was observed in cells exposed to ZnO NPs, which exhibits higher dissolution patterns compared to TiO₂ NPs. Another example is the lower toxicity of coated compared to uncoated quantum dots (QD) CdSe. The toxicity was related to the Cd ions released to the medium by the uncoated QD. Apparently, the toxicity exhibited on cell culture can be extrapolated to organisms. However, there is no data so far to corroborate this thought. In addition, it seems that the phase transformations of NPs are size related. For instance, TiO₂ NPs shows three crystalline structures, anatase, rutile, and brookite, which are

of different size. These size-dependent phase transformations are involved in the toxicity of TiO₂ towards single cell organisms [10]. As pointed out by Lubick [11] such variability “can make reference materials particularly hard to develop for agencies like the U.S. National Institute of Standards and Technology. That variability makes comparisons between studies difficult and lab protocols tricky to universalize.” The Gardea-Torresdey research group at the University of Texas at El Paso has reported that CeO₂ NPs are comparatively more toxic to soybean plants (*Glycine max* L.) than ZnO NPs [12]. This complicates the panorama about toxicity because the nanocerium are less soluble than ZnO NPs. There is a lack of information for several aspects of NMs such as use and handling of the nanowaste [13], life cycle of most of the NM in use [14], toxicity of NMs to human tissues [15], or how to do risk assessment [16]. Other aspects about NMs in need of study are: determination of bioavailability in different environments [17], levels of toxicity to tissues and individuals [18], and the scarcity of test materials for ecotoxicology studies [19].

Pertaining to nanomaterials synthesis and applications, 22 review papers were published in the biennium of 2008–2010 (Table 2). As seen in this table two detailed reviews described the application of QD in nanoelectronics [20,21]. The synthesis of NMs describing formation methods of oxide NPs, inorganic–organic NMs, carbon nanotubes, and chalcogenide NMs was also reviewed [22–26]. Catalysis was also extensively reviewed. The use of carbon nanotubes (CNTs) – inorganic materials [27], catalyst in fuel cell reaction [28], catalytic power of metal NPs [29] and silica-coated NMs [30] were worthwhile reviews to read. The use of NMs to determine soil properties [31] and detect persistent organic pollutants [32] was also summarized. Another area extensively reviewed in 2008–2010 was nanobioscience. Reviews on functionalization of plant viruses to form electroactive NPs [33], use of NMs in controlling the biochemical microenvironment of cells [34], *in vivo* nanocarriers for RNAi delivery [35], and starch NP formation [36] appeared in the biennium 2008–2010. Also, subjects like nano-optic [37], the fabrication and application of boron nitride nanotubes [38], electron-beam induced deposition [39], the use of NMs in lithographic techniques [40], and the use of NPs in medical applications [41] were also reviewed. Twenty-two reviews in 2 years is a clear indication of the number of publications and the activity in the field of nanotechnology.

2. Engineered nanomaterials: composition, characterization, and stability

2.1. Engineered nanomaterials composition

Engineered nanomaterials (ENMs) encompass those NPs synthesized and modified in order to enhance their performance in several technological and industrialized processes [42]. A number of ENMs are currently manufactured from different sources depending on their potential applications. Nanomaterial composition differs according to their formulation. Fullerenes and CNTs are NMs classified as carbon-based materials, QD as semiconductors, and metal oxides are considered as inorganic NPs [43]. ENMs are being synthesized as independent nanometric units, or modified by methods and solvents to arrange their structures to form wires, sheets, disks, rings, or fibers [1]. Carbon-based NMs are particles called fullerenes (nC₆₀), which typically are insoluble in water. These particles are capable of aggregating in nanotube structures or organic complexes that allow dispersion in aqueous solutions [44].

QD, regardless of their physical properties are considered semiconductors. The manufacturing of these materials is based on the strict control of the crystal size and shape which allows for con-

Table 2
Review papers describing nanomaterials synthesis and nanotechnology applications published in the biennium 2008–2010.

Nanoparticles	Nanotechnology/Research area	Major findings/Contents	Reference
Quantum dots	Complex charge transport nanoelectronic system	Methods to treat correlation effects, quantum fluctuations, non-equilibrium physics, and the time evolution into the stationary state of complex nanoelectronic systems are explained	[20]
Quantum dots	Graphene as a host for spin qubits	The advantages and challenges to use graphene quantum dots for spin qubits as compared to the more standard materials like GaAs. Graphene nanoribbons, a disk single layer graphene, and a disk in bilayer graphene are described	[21]
Nanomaterials in general	Synthesis of NMs	Recent developments and trends in combustion science towards the synthesis of NMs are described	[22]
Ceria-based nanomaterials	Controlled synthesis	Controlled synthesis of ceria-based NMs to manipulate the shape, crystal plane, and size is highlighted	[23]
Nanostructured materials	Synthesis of organic–inorganic NMs	Description of specific properties of supercritical fluids exploited for synthesizing functional nanostructured materials, especially in the field of inorganic and hybrid materials	[24]
Carbon nanomaterials	Synthesis of shaped NMs	Organometallic complexes such as ferrocene have been used as catalysts to make carbon materials with distinctive shapes. Reactor type and presence of heteroatoms (N, O, S, P) determine the final type of carbon	[25]
Chalcogenide nanomaterials	Fabrication of NMs	Two different approaches to create nanoscale transition metal chalcogenide materials: chemical nanofabrication (control of size and shape) and use of a molecular precursor to create one and two dimensional nanostructures of (NbSe ₂ and NbSe ₂ , TaS ₂ , TaSe ₂ , respectively)	[26]
Carbon nanotubes and inorganic NM	Applications of CNTs in catalysis, energy conversion, chemical sensors	Description of the preparation and applications of inorganic NM/carbon nanotube composites	[27]
Nanostructured catalysts	Nanocatalysis	Development and evaluation of the electrocatalytic performance of nanoengineered catalysts in fuel cell reactions are discussed	[28]
Metal nanoparticles	Synthesis and catalysis	Description of the new findings and challenges in the field of NP-based catalysis, including the role played by the particle structure and morphology, its chemical composition and oxidation state and the effect of the cluster support	[29]
Silica-coated nanomaterials	Spectroscopy, magnetism, catalysis and biology	Analysis of recent advancements in the synthesis of silica-coated NMs and their significant impact in different areas such as spectroscopy, magnetism, catalysis and biology	[30]
Nanomaterials	Environmental sciences	Describes a variety of nanostructures present in soil and their role to determine soil properties	[31]
Nanomaterials	Environmental sciences	Review of detection and treatment of persistent organic pollutants through NMs and analytical nanotechnology. Surface-enhanced Raman scattering, surface plasmon resonance, fluorescence, and electrochemistry in detection are some of the described techniques	[32]
Electroactive NPs	Nanobioscience	This review describes how a plant virus can be functionalized on its outer surface to form electro active NPs, can be used to construct monolayers on solid surfaces and multilayer arrays by a bottom–up, layer-by-layer approach to form monodisperse nanoparticles. The review also describes the potential application of the virus-derived NPs	[33]
Nanomaterials	Nanobioscience	NMs can provide a means to control the biochemical and mechanical microenvironment of cells. Hydrogel NMs, nanofibrous scaffolds, and layer-by-layer structures are depicted. Special features of NMs for in situ cell delivery and tissue regeneration and NMs for in situ cell therapeutics – caveats are also described	[34]
Nanocarriers	Nanomedicine	<i>In vivo</i> applications with special emphasis on the strategies for RNAi delivery in to immune cells. More than 20 nanocarriers are described	[35]
Starch NPs	Nanobioscience	This review contains an overview of starch nanoparticle preparation, characterization, properties, and applications	[36]
Zinc oxide nanorods	Nano-optics	Recent advances in growth of ZnO nanorods and results from both low temperature and high temperature growth approaches are presented	[37]
Boron nitride nanotubes	Fabrication and application of boron nitride nanotubes	Analysis of the up-to-date developments in boron nitride nanotubes, including theory, fabrication, structure, physical properties, chemical functionalization and applications. The use in hydrogen storage, biocompatibility tests, and composite materials fabrication is described	[38]
Functional nanostructures	Electron-beam-induced deposition	Review and comparison of techniques specifically aimed at purifying the as-deposited impure electron-beam-induced deposition structure	[39]
Nanostructures	Use of lithographic techniques	An overview of the best resolution obtained with several types of both organic and inorganic resists for the fabrication of nanostructures using lithographic techniques. The e-beam resist, hydrogen silesquioxane is described	[40]
Heparin-based nanoparticles	Chemical and biological properties	Anticoagulant activity, anticancer and antitumor therapy, tissue engineering and biosensors	[41]

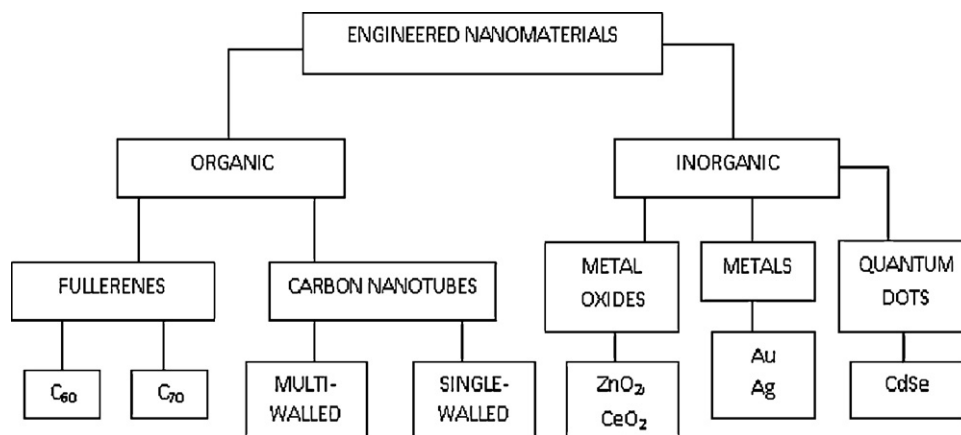


Fig. 1. Nanomaterial classification according to their physical and chemical properties.

control over the conductivity and energy release [45]. Some metal NMs are covered by surfactants in the manufacturing processes. This type of modification affects the dissolution behavior of the NPs because of their dissimilar agglomeration or aggregation in the media. Other processes allow alteration of the charge in atoms to form the external surface of the NPs. Furthermore, magnetic NPs are being synthesized and employed to remove Cr(VI) from contaminated waters [46].

As mentioned before, NMs are able to modify their shape, surface area, particle charge, and crystal arrangement due to their physical and chemical behavior [46]. Moreover, properties of ENMs can be tailored because of the amount of atoms lying on the surface of the material [45]. TiO₂ NPs represent a clear example of correlation between composition and chemical properties. Different phases in TiO₂ NPs were demonstrated to have dissimilar photocatalytic activities. Anatase, which is the predominant phase composition in TiO₂ NPs, shows the highest activity [43]. In addition, some NMs are coated or capped with small amounts of oxides to increase their chemical properties like dispersibility and conductivity, as well as to avoid aggregation of the NPs. When NPs tend to aggregate, the behavior of the cluster formed will be different. Moreover, syntheses of ENMs need to be specific in controlling size, shape, crystal structure, and aggregation. Fig. 1 shows NMs classification according to their composition [47].

ENMs are manufactured directly by chemical synthesis and/or sometimes by physical processes such as grinding or milling to obtain the appropriate size. However, NMs manufactured by physical methods usually require more control in order to obtain the adequate shape and size [1]. Manipulation of some chemical parameters in NMs synthesis such as pH, temperature, solute precipitation and concentration can produce NMs with magnetic properties which make them suitable for drug delivery and tissue restoration [48]. ENMs are monodispersed particulates dissimilar from the natural occurring NMs, which typically are polydispersed with more complex structures [45].

Numerous studies are currently being conducted to produce and to manipulate NMs for drug delivery, diagnosis, and targeting of several types of cancerous cells. Examples of these materials are mesoporous silica NPs, superparamagnetic iron oxide NPs, and Cd/Zn-selenides [48,49]. Due to their large surface as well as their atom's arrangement in their crystal structure, these materials are able to bind, absorb, or transport other compounds inside cells or tissues [43]. In addition, in the case of the iron oxide NMs which are extensively used in biomedical applications, the size of the core atoms also determines their magnetic properties [49].

In summary, size, shape, and crystal structure of NMs, as well as composition (single or complex), determine their mobility, chem-

ical, and physical properties in different systems. Despite the fact that the majority of NMs are produced by physical methods such as arc-discharge, evaporation, laser ablation, among others, chemical methods have demonstrated to be more effective in controlling size and shape [50].

2.2. Characterization of engineered nanomaterials

Appropriate physical and chemical characterization of natural and manufactured NMs is fundamental to determine their intrinsic properties [47]. Phase purity, particle and cluster size, surface chemistry, solubility, charge, and crystallinity are essential to elucidate the homogeneity, stability, reactivity, biodegradability, and potential application of NMs in different media [51]. Presently, numerous analytical techniques and instruments are being applied in NPs characterization. Besides, the most important physicochemical properties of NMs, which can be related with their behavior, are average size and elemental composition. Surface area, porosity, surface charge, hydrodynamic diameter, and agglomeration are additional properties not essentially determined by the manufacturers [19].

From electron microscopy techniques, one of the most valuable tools is high resolution transmission electron microscopy, which allows the corroboration of structure, morphology, as well as diffraction data for NMs [52]. Sometimes, transmission electron microscopes (TEM) are equipped with energy dispersive X-ray spectroscopy devices (EDS), which acquire the elemental analysis of NMs. X-ray absorption spectroscopy techniques, such as X-ray absorption fine structure, are specifically designed for determining three dimensional structures. Furthermore, atomic force microscopy (AFM) is employed simultaneously to measure particle surface morphology in three dimensions with high resolution.

AFM is applied in air or liquid media, and is based on the van der Waals forces between the NPs and the AFM tip [47]. Other techniques widely used to determine the NPs phase and size are X-ray powder diffraction (XRD), and small-angle X-ray scattering (SAXS). These techniques apply the Scherrer method to calculate particle size and the interplanar spacing d , to obtain lattice parameters of NMs. SAXS also provides dispersion of the particles, agglomeration, and morphology [47,48]. XRD coupled to TEM is commonly used to characterize mesoporous silica and silica nanospheres [53].

Dynamic light scattering (DLS), a spectroscopic technique, is also very valuable to determine the size, aggregation condition, and electrophoretic mobility of NPs. According to their size, NPs acquire different mobility which is referred to as hydrodynamic diameter. DLS measures the Brownian movement of the nanoparticles suspended in a liquid, while electrokinetic properties of the

particles, such as surface charge, are obtained jointly with laser Doppler velocimetry that measures the direction and speed [50]. DLS is particularly used to establish the size of the NPs and their agglomerates in solutions [52].

UV–vis, matrix-assisted laser desorption ionization, and Fourier transform infrared spectroscopy (FTIR) are spectroscopic techniques employed in characterization of fullerenes and derivatives particularly in water environments [44,54]. Coated nanomaterials such as microgel oxide NPs also are easily identified by FTIR due to changes in the characteristic absorption bands of Fe–O bond [55].

Chemical state and elemental composition of metal NMs can also be determined by X-ray photoelectron spectroscopy and thermogravimetric analysis (TGA), respectively [56]. TGA is very useful in obtaining weight composition in metal core–shell particles such as CuO–polystyrene NPs [57].

Electrophoretic light scattering spectroscopy (ELS) is a common technique employed in elemental analysis to estimate the NMs' dispersion through the attraction or repulsion between NPs (zeta potential). Net velocity of the NPs is obtained by applying an electric field which corresponds to the mobility in the media [47,48]. Vibrating sample magnetometry provides an insight in regards to the magnetization of the samples. This technique is widely used to measure the magnetization of Fe NMs [58].

Surface enhanced Raman spectroscopy (SERS) plays a very important role in the determination of the binding sites between functional groups of proteins and metal NPs. This technique is based on the excitation and vibrational modes of the surface plasmons and molecules close to the roughened metal surface. One disadvantage of this technique is the sample preparation and need for complementary measurements for SERS data interpretation [59]. SERS was reported to be very useful in identifying imidazole, sulfur, carboxylate, aromatic rings, and amine functional groups in microtubule protein filaments involved on the adsorption of gold NPs [60].

Secondary ion mass spectroscopy is another technique used to verify the elemental composition of NMs by ionization and sputtering of the surface atoms. Nevertheless, this is a destructive method which only allows the analysis of 1–3 nm layers [61].

It is well known that physical and chemical properties of NMs differ from bulk materials of the same composition, due to the fact that an appropriate characterization of manufactured NMs is needed. The most specialized techniques for characterizing NMs have been described; however, a detailed explanation about each one is beyond the scope of this review.

2.3. Engineered nanomaterials stability

Solubility is driven by physicochemical characteristics of NMs such as size, shape, and density. Essentially, water is the most important media used to study NMs behavior. For the most part, chemical transformations, redox activity, mobility, chemical interactions, and agglomeration of NMs in water need to be evaluated in order to determine their fate and transport as well as their potential toxicity [62,63]. Water ionic strength, hardness, pH, biochemical oxygen demand, alkalinity, organic matter presence, and water composition are some hydrological parameters which modify the NMs behavior.

Stability of ENMs in water is highly influenced by their solubility and dispersibility. Agglomeration and settling are common mechanisms to occur when ENMs enter into water systems, affecting their solubility. Some NPs tend to form agglomerates when they are in contact with aqueous systems and tend to settle with time. However, smaller NPs remain as colloids dispersed in the solution [46]. The rate of NPs aggregation in solution will depend upon the concentration, surface area, and forces involved in collisions like Brownian motion and van der Waals attractions [64]. Sometimes, in

order to increase NPs mobility and solubility in polymeric matrices, magnetic particles are often encapsulated with organic surfactants, particularly in biomedical applications like drug delivery [55]. Furthermore, metal oxide polyanions can also be incorporated to polymers in order to add charge-balanced species into the NP structure (nanocomposites) [54]. However, as mentioned before, mobility, diffusion, and transport of ENMs in water will be significantly influenced by their composition, chemical form, concentration, zeta potential, speciation, and NP shell, as well as water conditions like salinity, pH, organic ligands, and ionic strength [1]. Differences in natural organic compounds, pH, ionic strength, and surfactant presence in fresh, marine, and sea waters will have a significant influence on NPs aggregation and performance. Because of its ionic strength (due to salinity), seawater modifies the surface charge of NMs generating more particle collisions, aggregation, and precipitation. As a consequence, aggregation of NMs is more likely to occur in seawater than in freshwater where the presence of organic matter allows NPs coating and diffusion. In addition, viscosity and surface tension may also contribute toward trapping NMs on the ocean surface [64]. Polymeric substances secreted by marine microorganisms may induce agglomeration, stabilize NPs dispersion, or act as chelating agents for inorganic metal binding [65].

Fullerenes and CNTs tend to agglomerate due to their structural properties and hydrophobic character. Fullerenes are soluble in some organic solvents but their solubility in water is about 1.3×10^{-11} $\mu\text{g/L}$. As a result, numerous studies have been conducted in order to stabilize them in aqueous solutions. Capping agents, surfactants, and stabilizers are applied to decrease steric repulsions and form a stable aqueous dispersion. Inversely, physical methods such as ultrasonication and stirring are also employed to break up the agglomerates and increase NP dispersion [44]. Therefore, further studies of ENMs aggregation, deposition, and mobilization will help to better predict the NPs fate and stability in water systems.

3. Toxicity of nanomaterials

What makes NPs different from their bulk counterparts is mainly related to their high surface/volume ratio. It has been estimated that in a 20 nm NP only 20% of the atoms would be located on the outside, compared to 40% in a 10 nm NP [66]. As a consequence, physicochemical, optical, reactive, and electrical properties change. Besides, the milieu where NMs are present determines their behavior, reactivity, and their potential toxicity.

Essays to determine NPs toxicity involve their dispersion in different media. This aspect should be taken into account since different environments may stimulate different toxicities. In this section, the toxicity of a variety of NPs in several micro and macroorganisms is reviewed.

3.1. Nanoecotoxicity

Determination of NMs toxicity in different stages of the food chain should be assessed in order to obtain a more appropriate picture of the effects NMs in environmental and human health. Significant efforts have been made to assess the toxicity of different NMs in a variety of micro and macro organisms, what is within the scope of both, nanotoxicology and nanoecotoxicology [67]. However, to the authors' knowledge, there are no specific standardized protocols or certified reference materials for the NMs testing. Nevertheless, researchers are trying to find out the best methodologies to perform these kind of evaluations. This section summarizes what is known on the toxicity of several NMs to different organisms.

Difficulties in comparing NP toxicities in diverse systems are evident due to the lack of standardized protocols. In addition, differ-

Table 3
Selected nanoparticles tested in a variety of living organisms in the biennium 2008–2010.

Nanomaterial	NP size (nm)	Tested organism	Test	Reported results	Reference
ZnO	20	<i>C. elegans</i> (nematode)	24-h LC ₅₀	LC ₅₀ (2.3 mg L ⁻¹)	[68]
Al ₂ O ₃	6050			LC ₅₀ (82 mg L ⁻¹)	
TiO ₂				LC ₅₀ (80 mg L ⁻¹)	
Au	10	<i>Cucumis sativus</i>	Germination	No toxicity observed	[69]
Ag	2	<i>Lactuca sativa</i>	Bioluminescence		
Fe ₃ O ₄	7	<i>Photobacterium phosphoreum</i> <i>Anaerobic consortium bacteria</i>	Biogas production		
ZnO	60	<i>S. agalactiae</i> <i>S. aureus</i>	Bactericidal action	Inhibition of cell division (95% at 0.12 M)	[70]
CeO ₂	15 and 30	<i>D. magna</i> <i>C. riparius</i>	Genotoxicity Mortality, growth, and reproduction	CeO ₂ damaged DNA	[71]
SiO ₂	7 and 10			CeO ₂ , and SiO ₂ increased mortality	
TiO ₂	7 and 20				
Ag	20–37	<i>Oryzias latipes</i>	LC ₅₀ Developmental toxicity	LC ₅₀ (1.03 mg L ⁻¹) Edema abnormalities in the spine, fins, heart, brain, and eyes	[72]
TiO ₂	6	<i>D. magna</i>	24-h LD ₅₀	L-ALEX	[73]
Al (ALEX)	100	<i>V. fischeri</i>	48-h LD ₅₀	48-h LD ₅₀ of 107,588 mg L ⁻¹	
Al (L-ALEX)	100				
B	10–20				

ent parameters are assessed. For example, some researchers report LD₅₀ (lethal dose 50%) while others show LC₅₀ (lethal concentration 50%) or MIC (minimum inhibitory concentration). In other cases, none of these indices are used, instead other parameters are reported (Table 3).

3.2. Bacteria

Bacteria and algae are located on the bottom of the aquatic food chain, which are eaten by crustaceans such as *Daphnia* and *Cyclops*. These in turn are consumed by fish, making possible the process of biomagnification. Thus, the importance of determining nanotoxicity is evident in these organisms. Several reports are found in the literature concerning this issue. Battin et al. [74] explored TiO₂ (20 and 10 nm) nanotoxicity in planktonic and biofilms of a natural microbial aquatic community from surface water, using NP concentrations similar to those expected in realistic situations (5 mg L⁻¹). These researchers suggested that the negative effects on microorganisms are not only due to the effect of the exposure to individual NPs but also to the aggregates. They also observed that planktonic organisms were more susceptible to the NPs than biofilms. Cell membrane damage was among the toxic effects observed.

Battin et al. [74] and Choi et al. [75] determined a differential toxicity of nanosilver (15–21 nm) in planktonic and biofilm *Escherichia coli* cultures where biofilms were more resistant to the NPs. Choi et al. [75] also reported that minimum bactericidal concentrations were found to be 38 and 10 mg L⁻¹ for planktonic and biofilm *E. coli*, respectively. In addition, Ag NPs aggregation was observed as well as the penetration of the NPs following 1 h of exposure in a 40 μm thick biofilm, which suggested that the biofilm resistance might be due to retarded NPs diffusion.

Nanotoxicity in pathogenic bacteria has also been explored. Huang et al. [70] used *Streptococcus agalactiae* and *Staphylococcus aureus* to determine the toxicity of 60 nm ZnO NPs. In this case coating was polyvinyl alcohol. The main results that these researchers reported on had to do with cell membrane damage and NPs internalization, as well as the inhibition of bacterial growth.

3.3. Aquatic nanotoxicology: the importance of testing aquatic invertebrates

Aquatic invertebrates are the ultimate recipients of most contaminants released into the environment. Because of that, these

organisms are appropriate for nanotoxicity tests [67]. Nanotoxicity test in aquatic invertebrates should include acute and chronic assays as well as strengthen bioaccumulation studies. Geno and ecotoxicity of CeO₂ (15 and 30 nm), SiO₂ (7 and 10 nm), and TiO₂ (7 and 20 nm) have been evaluated in *Daphnia magna* and the larva of *Chironomus riparius* [71]. Results showed that CeO₂ NPs damaged the DNA. In addition, an increase in mortality was observed with CeO₂ and SiO₂ NPs. Moreover, significant correlation coefficients for DNA damage and potential reproduction reduction in *D. magna* were found in individuals treated with CeO₂ NPs. Conversely, TiO₂ did not affect these aquatic species.

Strigul et al. [73] tested the acute toxicity of TiO₂ (6 nm), Al (100 nm) (ALEX = NPs coated with Al₂O₃ and L-ALEX = NPs coated with carboxylate groups), and B (10–20 nm) NPs in *D. magna* and *Vibrio fischeri*. TiO₂ and L-ALEX displayed low toxicity in *D. magna*, because none of them allowed 24-h LD₅₀ determination. Besides, the former showed a 48-h LD₅₀ of 107,588 mg L⁻¹. However, those for ALEX were of 219.6 (24 h) and 7,483 mg L⁻¹ (48 h). Thus, non-hydrophobic nanoaluminum proved to be more toxic to these organisms than their non-hydrophobic counterparts. On the other hand, boron NPs in concentrations higher than 80 mg L⁻¹ were lethal to *D. magna*. In addition, LD₅₀ values were of 19.5 and 6.7 mg L⁻¹ for 24 and 48 h, respectively. With respect to *V. fischeri*, B NPs showed EC₅₀ values between 56 and 66 mg L⁻¹; while TiO₂, ALEX, and L-ALEX were not toxic to this bacterium. Thus, these researchers concluded that B NPs used in their study can be classified as harmful to aquatic organisms.

Silver NPs (20–37 nm) were used by Wu et al. [72] to determine LC₅₀, developmental toxicity, morphological, and histopathological changes in Japanese medaka (*Oryzias latipes*) at different developmental stages. The authors reported an LC₅₀ value of 1.03 mg L⁻¹ in a period of 48 h. In addition, developmental, morphological, and histopathological changes included edema production, abnormalities in the spine, fins, heart, brain, and eyes. Thus, these researchers concluded that Ag NPs showed toxicity for these aquatic organisms.

3.4. Nanotoxicity studies in terrestrial organisms

Tests of toxicity of nanomaterials in terrestrial organisms include nematodes. ZnO, Al₂O₃, and TiO₂ as NPs and bulk forms were tested on *Caenorhabditis elegans* [68]. Pertaining to LC₅₀, similar toxicity was reported for both forms of ZnO materials

(2.3 mg L⁻¹); however, LC₅₀ for the bulk forms of Al₂O₃ and TiO₂ was around twice as that observed for the NPs of these materials. Nevertheless, in all cases bulk and nanoparticulate materials affected the growth and reproduction capability of this nematode.

Silver NPs were also tested on *C. elegans* using wild type and mutant species [76]. Reports indicate growth inhibition as a consequence to Ag NPs exposure, as well as NPs internalization. To the authors' knowledge, these researchers have reported for the first time transgenerational transfer of Ag NPs, which evidences another potential hazardous consequence of NPs in living organisms.

3.5. Testing nanotoxicity in human and other mammalian cells

Mayer et al. [77] used human blood to determine the effects of size and surface charge of polystyrene NPs on coagulation induction, thrombocyte, complement, and granulocyte activation, as well as on hemolysis. They used polystyrene NPs ranging between 20 and 220 nm. They determined that activation of complement was stimulated when positive surface charges were present. NPs less than 60 nm in size with negative surface charges were more hemotoxic than larger sized NPs. Also, activation of thrombocytes, granulocytes, and hemolysis was provoked to higher levels by NPs around 20 nm in size. Results suggest that both particle size and surface charge should be taken into account when interpreting NPs toxicity results.

CdSe quantum dots (QD) with a ZnS shell and a coating of polyethyleneglycol were tested on intestinal cells [78]. They observed a change in NPs size and suggested a loss in coating when the NPs were exposed to gastric pH. The exposure to this low pH increased QDs toxicity, indicating that such toxicity might be determined by the route of exposure.

A study on human lung epithelial cells (line A549) compared the nanotoxicity of CuO, TiO₂, ZnO, CuZnFe₂O₄, Fe₃O₄, Fe₂O₃ NPs and multiwalled carbon nanotubes (MWCNT) [79]. Results indicated that all the NPs studied induced DNA damage to some extent, except for Fe₃O₄ and Fe₂O₃, which caused low or no toxicity. However, CuO NPs were the most toxic as they induced both DNA and oxidative lesions.

Another short-term exposure experiment demonstrated that CuO NPs (aprox. 52 nm) possess a potential for genotoxicity in A549 epithelial lung cells. CuO NPs reduced cell viability, and glutathione production was found along with an increase in oxidative stress and stimulation of lipid peroxidation, superoxide dismutase, and catalase [80]. Moreover, a biomarker of cellular damage was expressed (Hsp70) in the presence of this type of NPs.

Studies with RAW 264.7 (macrophage) and BEAS-2B (human bronchial epithelial) cell lines demonstrated that CeO₂ NPs (8 nm) acted as an antioxidant, and may display cytoprotective ability, while ZnO NPs (13 nm) generated the production of reactive oxygen species molecules, inducing toxicity expressed as inflammation and cell death. Also, evidence of dissolved ZnO NPs in the culture media as well as inside endosomes was found. TiO₂ (11 nm) and CeO₂ were found undissolved in the endosomal cavities [81]. Other studies demonstrated that TiO₂ NPs were not able to penetrate isolated porcine skin in a 24-h *in vitro* [82]. However, when applied *in vivo* for 30 days, 4 and 60 nm TiO₂ NPs entered the pork tissue. In addition, in a 30-day long study with hairless mice, TiO₂ NPs were found in various organs, including the brain and liver. Moreover, the collagen content in mice skin was reduced by TiO₂ NPs, what suggested that these NPs might induce skin aging.

NP toxicity studies have also been performed with mouse cells. Yang et al. [83] used primary mouse embryo fibroblasts to determine the nanotoxicity of carbon black (CB), single wall carbon nanotube (SWCN), SiO₂ and ZnO NPs. These authors [83] looked at cytotoxicity, oxidative damage, and genotoxicity, as related to particle size, shape, and chemical nature. Results demonstrated that

ZnO proved to be more cytotoxic than SiO₂ and carbon NPs, and suggested that particle shape might play a major role in inducing genotoxicity. On the other hand, it has been reported that coated (polyvinyl alcohol) and uncoated superparamagnetic iron oxide nanoparticles produced gas vesicle formation in mouse fibroblasts (L929) [84].

3.6. Studies in higher plants

Few nanotoxicity studies have been reported for higher plants. Lee et al. [85] proposed the use of agar media to perform nanotoxicity studies. Using this media they exposed *Phaseolus radiatus* (mung bean) and *Triticum aestivum* (wheat) to Cu NPs in order to perform a 48-h acute toxicity where the median effective concentration (EC₅₀) for seedling growth was determined. The authors observed NP aggregation inside plant cells, and 2-day EC₅₀ were of 335 and 570 mg Cu NPs L⁻¹ for *P. radiatus* and *T. aestivum*, respectively. Thus, *T. aestivum* was more tolerant to Cu NPs. These authors attributed toxicity to the Cu NPs rather than Cu ions.

The influence of nano-anatase (TiO₂) on plant oxidative stress has also been studied [86]. Results indicate that nano-anatase (TiO₂) reduced antioxidant stress in spinach chloroplasts by reducing H₂O₂, superoxide radicals, and malonyldialdehyde content, while increasing superoxide dismutase, ascorbate peroxidase, guaiacol peroxidase, and catalase activities [86]. Studies performed in hydroponics with rye grass (*Lolium perenne*) demonstrated that ZnO NPs (20 nm) reduced biomass production and root elongation. In addition, root cells showed high vesiculation or collapsing and were found attached to the root surface as well as in root endodermis. Low Zn translocation from root to shoot was also reported [87]. Because the authors observed low Zn ions in solution, the toxicity was mainly attributed to the NPs rather than to Zn ions. Contrasting effects have been reported from soil experiments. Doshi et al. [88] treated *Phaseolus vulgaris* (variety California red kidney bean) and *L. perenne* with Al NPs (Al₂O₃, ALEX, and L-ALEX). In this case no adverse effects were observed.

Asli and Neumann [89] exposed corn roots to colloidal suspensions of either natural or engineered TiO₂ NPs (30 nm). Bentonite clay was used as natural TiO₂ NP source (sizes between 1 and 6000 nm). They performed short-term experiments and measured root hydraulic conductivity, leaf and root growth rates, transpiration, as well as root cell wall pore size. They reported that almost all the parameters measured were reduced in the presence of both natural and synthesized TiO₂ NPs. In addition, in long-term exposures performed in pot experiments, they found out that no significant inhibitory effects occurred. These researchers have hypothesized that differences in the observed effects in hydroponics and soil experiments might be the effect of soil acting as a filter for the NPs avoiding direct contact with corn roots.

Recently, López-Moreno et al. [90] reported a differential toxicity of CeO₂ NPs on four edible plant species. These authors found that 2000 mg CeO₂ L⁻¹ significantly reduced corn, tomato, and cucumber germination. In addition, when CeO₂ was present in the germination media in concentrations between 500 and 4000 mg CeO₂ L⁻¹, corn and cucumber root growth increased; however, that of alfalfa and tomato decreased. In the wild plant mesquite (*Prosopis sp.*), coated and uncoated Ni(OH)₂ did not affect plant growth or chlorophyll production, suggesting that this wild plant could be tolerant to these NPs [91]. On the other hand carbon nanotubes (CNTs) might have positive effects on plant growth as shown by Khodakovskaya et al. [92], who observed that CNTs enter tomato seed coat and might be able to maintain water uptake promoting seed germination. It has also been reported that CNTs enter plant cells [93] and might be used as molecular transporters for plants. However, multiwalled carbon nanotubes (MWCNTs) penetrate wheat cells by perforating the cell wall [94].

3.7. Evidence of biotransformations

X-ray absorption spectroscopy is a powerful tool that allows the direct determination of elemental oxidation states in a wide variety of samples. This technique also provides important information for the elucidation of the coordination environment of elements in environmental samples. Since amorphous and crystalline samples can be analyzed, it is widely used for the study of biological samples, including plants. It appears that NPs' biotransformation has not been extensively studied as few reports appear in the literature. Through XAS, López-Moreno et al. [90] were able to prove that CeO₂ NPs are stored within soybean tissues with no biotransformation. In addition, Parsons et al. [91] demonstrated that NPs coating influences biotransformation of Ni(OH)₂ NPs. These researchers reported that in mesquite seedlings treated with uncoated Ni(OH)₂ NPs, the NPs were detected in roots and shoots. However, in leaves, Ni was bound to an organic acid ligand. Inversely, when mesquite was treated with sodium citrate-coated Ni(OH)₂ NPs, the NPs were only detected in roots, whereas in shoots and leaves a Ni-organic acid complex was identified.

4. Fate and transport of NPs in terrestrial ecosystems

Due to the rapid development of nanotechnology, there has been a significant increase in the amount of various engineered ENMs annually released into the environment. It is estimated that a significant fraction of these ENMs will enter terrestrial ecosystems through both direct and indirect modes: through zero-valent metal for remediation of contaminated soil [95–97], through photocatalyst for water treatment [98,99], or via human activities such as biomass burning, fossil fuel combustion, or waste incineration.

4.1. Sources and environmental amounts of NP in terrestrial ecosystems

For natural terrestrial ecosystems, NPs have an extensive history. It has been long known that soil contains material less than 2 μm in particle size, which is loosely called colloidal soil. Colloidal soil contains phyllosilicates, humic acids, and iron oxides, and has nanosized particles [31]. Components of the colloidal soil include nanosized iron oxides as colloidal phases of ferrihydrite of 2–5 nm in length and also circa 1 nm particles of soil organic matter [31]. All of the naturally occurring nanoscale particles could potentially play an important role in ecosystem dynamics [100].

However, the environmental concentrations of both natural and anthropogenic sources of NPs in terrestrial ecosystems are almost completely unknown. In soil ecosystems only a small proportion of NPs occur as discrete entities. Organic colloids in soil, for example, are largely associated with their inorganic counterparts and form caps over mineral surfaces. For this reason, individual NPs are difficult to separate and collect from the bulk soil, and extraction yields are generally low [101]. Additionally, the lack of analytical methods capable of quantifying trace concentrations of NPs is also the reason for the lack of knowledge [102,103]. Gottschalk et al. [103] calculated environmental concentrations of NPs based on a probabilistic material flow analysis from a life-cycle perspective of ENMs containing products. They found the simulated models range from 0.003 (fullerenes) to 21 ng L⁻¹ (nano-TiO₂) for surface waters, and from 4 ng L⁻¹ (fullerenes) to 4 μg/L (nano-TiO₂) for sewage treatment effluents. In addition, Mueller and Nowack [102] used a life-cycle perspective to model the quantities of three NPs in the environment nano-Ag, nano-TiO₂, and CNT. They use variables such as estimated worldwide production volume, location, particle release, and flow coefficient. They found that only in the case of TiO₂ the expected concentration in water (0.7–16 μg/L) was close

to or higher than the predicted no effect concentration (<1 μg/L). This suggests that more detailed studies are required to predict the effects of TiO₂ in the environment.

So far, most of the studies on fate and transport of NPs in terrestrial ecosystems lead to the conclusion that increased entry into the soil of engineered and anthropogenic NPs raises concern about their fate, transport, and potential adverse effects on animal and human health. Before 2008, however, no direct and relevant data pertaining to the fate and behavior of manufactured NMs in terrestrial systems existed. Due to soil and sediment being more complex systems, it is still difficult to determine the concentration of NPs in terrestrial ecosystems. Furthermore, Kline et al. [1] pointed out that for some kinds of NPs, such as iron oxide NPs, a large background of naturally occurring iron in the dissolved phase exists, which makes difficult to differentiate the natural and manufactured material. More studies are needed to understand this matter.

4.2. Possible behavior of NP in soil media

Terrestrial ecosystems are composed of soil and organisms. Soils are mainly composed of air, water, organic matter, and minerals [104]. Among them, air and water compose soil pore space, where dispersed NMs are mobilized or stabilized in the soil solution. Organic matter and minerals make the solid soil. When NPs are released into the soil, they may interact with solid components, e.g. soil organic matter and minerals.

It is usually thought that the fate of NPs released into the soil vary depending on the physical and chemical characteristics of the NPs [105]. Solovitch et al. [106] demonstrated that nanoscale particle dimensions may favor aggregation kinetics, thus altering the transport and retention of these materials in saturated porous media. On the other hand, soil factors such as ionic strength, pH, zeta potential, and soil texture greatly dominate the fate and transport [107–109]. Under those factor, multiple behaviors of NPs in soil occur: aggregation, transport and deposition, sorption, desorption, stabilization, and dissolution. In addition, NPs are small enough to fit into smaller spaces between soil particles and might therefore travel further than the larger particles before becoming trapped in the soil matrix [46]. Evidence of electrostatic interactions was observed between the negatively charged citrate gold NP attached to positively charged particulates in soil [105]. Fabrega et al. [110] found that the interaction of bacteria with NPs potentially affects the transport of NPs in soil environment.

4.3. Behavior and transport of NPs in soil solution

In soils, the mobility of NPs in pore water is an essential condition for the interaction with plant roots or fungi hyphae [111]. Soil solutions contain colloids; those colloids with high specific surface areas are of great environmental importance because can carry many sorbed substances and facilitate the transport of pollutants and other materials [31]. In addition, soil solution is normally rich in dissolved organic molecules (e.g. humic and fulvic acid) that can enhance the colloidal stability of nanomaterials and, therefore, increase their travel distances [109]. Ghosh et al. [112] found that the stability of humic acid-coated nano-Al₂O₃ was enhanced due to strong steric stabilization. On the other hand, soil solution chemistry (e.g. ionic strength, pH, presence of natural organic matter) strongly affects the interactions between NPs and the solid media, thus influencing the balance between the free migration of particles and the deposition of NPs [106].

The mobility in aqueous media is highly influenced by natural organic matter and ionic strength but independent of pH [63]. Organic matter adsorbed on nanoparticles reduces their aggregation, which could influence their movement in soil solution.

4.4. Interactions of NPs with soil organic matter

Soil organic matter includes humic and fulvic acids which are soluble in soil solution and humin that exists in solid particles. It is expected that dissolved soil organic matter will interact with NPs and thereby potentially alter their fate, transport, and bioavailability in soil. On the other hand, the colloidal surfaces of humus are negatively charged as a result of H^+ dissociation from carboxylic ($-COOH$) or phenolic ($-OH$) groups. Solid-state organic matter will possibly adsorb positively charged NPs by electrostatic attraction and ligand exchange.

Soil organic matter may also influence the surface speciation and charge of NPs, and thus affect their aggregation/deposition properties. In addition, in aquatic systems soil organic matter will increase mobility and bioavailability of NPs [50,111]. Pelley and Tufenkji [50] reported the effect of natural organic matter on the migration of NPs in saturated porous media. They found that the presence of river humic acids generally resulted in a decrease in attachment efficiency. Furthermore, they discovered that the decrease in colloid attachment in the presence of humic acids is related to the combined influence of the mechanisms of charge and steric stabilization [50]. Yang et al. [113] found that humic acids were sorbed on the surface of nanosized TiO_2 , Al_2O_3 , and ZnO . The decreased zeta potential indicated that humic acid-coated nano-oxides could be more easily dispersed and suspended in solution because of their enhanced electrostatic repulsion.

4.5. Interactions of NPs with soil minerals

There is no direct evidence pertaining as to how NPs interact with soil minerals in soil media. Recently Scheckel et al. [96] determined the speciation and chemical stability of silver and zinc oxide NPs in pure kaolin suspensions over an 18-month period. These researchers reported that silver NPs did not change in sodium nitrate suspension, while the stability was lower in sodium chloride suspension. On the other hand, ZnO NPs rapidly dissociate to $Zn(II)$ within 1 day of reaction.

Joo et al. [98] investigated the interactions of carboxymethyl cellulose-coated anatase TiO_2 NPs (CMC-ANTNP) with the mineral surface of iron-and-aluminum-oxides. The study revealed that the mobility of CMC-ANTNP was retarded by the presence of amorphous Fe and Al hydroxide, which means that CMC-ANTNP was adsorbed on the surface of soil mineral. During this process, the surface charge of both NPs and soil minerals played an important role in the sorption behavior.

4.6. Interaction with existing soil contaminants

Nanoparticles can absorb both organic (herbicides and pesticides) and inorganic pollutants (heavy metals) due to their high surface area. To date, there is a lack of studies as to how the NPs interact with existing contaminants in polluted soils. Because of this, the fate of existing pollutants could possibly be affected by NPs, and at the same time, potentially change the fate and behavior of NPs. Superparamagnetic iron oxide (Fe_3O_4) NPs with a surface functionalization of dimercaptosuccinic acid (DMSA) have been found to adsorb toxic soft metals such as Hg, Ag, Pb, Cd, and Tl, which bind to the DMSA ligands. In addition, As can be removed by Fe_3O_4 because it binds to the iron oxide lattices [114]. Many papers describe the degradation of herbicides by NMs; here are some examples. Joo and Zhao [115] reported that under anaerobic conditions iron-palladium nanoparticles completely reduce 1 mg L^{-1} of lindane at an iron dose of 0.5 g L^{-1} or 1 mg L^{-1} of atrazine with 0.05 g L^{-1} iron with a trace amount of Pd as a catalyst. However, under aerobic conditions only 65% of lindane was degraded. Palladium-iron bimetallic nanoparticles have been also reported

as useful for dechlorination of dichloromethane, chloroform, and carbon tetrachloride [116]. Iron and nitrogen doped titanium dioxide nanoparticles have shown to be effective to degrade herbicides such as mecoprop, (4-chloro-2-methylphenoxy)acetic acid, and 3,6-dichloropyridine-2-carboxylic acid under the visible light [117]. However, references on field applications were not found; furthermore, Grieger et al. [118] have pointed out the scarcity of risk assessment studies and environmental risks for field scale applications of nanomaterials like zero-valent iron NPs.

4.7. Transport of NP in soil columns

To date, there are only a few reports in the scientific literature about the behavior of NPs in real soil systems. In 2009, a paper reported on the stability of titania NPs in soil suspensions, as well as their transport in saturated homogeneous soil columns [99]. They found that the transport distances of TiO_2 in some soils ranged from 41.3 to 370 cm, meaning that there is a potential risk of TiO_2 transfer from soil media to underground water. It was also revealed that suspended TiO_2 contents in soil suspensions were positively correlated with the dissolved organic carbon and clay content of the soil, but were negatively correlated with ionic strength, pH, and zeta potential.

Jaisi and Elimelech [109] investigated the transport behavior of single-walled, carbon nanotubes in soils under saturated flow conditions. Results suggest that carboxyl-functionalized, SWCNTs will not exhibit substantial transport and infiltration in soils because of an effective retention by the soil matrix. The transport was limited to 5.5 and 4.6 cm at 1 and 19 mM KCl, respectively.

Some NPs are coated with inorganic or organic compounds, such as citrate, cysteine, carbonate, or surfactants to maintain the NPs stability. Surface coatings on the NPs are important determinants of mobility and may enhance the transport. Presently, there is a lack of such information related to coated or capped NPs' behavior in terrestrial ecosystems. To date, there are only a few papers describing the transport of NMs in soil. Since many coated NPs will enter into terrestrial ecosystems, more research is needed to better understand the environmental behavior of these NPs [98,107].

4.8. Transport by terrestrial organisms

C. elegans, a nematode living in the soil, is usually taken as a model organism to studying the bioaccumulation and toxicity of NPs. Evidences have revealed that ZnO , Al_2O_3 , and TiO_2 and Ag NPs could be taken up by *C. elegans*, causing different degrees of toxicity including decreasing reproduction and inhibition of growth [119,68]. By far, few publications have documented the uptake of NPs by living organisms. There is no clear evidence yet if the toxicity and absorption can be attributed to the NPs or the dissolved ions. Pipan et al. [120] reported that the Zinc bioaccumulation in a terrestrial isopod probably depends on Zn dissolution from ZnO NP, and not on bioaccumulation of particulate ZnO . To the authors' knowledge, there are no publications describing the transport of NMs by soil microorganisms, including *C. elegans*.

Pertaining to plants, most of the articles explore the toxicity of NPs on seed germination and root elongation [12,87]. Kurepa et al. [121] found evidence that modified TiO_2 entered into plants cells and accumulated in specific subcellular locations. Lin and Xing [87] observed the root uptake and phytotoxicity of ZnO NPs in various plants. In the presence of ZnO NPs, ryegrass significantly reduced biomass production; root tips shrank, and root epidermal and cortical cells were highly vacuolated or collapsed. They also revealed that the phytotoxicity of ZnO NPs was not a direct result of their limited dissolution in the bulk nutrient solution or rhizosphere; the NPs greatly adhered to the root surface. Ma et al. [122] compared the effects of rare earth oxide NPs on the root elongation of

Table 4
New nanomaterials produced in the biennium 2008–2010.

Nanomaterial	Production method	Properties/Applications	Reference
Cobalt ferrites ($\text{Co}_x\text{Fe}_{3-x}\text{O}_4$)	Non-aqueous synthesis method	Small NPs with catalytic power; candidates for the combustion of methane	[125]
Magnetic nanocarriers	Grafting 2-hydroxypropyl- β -cyclodextrin to gum Arabic modified iron oxide NP	Capability to load the anticancer agent all-trans-retinoic acid	[126]
Colloidal-supported metal NP	(1) Synthesis of silica colloids, (2) synthesis of palladium NP, (3) functionalization of silica colloids with 3-mercaptopropyl trimethoxysilane or 3-aminopropyl triethoxysilane, (4) covalent attachment of palladium nanoparticles onto functionalized silica colloids	Intermediate nanocatalyst in liquid-phase reactions	[127]
Cryptomelane-type manganese dioxide	Solid-state reaction between Mn^{7+} and Mn^{2+} species in a high-energy ball milling with stainless steel balls (12 balls, 20 mm diameter) and jar	Modified cryptomelane solids with catalytic activity in the preferential oxidation of CO reaction in the presence of hydrogen	[128]
Anatase/brookite mixtures and pure brookite TiO_2 nanorods	Reaction of aqueous solutions of the titanium(IV) bis(ammonium lactate) dihydroxide complex with urea	Anatase/brookite mixtures and brookite nanorods with higher photocatalytic activity than anatase nanoparticles and even higher than Aeroxide (Evonik) TiO_2 P25 for the photocatalytic H_2 evolution from aqueous methanol solution	[129]
Magnetically recyclable Au@Co core-shell NP	HAuCl_4 and CoCl_2 with a molar ratio of 0.06:0.94 in polyvinylpyrrolidone mixed with ammonia borane solid	Catalytic activity and long-term stability to hydrolytic dehydrogenation of aqueous ammonia borane at room temperature	[130]
Bismuth subcarbonate ($(\text{BiO})_2\text{CO}_3$)	Bismuth nitrate via simple solvothermal method	Antibacterial properties against <i>H. pylori</i>	[131]
Lipid-modified cationic poly(flourenylene phenylene)	Polymer synthesis	Uniform 50 nm NP in water excellent photostability, little cytotoxicity; deliver plasmids into cancer cells	[132]
Celecoxib NP dry powder	n-butyl acetate + sec-butyl alcohol + ammonium glycyrrhizinate + soybean phosphatidylcholine equilibrate at 25 °C for 24 h + gradually dilution with water	Powder may be incorporated into tablets, capsules, or other orally administered dosage forms	[133]
Metastable γ -FeNi NP	Mechanical alloying of melt-spun ribbon followed by a solution annealing treatment in the γ -phase region and water quenching	Use in applications such as polymer curing and cancer thermotherapy	[134]
Silver complexes of N-heterocyclic carbene	Benzimidazolium salts reacted with Ag_2O in dichloromethane as a solvent	Activity against Gram-positive and Gram-negative bacteria; antifungal activity against <i>Candida albicans</i> and <i>Candida tropicalis</i>	[135]
$\text{YF}_3:\text{Yb}^{3+}/\text{Er}^{3+}$ functionalized with poly(acrylic acid) (PAA)	Nanocrystals prepared using lanthanide nitrate salts and sodium fluoride in ethylene glycol and ethanol with PAA as surfactant	Potential to be used <i>in vivo</i> fluorescence imaging, due to the deep penetration of NIR radiation	[136]
Lithium–vanadate-phosphate (LVP) and lithium–iron-phosphate (LFP) glasses	Mixture melted at 900 °C poured on a stainless-steel plate held at room temperature, immediately covered by a second stainless steel plate	Electronic conductivity of 10^{-1} S cm^{-1} at 300 °C. New way for electronic conductivity improvement of olivine-like cathode materials	[137]
Copper selenide (CuSe , Cu_{2-x}Se , β - Cu_2Se and Cu_2Se) hexagonal nanoplates	Several copper sources + elemental selenium, ethylene glycol and hydrazine hydrate in water at 100 °C (12 h)	Nanoplates in the range 200–450 nm. Potential building blocks to construct functional devices and solar cell	[138]
Chain-like and rod-like Co-B NM	Chemical reduction in CTAB and PVP aqueous solution, respectively	Both NMs show high discharge capacity, excellent electrochemical reversibility and high rate discharge capability comparable to Ni-MH battery	[139]
Natural layered silicates (Na^+ -MMT), natural rubber (NR), and polypyrrole (PPy)	Electrolytic admicellar polymerization pyrrole monomer and the Na^+ -MMT varied from 100 to 800 mM and 1–7 parts per hundred of rubber, respectively	Mechanical and DC electrical conductivity properties significantly improved with the inclusion of the layered silicates	[140]
Spinel $\text{Zn}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ NM	Synthesized by sol-gel citrate method	30–35 nm for Mn-Zn ferrite. Sensor very promising for ethanol detection in the range 0–200 ppm with a response time in the order of 10 s	[141]
$\text{NaYF}_4:\text{Yb}^{3+}$, Tm^{3+} NP	$\text{NaYF}_4:\text{Yb}^{3+}$, Tm^{3+} NP coated with an Ru(II) complex doped SiO_2 shell with a thickness circa 30 nm; surface of SiO_2 functionalized with amines	Applicable as biolabels and optical oxygen sensors, in biological fluids	[142]
Ag-L-cysteine	Mixing equal volumes of AgNO_3 (20 mM) and L-cysteine (22 mM) aqueous solutions under sonication in a water bath at 37 °C for 30 min	Directly used to detect Hg^{2+} without further purification and separation	[143]
$\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors	Low temperature solution combustion + metal nitrates as oxidizers fueled by oxalyl dihydrazide (ODH)	Particles show red emission at 611 nm corresponding to $^5\text{D}_0$ – $^7\text{F}_2$ transition	[144]
CdS covalently functionalized polyacrylonitrile nanocomposite	CdS covalently functionalized polyacrylonitrile (CdS-PAN) was prepared in the presence of azobisisbutyronitrile under ultrasonic radiation	Positive nonlinear absorption of incident light	[145]

Table 4 (Continued)

Nanomaterial	Production method	Properties/Applications	Reference
CdTe quantum dots complexed with FeP	Fe(CO) ₅ and trioctylphosphine precursors + CdTe in the same reactor	Optical and magnetic properties	[146]
Cellulose–nanoscale–manganese oxide composite	Impregnating KMnO ₄ solution into cellulose fiber matrix for 30 min followed by reduction with ethanol	Application for Pb(II) removal from aqueous solutions	[147]
Nanometric LiMO ₂ (M = Co, Fe) powders	LiNO ₃ alcoholic solution and either Co(NO ₃) ₂ or Fe(NO ₃) ₃ added under constant stirring into a 3 mol L ⁻¹ KOH alcoholic solution (methanol, ethanol or 2-propanol)	High voltage cathode materials	[148]
Polymer electrolyte	Coprecipitation using nanoparticles of hydrotalcite (anionic clay) as filler	Ionic conductivity 1.1 × 10 ⁻⁵ S cm ⁻¹ for 3.6 wt.% nanoparticle doped sample	[149]
Acrylic-based luminescent NM	In situ emulsifier-free microemulsion copolymerization	Particles with 20–100 nm, blue luminescent NMs potential use in electronic inks	[150]
Fe ₃ O ₄ @γ-Fe ₂ O ₃ core/shell nanomaterials	Thin layer of α-FeOOH absorbed on surface of iron oxide nanoparticles	Higher magnetic saturation value	[151]
Fe ₃ O ₄ /CdTe magnetic/fluorescent nanocomposites	Fe ₃ O ₄ nanoparticles functionalized with thiol groups + chemical conjugation with multiple thioglycolic acid modified CdTe QDs to form water-soluble Fe ₃ O ₄ /CdTe	Nanocomposites with magnetic and fluorescent properties applicable in magnetic separation and fluorescent imaging	[152]
Carbon–zirconia quantum dot	High-temperature annealing (1200 °C) of synthetic opal infiltrated with zirconia and a small amount of carbon	Might be used to convert short-wavelength broadband radiation to quasi-mono-chromatic light in the visible range	[153]

test plants. The study indicated that suspensions of nano-La₂O₃, nano-Gd₂O₃, and nano-Yb₂O₃ severely inhibited the root elongation of seven plants species, while nano-CeO₂ at 2000 mg L⁻¹ had no effects on the root elongation of six plants species, barring lettuce. Stampoulis et al. [123] tested five NPs (MWCNT, Ag, Cu, ZnO, and Si) on *Cucurbita pepo*. Phytotoxicity was evaluated on seed germination, root elongation, and biomass production. Seed germination was found to be unaffected by any of the treatments, but Cu NPs reduced root length, while biomass production was reduced by MWCNT and Ag NPs. López-Moreno et al. [90] reported that the nanoceria differentially affected plant organs. While in some plants promoted root and shoot elongation, in other plants produced inverse effects in roots and shoots. López-Moreno et al. [90] obtained evidence of the differential biotransformation and genotoxicity of ZnO and CeO₂ NPs on soybean plants. Although the NPs did not affect soybean germination, some genotoxic effects were found. To the authors' knowledge, only one publication with CNTs described the possible dispersion of NP through terrestrial plants [124]. These authors found that C₇₀ were detected in the leaves of the second generation of rice plants, which suggest that NPs could be potentially spread by terrestrial plants. As shown above, studies including ENMs have been mainly focused on the impact of NPs on individuals. The ecological impact and movement of NPs on whole terrestrial ecosystems still remains unreported. It is very important to know how high is the impact of NPs on soil, what the sinks are, and how much leaches to the underground water. It is supposed that after information pertaining to NPs and their impact on terrestrial biota become available, ecosystem-scale impact studies will emerge.

5. New nanoproducts

Several new ENMs were produced in the biennium 2008–2010. Table 4 includes those NMs with specific properties or applications. NMs reported in the literature but with no definite applications were not included in this review. From the listed NMs, cobalt ferrites [125], organically modified iron oxide NPs [126], colloidal-supported metal NPs [127], cryptomelane-type manganese dioxide NMs [128], TiO₂ nanorods [129], and magnetically recyclable Au@Co core–shell NPs [130] show catalytic activity. The new nanoproducts with potential medical applications include bismuth subcarbonate NPs [131], lipid-modified cationic poly(flourenylene phenylene) [132], celecoxib NPs [133], metastable Fe–Ni NPs [134],

silver–carbene [135], functionalized YF₃:Yb³⁺/Er³⁺ [136]. Nanomaterials with applications in electronics include lithium complexes [137], copper–selenium complexes [138], Co–B NMs [139], and silicates–rubber–polypyrrole complexes [140]. Nanomaterials for sensors applications were Zn–Mn–Fe NMs [141], NaYF₄:Yb³⁺ coated NM [142], Ag–L-cysteine NPs [143]. New NMs with optical applications were Gd₂O₃:Eu³⁺ nanophosphors [144], CdS nanocomposite [145], and CdTe quantum dots [146]. Other NMs included cellulose–manganese oxide composite for Pb removal from aqueous solution [147], Li compounds for high voltage cathode [148], polymer electrolytes [149], acrylic-based luminescence NM [150], Fe complexes with higher magnetic saturation value [151], Fe/Cd Te nanocomposites with magnetic properties [152], and carbon–zirconia QD to convert short-wavelength radiation to quasi-monochromatic light in the visible range [153]. Many more new NMs were reported but still are without practical applications. This is the reason why they were not included in this review.

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