

# Bioavailability of Engineered Nanoparticles in Soil Systems

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**Abstract:** Nanotechnologies form a field of research that is still emerging with major gaps in knowledge regarding the behavior and potential toxicological risks of engineered nanoparticles (ENPs) in soils. While most of the studies are conducted in porous media (quartz and glass beads) and culture media, less frequently are the studies carried out in natural soils. However, the complex interactions occurring in soils, mediated by both soil components and soil organisms, are essential in bioavailability processes. Therefore, this paper is intended to highlight particularly the bioavailability of ENPs in soils. The potential release pathways of ENPs to soils are described and are faced with a lack of specific regulation and definitive nomenclature. This paper reviews a number of studies regarding ENP toxicological bioavailability on microorganisms and microfauna, mesofauna, and macrofauna inhabiting the soil, as well as on soil-plant systems. The paper especially discusses ENP behavior in soils that affect ENP bioavailability to the edaphic biota. Particular attention is paid to the factors regulating these processes [i.e., (1) ENP-dependent factors, (2) soil properties, and (3) soil components], focusing on organic matter. DOI: 10.1061/(ASCE)HZ.2153-5515.0000263. © 2015 American Society of Civil Engineers.

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## Introduction

Soil is a complex, variable, and living system, essentially regarded as a nonrenewable resource. The sustainable use of soil is defined by the temporal and spatial harmonization in the use of its ecological (biomass production, protection of humans and the environment, and gene reservoir) and nonecological functions (physical basis of human activities, source of raw materials, and geogenic and cultural heritage; Blum 2005). These functions are linked to the ecosystem services provided by soil and are determined by soil type, condition, and functional biodiversity (Finvers 2008). From more than 200 years of industrialization, soil pollution is now a widespread phenomenon, which has negative impacts on human

health and natural ecosystems, as well as on the economy (European Commission 2014). It is estimated that soil degradation, including soil pollution, has an approximate global economic loss value of U.S. \$66 billion annually (Suppan 2013). Pollutant persistence in soils is much higher than in other environmental compartments, soil pollution appearing to be almost constant (Kabata-Pendias and Pendias 2001). In this scenario, the soil becomes more vulnerable and some of its functions negatively affected.

Anthropogenic nanoparticles (NPs) have been released into the environment for centuries from combustion processes as well as mining, industrial, and construction activities, but current concern regards intentionally manufactured or engineered nanoparticles (ENPs; Plant et al. 2012). Over the last decades, there has been an extremely rapid expansion of nanotechnology, with a wide range of applications and benefits in various areas. Currently in the market there are more than 800 nanotechnology-based products and it is expected to increase in the coming years (Bystrzejewska-Piotrowska et al. 2009). Despite the rapid growth of nanotechnology, there are major gaps in knowledge regarding the potential toxicological risks of exposure to ENPs (Wijnhoven et al. 2009). One of the major challenges is to establish standardized methodology to examine the implications for human health and the environment. This is especially true in the soil environment, where the low number of studies is particularly noticeable (Ostrowski et al. 2009). The environmental risks of ENPs in different environmental compartments including soils have been probabilistically quantified (Gottschalk et al. 2013). Results showed that there is only a marginal risk for metal-based ENPs in sewage-treatment plant effluents and no risk in soils. However, from the literature reviewed (years 2006–2011), fewer environmentally relevant toxicity studies were found for soil environments and the researchers concluded that risk levels in soils must be constantly monitored due to the continuous ENP deposition combined with an increasing volume of ENP production. Risk assessment of chemicals is often based on the quotient predicted-environmental

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concentration (PEC) to predicted-no-effect concentration (PNEC; Frische et al. 2003). Mueller and Nowack (2008) reported that PEC-to-PNEC was smaller than 1 (i.e., no risk is assumed) for nano-TiO<sub>2</sub>, carbon nanotubes (CNTs), and nano-Ag. However, models often neglect the ENPs behavior in the environment (such as transformation, degradation, dissolution, and bioaccumulation) despite the key role played in the actual and potential bioavailability.

Bioavailability is a necessary precondition for bioaccumulation but the latter is not a precondition for toxic effects, which are possible without uptake of contaminants into the organism (Frische et al. 2003). The bioavailable contaminant fraction in the soil represents the relevant exposure concentration for the edaphic biota and it depends on the substance properties, soil properties, and uptake route of the target organism (Frische et al. 2003). The physical properties of ENPs differ from those of the same (yet larger) chemical structure and are essential in determining their behavior in soils. Furthermore, transformations that occur when introducing ENPs in soils determine their behavior and therefore their bioavailability. These processes are largely regulated by soil components and properties, especially organic matter (OM), ionic strength, water regime, pH, and texture. However, most studies on ENP bioavailability mainly refer to porous media (pure quartz and glass beads) or pure culture media; there is less information in natural soils, particularly with a broad range of characteristics. This makes it difficult to extrapolate and understand the comportment of ENPs under realistic field scenarios. Soil is a structured, heterogeneous, and discontinuous system where the biological population is very diverse (Nannipieri et al. 2003). Edaphic biota has a broad variety of exposure routes (e.g., soil pore water, soil particles, and particulate OM) and closely reacts with the medium releasing chelates or exopolymers to counteract the toxic effect of a given pollutant (Navarro et al. 2008a). Interactions between ENPs, soil components, and organisms are essential in bioavailability processes.

This paper provides an overview of existing research studies focusing on the bioavailability of ENPs to edaphic biota linked to their transformation and behavior in soils, with particular emphasis on the role played by the ENP-dependent factors as well as on the soil properties and components. Papers conducted in artificial media or in the aquatic environment were employed to support the discussion.

## Engineered NPs in Soils: Pathways and Regulation

Engineered NPs are used in a wide range of applications, including nanomedicine and pharmacy, chemicals and cosmetics, the food industry, agriculture, coatings, materials, transportation, telecommunication, scientific tools, imaging, mechanical engineering, energy, electronics, military and security, and pollution remediation (Buzea et al. 2007; Chau et al. 2007; Patel 2008). Currently, there is no international definition for NPs but the term nanomaterial (NM) is defined by the ISO; the European Commission (2011) recommended on October 18, 2011, the definition, "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm. [...] By derogation from the above, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials." From the literature (Buzea et al. 2007; Gladkova and Terekhova 2013), several classifications of ENPs can be found, based on the following: (1) dimensionality,

(2) morphology [i.e., flatness, sphericity, and aspect ratio, either high (e.g., helices, zigzags, belts, and nanowires) or low (spherical, oval, cubic, prism, helical, and pillar)]; (3) uniformity and agglomeration (such as dispersed aerosols, suspensions/colloids, in an agglomerate state), or (4) composition [e.g., carbon-based NPs such as fullerenes, multiwalled carbon nanotubes (MWCNTs), and single-walled carbon nanotubes (SWCNTs); metal-based NPs (e.g., inert metals like Fe, Ag, and Au; or metal oxides like TiO<sub>2</sub>, ZnO, and CeO<sub>2</sub>); quantum dots (e.g., CdSe, CdTe, and ZnSe); and dendrimers or multifunctional polymers].

## Environmental Release Pathways of ENPs: Focus on Soils

Besides combustion processes, ENP release (unintentional or deliberate) into the environment occurs during ENPs production, their incorporation into products, ENP-containing product use, as well as any disposal processes like sewage treatment, recycling, waste incineration, or landfilling (Gottschalk and Nowack 2011).

Engineered NPs can be unintentionally released during production, packaging, transportation, and/or use of ENPs-containing consumer products, including clothing, food, care products, sporting goods, tires, paints, or detergents (Buzea et al. 2007; Gladkova and Terekhova 2013). These products have different lifecycles, causing wide variations of the expected ENPs concentrations in the environment (Mueller and Nowack 2008). The product's material matrix affects largely the release of ENPs to the environment, i.e., being lower from solid matrices; higher from liquid, paste, cream, and/or powder matrices; and directly when they are incorporated into aerosol spray matrices (Gottschalk and Nowack 2011). Nonetheless, the original ENP formulations can change during their lifecycle. Moreover, ENP release from consumer products is considerably affected by the consumer behaviors (washing habits, use of product, and mechanical stress), washing-water-quality parameters (pH, redox potential, temperature, particulate matter, detergents, and bleaching agents), and environmental conditions (temperature, rainwater, and pH; Benn et al. 2010; Gottschalk and Nowack 2011). In this regard, Benn et al. (2010) simulated Ag release in so-called real-world scenarios (such as landfilled conditions) from a wide range of nano-Ag-containing consumer products using the toxicity characterization leaching procedure (TCLP) method. Results showed that significant Ag concentrations could be released into the environment at some point of the product lifecycle.

Engineered NPs can also be deliberately released into the environment. More specifically, ENPs directly reach soils when using ENP-containing agrochemicals, including nanofertilizers, nanopesticides, seed treatment preparations, materials for agrofilms, and hydroponic solutions (Gladkova and Terekhova 2013). Engineered NPs deliberate release also includes their use for in situ remediation of a wide range of pollutants in soils and groundwater, including metals, metalloids, chlorinated organic solvents, organochlorine pesticides, polychlorinated biphenyls, or polynuclear aromatic hydrocarbons (Klaine et al. 2008; Shipley et al. 2010; Tungittiplakorn et al. 2004; Zhang 2003). Moreover, ENPs use in wastewater treatment is likely to result in direct emissions to soil water, surface water, and groundwater (Boxall et al. 2007). Because ENPs can concentrate in wastewater sludge, during clarification processes (and when the digested dewatered sludge is sent to the landfill or as biosolids for agricultural application), the leachability of ENPs is likely to cause contamination (Brar et al. 2010). Land application of organic amendments (including biosolids, sewage sludge, and horse manure) represents a significant environmental

exposure route for specific ENPs (Ganzleben and Hansen 2012; Yang et al. 2014). Courtris et al. (2012a) subjected horse manure spiked with Co ENPs, Co ions, Ag ENPs, or Ag ions to a sequential extraction procedure, and they observed that ENPs were less mobile than their ionic counterparts. Nonetheless, although the released ENPs amount is estimated to be low, it must not be neglected due to (bio)accumulation in soils in the long term with unpredictable future consequences (Benn et al. 2010). Engineered NPs spilled or disposed into the soil are inevitably exposed to environmental factors. Ma et al. (2011) demonstrated that phototoxicity of nano-ZnO was dramatically enhanced under natural sunlight illumination with great environmental implications. Furthermore, certain ENP-containing products such as food (additives, nutraceuticals, disinfectants, and toxin detectors) or healthcare goods (sunscreens, pharmaceuticals, cosmetics, toothpastes, and deodorants) can be also emitted to the sewage system after human (or animal) excretion or during washing and showering, being easily released to soils and surface waters either by landfilling or atmospheric deposition after incineration (Boxall et al. 2007; Brar et al. 2010; Chau et al. 2007; Cushen et al. 2012).

## Legislation

There is no international law or policy about the nanotechnology, but some countries define standards and regulation using ISO standards (Bergeson and Hester 2008). In North America, Environment Canada and Health Canada policies are based on the Canadian Environmental Protection Act (1999) to regulate imported or manufactured NMs in Canada (Government of Canada 2013). In the United States, the regulation of new nanoscale substances is the prerogative of the U.S. EPA and the U.S. Food and Drug Administration (FDA). Under the Toxic Substance Control Act (TSCA) and the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), the U.S. EPA issues regulations concerning NMs regarded as so-called chemical substances and nanopesticides, respectively. All nanoscale products covered by the Federal Food, Drug, and Cosmetic Act (FFDCA) fall under the authority of the U.S. FDA. In the European Union, the legislation is based on regulations and directives related to the nature of the product (i.e., chemical, cosmetic, food, biocide, and plant protection). For example, as a chemical, ENPs must comply with the Registration, Evaluation, and Authorization of Chemicals (REACH) regulations. Until now the criteria defining NMs may differ among countries, complicating implementation of international regulations (Lanoy 2014).

There is no definitive system nomenclature for NMs but several countries work together to find a specific nomenclature (Environment Canada and Health Canada 2007), and there is neither legislation nor regulation about the NMs that are problematic in soils (Ganzleben and Hansen 2012; Suppan 2013). The main contributions of NPs to agricultural soils are sewage sludge and biosolids, as discussed previously. Directives like the European Directive 86/278/EEC set heavy metal (Cd, Cu, Ni, Pb, Zn, Hg, and Cr) threshold concentrations in sewage sludge used for agricultural application (Council Directive 1986). However, these limits do not exist for metal-based NPs and other specific NPs. Some recommendations could be defined to include NPs in this type of directive in order to improve soil management and quality monitoring. Although finding an agreement on NP regulations is remote (Van Calster 2006), the European Commission launched a public consultation on the modification of the REACH Annexes on NMs but the report has not been made public yet.

## Toxicity and Bioavailability in Soils Exposed to ENPs

Soil organisms are one of the most important factors governing soil quality. Nonetheless, soil is a complex and dynamic biological environmental compartment that today still requires a better understanding of the interactions between biodiversity and soil functions. The soil living population includes macrofauna, mesofauna, microfauna, and microflora, where microbes mediate 80–90% of the soil processes (Nannipieri et al. 2003). Microorganisms secrete soil enzymes that play a fundamental role in soil nutrient cycling, transformation of plant and microbes debris, mineralization and transformation of OM, and transformation and degradation of pollutants (Rao et al. 2014a). Earthworms positively interfere with the activity and the underground plant competition for nutrients (Eisenhauer et al. 2009), and play a major ecological role, in terms of both microaeration and drainage in soils (excavation activities and excretion of macroaggregates) as well as dispersion of contaminants, soil constituents (OM and clay), and microorganisms, including bacteria. In contaminated soil remediation, earthworms play an important role as pioneers, with bioturbation effects that can alter the kinetics of some environmental pollutants (Eijsackers 2010). Acting on their habitat, earthworms indirectly regulate the activity, diversity, and spatial distribution of soil microorganism communities responsible for the OM mineralization into nutrients that may ultimately be available for plant uptake through roots. Meanwhile, plants provide the OM required for the functioning of the decomposer subsystem, which in turn breaks down dead plant material, and indirectly regulates plant growth and community composition by determining the available soil nutrient supplies (Wardle et al. 2004).

Engineered NPs can affect the structure, diversity, and activity of soil organisms including microorganisms and invertebrates, largely responsible for plant development. Quantitative and qualitative changes in soil biological community involve all trophic levels of the soil food web by direct, indirect, and cumulative impacts with the potential for biomagnification (Judy et al. 2011). Moreover, the lack of soil biota could further reduce the soil quality of an already contaminated and degraded soil (Coleman et al. 2010).

## Soil Microorganisms

Toxicity of ENPs can occur directly on soil microorganisms [disruption of membranes, genotoxicity, formation of reactive oxygen species (ROS), and phototoxicity] and/or by changes in the bioavailability of nutrients, water, or toxins (Dinesh et al. 2012; Simonet and Valcárcel 2009). Through their interactions with natural organic matter (NOM) and with toxic compounds, which may amplify or alleviate their toxicity, ENPs may also indirectly impact microorganisms (Simonet and Valcárcel 2009). Nonetheless, in this respect there is no unanimity in the literature. For instance, Ge et al. (2013) concluded that TiO<sub>2</sub> NP toxicity to soil bacteria was a result of direct toxicity (mediated by soil water) rather than indirect effects due to NPs affecting soil water and OM pools. In a similar way, Chunjaturas et al. (2014) observed no change in soil parameters [OM, pH, electrical conductivity, and cation-exchange capacity (CEC)] after spiking soils with Ag NPs. Nonetheless, the researchers observed a significant decrease in the bacterial community with increasing Ag NP concentration. This response was accompanied by a decrease in the amount of CO<sub>2</sub> emissions, but not in N mineralization. Although Ben-Moshe et al. (2013) observed a change in neither the total amount of OM in the soil nor the soil extract, three-dimensional (3D) fluorescence spectroscopy

demonstrated changes in humic substances. So, studies aimed to elucidate the impact of ENPs on key soil properties regulating bioavailability are required.

Several papers discuss the ENP toxicity to microbial communities in the soil. Mohanty et al. (2014) spiked some agricultural soil samples with CuO NPs, ZnO NPs, CuCl<sub>2</sub>, or ZnCl<sub>2</sub> to evaluate the effects on the CH<sub>4</sub> oxidation activity and the abundance of heterotrophs, methane oxidizers, and ammonium oxidizers. Results showed that CuO and ZnO NPs were highly toxic for the microbial-mediated CH<sub>4</sub> oxidation, compared with the ionic form, and that the microbial abundance was impaired. In the same way, Vittori Antisari et al. (2013) reported an alteration of the microbial biomass-C/N ratio and an increase of the qCO<sub>2</sub> values in a soil spiked with SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub> NPs, attributed to microbial stress and changes in the bacterial/fungal biomass ratio. The imbalance in fungal and bacterial populations has been previously reported for polluted soils with trace metals (de Santiago Martín et al. 2013) and can involve a disturbance of key soil processes, such as OM decomposition. In contrast, He et al. (2011) reported that the addition of Fe oxide magnetic NPs could potentially stimulate bacterial growth and change the soil bacterial community structure, without altering the bacterial abundance. Depending on the study, the impacts of ENPs on soil microbial communities appears conflicting. Thus, while Chung et al. (2011) observed that microbial activity and biomass in soils was significantly lowered after spiking with MWCNTs, Zhang et al. (2013) demonstrated the ability of some bacteria to degrade acid-treated MWCNTs which would decrease their environmental persistence. Zhang et al. (2013) concluded that MWCNT degradation appears to require an external C source involving cometabolism and the cooperation of several microorganisms. In a similar way, Johansen et al. (2008) observed that the addition of C<sub>60</sub> fullerenes in a clay loam soil induced only minor perturbations on microbial community (bacteria and protozoans). The researchers nonetheless concluded that the character extremely recalcitrant of C<sub>60</sub> to be degraded should be kept in mind in C<sub>60</sub> long-term persistence. Moreover, microorganisms may develop noteworthy physiological defense mechanisms against ENPs, such as exopolysaccharide production for capping ENPs (Khan et al. 2011; Sudheer Khan et al. 2011).

Soil enzymes are useful bioindicators of soil quality as they give information not only on the pollution extent on the soil quality but also on soil remediation efficiency (Rao et al. 2014b). Tong et al. (2007) reported that the soil enzyme activity was not adversely affected after spiking with C<sub>60</sub> fullerenes. However, some works have reported significant negative impacts. Thus, Shin et al. (2012) evaluated the inhibition of some soil extracellular enzyme activities (urease, acid phosphatase, arylsulfatase and  $\beta$ -glucosidase) and the overall microbial activity (dehydrogenase and fluorescein diacetate hydrolase) after spiking a soil with Ag NPs. The researchers observed that Ag NPs negatively affected all the enzyme activities tested, the urease activity being especially sensitive. Altering the soil enzymatic activity can directly occur by inactivation of the enzymes through the interaction of pollutants (such as metals) with the active site, the substrates, the enzyme-substrate complex, and/or the enzyme products. However, Shin et al. (2012) reported that the observed adverse effect on soil enzyme activities was caused due to Ag NPs toxicity and not to Ag ions. So, a change of the microbial community synthesizing enzymes is likely to occur. Jin et al. (2013) observed that SWCNTs lowered the activity of some soil enzymes and that the inhibition persisted within the time frame studied. The researchers concluded that both the direct enzyme inhibition and the damage to soil microorganisms producing enzymes could explain the observed patterns. Subsequently, a decrease in bacterial and fungal communities exposed to SWCNT which could

explain the reduction in the enzyme activity previously reported was noted in Jin et al. (2014). Nonetheless, studies aimed at elucidate the mechanisms of enzyme inhibition in soils are required.

## Soil Invertebrates

Studies on the impact of ENPs on microfauna, mesofauna, and macrofauna are beginning to emerge. Although most of the studies were carried out on earthworms and nematodes, several studies within the edaphic biota were performed on isopods (*Porcellio scaber*; Novak et al. 2012a, b; Tkalec et al. 2011), collembola (*Folsomia candida*; El-Temsah and Joner 2013; Kool et al. 2011; Waalewijn-Kool et al. 2013), and ostracods (*Heterocypris incongruens*; El-Temsah and Joner 2013). The toxicity studies performed with natural soils are scarce but preliminary works have highlighted the varied nature of responses to ENPs types on different species. Manzo et al. (2011) observed different toxicity responses to ZnO NPs in a wide range of terrestrial organisms [plants (*Lepidium sativum* and *Vicia faba*), ostracods (*H. incongruens*), and collembolans (*F. candida*)] and they reported that *H. incongruens* was the most sensitive organism. While toxicity mechanisms are similar to that for soil microorganisms, the routes of exposure to soil invertebrates are not always equivalent. Overall, direct (dermal) uptake is a possible route of exposure, but the ingestion of contaminated particles or contaminated food is likely to be the major route. Collembolans will mainly be exposed to soil pore water, earthworms to both pore water and soil particles (by dermal and oral contact), and woodlice to food (decaying leaf material) and soil particles by ingestion [and to a limited extent to soil pore water (Tourinho et al. 2012)]. Besides, the internalization of ingested ENPs could be determined by the integrity of the cell membrane, as observed by Novak et al. (2012a), who studied the toxic effect of TiO<sub>2</sub> NPs on *P. scaber*.

Earthworms seem to avoid soil containing ENPs which may minimize toxic effects such as decrease in survival, growth, or cocoon production (McShane et al. 2012; Shoults-Wilson et al. 2011b). It has been suggested that this response could be used as a sensitive indicator of harmful conditions. Coleman et al. (2010) evaluated the effects of long-term exposure of *Eisenia fetida* to nanoscale and micrometer-scale Al<sub>2</sub>O<sub>3</sub> in spiked soils. They observed that only high levels of nanoscale Al<sub>2</sub>O<sub>3</sub> (>5 g/kg) resulted in reductions of both reproduction and habitat avoidance. Similarly, Hu et al. (2010) reported that TiO<sub>2</sub> and ZnO NPs could be bioaccumulated in *E. fetida* placed in spiked artificial soils at high exposure levels (>5 g/kg). These researchers concluded, nonetheless, that other parameters [such as response of antioxidant system and deoxyribonucleic acid (DNA) damage] were more predictive of impacts than tissue levels of ENPs. While Lapied et al. (2011) observed no mortality or bioaccumulation of TiO<sub>2</sub> NPs in the earthworm *Lumbricus terrestris* exposed to an aged TiO<sub>2</sub> nanocomposite used in sunscreen cosmetics (at levels  $\leq$ 100 mg/kg), toxic effects were noted, such as an enhanced apoptotic frequency in the cuticle, intestinal epithelium, and chloragogenous tissue. In contrast, Schlich et al. (2012) reported that uncoated TiO<sub>2</sub> stimulated *Eisenia andrei* reproduction (up to 50%) in a concentration-dependent manner during winter testing. Nevertheless, there was no stimulation when the test was performed in summer, suggesting that TiO<sub>2</sub> affect earthworm reproductive activity by abolishing the circannual rhythm. Scott-Fordsmand et al. (2008) evaluated the lethal and sublethal toxicity of double-walled carbon nanotubes (DWCNTs) and C<sub>60</sub> fullerenes to *Eisenia veneta*, and reported that DWCNTs impaired the cocoon production, but not the hatchability, growth, and mortality. Similarly, García-Gómez et al. (2014)

observed neither mortality nor differences in *E. fetida* body weight exposed to ZnO NPs, although the production of cocoons was impaired.

Besides earthworms, most of the studies were conducted on nematodes, primarily on *Caenorhabditis elegans*, reporting toxicity (Khare et al. 2011; Kim et al. 2012; Ma et al. 2011; Roh et al. 2010; Wang et al. 2009). Wu et al. (2012a) observed that TiO<sub>2</sub> NPs exhibited chronic toxicity to *C. elegans* at predicted environmental relevant concentrations. Nematodes showed alterations of locomotion behaviors and ROS production as endpoints. Similarly, these researchers observed an equivalent toxicity response pattern in *C. elegans* exposed to dimercaptosuccinic acid (DMSA)-coated Fe<sub>2</sub>O<sub>3</sub> NPs (Wu et al. 2012b). Linear regression analysis confirmed the close relation between the ROS production and lethality, growth, reproduction, locomotion behavior, pharyngeal pumping, defecation, and intestinal autofluorescence. Thereafter, comparisons between a range of metal oxide ENPs (30 nm in all cases) showed different toxicity patterns (ZnO > TiO<sub>2</sub> > SiO<sub>2</sub>) as well as subtle toxicity differences in *C. elegans* (Wu et al. 2013).

## Soil-Plant Systems

Plants are potential pathways for the translocation of ENPs into the food web. The aboveground surface of plants, or also below ground by organs such as roots and tubers, are the main interfaces between the soil environment and ENPs where they are absorbed inside plants (Dietz and Herth 2011).

Cell walls formed of cellulose constitute the primary interacting system and barrier for ENP entrance in plants. The cell wall pore diameter ranging from 5 to 20 nm (Fleischer 1999; Nair et al. 2010) directly influences the kind of ENP which could be transferred into roots. Only ENPs with a size smaller than the pore diameter can penetrate inside plants (Moore 2006; Navarro et al. 2008a). More, ENPs have properties that can enhance their ability to be absorbed by roots like, for example, self-assembly, structure, concentration, aggregation, surface characteristics, and dissolution (Chang et al. 2012; Yan et al. 2011). Engineered NP absorption by plants could be supported by a change of cell wall permeability during reproduction or under stress conditions (Lin and Xing 2008). Furthermore, a new pore can be developed by interaction between ENPs and cell walls, increasing ENPs movement towards roots (Navarro et al. 2008a). Few studies have examined the bioavailability of ENPs from soil to plants, making determination of ENP uptake [affecting environmental variables such as soil type and soil chemistry (Judy 2013)] difficult. Also, ENPs can develop several effects (mechanical, chemical, catalytic, and surface) due to interactions with biological systems (Dietz and Herth 2011). Some of these effects are shown in a study by Lin and Xing (2007) on six higher plant species, as follows: (1) radish, (2) rape, (3) ryegrass, (4) lettuce, (5) corn, and (6) cucumber. That study showed that ENPs such as Al, alumina, Zn, ZnO, and MWCNTs affect differently seed germination and root growth depending on the plant species, but conversely that the plant species may influence the ENP behavior.

Engineered NPs can have both positive and negative effects on plants. Asli and Neumann (2010) and subsequently Wang et al. (2011b) showed that TiO<sub>2</sub> NPs can produce disturbances in the root system in *Arabidopsis thaliana*, in addition to changes in the hydraulic conductivity and water flow through the roots of maize. Water-soluble fullerenes may tend to produce changes in microtubule networks and inhibitory effects in seedling roots in *A. thaliana* (Liu et al. 2010). A large number of researchers (Lin and Xing 2007; Stampoulis et al. 2009; Yang and Watts 2005) have

studied the negative effects of metallic ENPs (e.g., Cu, Al<sub>2</sub>O<sub>3</sub>, Al, Zn, and ZnO) in the soil-plant system and several findings lead to damage, modifications on root elongation, and development inhibition. A bioaccumulation effect has also been demonstrated based on the distribution of Ag NPs in (1) *Brassica juncea*, and (2) *Medicago sativa* (Harris and Bali 2008). The two species had different reactions compared to the concentration of nano-Ag (AgNO<sub>3</sub>), but the researchers showed that hyperaccumulation of Ag is possible in many plant species. That study highlighted that ENPs from metallic origin could be transported in plants, being transferred into the food web. Engineered NPs can also be used in soil remediation practices. As previously mentioned, the use of biosolids in agricultural activities is an important source of ENPs in soils. Soybean is highly exposed to ENPs from pharmaceuticals (Wu et al. 2010) and to trace metals (Berti and Jacobs 1996) contained in biosolids. Priester et al. (2012) studied the accumulation of CeO<sub>2</sub> and ZnO NPs in different tissues of soybean plants, and they observed that those ENPs significantly decreased soybean production. The researchers concluded that nano-ZnO bioaccumulation in the edible tissues of plants impacts the food quality and that nano-CeO<sub>2</sub> degrades soil fertility.

The positive responses are less documented but some researchers reported the benefits of ENPs in the soil-plant system. Generally, the benefits of ENPs in the soil environment are developed for agricultural activities and agrobiotechnological applications. Engineered NPs can potentially reduce pesticides and fertilizers or be used in sensor systems for applications in agriculture (Ghormade et al. 2011; Jatav and De 2013). Studies on crops showed that CNTs can stimulate the seed germination and growth of tomato and tobacco (Khodakovskaya et al. 2009, 2012; Lin and Xing 2007), CeO<sub>2</sub> NPs induce root growth in tomato and alfalfa (López-Moreno et al. 2010), and TiO<sub>2</sub> NPs enhance the biomass growing of spinach by increasing the activity of rubisco (Gao et al. 2006, 2008). Moreover, nano-TiO<sub>2</sub> can work on the photochemical reaction of chloroplasts, increase the Hill reaction, and increase the activity of chloroplasts, which caused iron ferricyanide (FeCy) reduction and oxygen evolution [as per a study on *Spinacia oleracea* by Hong et al. (2005)].

## Retention and Mobility Processes Affecting ENP Bioavailability

Several studies evidenced ENPs toxicity on soil organisms using laboratory cultures; however, ENPs mobility and their transformations occurring in the soil may alter their bioavailability and thus their toxicity. Even considering that the route of exposure is species-specific, the transport of ENPs in the soil could be associated to their potential bioavailability as poorly mobile ENPs may be less available for sessile biota like plant roots and are fungi hyphae-dependent (Navarro et al. 2008a). Briefly, the mobility of colloidal particles in porous media is described by particle transport to the immobile grain surface (termed the collector), and next is attachment that removes particles from solution by interception, diffusion, and sedimentation (Elimelech and O'Melia 1990). Because of their nanoscale size, ENP transport is governed by Brownian diffusion and their attachment is mainly due to diffusion, as their high diffusivity increases the collision rate (Dunphy Guzman et al. 2006; Lecoanet et al. 2004; Lin et al. 2010). Moreover, ENP deposition on collector depends also on several kinds of interactions such as (1) van der Waals forces, (2) electrical double-layer interactions, (3) steric interactions, (4) hydration forces, and (5) hydrophobic interactions (Lecoanet et al. 2004; Navarro et al. 2008a). Furthermore, during transport, different transformations may occur,

affecting the ENPs behavior and thus their bioavailability. These include aggregation/agglomeration, dissolution, and sorption processes (Tourinho et al. 2012), as shown in Fig. 1.

## Aggregation and Agglomeration Processes

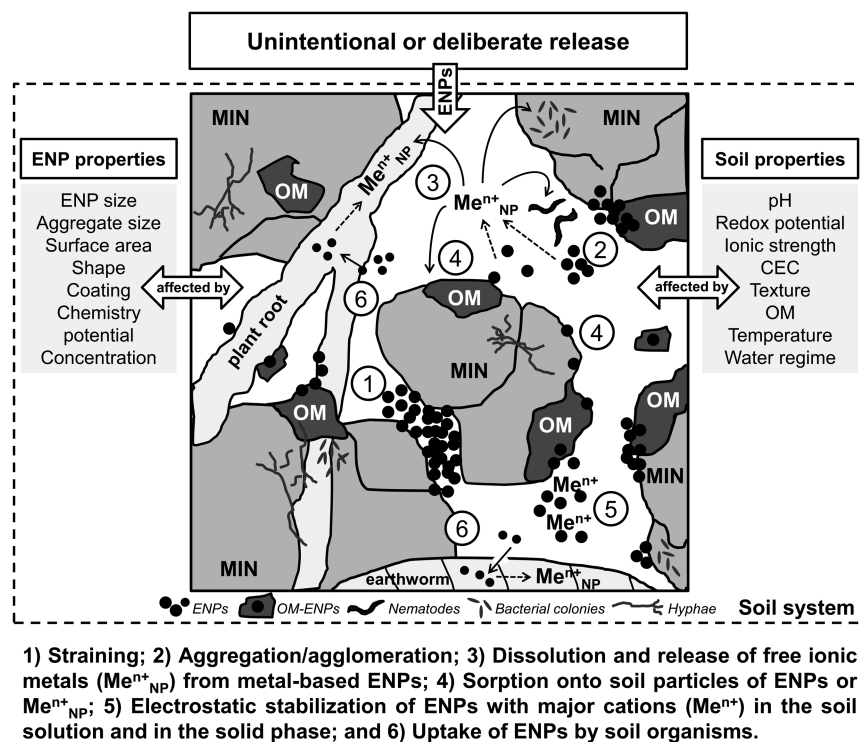
As Brownian motion is responsible for NP collision rate with collectors, it also causes collisions between ENPs, leading to the formation of agglomerates in the case of weak bonds (van der Waals forces) or the formation of aggregates in the case of strong chemical bonds (Jiang et al. 2008). The kind of bonding may influence the associated NP fate due to possible shear forces (Dunphy Guzman et al. 2006) and may affect their bioavailability (Jiang et al. 2008). In the subsequent text, aggregation will refer to either aggregation itself or agglomeration, as most of the reviewed ecotoxicological studies did not investigate the NP aggregation/agglomeration state. Moreover, NPs may attach to an identical particle (homoaggregation) or to natural colloids (heteroaggregation) to form larger particles that are subject to physical straining (Darlington et al. 2009; Hydutsky et al. 2007; Jaisi and Elimelech 2009; Jiang et al. 2012b). Natural NPs are numerous in soil pore water; thus, heteroaggregation may to a certain extent change ENPs transport and bioavailability (Cornelis et al. 2012).

Several studies showed that aggregation process influences ENP toxicity to different soil organisms. Lyon et al. (2006) studied the antibacterial activity of a fullerene aqueous suspension ( $\text{aq/nC}_{60}$ ) obtained by stirring that is supposed to mimic a spill scenario. First, particles were separated in two fractions, as follows: (1) a so-called small fraction with a mean diameter of around 2 nm, and (2) a so-called large fraction with a mean diameter of 142.3 nm. Then each fraction was inoculated with culture of *Bacillus subtilis*, a soil microorganism used as an indicator for Gram-positive and Gram-negative bacteria (Lyon et al. 2006). The minimal inhibitory concentration was 6.8-fold greater for the so-called small fraction.

This indicates that the aggregation process contributes to a lower antibacterial activity of fullerene water suspensions. However, there was no linear relationship between bacteria response and particle size, so the researchers suggest that besides aggregation some other properties may increase small particles. Metal-based ENPs such as Au, Ni, and Ti may also aggregate in soil (Du et al. 2011; Heckmann et al. 2011; Unrine et al. 2010a). Regarding plants, Du et al. (2011) assessed the toxicity of  $\text{TiO}_2$  NPs towards wheat in agricultural soil and observed wheat roots by transmission electron microscopy (TEM). Examination with TEM before spiking in soil showed two size fractions of  $\text{TiO}_2$  NPs in which the mean diameters were (1)  $20 \pm 5$  nm (93.3%), and (2)  $50 \pm 10$  nm (6.7%). Although TEM revealed some small particles in the cortex cell, larger particles adhered to the cell wall of periderm cells; thus, they did not penetrate the wheat root cell. The researchers assumed that  $\text{TiO}_2$  NP aggregation occurring in the soil and in the cell media, previously observed in water suspension reflecting soil solution in French et al. (2009), was responsible for reduced uptake by wheat root (Du et al. 2011). Synchrotron X-ray microspectroscopy revealed Au NP aggregation in an artificial soil solution for two particle sizes [i.e., (1) 20 nm, and (2) 55 nm] at 5, 20, and 50 mg Au/kg dry mass (Unrine et al. 2010a). As a consequence, earthworms (*E. fetida*) accumulated higher amount of the less-aggregated particles, leading to decreases in reproduction.

## Dissolution Processes

Engineered NP dissolution has received a lot of attention, especially in the case of metal-based ENPs, as the released metallic ions may produce toxicity. Dissolution occurs when the ENP is thermodynamically unstable, so ions move from the particle core to the soil solution through the double layer (Borm et al. 2006). This process can take place either in the soil environment or in organism



**Fig. 1.** Processes and factors affecting the behavior and bioavailability of engineered nanoparticles in soils (CEC = cation exchange capacity; MIN = soil mineral particle; and OM = organic matter).

tissues where ENPs release ions inside the cell, acting as “Trojan-horses” according to Dinesh et al. (2012).

Whether the patterns of toxicity may be related to the release of free metal ions is not resolved yet due to the low dissolution rate. Moreover, aggregation may alter negatively dissolution processes as it reduces the surface area and hampers diffusion of free ions from NP aggregates, as noted by Borm et al. (2006) for Ag NPs. This interaction, however, must be further studied, as nanoscale and bulk forms of  $\text{Al}_2\text{O}_3$  and ZnO have similar dissolution rates despite extensive aggregation of the NPs in ultrapure water suspensions (Wang et al. 2009). While some studies observed that the free-metal-ion concentration originating from the ENPs cannot explain the toxicity patterns (Navarro et al. 2008b), other researchers suggested that the toxicity of free ions cannot be discounted (Neal 2008), being even considered in some cases the main mode of action (Ma et al. 2013).

Silver NP toxicity is likely due to the ionic Ag released in pore water (Yang et al. 2012). Shoultz-Wilson et al. (2011a) demonstrated that polyvinylpyrrolidone (PVP)-coated Ag NPs are less toxic to *E. fetida* in artificial and natural sandy loam soils than the equivalent quantity of  $\text{AgNO}_3$ , ENPs toxicity occurring at concentrations 10× greater than those observed for  $\text{AgNO}_3$ . Moreover, X-ray absorption spectroscopy showed that the amount of oxidized Ag from Ag NPs after 28 days fits approximately with the difference in toxic concentrations between  $\text{AgNO}_3$  and Ag NPs, indicating that Ag NP dissolution was the main reason for its toxicity. While assessing  $\text{AgNO}_3$  and Ag NPs toxicity to *E. fetida* in a sandy loam soil, Heckmann et al. (2011) observed that both Ag forms caused the formation of grey shiny particulates on the soil surface, which was delayed and less pronounced for Ag NPs, suggesting that the latter released ionic Ag. Cobalt NPs may also dissolve in soil but both Co NPs and ionic Co are bioavailable to *E. fetida*, suggesting that Co NPs may also dissolve after ingestion in earthworms (Coutiris et al. 2012a). Concerning Cu NPs, both NPs and released Cu ions contribute to their toxicity to *E. fetida* (Heckmann et al. 2011; Unrine et al. 2010b). However, dissolution may be less extensive as Cu NPs and  $\text{CuCl}_2$  caused different gene responses in *Enchytraeus albidus* (Oligochaeta; Gomes et al. 2012). Like Cu NPs, it is not clear to which extent dissolution contributes to ZnO NPs toxicity as the latter cause higher toxic effects than the equivalent amount of ionic Zn towards for some soil organisms (Manzo et al. 2011; Mohanty et al. 2014), despite the fact that several studies established that ZnO NPs toxicity is related to the released ionic Zn (Du et al. 2011; Hooper et al. 2011; Kool et al. 2011; Pipan-Tkalec et al. 2010).

## Sorption Processes

Engineered NPs sorption processes onto soil colloids control their transport (Batley et al. 2013; Cornelis et al. 2010, 2011; Darlington et al. 2009; Jaisi and Elimelech 2009; Pennell et al. 2008), which may affect their bioavailability (Navarro et al. 2008a; Oberdörster et al. 2006; Peralta-Videa et al. 2011; Tong et al. 2007). Nonetheless, it should be considered that the exposure route is species-specific and that certain species like earthworms can counteract the toxic effect of pollutants by moving away from the contaminated area. The role played by soil components in ENPs sorption processes is discussed in a subsequent paragraph.

Sorption will decrease ENPs bioavailability in pore water (Kool et al. 2011) and the presence of a biofilm, a community of microorganisms embedded in matrix of self-developed biopolymers, will promote ENP retention regardless of ENP size and surface chemistry (Jiang et al. 2013; Lerner et al. 2012;

Tong et al. 2010; Tripathi et al. 2012). The biofilm coating porous media may increase ENP retention as it may decrease pore size, and increase deposition and agglomeration, leading to greater straining, as observed by Jiang et al. (2013) for ZnO NPs in quartz sand porous media coated with *Escherichia coli*. In contrast, Mittel and Tufenkji (2014), studying the transport of polyvinylpyrrolidone-stabilized Ag NPs, reported that the retention of PVP-Ag NPs was significant reduced in *Pseudomonas aeruginosa* strain PAO1-coated quartz sand. The researchers concluded that the decreased retention was likely due to repulsive electrostatic forces between the PVP coatings and extracellular polymeric substances of the biofilm grown with a modified method. Thus, further studies are required under natural soil conditions.

## Particle-Dependent Factors Regulating ENP Bioavailability

### Engineered NP Size and Aggregate Size

Engineered NP size directly affects their behavior, transport, and fate in the environment. Engineered NPs that are of small diameter can be highly mobile, which could enhance their bioavailability compared to larger particles (Buffet 2012). Although in general larger ENPs have higher retention (Darlington et al. 2009; Dunphy Guzman et al. 2006; Lecoanet et al. 2004; Phenrat et al. 2009), ENPs may aggregate, resulting in potentially different ENP behavior. The surface properties of ENPs are of essential importance for their aggregation behavior and thus for their mobility in aquatic and terrestrial systems (Farré et al. 2009). Several researchers demonstrated that the stability of ENPs is inversely proportional to their tendency to aggregate (Farré et al. 2009; Mackay et al. 2006). Wang et al. (2012) pointed out the difficulty to evaluate the effect of ENP size on their mobility and subsequent bioavailability because of aggregation processes; thus, accurate characterization of ENPs' state in complex media such as soil is necessary. In addition, Ma et al. (2011) suggested that initial particle size may be more important for toxicity than aggregate size. They reported greater phototoxicity of ZnO NPs to *C. elegans* compared to bulk-ZnO at identical mass concentration, despite the fact that both ZnO forms formed similar-sized aggregates (about 2  $\mu\text{m}$ ) in test solution. The researchers suggested that ZnO NPs packing led to a higher accessible surface area for ROS production. Hydrodynamic diameter determination may also be relevant in certain cases as ENPs of close size classes may have the same hydrodynamic diameter, resulting in similar uptake (Judy et al. 2011). The tendency to form aggregates may vary depending on the kind of ENP, its concentration, and the chemistry of the environment (Tourinho et al. 2012). At a higher exposure concentration in soil, smaller ENPs may aggregate to a greater extent compared to larger primary particles, leading to a lesser accumulation by soil organisms (Unrine et al. 2010a). Particle size may affect also oxidation and dissolution processes, as smaller metal ENPs will dissolve more extensively, leading to a higher exposure concentration of the toxic ionic metal and thus greater toxicity (Masrahi et al. 2014; Unrine et al. 2010b). Nevertheless, this size-dependent toxicity might be possible only between very different size classes (Shoultz-Wilson et al. 2011a). Some exceptions to this relationship may occur, depending on the metal speciation. Dahle and Arai (2014) showed that larger  $\text{Ce(IV)O}_2$  having much greater amounts of Ce(III) impurity were more toxic to denitrifying bacteria because Ce(III) was more toxic than the insoluble  $\text{Ce(IV)O}_2$ . Moreover, the small size and large surface area per unit mass of ENPs induce important binding phases, for both organic

and inorganic pollutants (Klaine et al. 2008), the behavior and toxicity of which are difficult to determine (Moore 2006).

### Engineered NP Concentration

Retention processes are largely dependent on ENPs concentration and ionic strength (Rahman et al. 2013) which may affect ENPs bioavailability. The concentration can be understood in two ways, as follows: (1) mass concentration (milligrams per liter), or (2) particle number concentration (particles/milliliter; Wang et al. 2012), but these researchers suggested using particle number concentration as the basis for comparisons of ENP fate and toxicity. As reported in aerosol research, the surface area and particle number concentrations are better predictors than mass concentrations of risks associated with ENP exposure and toxicity in air (Park 2009; Park et al. 2010).

As mentioned previously, formation of aggregates depends greatly on collisions between ENPs. Increasing particles number concentration will increase the likelihood of creating these contacts. For instance, increasing citrate-coated Ag NP concentration in nematode growth in agar medium led to more extensive ENP aggregation and a decrease in Ag NPs dissolution, which finally caused a weak increase in the toxic effect regarding reproduction and survival of nematodes (*C. elegans*; Kim et al. 2012). However, data relating ENPs concentrations to aggregation processes in soil are very scarce. By focusing on mechanisms of TiO<sub>2</sub> NP transport in porous media, Chowdhury et al. (2011) showed that the role of ENPs concentration is pH-dependent. They demonstrated that at pH 5, ENP concentration contributes to delayed ENP breakthrough. This lag is due to blocking and subsequent NP-NP repulsion. Blocking refers to a decline in the deposition rate due to reduced availability of attachment sites on the collector surfaces and leads to greater elution with ENP concentration. Combined to straining, aggregation, Derjaguin-Landau-Verwey-Overbeek (DLVO)-type interactions, blocking constitute a mechanism of transport and removal of ENPs through porous media. Besides pH, flow rate, and ionic strength, removal mechanisms are supposedly dependent on NP concentration. Bradford and Bettahar (2006), Bradford et al. (2009), Park (2009), and Park et al. (2010) investigated the concentration-dependent colloid retention and transport to understand ENP environmental fate and toxicity. They hypothesized that two main factors are controlling the concentration-dependent colloid retention and transport, as follows: (1) concentration-dependent filling of retention sites, and (2) concentration-dependent mass transfer of colloids to the retention site. In contrast with these results, Zhang et al. (2010) observed that greater input concentrations resulted in increased relative colloid retention at ionic strength >0.1 mM. Furthermore, they attributed that the retained colloids acted as new retention sites for other suspended colloids, i.e., the ripening effect.

### Surface Coating

Engineered NPs surface modifications involve modifications of their interfacial interactions with natural compounds. For inorganic NPs, two ways to carry out surface modifications exist, as follows: (1) surface absorption or reaction with small molecules (such as silane coupling agents), and (2) grafting polymeric molecules through covalent bonding to the hydroxyl groups existing on the particles. This has several engineering applications, such as (1) dispersion of surface-modified NPs in organic solvents, (2) photocatalytic and antibacterial applications, (3) biomedical applications, and (4) removal of trace metal ions (Kango et al. 2013). Related to ENPs, surface coating plays an important role in the

modification of their surface and their retention in different media, and hence their bioavailability. Another consequence of ENPs coating is stabilization; engineered surface modifications providing electrostatic, steric or electrosteric repulsive forces between NPs enable reduced aggregation in order to enhance their transport properties (Jackson et al. 2013; Jiang et al. 2008; Levard et al. 2012; Liu et al. 2012). Moreover, ENPs coating may also affect dissolution processes and thus toxicity mechanisms. For instance, citrate coating of Ag NPs reduced dissolution of the latter, allowing researchers to observe toxicity related to ROS (Yang et al. 2012). In contrast, Coutris et al. (2012b) concluded that uncoated Ag NPs can be more bioaccessible than Ag ions or citrate stabilized Ag NPs, since uncoated Ag NPs can act as a constant source of relatively stable and bioaccessible Ag.

### Soil Properties Affecting ENP Bioavailability

Soil parameters largely affect ENP behavior, either directly (by regulating sorption, dissolution, and aggregation processes) or indirectly (by modification of the particle surface properties). Soil reactive phases such as OM or clay minerals have themselves charged surfaces, which influence the interaction of ENPs with the soil components (Tourinho et al. 2012; Wang et al. 2010). Overall, as previously reported for other soil pollutants, the most important parameters controlling these processes are generally pH, redox potential, ionic strength, CEC, texture, OM, mineral composition, temperature, and the water regime (Kabata-Pendias 2004).

In soils, OM is present in the solid phase (particulate form or as coatings on mineral surfaces) and in the soil solution [dissolved organic matter (DOM)]; the proportion depends on its nature, and on pH and redox conditions (Staunton 2002). The adsorption of DOM to the ENP surface significantly alters its physicochemical characteristics and therefore its behavior in the environment. Humic acid (HA) and fulvic acid (FA) stemming from biomass degradation processes are important in DOM, as well as intermediate degradation products or exudates from soil organisms (Cornelis et al. 2014; Navarro et al. 2008a). The adsorption of HA onto ENPs is much higher than the FA adsorption, both being pH-dependent (Liang et al. 2011; Yang et al. 2009). The interaction of ENPs with HA leads to electrostatic repulsion and steric hindrance, which increases the suspension stability (Deonarime et al. 2011). This alteration of the surface charge of ENPs could decrease their affinity for cell membranes and thus reduce their bioavailability and uptake (Tourinho et al. 2012). Glenn and Klaine (2013) found that DOM was associated with 4 and 18-nm Au NPs in suspension, and form NP-OM complexes that resulted in (1) minimized NP aggregation, and (2) a decrease of NP absorption by aquatic plants. The same effect was not observed with 30-nm Au NPs. Likewise, nutrients may be sorbed onto ENPs and/or HA-ENPs, being less available to organisms which indirectly inhibit microbial growth. However, the presence of divalent and trivalent cations in the soil solution could suppress the electrical double layer at the ENPs surface, leading to aggregation and coating of the ENPs with organic components, which could mitigate ENP toxicity (Calder et al. 2012). Hence, ionic strength and cation nature strongly affect this process (Fig. 1). As observed by Wang et al. (2011a), Cu<sup>2+</sup> had a greater effect on the transport behavior of nanohydroxyapatite (nHAP) than Ca<sup>2+</sup> and K<sup>+</sup> cations, attributed to its strong competition and exchange with Ca<sup>2+</sup> of nHAP. and its surface complexation with nHAP. Moreover, electrostatically stabilized systems are more affected by the ionic strength than those which are sterically stabilized, which particularly occurs in the case of carbon-based ENPs (Cornelis et al. 2014).



Whether an ENP can be hazardous in soil depends largely on the probability of contact with organisms (Dinesh et al. 2012; Neal 2008). Ben-Moshe et al. (2010), while studying the transport of metal oxide ENPs in porous media, observed that the addition of HA stabilized particle dispersion, which in turn led to increase the percentage of ENPs mobility;  $98\% \text{ TiO}_2 = 98\% \text{ CuO} > 74\% \text{ ZnO} > 62\% \text{ Fe}_3\text{O}_4$ . In a similar way, Jiang et al. (2012a) reported that the presence of NOM (including HA and alginate) enhanced ZnO NP mobility, attributed to the electrosteric interaction in the presence of NOM, which reduced the ZnO NPs deposition and NP-NP aggregation. This increase in ENPs mobility due to the interaction with low-molecular-weight NOM compounds in the soil solution could be responsible for the toxicity to soil organisms. In contrast, the formation of larger agglomerates of ENPs by high-molecular-weight NOM compounds may decrease the ENPs bioavailability (Navarro et al. 2008a). Regarding this, Shah and Belozero (2008) attributed the lack of significant influence of Si, Pd, Au, and Cu NPs on soil microbial communities to the immobilization of the ENPs on the soil organic fraction. As these researchers concluded, the ENPs were not able to freely move around the soil, so they were not able to exert a strong influence on the soil microbial diversity. A similar conclusion was reached by other researchers. Thus, Johansen et al. (2008) noted that the toxic effect of  $\text{C}_{60}$  fullerenes on soil bacteria may have been diminished by  $\text{C}_{60}$  adsorption onto soil particles and saturation of their surface with various compounds. As mentioned previously, Tong et al. (2007) observed no significant affectation of  $\text{C}_{60}$  fullerenes on some soil biochemical and microbial properties (respiration, microbial biomass, bacterial diversity, and enzyme activity) in a spiked drummer soil (silty clay loam, 4% OM, pH 6.9). The researchers attributed this result to both OM and salts in soil controlling the  $\text{C}_{60}$  availability, and ultimately the exposure level and toxicity. Likewise, Frenk et al. (2013) observed an alteration on the hydrolytic activity and the bacterial community in two contrasting soils spiked with (1) CuO NPs, and (2)  $\text{Fe}_3\text{O}_4$  NPs, being more evident in the soil with lower clay and OM contents. The same soil components as previously reported for trace metals could regulate the ENP bioavailability to plants (de Santiago-Martín et al. 2014). In this respect, El-Temsah and Joner (2012) observed that Ag NPs were more toxic to ryegrass in a sandy soil than that grown in a clay soil.

Similar results were obtained by other researchers; however, they cannot be always attributed to soil colloids. Thus, despite the low soil OM content, Shrestha et al. (2013) observed no effects of MWCNTs on soil respiration, enzymatic activities, and microbial community composition at 10, 100, and 1,000 mg/kg rates in a sandy loam soil (1% OM, pH 7.34), although an increase of fungal communities was noted at 10,000 mg/kg. In contrast, Jin et al. (2013) reported a significant negative response of soil microbial activity when spiking a sandy loam soil with higher OM content (~3% OM, pH 6.98) with SWCNTs. The researchers also obtained significant negative relationships between the surface area of SWCNTs and certain soil microbial properties (enzyme activity and microbial biomass). As discussed previously, ENPs-dependent factors such as size and surface area of ENPs could be determinant in affecting the bioavailability patterns.

While soil natural colloids (OM and clay) play an important role in decreasing ENPs mobility and toxicity (Pawlett et al. 2013; Shoults-Wilson et al. 2011a), the interaction with soil colloids could concentrate ENPs at specific sites where soil organisms may be particularly exposed (Johansen et al. 2008). In this sense, Vittori Antisari et al. (2013) observed that metal-oxide ENPs ( $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CeO}_2$ ) were associated to small-size (2–53 and  $<2 \mu\text{m}$ ) aggregates in soils (often rich in labile organic C,

microbial biomass C, and clay) and they suggested that the presence of ENPs in the clay fraction negatively affected the soil microbial communities. Similarly, hydrophobic ENPs like fullerenes retained in the organic fraction could be readily bioavailable to bacterial and fungal populations as they use OM as a substrate (Navarro et al. 2008a; Oberdörster et al. 2006). In contrast, moderate contents of soil natural colloids (<30% clay and moderate OM content) possibly create favorable conditions of substrate availability and aeration for microbial populations, which may favor dealing with the resulting stress of ENPs contamination, as observed by Martin Calvarro et al. (2014) for trace metals.

Soil properties or constituents, such as pH, HA, or water content (Benoit et al. 2013; Cornelis et al. 2012; Li et al. 2011), and the action of organisms (Navarro et al. 2008b) can mediate the dissolution processes of metal-based ENPs, being a potential source of free-metal-ions. Waalewijn-Kool et al. (2013) observed that soil pH affected the toxicity of ZnO NPs to *F. candida* and that ZnO NPs and  $\text{ZnCl}_2$  were more toxic in acidic soil than in basic soil. An increase in the dissolution rate could explain this result. However, in the soil environment a rapid reduction of the concentration of free-metal-ions released from metal-based ENPs is likely to occur upon contact with the soil components (such as chloride, phosphate, carbonate, OM, or clay minerals), highlighting the protective role exerted by the soil matrix (Calder et al. 2012; Coutris et al. 2012b). Li et al. (2011) drew similar conclusions as they observed that  $\text{Zn}^{2+}$  released from ZnO NPs and subsequently complexed by DOM had lower toxicity to *E. fetida*. As stressed by these researchers, the effects in these ternary systems [i.e., comprised of (1) ENPs, (2) NOM, and (3) salts] are difficult to predict. Whereas the ion bioavailability is expected to decrease in soils over time, ENPs could effectively act as ion pumps and represent a continuous source of metals (Coutris et al. 2012a). The complex interactions occurring in soils point out the importance of studying ENPs behavior and toxicity in natural soils rather than pure quartz, glass beads, culture media, or extrapolation from water-phase studies (Cornelis et al. 2014; Gladkova and Terekhova 2013; Sagee et al. 2012).

## Conclusions

The field of nanotechnology is still incipient and specific legislation, standardized methodology, and soil reference material is required. Engineered NPs may be bioavailable in soils depending on the routes of exposure of the target organism, thus causing bioaccumulation and/or toxicity (structure, diversity, activity, reproduction, locomotion, and nutrient imbalance) and possibly biomagnifications. The transport of ENPs is often associated with their bioavailability to edaphic biota. However, ENPs suffer different transformations from their interactions with organisms and constituents in soils. Surface coating of ENP with HA could increase the suspension stability and thus ENP mobility. However, alteration of the ENP surface charge could decrease the affinity for cell membranes. Aggregation processes are likely to decrease the bioavailability of ENPs, except in case of membrane disruption or small aggregates (<20 nm) that could penetrate the plant cell wall. These processes are enhanced in the presence of OM, clays, and major cations, and are highly dependent on the kind, size, and concentration of ENPs. Sorption processes seem to decrease the ENPs bioavailability, but a concentration of ENPs at specific sites where soil organisms are exposed may occur. Dissolution of metal-based ENPs can take place either in the soil or inside the cell, and is mediated by soil properties (pH, humified OM, and water content), the action of organisms (plant exudates), and the ENP characteristics

(coating and aggregation). Whether the bioavailability is primarily due to the ENP or to the release of free-metal-ions is not resolved in the literature yet, since (1) dissolution rate may be low, (2) metal concentration can rapidly decrease by sorption processes onto soil particles, and (3) toxicity may be specific to the nanoscale size. Nonetheless, high ENPs accumulation in soils may represent a continuous source of metals. The complex interactions occurring in soils point out the importance of studying the bioavailability of ENPs in natural soils.

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