Impact of the Nanomaterials on Soil Bacterial Biodiversity

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Sandra I. Concha-Guerrero, Elcia M.S. Brito,
and César A. Caretta

Abstract

In this chapter we first review some characteristics of the nanoparticles and nanomaterial. We will explain their definition, main properties, applications, availability, and toxicity to the prokaryotes. Then, we define the soil as a very complex ecosystem and consider some of its physicochemical-biological properties, in order to discuss the action of the nanoparticles and nanomaterials present. We discuss the use of these substances in agriculture and their ecotoxicological effect. We also examine methodologies and techniques currently used for measuring their interaction with microorganisms and microorganism communities and argue that they are indeed potential contaminants. Since their use, especially in agrochemicals, has largely grown in the last years, and there is still not enough data to support the necessary decisions in local and international regulations concerning human health and the environment, it is urgent to develop and extend this kind of studies.

Keywords

Nanoparticles • Toxicity • Ecotoxicology • Soil • Agriculture

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S.I. Concha-Guerrero (✉) • E.M.S. Brito
Environmental Engineering Department, Universidad de Guanajuato,
Guanajuato, Gto., México
e-mail: ixmucame.guerrero@gmail.com; emsbrito@gmail.com

C.A. Caretta
Astronomy Department, Universidad de Guanajuato, Guanajuato, Gto., México
e-mail: caretta@astro.ugto.mx

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10.1 Nanotechnology

The US Environmental Protection Agency (US EPA 2007) defines *nanotechnology* as the understanding and controlling of matter at dimensions of roughly 1–100 nm, where unique physical properties make novel applications possible (Nowack and Bucheli 2007). This knowledge branch emerged from the physical, chemical, and engineering sciences with the aim of developing new materials, structures, devices, and systems that present properties and functions different from the similar ones at macroscales. A typical example is carbon, a nonmetal that, when forming nanotubes, is one of the best conductors.

According to Santamaria (2012), the first observation and size measurement at a nanoscale was made in 1914 by Richard Adolf Zsigmondy. Thereby, the rise of this science is associated to the development of the scanning tunneling microscope (STM) and the atomic force microscope (AFM), which allowed the manipulation and control of atoms and molecules individually (Prathna et al. 2010; Santamaria 2012). There were exciting news when it was announced that Eigle and Scheweizer could manipulate, in 1989, 35 xenon atoms on a nickel surface to form the IBM logo, initiating the use of applied Nanotechnology.

10.2 Nanomaterials and Their Properties

Nanomaterials (NMs) are materials with morphological characteristics that measured less than 1 μm in at least one dimension. Such materials are usually classified by, beyond their dimensionality, their morphology, composition, uniformity, and agglomeration properties (Nowack and Bucheli 2007). On the other hand, *nanoparticles* (NPs) are substances that have less than 100 nm of size in more than one dimension (Nowack and Bucheli 2007).

The NPs can be divided into natural, incidental, and engineered. The natural ones are ubiquitous in the environment and are produced by natural processes (without human influence); while the incidental are coproduced by processes associated to anthropogenic activities; on the other hand, engineered NPs are produced industrially with specific purposes (Nowack and Bucheli 2007).

The exceptional “abilities” of NPs are associated to the manifestation of quantum effects. When the size of a particle becomes comparable to its fundamental scale (i.e., its wave function), for example, roughly like the Bohr radius for an electron forming an exciton (excited in a lattice), quantum confinement occurs and the energy needed to move an electron (that is, to form the exciton) starts to increase. One of the consequences of it is that, since the energy band gets wider, the wavelength gets shorter, and the ratio of the surface area over the volume becomes larger (Prathna et al. 2010; Dinesh et al. 2012). This can enhance the agglomeration rate, at the same time that the diminution of the particle size leads to more reactivity. Also, the surface charge can facilitate their binding to the targeted biological system (e.g. macromolecules, microorganisms, ions) (Dizaj et al. 2014).

Concerning the NPs' toxicity, there is a clear relation between it and the NP sizes: smaller NPs show a higher toxicity. Due to their small dimensions, they easily enter biological systems and can interact with the macromolecules of the organisms. These interactions can produce ions or free radicals that cause damage to cells, mainly to the DNA itself (Gatoo et al. 2014). Thus, it is important to keep in mind that the physicochemical properties of the NPs depend on a great variety of factors which are strongly influenced by the surrounding environment.

10.3 The Many Applications of Nanoparticles

Different synthesis procedures can manufacture NMs with very particular electronic, optical, physical, and chemical properties (Prathna et al. 2010). These properties, such as size, shape, surface area and charge, crystal structure, chemical composition and reactivity, hydrodynamic diameter, agglomeration, concentration, and porosity and purity, determine their behavior and can be tailored to adjust them for special needs in their targeted application.

Based on quantities in the market, industrial production, and life cycle of NPs, Piccinno et al. (2012) estimate that worldwide NP production is dominated mainly by the ones of TiO_2, ZnO, FeO_x, AlO_x, SiO_2, CeO_2, Ag, quantum dots, carbon nanotubes (CNT), and fullerenes. They found that NMs containing TiO_2 are the largest produced, with approximately 10,000 ton/year, followed by CeO_2, FeO_x, AlO_x, ZnO, and CNT with 100 and 1000 ton/year. According to the literature, NPs are being applied mainly on the areas of engineering, agriculture, electronics, and medicine, particularly on the production of materials for health and fitness, home and garden, electronics and computers, food and beverage, automotive, and appliances (see, e.g., Petersen and Nelson (2010); Santamaria (2012) and Table 10.1). And the commercialized products containing the NMs or NPs are mainly cosmetics, clothing, shoes, detergents, dietary supplements to surface coatings in respirators, water filters, phones, laptops, toys, and commercial home water purification systems (e.g., Nowack et al. 2011; Bondarenko et al. 2013).

10.4 Nanoparticles in the Environment

Undoubtedly, nanotechnology has provided several applications and has driven many innovative developments, becoming important in the global economy (Scott and Chen 2013). However, they may also represent a new source of environmental contamination, not yet controlled or even understood.

NPs released to the environment may come from punctual or non-punctual sources (Table 10.2). Examples of the first sources are production facilities, landfills, and wastewater treatments. While for the second, we can mention the wearing materials containing NPs (Nowack and Bucheli 2007). Also, NPs can be released to natural compartments via sewage treatment plants and waste handling reaching the soil or water bodies, or arrive to them indirectly, for instance, via aerial deposition or

Table 10.1 Use and applications of NPs

Kind of NPs	Applications or potential use	References
Pt, Ag, Au, Cu, Pd, Ni and Rh	Used to modify the semiconductor properties and enhance their photocatalytic activity	Devi and Kavitha (2014)
Fe_3O_4	Drug delivery promise	Guo et al. (2009)
Au and Ag	Candidate to photothermal therapy and promising contrast agent for dark-field image studies	Sau et al. (2010)
MoS_x, Cu, CuO, PbS, TiO_2, ZnS, LaF_3, and WS_2	Lubricant/oil additives	Bakunin et al. (2004), Liu et al. (2004), and Wu et al. (2007)
Cu, CuO, Al_2O_3, TiO_2, and Ni	Used to enhance the heat transfer on fluids, for instance, on solar cells	Ebrahimnia-Bajestan et al. (2011)
CuO and ZnO	NPs' deposition on textiles	Abramova et al. (2013, 2014)
TiO_2	Used as photocatalysts for degrading many organic contaminants	Ohko et al. (2001) and Dasari et al. (2013)
ZnO, TiO_2 and Ag	Used in cosmetics and skin care products	Patel et al. (2011) and Nipane et al. (2012)
Co_3O_4	Used as catalysts, in electrochromic devices, gas sensors, solar energy absorbers, and magnetic materials	Li et al. (2005, 2011), Liang et al. (2011), Zhong et al. (2012), and Dasari et al. (2013)
Al	Potential use as fuels for space launch vehicles, rockets, and missiles	Ohkura et al. (2011) and Ahn et al. (2013)

Table 10.2 Main sources of NPs or NMs released to the environment

NM production	Laboratories or factories can release the NPs during their synthesis processes
Nanoproducts	Released from products containing NMs, such as cleaning products, clothes, detergents, personal care (cosmetics, sunscreens, etc.), technological products (electrodes, conductors, semiconductors, dielectrics), etc.
Intentional discharges	Release of nanopesticides or materials containing NMs, such as municipal wastewater
Transport and storage products	Through the accidental spills, discharges, and leakage

Adapted from Keller et al. (2013)

runoff (Nowack and Bucheli 2007). Nevertheless, previous studies have suggested that the concentration of NPs is higher in soils than in water or air systems; while the soil microbiota and plants are the major eco-receptors of soil NPs (Maurice and Hochella 2008; Klaine et al. 2008; Gottschalk et al. 2009; Tiede et al. 2009).

Concerning the effect of NPs over the biota, in natural compartments, their persistence seems to be an important characteristic, besides their toxicology.

NPs may persist in the system for a long time, be taken by the organisms (possibly bioaccumulated), or even be transferred among organisms of different trophic levels (Anjum et al. 2015).

10.5 Soil

Soil constitutes one of the most fascinating ecological systems, where the microorganisms; micro-, meso-, and macrofauna; microflora; and plant roots interact among themselves and also with the abiotic part, modifying their surroundings although usually on a perfect homeostasis. Following this view, it is appropriate to mention the soil definition proposed by Atlas and Bartha (1986): "The soil is a structured, heterogeneous and discontinuous; fundamental and irreplaceable system; developed from a mixture of organic matter, minerals and nutrients capable of supporting the growth of organisms and microorganisms." It has been recognized that the soil is not an inexhaustible resource and that it may, if inappropriately used or mismanaged, be rapidly lost (Nortcliff 2002). It governs plant productivity of terrestrial ecosystems and is very important for the maintenance of most the biogeochemical cycles (Nannipieri et al. 2003).

The main problems associated to the soil are soil degradation and contamination. *Soil degradation* can be defined as "a process which lowers the current and/or future capacity of the soil to produce goods or services" (Oldeman 1994) and is related to: (a) the displacement of the soil material and (b) the deterioration of the soil in situ. Soil degradation can be caused by erosion and by chemical and/or physical factors. From these, soil degradation caused by the erosion is the most studied process and has been recorded since ancient times, reason for it to be recognized as a classical problem of soil loss. Soil erosion is a complex process that depends on soil chemical properties, ground slope, vegetation coverage, and rainfall amount and intensity (Montgomery 2007), usually associated to the changes in land use, such as demographic pressure, deforestation, and/or agriculture. The physical factors that can cause soil degradation are, for instance, waterloggings, subsidence, soil compaction, crusting, and sealing. Chemical factors that can disturb the soil are the loss of nutrients and organic matter, soil salinization, acidification, and pollution (Oldeman 1994).

Highlighting the *soil contamination* topic, there are a vast list of products and processes that can cause some damage to the soil's health, such as waste accumulation, excessive use of pesticides, excessive manuring, oil spills, deposition of airborne pollutants, such as heavy metals like lead (metal refineries), arsenic, zinc, cadmium (motor vehicle emissions) etc. (Montgomery 2007). The NMs must also be included on this list, since their production and applications have grown extensively in recent times and thus their environmental input as a consequence. However, while other kinds of contaminants can easily be recognized as contaminants, it is difficult to make evident that NMs or NPs are the pollutants. For this reason, NPs' contamination is "a kind of invisible pollution" (Gao et al. 2013; Anjum et al. 2015).

10.6 Interaction of Nanomaterials and Nanoparticles with the Soils

Since the soil is a very complex ecological system, composed by different minerals, organic material, and living beings, the interaction of the NPs with it will strongly depend on the soil's parameters, as well as on the properties of the NPs.

The main properties of the soil, that is, the ones that define its fertility (porosity, hydraulic conductivity,[1] cation exchange capacity,[2] pH, and amount of organic carbon), are also important factors for defining the interaction NPs-soil (Nowack and Bucheli 2007; Ben-Moshe et al. 2013). Moreover, the total soil biota (microbial communities, earthworms, nematodes, protozoa, fungi, arthropods, and plants) can affect strongly this interaction (El-Temsah and Joner 2012; Concha-Guerrero et al. 2014; Servin and White 2016). Particularly, the soil retention capacity may be affected by its ionic strength, pH, zeta potential, and texture (Pachapur et al. 2016), while the aggregation ability of soil particles, transport, and eco-toxicity of NMs in the environment may depend on the soil ionic strength, pH, and surface charge (Joo et al. 2009). On the other hand, NPs' mobility inside the soil (mean free path) is probably the main parameter governing their interaction. This is directly related to their relationship with the water; their ability for aggregation or dispersion, adsorption or desorption, and dissolution or precipitation; as well as with their decomposition rate (Dinesh et al. 2012).

Although there is a consensus about the importance of the above parameters, the interaction of NPs-soil itself and the level of toxicity of the NPs are not well defined and sometimes prone to debate. On the case of the organic matter, for instance, while Ben-Moshe et al. (2013) verified no effect of it over the reactivity of the NPs, Nowack and Bucheli (2007) observed that the organic matter could lead to the formation of aggregates of NPs, favoring their precipitation and, consequently, decreasing their bio-disponibility. On the other hand, other authors have shown that the adsorption of NPs to the soil organic matter may enhance their suspension in aqueous solution, therefore increasing the NPs' mobility (Mansouri et al. 2015; Pachapur et al. 2016). Finally, all these studies agree that the capacity of the NPs for acting as sorbents depends on their surface area, reactivity, and ionic charges, as already pointed out.

Anyway, it is paramount to expand our knowledge about the interaction, toxicology, and degradation mechanisms of NPs in the soil and other ecosystems. Only then will we be able to define politics and make informed decisions about the use, risks, advantages, and consequences of the use of NPs in the soil or general release of them to the environment.

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[1] Capacity of a soil, rock, or plant of letting the percolation of a fluid, usually the water

[2] CTC is the total amount of cations ($Ca^{2+} + Mg^{2+} + K^{+} + H^{+} + Al^{3+}$) retained on the surface of the soil colloids (clays, humic substances, and oxides of Fe and Al).

10.7 Use of Nanoparticles in Agriculture

An agrochemical (or agrichemical) is any chemical substance used in agriculture, even if its use is also extended to non-agronomic applications (home and garden, forestry and industry), with the aim to control seeds, competing herbs, insect pests, and diseases in crops (McDougall and Phillips 2003). Examples of agrochemicals are fertilizers, pesticides, herbicides, fungicides, and feed supplements. Once an agrochemical has been applied, one part of it may be volatilized, while the remaining part will be integrated to the soil. Depending on its chemical and physical characteristics, it will be solubilized in the water soil and can be translocated into the plants; but, the excess will remain and be incorporated into the water ground, becoming a great environmental problem hard to mitigate. Besides the contamination of water resources and residues on food products, there are also the health and social problems associated to their application. Nevertheless, agrochemicals have been extensively used to do different degrees in various countries, under different health and environmental laws.

The interest on using NPs in the agriculture has flourished recently, with innumerable applied research projects developing novel nanoagrochemicals, especially the ones known as “nanopesticides” and “nanofertilizers” (Kah 2015). Nanotechnology is a new science which promises a revolution over the old techniques with the introduction of new materials and products better than those that already exist. Specifically for the agriculture, it may improve the area of “precise farming” (e.g., Table 10.3), which searches the means for maximizing agricultural production outputs while minimizing production input, by also meeting the increased needs of the world’s sustainability (Chen and Yada 2011).

However, the use and application of such nanoagrochemicals must be regarded as a particularly critical case in terms of environmental impact since they represent a direct source of NPs to the environment. This caution is reinforced by our lack of knowledge of the risks and consequences of these new NMs into the ecosystems. There is a certain consensus that the data to allow a clearly safe assessment for the use of nanoagrochemicals is still insufficient. This leads some to defend that “the application of nanopesticides should be prohibited until they are proven to be entirely safe,” although this is, in some sense, unrealistic because all pesticides are inherently toxic (Kah 2015). Also, the use of NPs and NMs is already a reality, as far as the direct contact of people with products that contain them and their release to the environment (Musee 2011; Raj et al. 2012; Keller et al. 2013). The scientific community has different viewpoints: while some tend to convey a very positive image of the nanotechnology (as usually do the material scientists), others prefer to focus on the risks to the environment and human health associated to the use of the NPs (as usually do the environmental scientists) (Kah 2015; Prasad et al. 2017). This debate is important to support decision-making processes, e.g., for local or international regulations, but also for giving objective information to the population and direct users.

Table 10.3 Possible advantages of nanotechnology for agriculture

Nanotechnology	Description	Advantages
Nanoscale carriers	Carriers to store, protect, deliver, and release the intended payload, in the desired specific amount, for crop production process (improves stability against environmental degradation)	May enable the controlled application of agrochemicals, reducing the total amount applied, avoiding overdoses, and minimizing the waste
Field nanosensors	Field sensing systems to monitor the crop conditions and environmental stresses	Real-time monitoring of crop growth, allowing optimal planning and control ling the level of water, fertilizers, pesticides, herbicides, etc.
Nonintrusive nanocomponents	Characterization tools to study physical, chemical, and biological inter actions between plant cell organelles and disease-causing pathogens	Enables the study of plant disease mechanisms for developing treatment strategies
Nanotechnology gene sequencing	Study of genomes of crop cultivates and genetic engineering	Improves plant resilience against environmental stresses and diseases
Lignocellulosic nanomaterials	Development of new nanoscale cellulosic nanomaterials from crops and trees	New nano-biomaterials for food, packaging, construction, and transportation

Adapted from Chen and Yada (2011)

10.8 Ecotoxicology of Metallic NPs to Prokaryotes

It is well known that the microbial abundance in soils[3] is greater than the abundance of eukaryotic organisms (Torsvik and Øvreås 2002). Another point of common consensus is the importance and integrity of the soil microbial pool for the good health of these ecosystems. Thus, it is preeminent to understand the toxicology of NMs and NPs to these microorganisms. Agrochemicals may contain metals (Dizaj et al. 2014), as well as their counterpart containing NMs (Chen and Yada 2011). In this section, we will focus on the understanding of ecotoxicology of mettalic NPs on prokaryotes of soils.

The starting point is the direct interaction between the NPs and the cellular surface. Since the bacterial membrane is negatively charged, when positively charged NPs, such as NPs of Al_2O_3 and SiO_2, are available, they may be attracted by the cells and the interaction is favored, as was observed by Jiang et al. (2009). The negativity of the membrane is usually generated by carboxyl, amide, phosphate, hydroxyl groups, and carbohydrate-related moieties aggregated to the bacterial cell wall, providing sites for molecular-scale interaction with NPs.

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[3] Estimated to amount 26 Pg in cellular carbon, or about 5–7% of the total mass of prokaryotes in the Earth (Whitman et al. 1998).

The studies focused on the cytotoxicological mechanisms caused by metal NPs have pointed mainly two possibilities: free metal ion toxicity coming from the dissolution of the metals by the NPs and oxidative stress via the generation of *reactive oxygen species* (ROS), both on the surface of NPs (Dizaj et al. 2014). Other mechanisms, such as van der Waals forces and electrostatic, hydrophobic, and receptor-ligand interactions, have also been considered as possible explanations for cell damage caused by NPs.

The oxygen-derived prooxidants, or ROS, are long known to cause biological damage, especially to lipids, DNA, and proteins. They can be classified into two groups of compounds: radicals and nonradicals (Kohen and Nyska 2002). The ones in the *radicals group* contain at least one unpaired valence electron and are capable of independent existence (Rice-Evans 1994; Halliwell and Gutteridge 2015). Examples of them are the nitric oxide radical ($NO^{\bullet}$), superoxide ion radical ($O_2^{\bullet-}$), hydroxyl radical ($OH^{\bullet}$), peroxyl ($ROO^{\bullet}$), and alkoxyl radicals ($RO^{\bullet}$) and one form of singlet oxygen ($^1O_2$). The occurrence of one unpaired electron results in high reactivity of these species by their affinity to donate or obtain another electron to attain stability. The ones in the *group of nonradicals* are also extremely reactive, even though they are not radicals. Among the compounds produced in high concentrations in living cells that can be considered on this group are the hypochlorous acid (HClO), hydrogen peroxide (H_2O_2), organic peroxides, aldehydes, ozone (O_3), and O_2 (Cao and Prior 1998; Halliwell 1990, 1995).

Studies of the generation of ROS on NP surfaces in model microorganisms (Jiang et al. 2009; El-Temsah and Joner 2012; Dizaj et al. 2014; Wyszogrodzka et al. 2016) have pointed that the bactericidal potential decreases as $OH^{\bullet} > O_2^{-} > H_2O_2$ (Maness et al. 1999; Anjum et al. 2015). These studies have shown that ROS can cause deterioration of the membrane architecture, leading to alterations in cell-membrane properties; they also interfere on the activity of metalloenzymes and damage the integrity of DNA. Apparently, ROS formation by metallic NPs is a photoinduced mechanism (Dasari et al. 2013; Wyszogrodzka et al. 2016). Indeed, Wyszogrodzka et al. (2016) state that metal NPs cannot be active in the formation of ROS unless directly illuminated by ultraviolet (UV) light and argue that, when ROS is generated, it is probably a defense mechanism. On the other hand, Jiang et al. (2009) and Dasari et al. (2013) verified the production of free radicals by metal NPs, that is, even under dark conditions.

The general action mechanisms of NPs, that is, their capacity to produce ROS, to link to the membrane components, and to be internalized by the cells, are wide and depend on several factors. Overall, it is related to chemical speciation, stability and aggregation of NPs, and their size, shape, and concentration, besides the surrounding physicochemical characteristics (such as pH, luminosity, etc.). As can be seen in Table 10.4, ZnO and TiO_2 are examples of NPs capable to produce ROS (Dasari et al. 2013; Carré et al. 2014). However, it is already unclear if some other NPs, such as CuO, can do the same. For instance, Dimkpa et al. (2011), Dasari et al. (2013), and Concha-Guerrero et al. (2014) verified that bacteria exposed to different concentrations of CuO NPs presented cellular damage and even cell death. Nevertheless, Dasari et al. (2013) and Concha-Guerrero et al. (2014), who used low concentrations of CuO NPs, did not detect ROS production, while Dimkpa et al. (2011)

Table 10.4 Some studies on the toxicology of NPs by using single-species experiments

Results	Reference
TiO_2 photocatalytic reaction causes the lipid peroxidation reaction; as a result, normal functions associated with an intact membrane, such as respiratory activity, are lost	Maness et al. (1999)
On Gram-negative bacteria, the AgNPs (1–10 nm) attach to the surface of the cell membrane disturbing its basic functions, like permeability and respiration; they penetrate the cell where they can interact with sulfur- and phosphorus-containing compounds (such as DNA); they release Ag^+ with bactericidal power	Morones et al. (2005)
AgNPs may target the bacterial membrane leading to a dissipation of the proton motive force	Lok et al. (2006)
NPs’ surface changes play a dominant role on adsorption processes	Nowack and Bucheli (2007)
Antibacterial activity of metallic NPs (Al_2O_3 , SiO_2, and ZnO) was observed, indicating possible production of free radicals under dark conditions	Jiang et al. (2009)
Metallic NPs of Ag and CuO showed bactericidal effect, while ZnO NP caused bacteriostasis (≤1 mg Ag/L and ≈10 mg CuO and ZnO)	Gajjar et al. (2009)
Accumulation of intracellular ROS only when the cells were treated with toxic levels of CuO NPs and Cu ions, respectively 500 mg/L and 2.5 mg/L	Dimkpa et al. (2011)
Nano-sized zero-valent iron (nZVI) at ≥500 mg.kg^{-1} showed negative effects on the soil invertebrates	El-Temsah and Joner (2012)
NPs of TiO_2 (1.7 mg/L) and ZnO (0.05 mg/L) produced ROS inducing damage on the *E. coli* cells, while any ROS production was observed by CuO (0.2 mg/L) and Co_3 O_4 (35.0 mg/L)	Dasari et al. (2013)
CuO NPs (160 mg/L) were observed to cause strong damage (e.g., holes and cavities on the membrane cells and cellular death) on soil native bacteria strains (*Brevibacillus laterosporus* CSS8, *Pantoea ananatis* CSA35, *Chryseobacterium indotheticum* CSA28 strains), probably due the formation of Cu^{2+} ions	Concha-Guerrero et al. (2014)
Some evidence of oxidative stress was observed when *E. coli* strains were exposed to MgO NP (1 mg/mL). The cells exhibited severe membrane damage	Leung et al. (2014)
TiO_2 NPs (0.4 g/L) induced production of ROS on *E.coli* culture modifying the membrane structure (proteins and lipids); the $O_2^{\bullet-}/^1O_2$ were the main compounds involved in the lipid peroxidation	Carré et al. (2014)
NPs of metal oxides, specially ZnO, NiO, CoO, CuO, and Cu_2O, and their antibacterial activity have been attributed to the formation of reactive oxygen species (ROS)	Wyszogrodzka et al. (2016)
At low concentrations of ZnO NPs (50–100 mg/L), cellular growth was stimulated; at median concentrations (500–900 mg/L), damage on the membrane cells was observed, mainly holes and cavities on the membrane cells; finally, at concentrations as high as 1000 mg/L, cellular death is observed	not yet published

observed the accumulation of intracellular ROS, but only when the cells were treated with hyper-toxic levels of CuO NPs (500 mg/L).

The ability of the microorganisms to grow on biofilms may also affect the interaction of NPs with them. The biofilms usually act as protective layers and are composed by exopolysaccharides (EPS); however, proteins, nucleic acids, (phospho) lipids, and humic substances have also been found on them (Denkhaus et al. 2007). All these compounds may interact with the NPs, probably by reducing their electrostatic interaction and, thereby, decreasing their availability to interact with the cells. Dimkpa et al. (2011), for instance, verified that the presence of EPS could in fact protect bacterial strains against the action of CuO NPs and Cu ions. Similar results were obtained for Cu-doped[4] NPs and TiO_2 NPs by Wu et al. (2010).

10.9 Evaluation of NPs' Toxicology over Soil Microbial Communities

Most published works on the potential ecotoxicology of NPs are based on experiments that use single species. Also, they usually prove laboratory or type strain representatives of a model group (such as *E. coli*, *Pseudomonas* sp., *Paracoccus* sp., *Bacillus* sp., etc.), with very few works using native strains. The advantages of working with model strains are that they are very adapted to laboratory conditions and their physiology is well known, which makes it easier to analyze and compare the results. On the other hand, native strains do not have these advantages, and, worse, they need to be isolated from the environment and characterized to determine their best growth conditions, before the toxicity assays are carried out. Nevertheless, the use of native microorganisms is much more realistic: native strains behave differently from laboratory ones (growth rate, nutritional requirements, etc.) and may respond in a distinct way to any determined environmental stress. Thus, the results obtained with these strains must be used to validate the assays with model strains.

Moreover, single-species experiments only give a glimpse about the effects of the compounds over the microorganisms. As mentioned before, soil is a very complex biological system, and it is necessary to construct experiments as realistic as possible taking into account all the variables and conditions that occur in the environment. An alternative is the use of soil microcosms. By definition, *soil microcosm* is a "replicable experiment unit containing soil and which allow the observation of the ecosystem structure and function." Thus, it must be sufficiently complex to really reproduce the ecosystem under study; that is, it must be self-perpetuating or, at least, have relatively stable communities (Giesy Jr. and Odum 1980; Tarradellas et al. 1996).

In practice, these conditions are hardly obtained since frequently the drying, sieving, and storing of soils for preparing the microcosms change their physical characteristics, as well as the difficulty to maintain the expected humidity and temperature. In order to alleviate these problems, the American Society for Testing and

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[4] Cu NPs to which specific impurities (called "dopants") were added for giving them desired properties.

Materials (ASTM) described a standard method for a minimum soil microcosm (Van Voris 1988). This includes the use of an intact soil core in a system that lets water and sunlight as input and collects the leakage output. Some improved soil-core microcosms were also suggested, as the one proposed by Checkai et al. (1994). Specifically, they incorporate to the standard microcosm: sampling core retrieving techniques for minimal disturbance and controlling of the environmental parameters of the soil – including soil moisture regime (matric tension, rainwater quality, quantity and rate of application) – and soil temperature.

To evaluate the cytotoxicity of NPs, the most frequently reported measurements are the lethal doses (LD) and the inhibitory concentration doses (IC_{25}, IC_{50}), always accompanied by at least one or two chemical, physical, biochemical, and/or physiological additional tests. To directly inspect the physical damage caused to the membrane cells (cavities, holes, membrane degradation, blebs, cellular collapse, and lysis), electronic microscopy observation is often used. Specifically, to evaluate NPs' toxicity in soil microcosms, there are additional techniques that measure the metabolic response of a system (like the Biolog EcoPlates™) and the changes on the community pattern (Brito et al. 2007). Traditional fingerprint molecular tools, such as denaturing gradient gel electrophoresis (DGGE), terminal restriction fragment length polymorphism (TRFLP), clone libraries, and patterns of neutral lipid fatty acids (NLFAs) and phospholipid fatty acids (PLFAs), are frequently used. Pointing to the future, next-generation high-throughput DNA sequencing techniques (MiSeq and HiSeq) will probably replace previous ones for studying the genetic diversity of environmental samples. The combined use of several methods to evaluate the toxicity, especially in the case of the NPs, which have many possible action mechanisms not completely understood, gives more reliability to the results.

Dasari et al. (2013), for instance, measured the metal ions and ROS production, the concentration of specific enzymes (e.g., glutathione), and the peroxidation of lipids for molecular level evaluation. Carré et al. (2014), in turn, used proteomic assays, verifying that TiO_2 NPs modified the protein pattern of the membrane. By using LD, IC_{25}, and IC_{50} indices, the level of exoenzyme esterases (as soil metabolism indicators), the ROS concentration, the metabolic activity, and the direct observation of the cells by electron microscopy analysis, Concha-Guerrero et al. (2014) and Concha-Guerrero (2015) studied the toxic effect of Cu NPs over soil native bacteria. Their results showed no ROS detection although significant cellular death was present suggesting a strong toxicity to the cells. They attributed this damage to the generation of nitrogen reactive species, a hypothesis that still needs to be verified by molecular approaches, by studying the genes involved in nitrogen cycles or by the expressed protein pattern. Another relatively simple technique is the use of Biolog EcoPlates which make possible to perform a screening of metabolic activity of the sample. By applying this approach, our group is studying the effect of the CuO NPs on native strains isolated from agricultural soil samples (Concha-Guerrero et al. 2014) and on microbial communities using soil microcosms (Concha-Guerrero 2015).

Table 10.5 summarizes some results on NPs' toxicity by using model microcosms. These studies show that the NPs tend to form aggregates on soil. The depth on the soil where the contaminant is found, soil texture, and movement of water and

Table 10.5 Soil toxicology assays using microcosms

Soil system	Probed NP(s)	Observations	Methods	Reference
100 g dw of soil (18% water)	CuO	The total number of soil bacterial communities was reduced significantly (48%); also a drift on the composition of the soil community pattern was observed after 30 days	TRFLP[a] metabolic and enzymatic activities	Concha-Guerrero (2015)
6 g dw of soil (80% water)	TiO_2, $TiSiO_4$, FeCo, Ag	All NPs tended to form large aggregates when in soil suspension; all NPs drifted the soil population	DGGE[b]	Nogueira et al. (2012)
5 g soil-sludge (95:5)	PVP-Ag[c], Ag_2S, Ag^+	Ag, populations of actinomycetes, and Gram-negative and Gram-positive bacteria and fungi were impacted, mainly by PVP-Ag and Ag^+ treatments	NLFAs[d] , PLFAs[e]	Judy et al. (2015)
Dry soil	CuO, Fe_3O_4	CuO NPs affected more strongly the bacterial community than Fe_2O_4 NPs; the NPs affected the microscopic properties of the soil	SMP[f] , FTIR[g] and DGGE[b]	Ben-Moshe et al. (2013)
50 g of soil	Fe_3O_4	The NPs stimulated the soil urease and invertase activities and the growth of some bacterial groups (*Duganella*, *Streptomycetaceae*, or *Nocardioides*), although not their relative abundance in the soil	DGGE[b], clone library, RT/qPCR[h], soil enzyme activities	He et al. (2011)
Soil	CNT (C_{60} – Fullerene)	Induced a drift on the soil bacteria community between 20 and 30%	Biomass, DGGE[b], soil respiration	Tong et al. (2007)
200 g of soil	Functionalized CNT	The FMWCNT[i] caused a low shift on the bacterial community composition	RT/qPCR[h]	Kerfahi et al. (2015)
100 g soil + *Cucumis sativa* and *Zea mays* plants	CuO and ZnO	More toxicity was observed from CuO than from ZnO NPs, reducing the biomass of the plants	Metabolic and enzymatic activities	Kim et al. (2013)

(continued)

Table 10.5 (continued)

Soil system	Probed NP(s)	Observations	Methods	Reference
2 kg of soil + maize seeds	ZnO	The arbuscular mycorrhizal fungi may help to alleviate the ZnO toxic effect in plants; the NPs were accumulated on roots and shoots of maize plants	Root colonization, EM [j] , photosynthetic pigments	Wang et al. (2016)
2 kg of soil + soybean seeds	ZnO	Electro-dense ZnO NP deposits in stem and root cells were observed; the ZnO NPs inhibited the elongation and growth of the plant	EM [j], metals	Yoon et al. (2014)
Soil + earthworms	Al_2O_3	The Al_2O_3 NPs can impact on the reproduction and cause earthworm behavior changes (*Eisenia fetida*)	Biomass, metals	Coleman et al. (2010)

[a] *TRFLP* terminal restriction fragment length polymorphism
[b] *DGGE* denaturing gradient gel electrophoresis
[c] *PVP-Ag* polyvinylpyrrolidone coated with AgNP
[d] *NLFAs* neutral lipid fatty acids
[e] *PLFAs* phospholipid fatty acids
[f] *SMP* soil macroscopic properties (porosity, hydraulic, conductivity, amount of organic matter, cation exchange capacity)
[g] *FTIR* Fourier transform infrared spectroscopy
[h] *RT/qPCR* real-time qPCR
[i] *FMWCNT* functionalized and raw multiwalled carbon nanotubes
[j] *EM* electron microscopy analysis

pollutants on it also affected, in different ways, the toxicity of a contaminant (El-Temsah and Joner 2012). The behavior of the exposed biota, such as its home range, also defines its exposition to the xenobiont (El-Temsah and Joner 2012). In almost all of these experiments NPs did modify the structure of the microbial soil communities.

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