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Review

Behavior and characterization of titanium dioxide and silver nanoparticles in soils

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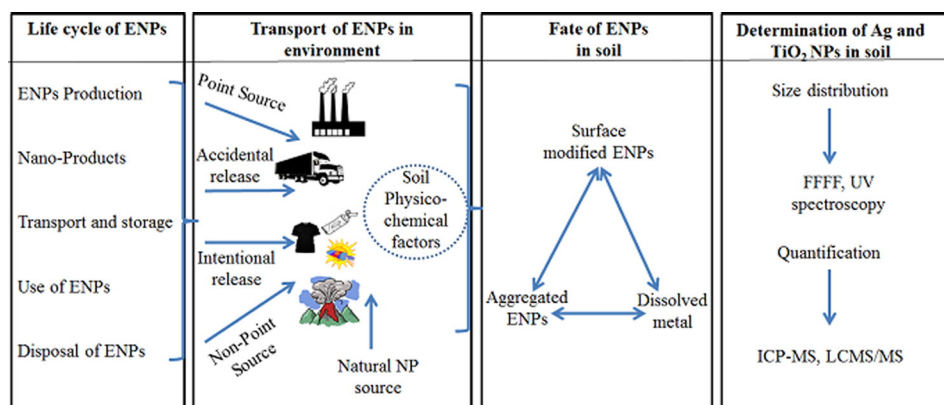
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HIGHLIGHTS

- Humic acids modify coating affecting mobility of nano Ag and TiO₂.
- Bio-availability and toxicity are also affected by coatings.
- Increase mobility increases risk of negative effects.
- Interaction ENPs-environment need to be addressed in a conservative way.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence and transport of emerging Engineered Nano Particles (ENPs) in the environment is driven by combination of multiple factors comprising their size, charge and aggregation/agglomeration rate along with interactions with different soil types. Due to the complexity of the soil, it is difficult to associate an exact concentration with the possible transport pathways, interactions and transformation mechanisms. Major uncertainties arise with the increased number of extraction and filtration steps required for determining the exact toxicity doses of ENPs. Due to these issues, TiO₂ and Ag behavior, characterization, transport, and environmental effects in soils are still not clear. In soils, TiO₂ and Ag have been mainly reported to be present in the surroundings of point sources and are driven by their aggregation/agglomeration rate in combination with different soil types. TiO₂ and Ag are mainly transported by interstitial water depending on their zeta-potential in the local soil. Along the transport route, TiO₂ and Ag undergo alteration in dissolution, corrosion, redox reaction and coatings with the soil matrix. Their mobility is better across mineral soil in comparison to soil rich in organic colloids. The bioavailability gets modified and, in consequence, they are retained until complete degradation of the organic matrix. Depending on the soil matrix composition in terms of water content, minerals, and biological structure, the current most used methods for TiO₂ and Ag characterization are FFFF and UV spectroscopy coupled with

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ICP-MS and LCMS/MS. The increased flux of TiO₂ and Ag across soil is significant in understanding/accessing the viable threats, in particular their release affects the natural ecosystem.

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1. Introduction

Particle sizes with at least two dimensions between 1 and 100 nm are defined as nanoparticles and are commercially used across several industrial processes (Cumberland and Lead, 2009; Klaine et al., 2008). Over the last 30 years, nanotechnology has engineered many structures (Bartłomiejczyk et al., 2013), with 1750 types in 2012 compared to 212 types in 2006 (Peyrot et al., 2014). Market potential of engineered nanoparticles (ENPs) is doubling every three years, for instance Ag NPs (antibacterial) market will rise from 0.79 billion in 2014 reaching \$2.54 billion by 2022 (Grand View Research, 2015). In contrast, TiO₂ annual production is around 6 million tons (Jovanović and Guzmán, 2014), being already a billion dollars market with a price of approx. 2000\$ per ton (ICI, 2015). The term of ENPs usage throughout the study is in with respect to TiO₂ and Ag nanoparticles. The number of nano based products will reach an estimated \$3 trillion market by 2020. Their properties, size, surface area, zeta potential, and quantum effects can be tailored to adjust to special needs enabling dual-use technology applications, such as nano-electronics, -coatings, -optics, -sensors, -monitors, -textiles and nano-weapons (Anne and Kirsten, 2014). ENPs are frequently used in electronic devices, cosmetics, environmental remediation, energy and textile industry (Bindhu and Umadevi, 2015; Peyrot et al., 2014). The possibility of feature engineering has shown a great potential with increased interest in medicine and health-related areas, such as cancer treatment and targeted drug delivery systems due to their antibacterial and antiviral properties (Cumberland and Lead, 2009). ENPs have become a general-purpose technology, expected to increase with innovation and commercialization to generate economic value. However, there is a need to create social and environment value for the society (Roco et al., 2011).

During production, at the time of land application for biosolids wastewater treatment, accidental spills or applications of nano-pesticides, ENPs find their way into the soil environment Fig. 1 (Cornelis et al., 2013). Most studies related to transport of ENPs have been performed using well-defined lab conditions, although their relevance with transport of ENPs in the natural soil environment is questionable. Only few studies have examined ENPs transport in natural soils and no systematic research of the effect of soil properties and its microbial community was conducted (Cornelis et al., 2013; Sagee et al., 2012).

Depending on exposure modeling, soil is the major sink for most of the ENPs released into the environment and their concentrations were higher in comparison to water or air (Dale et al., 2015; Suresh et al., 2013). Since the fate and transport of ENPs in the environment also involves interactions with soil microbial systems, it is widely recognized that nanomaterial-microbial interactions may also impact human health (Suresh et al., 2013).

ENPs have been examined for their potential toxicity (Table 1), associated environmental risk and consequently considered as emerging pollutants (Cañas et al., 2011; Chai et al., 2015; Choi and Hu, 2008; Throbäck et al., 2007). Understanding ENPs behavior requires better elucidation of environmental and human health risks for establishing tailored regulatory guidelines (Peyrot et al., 2014). The recent studies for hazard assessment of ENPs on different food-chain level organisms, such as bacteria, algae, fish, crustaceans and nematodes indicated that metal ENPs (such as Ag, TiO₂, ZnO and Cu) are toxic at environmentally relevant concentrations (Cupi et al., 2015; Holden et al., 2014).

ENPs are often used for their powerful antimicrobial and antiviral properties and have adverse effects on the survival, reproduction and mobility functions of soil organisms (Cornelis et al., 2013), depending upon the ENPs dose, size, shape and reaction with the soil environment (Cumberland and Lead, 2009). ENPs colloidal stability dominates their toxicity and is affected by many factors, such as capping agent, background electrolyte composition, environmental pH and ionic strength (Cornelis et al., 2013; Sohn et al., 2015). The behavior of ENPs across soil environment also varies with different forms of ENPs, which results in bio-availability, chemical changes and possible transformations in the soil environment (Cornelis et al., 2013).

In this study the emphases on the most commonly used nanoparticles, TiO₂ and Ag as examples, considering their transport into the soil, their influence on soil quality and effect on soil organisms. Information related to its characterization and development of these ENPs for their release into the environment is also discussed.

2. Presence of engineered nanoparticles

TiO₂-NPs used as white pigment in body tattoos date from ancient times (Sciau, 2012). There are many natural NPs originating from

constituents of soil, coal, dystrophic lakes, ocean water, surface ground water and some from interstellar origin caused due to impact of comets and asteroids on earth (Heck et al., 2014; Neubauer et al., 2011). The behavior of these natural NPs resulting from weathering in the presence of humic acids is almost identical to ENPs developed in laboratory (Ciglenečki et al., 2014; Rana and Kalaichelvan, 2013) creates a background from which ENPs can be hardly discriminated.

Man-made engineered nanoparticles are produced at a nano-scale (above 1 nm and < 100 nm) with its physical-chemical properties differing from the same material having larger particle size. TiO₂ finds its application across medicine for burn treatment, dental compositions, antibacterial agents and sunscreen lotions (Bindhu and Umadevi, 2015). Applications of AgNPs are also spread across varied consumer products, which include cosmetics, textiles, water purifiers, food packaging surfaces, linings in dishwashers or washing machines, coolants in refrigerators/air conditioners. In addition to biomedical applications, such as antibacterial, sensors and detectors (Bindhu and Umadevi, 2015; Calder et al., 2012). Moreover, multiple potential applications in agriculture has been developed as nanosensors for detection of animal and plant pathogens, in food processing as nanocapsules for flavor/taste enhancement, in food packaging as nanofilms to avoid. The latest addition of ENPs across edible products or that could be ingested, such as canola active oil, nanotea, nanoceticals slim shake chocolate, maternal water, nanosupplements, nano toothpaste and toothbrush with registered companies across the world under the project on emerging nanotechnologies increased not only the range of applications but also the exposure scenario (Weir et al., 2012; Wijnhoven et al., 2009). In this context, human exposure to ENPs is inevitable.

Once ENPs are released into the environment, they find their way into the soils; depending upon the composition and nature of the soil type, the transport and transformation process of ENPs initiates. ENPs not only react with soil but also interfere with various aspects of soil organisms. Hence, determining total amount of ENPs in soil may not provide the full picture with respect to their exposure and bioavailability estimation. In this sense, the bio-accessibility can be defined as the fraction of available ENPs to cross an organism's cellular membrane from the soil at a given time (Baláž et al., 2013). Bio-accessibility encompasses both bioavailability and potential availability of ENPs and it is mainly determined for metals content in soil (Peijnenburg et al., 2007; Riding et al., 2015). In this sense, partitioning and aging of ENPs drive their behavior in contact with different environment matrices (Couttris et al., 2012; Tavares et al., 2015).

To calculate their environmental concentration, researchers came-up with several analytical techniques, such as probabilistic material flow analysis considering the life-cycle of ENPs products. On surface waters,

the concentrations have been estimated to range from 0.003 ng/L (fullerenes) to 21 ng/L (nano-TiO₂) while in sewage treated effluents they range from 4 ng/L (fullerenes) to 4 µg/L (nano-TiO₂) (Gottschalk et al., 2009). Using various variables, such as production volume, location, particle release with their flow coefficient, researchers have created a life-cycle perspective model for quantification of nano-silver in rivers reached 0.002 ng/L and 1.5 ng/L respectively (Dumont et al., 2015) which underlined the current need of addressing this emerging problem.

It is very difficult to determine the exact concentration of ENPs in soil due to its complex nature. Across the studies (Cornelis et al., 2013; Couttris et al., 2012; Dumont et al., 2015), the natural NPs presence tends to behave and show similar background signals to that of ENPs. This complicates their differentiation and use of control sample populations would allow estimating the man-made contribution.

3. Transport of engineered nanoparticles

During manufacturing, transportation, application and disposal, the ENPs are inevitably released into the environment (Lin et al., 2010; Sun et al., 2015a). These ENPs enter the environment through direct: metal remediation of contaminated soil, photocatalyst during water treatment or indirect modes human activities, such as fuel combustion or waste incineration accidental spillage, industrial effluent and release from nano-products (Bakshi et al., 2015; Soni et al., 2015; Sun et al., 2015b; Yin et al., 2015) and many others mentioned above.

The discharged ENPs get transported and transferred through the different environmental reservoirs i.e. water, soil, air, organisms and can play a very important role in the environment along the life cycle that can affect the balance of the communities. The entry, cycling and deposition of ENPs in the environment are schematically represented in Fig. 1. If released into the air, ENPs behave like an aerosol, traveling some distance from the source and finally depositing into soil and water bodies. More precisely, when they enter the water bodies, ENPs may get aggregated and precipitate to sediments which depend on the properties of ENPs and conditions of water chemistry. Altered ENPs break through soil-matrix to reach ground water and are transported by water flow (Dumont et al., 2015; Lin et al., 2010). ENPs get retained by soil particles due to the particular soil features, such as ionic strength, pH, zeta potential and soil texture which dominate the ENPs transport process. Due to these factors, diverse behavior of ENPs in soils occurs, such as aggregation, deposition, and stabilization (Darlington et al., 2009; Peralta-Videa et al., 2011; Sun et al., 2015a). ENPs can be subjected to transformation and degradation steps, such as dissolution in aqueous phase, oxidation, photo-degradation and passivation by coexisting matter. Different

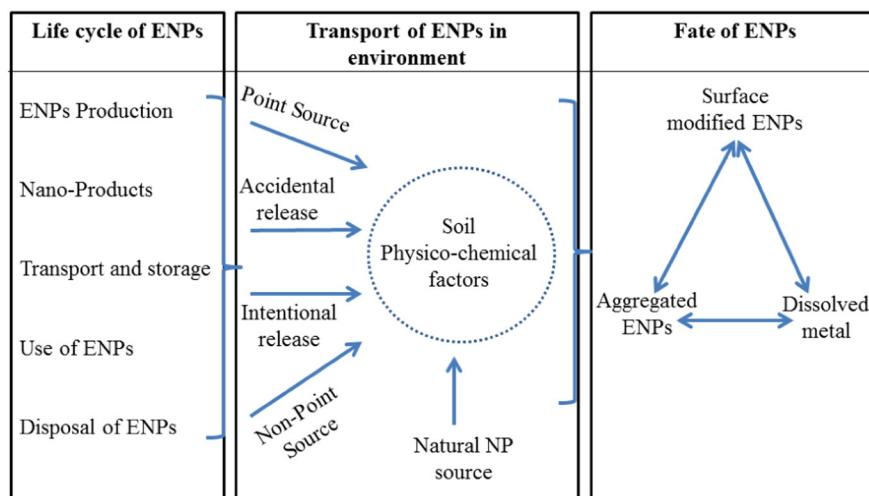


Fig. 1. The entry, transport, and fate of engineered nanoparticles in environment.

organisms may take-up the ENPs, which may lead to bio-accumulation (Kim et al., in press; Lin et al., 2010).

3.1. ENPs behavior with soil organic matter

Due to the high specific surface area of the natural colloids present in soil, ENPs get adsorbed to these substances, which in-turn facilitates their transport. Most of these colloidal surfaces are negatively charged and adsorb positive ENPs by electrostatic attraction and ligand exchange. In the presence of dissolved organic matter (e.g. humic and fulvic acid), the colloidal stability of ENPs increases along the distance traveled (Cornelis et al., 2013; Peralta-Videa et al., 2011; Wuithschick et al., 2015). The enhanced stability of humic acid-coated ENPs occurs due to strong steric stabilization and the adsorbed humic acid swells with increase in osmotic potential (Ghosh et al., 2009; Nielsen et al., 2015). This is because humic acid is sorbed on the surfaces of nanosized TiO₂ and ZnO, with a decrease in their zeta potential indicating the fact that humic acid-coated nano-oxides could easily disperse and suspend in solutions (Mansouri et al., 2015; Yang et al., 2009). In contrast, deposition and collision efficiency between soil media and ENPs may result in reduced AgNPs mobility with potential risk from off-site transport (Cornelis et al., 2013; Watson et al., 2015). Free migration and deposition of ENPs depended on several interactions, which are affected by soil solution chemistry, such as ionic strength and presence of organic matter (Peralta-Videa et al., 2011; Philippe, 2015). The ionic strength of soil organic material is important parameter and investigated extensively across TiO₂ and AgNPs. The interaction is depended on spherical particles with van der Waals and electrical double-layer interactions (Cornelis et al., 2013; Lin et al., 2010; Saleh et al., 2015). Thus, the interactions between ENPs and soil media strongly influence the balance between free mobility of particles and the deposition of ENPs across the soil environment.

3.2. ENPs interaction with soil minerals

Chemical stability studies of AgNP and nano-ZnO were carried out in the presence of mineral suspensions indicating no change in AgNP during several months, but nano-ZnO rapidly dissociated within 1 day. Hence, there is no direct evidence on ENPs interactions with soil materials (Dror et al., 2015; Peralta-Videa et al., 2011). In some cases, the mobility of ENPs might be retarded due to adsorption of ENPs on the

surface of soil minerals. Therefore, the interaction between soil minerals and ENPs depends on the surface charge and presence of soil minerals which play an important role in sorption behavior (Joo et al., 2009).

3.3. ENPs interaction with existing soil contaminants

Soil contaminants mainly consist of herbicides and pesticides along with inorganic pollutants, such as heavy metals and trace elements from mining, industrial and technological activities. Due to their large surface area most of the soil contaminants get removed from the environment by using the high specific surface area of the ENPs with their super paramagnetic property along with their elevated sorption capacity (Martínez-Fernández et al., 2015). The toxic soft metals, including Hg, Ag, Pb, and Cd tend to adsorb on the specific surface functional ligands of ENPs (Mahdavi et al., 2015). The ENPs tend to behave like receptors by transformation into porous microstructures controlling the transport of trace contaminants (Bakshi et al., 2015). Such functional ligands are indirectly used for the degradation of herbicides. In this case, ENPs tend to degrade them efficiently under aerobic conditions, but degradation is complete for instance in the presence of Pd catalyst under anaerobic process (Zahedi et al., 2015). ENPs interaction with trace contaminants depends on several factors, such as nanoparticle transportation, environment effect, aggregation and contaminant uptake rate (Bakshi et al., 2015; Cruz et al., 2015).

3.4. Transport of ENPs in soil columns

When it comes to behavior of ENPs in soil systems, only few research studies have been carried out. The stability of TiO₂ NPs was studied in saturated homogeneous soil columns collected from different regions possessing various physical and chemical characteristics. The soil sample was air-dried for 1 week at room temperature and sieved (across 2 mm) to remove debris before carrying out experiments (Fang et al., 2009; Wang et al., 2014, 2015). The transport distance of TiO₂ ranged from 41.3 to 370 cm, suggesting a potential risk of underground water contamination (Fang et al., 2009). On the contrary, inorganic and organic coated ENPs are important determinants of mobility and may enhance the transport of ENPs (Jaisi and Elimelech, 2009). The dissolved forms of AgNPs are toxic to many organisms, such as microbes, invertebrates and somewhat less for fish and humans (Osborne et al., 2015) but the magnitude of these effects depends on the amount of AgNPs,

Table 1
The toxicity effect of engineered nanoparticles on microorganisms in soil.

ENP	Objective	Size (nm)	Dosage	Bacterial strains	Observation	Ref.
Ag	To study the size-dependent inhibition and evaluate inhibition with ROS on Nitrifying bacteria	9–21	0.05–1 mg/L	Nitrifying bacteria	Inhibition to nitrifying organisms with AgNP <5 nm being more toxic	Choi and Hu (2008)
Ag	To study dose dependent effect on denitrifying bacteria	–	0.003–100 mg/kg	Soil denitrifying bacteria	Sigmoid dose-dependent reductions in denitrification activity with no recover till 90 days	Throbäck et al. (2007)
Ag, Cu, SiO ₂	To study the toxicity effect on plant-associating bacteria	15–20	0.066% (w/w)	Soil bacterial communities	High latitude soil contaminated with NP induced respiration and DNA damage	Kumar et al. (2011)
ZnO	To study chronic toxicity of nano-ZnO and ionic-Zn on soil earthworm	<100	250–750 mg/kg	Soil earthworm	Survival rate, immune activity decreased with effects on life history traits	Hooper et al. (2011)
ZnO, TiO ₂	To study acute and reproductive toxicity of NP on soil earthworms	40–100	0.1–10 ⁴ mg/L (acute) 0.1–10 ³ mg/kg (reproduction)	Soil earthworm	No acute toxicity but reproductive effects to earthworms in soil	Cañas et al. (2011)
Ag	To study the concentration effect on bacterial growth colony	–	0.1–0.5 g/kg	Soil dehydrogenase activity	Survival rate and soil dehydrogenase activity decreased	Murata et al. (2005)
Nano-Ag	To study the effects of silver NPs on soil microorganisms	20 nm	100 mg/kg	Bacteria and fungi	Reduced enzymatic activity and decreased substrate uptake	Sillen et al. (2015)
ZnO, SiO ₂ , TiO ₂ and CeO ₂	To study the effect of metal oxide NPs on bacteria	–	1 mg/g	Bacteria	Reduced abundance of functional bacteria and enzymatic activity	Chai et al. (2015)
Ag-NPs	To study effects of silver NPs on soil invertebrates	10 nm	1500 mg/kg	<i>Eisenia fetida</i>	glutathione reductase and oxidative damage	Gomes et al. (2015)

colloidal stability, its bio-availability, chemical changes and possible transformations in the soil environment (Cornelis et al., 2013). The behavior of ENPs is largely dependent on soil media transport and it also varies with different forms of ENPs. For instance, a recent study on PVP coated AgNPs indicated that mobility increased with pH, the capacity of exchanging ions, and the content of organic matter in the soil matrix, while iron oxide decreased mobility as well as calcium and potassium (Wang et al., 2015).

4. Fate of engineered nanoparticles

ENPs aggregation is an association of colloid particles and adhering surface by forces, such as electrostatic repulsions and van der Waals forces. Aggregation of similar ENPs creates homo-aggregation and dissimilar ENPs with clay materials create hetero-aggregation. Aggregation plays a significant role in ENPs transformations, which depends on critical coagulation concentration, aggregation attachment efficiency, capping agents, and preparation methods of ENPs and pH conditions of soil environment (Dwivedi et al., 2015). ENPs collide through Brownian motion increasing their size with repeated collisions forming agglomerates of ENPs. The collision rates of ENPs during agglomeration by Brownian movement have more influence during the transport in comparison to turbulence force. Agglomeration is directly related to the number of primary ENPs that form agglomerates, as well as the presence of dissolved organic carbon (DOC) and depends on media with high ionic strength (Soni et al., 2015). The clustering process of nanoparticles can occur through irreversible aggregation or reversible agglomeration. Distinguishing among them is not an easy task using conventional techniques and therefore an electrochemical nano-impact technique was recently described for Ag clusters (Sokolov et al., 2015). A schematic representation of the aggregation and agglomeration processes is shown in Fig. 2. ENPs aggregation and agglomeration are affected by environmental physical forces, such as Brownian motion, gravity and fluid motion (Casals et al., 2012) and the probability of collision between two ENPs is believed to be directly proportional to the rate of the aggregation (Tourinho et al., 2012). Resulting aggregates lead to formation of particle flocs and are of sufficient size to get sedimented by gravity. Aggregation rate and size of formation depend on the concentration of ENPs. Nevertheless, not all ENPs form

aggregates; few ENPs were detected in suspensions suggesting variation in size distribution among particle types (Casals et al., 2012). Agglomeration leads to different surfaces, concentrations, and mobility behavior of ENPs, which are very specific but differ from the initial ENPs. The highly agglomerated ENPs may be less mobile than the well-stabilized ones during transportation (Casals et al., 2012; Tourinho et al., 2012). ENPs aggregation and agglomeration are time-dependent processes requiring few seconds to weeks and this property must be considered in the biological tests. During evaluation of ENPs for toxicity assay, the aggregation and agglomeration can create confusion. Thus, it is necessary to control aggregation/agglomeration degree and colloidal stability in soil (Casals et al., 2012).

Dissolution and corrosion processes for ENPs are also widely studied (Lin et al., 2010). They are derived from the interest of the metallurgical industry for presence of metal ions and its biological impact on the environment. Corrosion is nothing but rust associated with degradation of iron from iron-based tools. In the case of ENPs, the corrosion ability of metallic ENPs (Ag, Fe and Au) releasing metal ions for their induced toxicity is studied. Corrosion of ENPs with its release of ions ends up in different chemical species (Ito et al., 2001; Stack et al., 2011). The ions released from inorganic NPs cause more detrimental effects with higher biological implications in short-term period. ENPs with reduced size, high surface-to-mass ratio, and high radii present less coordinated atoms at the surface tend towards dissolution during the oxidative process (Casals et al., 2012; Stack et al., 2011). The dissolution of ENPs is subjected to various events, such as chemical reactions due to exposure to oxygen or chlorine or enzymes and also due to thermodynamic/kinetic favorable conditions which tend to disintegrate ENPs (Ag, Fe and Au) into their constituent atoms (Casals et al., 2012). Due to their size distribution, released ions lose their chances to return to pure ENPs and are driven towards dissolution in the environment (Casals et al., 2012; Tourinho et al., 2012).

On the other hand, ENPs can get trapped between the soil pores influencing particle retention in soils, which depends on particle size and pore size distribution. Only few ENPs show higher travel distance and they are potential risks to groundwater contamination. The transport gets affected due to electrostatic interactions between charged particles of soils (Tourinho et al., 2012) and also with microorganisms leading to bioaccumulation which slows down their transport.

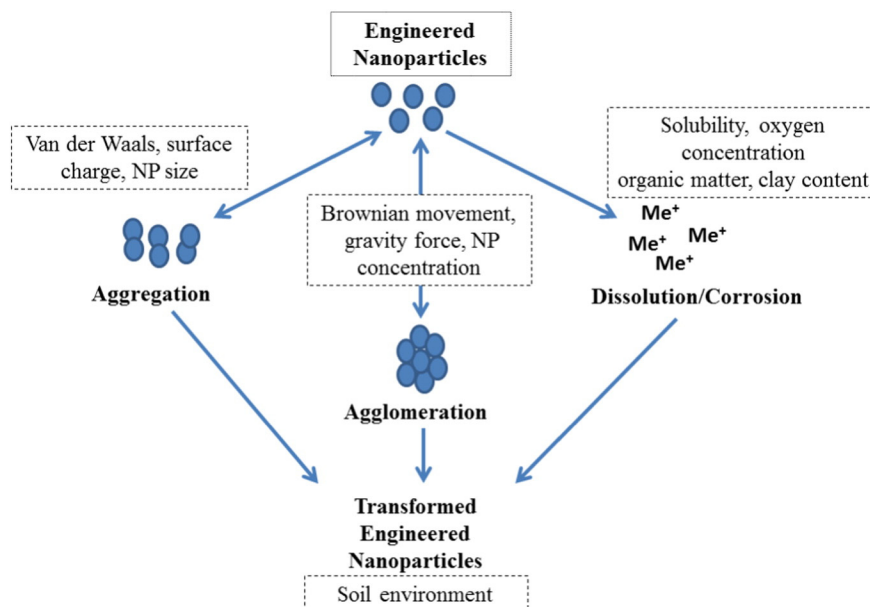


Fig. 2. A schematic representation of the aggregation and agglomeration process along with dissolution and corrosion process are represented for an engineered nanoparticle.

The studies on the negative effects of ENPs are increasing along with the increase in the production of these ENPs. To minimize the negative effects and also to understand the future of ENPs, it is necessary to assess their fate, toxicity and biological effects on an urgent basis (Lopez-Serrano et al., 2014). All this depends on the oxidative aging of ENPs surface over exposure to UV light or aggressive soil chemistry (Mittelman, 2015). The nanomaterial-microbial interactions may also impact on the human health by external or internal ways of exposure. External exposure is nothing but the bioavailability of ENPs in the surrounding environment. Internal exposure refers to the ENPs intake, which might be metabolized and transferred to different organs and tissues (Lopez-Serrano et al., 2014) causing different effects with varying size and dosage as seen in Table 1. In the microbial communities, the indirect effects can occur due to the interaction with natural organic matter, as well as direct interaction with toxic compounds which would cause a synergistic toxic effect (Dinesh et al., 2012). The uptake of ENPs by microorganism depends on the pH, which results in ecotoxicological toxicity associated with solubility/dissolution kinetics of ENPs (Milani et al., 2015; Read et al., 2015).

To study the toxic effect and bioaccumulation of ENPs in soil biota, the nematode *Caenorhabditis elegans* is the model organism selected in most cases. The exposure of *C. elegans* to nano-ZnO, TiO₂ and AgNPs decreased its reproduction rate, growth inhibition, cell rupture, altered enzyme activity, apoptosis, etc. (Peyrot et al., 2014). The soil worm, *Eisenia fetida* was exposed to ENPs, triggered glutathione reductase activity and caused oxidative damage at higher dosage as result of bioavailability of metal in salt-form along with a partial effect caused by release of metal ions from the ENPs (Gomes et al., 2015). The nano-silver exposure (100 mg/kg) and TiO₂ (1 mg/g) on soil fungi and bacteria caused decreased enzymatic activity, altered substrate uptake rate and abundance (Chai et al., 2015; Sillen et al., 2015). Till date, however, there are no publications describing the transport of ENPs by soil microorganisms.

The toxicity of ENPs on soil microorganisms depends on the mode of intake by the cell, through endocytosis or phagocytosis (Bartłomiejczyk et al., 2013). Eventually, molecular mechanisms of toxicity within the cell may differ for different ENPs and living organism. But the primary and common cause of ENPs toxicity is the dissolution of ENPs into ions (Suresh et al., 2013). Fig. 3 represents different potential interactions of ENPs and modes of toxicity in bacterial cell. The surface bonding of ENPs, cellular internalization, dissolution process, membrane rupture, oxidative and DNA damage are few of the molecular mechanisms of toxicity. In a mesocosms study, the ENPs homo-agglomerated with the organic matter fraction of bacteria DNA and the adsorption rate resulted in persistence of ENPs across the bacterial community (Furtado et al., 2015). These experiments revealed the ENPs toxicity mechanisms across various

cellular levels depending on release, exposure, physical-chemical characteristics of ENPs, agglomeration transport rate and the possible combination of multiple events along with soil properties (Saleh et al., 2015; Soni et al., 2015). The measurements of ENPs particle number concentration with their accurate detection across soil media at natural concentrations will demonstrate and improve our understanding of fate of ENPs (Prasad et al., 2015). It is important to determine the exact concentration of the expected ENPs present in soil, their mode of contact, direct or indirect intake and also different pathways which affect humans.

5. Characterization of engineered nanoparticles

The phase purity, particle and cluster size, surface chemistry, solubility, charge, and crystallinity are the essential characteristics to elucidate NPs homogeneity, stability, reactivity, application, behavior and fate by different means (Kahru and Dubourguier, 2010). Soil consists of solid (minerals and organic matter) and a porous phase that holds gases and water. Through this porous phase, the ENPs are dispersed or mobilized. Hence, the variable nature of each soil makes it difficult to separate extract and collect individual ENPs and their characterization often requires advanced analytical techniques (Ju-Nam and Lead, 2008). Besides, the stability of ENPs in soil is related with its exposition to environmental conditions during their life cycle and fate. Oxidation is likely to be one of the main degradation factors of ENPs in soils (Sanchís et al., 2013). Table 2 describes some ENPs, their specific evaluated conditions and their characteristics identified in soil (Farré et al., 2011; Forouzangohar and Kookana, 2011; Peralta-Videa et al., 2011; Wilson et al., 2008).

The hydrodynamic diameter of ENPs reflects the agglomeration level and it has great impact on the transport and bioavailability, which is the main problem in the characterization of ENPs as seen in Table 2. Nowadays, there is no available general method to characterize or describe ENPs present in soil, as it has multiple geological and environment factors affecting the behavior of ENPs.

A very important step for the ENPs characterization is the physico-chemical analysis of soil, because its water ionic strength, hardness, pH, biochemical oxygen demand, alkalinity and organic matter are the parameters which modify the ENPs behavior (Peralta-Videa et al., 2011). Two key steps for the characterization of ENPs are the extraction-fractionation and separation Fig. 4. In this sense, it has been reported that during the extraction, the solubility is driven by physico-chemical characteristics of ENPs, such as size, shape, and density. Although water is the most important media used to study ENPs behavior, there are also some reports using toluene, ethanol and mixtures (Fang et al., 2009; Sanchís et al., 2013).

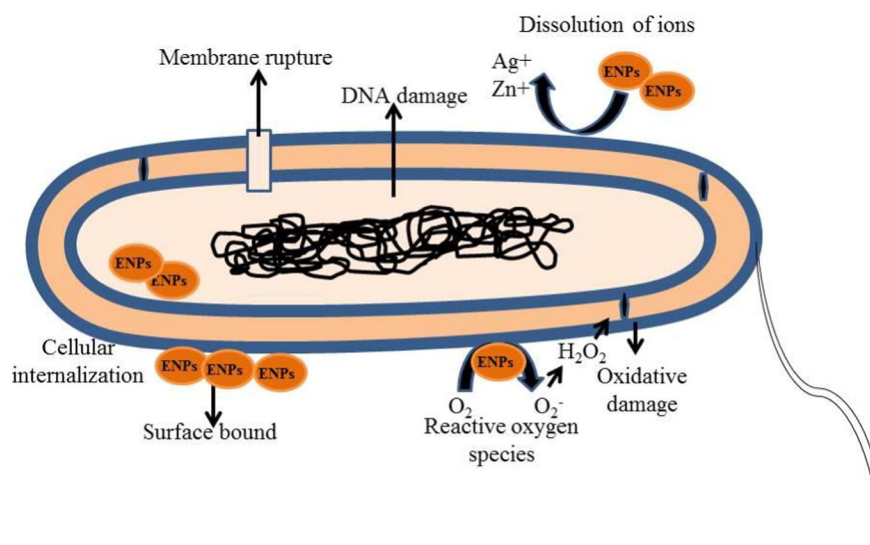


Fig. 3. Schematic representation of bacterial cell with different potential interactions of engineered nanoparticles and modes of toxicity.

Table 2
Characteristics of some NPs identified in soil.

ENPs	Some reported characteristics	Reference
Fullerene C60	<ul style="list-style-type: none"> Hydrophobic compound. Soluble in some organic solvents. Emit fluorescence at room temperature when dissolved in organic solvents. Their solubility in water is about 1.3×10^{-11} g/L. Oxidation when it is exposure to water for a prolonged period. Its surface charge is sensitive to the pH of the system. Tend to agglomerate due to their structural properties and hydrophobic character. Its colloidal properties would be a function of pH and salt content and their deposition would depend on the soil mineral and their charge characteristics. 	Forouzanoghar and Kookana (2011), Peralta-Videa et al. (2011)
TiO ₂	<ul style="list-style-type: none"> Absorb light in the 300–350 nm range. Aggregation and deposition processes soil-dependent, it could remain suspended in soil suspensions even after settling for 10 days. Significantly retained by soils with higher clay contents and salinity. 	Fang et al. (2009)
Al ₂ O ₃	<ul style="list-style-type: none"> Hydrodynamic diameter = 50–99 nm. Zeta potential = strongly positive (30 mV). 	Darlington et al. (2009)
Ag, Hg, Pb, Cd, TI	<ul style="list-style-type: none"> Hydrodynamic diameter of 30 nm. Tendencies for agglomeration in media with higher ionic strength. 	Hagendorfer et al. (2012)

5.1. In-situ extraction of nanoparticles

Stability of ENPs in water is highly influenced by their solubility and dispersibility. The agglomeration and settling are common mechanisms that occur when they enter natural systems, affecting their solubility and mobility (Peralta-Videa et al., 2011). This group of researchers developed a liquid nebulization-differential mobility method to measure

the distribution of sizes and quantitative mass concentrations of twelve nanomaterials in aqueous matrices with a limit ranging from 0.01 mg/L to 3 g/L depending on diameter and matrix complexity. Further, the formation of agglomerates will increase the settling rates in suspension and may impact the deposition from a colloidal suspension to a solid surface (Darlington et al., 2009) misleading actual measurements. To improve the extraction efficiency, Sanchís et al. (2013) suggested that changing the polarity of the extractant solvent (adding methanol) would increase extraction efficiency. More recently, the extraction of nano Ag with different methods resulted in an efficiency of about 50% with 2 M HNO₃, indicating low reactivity, while the Simplified Bioaccessibility Extraction Test gave the highest yields of interaction with organic ligands (Cruz et al., 2015). In addition to solvent effect, the selection of an appropriate technique for the extraction is very important for the adequate characterization of ENPs. Lopez-Serrano et al. (2014) described different techniques for this purpose but only a few have been evaluated for the extraction of ENPs from soils.

5.2. Size distribution of ENPs

Different microscopic techniques, light scattering, X-ray-based and spectroscopy have been used for determination of size distribution of ENPs. Although microscopy techniques are the most well-known, yet they have not been discussed in details in research on ENPs in soils, probably because of the difficulty detecting of ENPs mixed with soil particles.

Flow field-flow fractionation (FIFFF) is a technique reported to characterize particle size distributions (PSDs) in the <1- μ m fraction of 'colloidal' soil suspensions. Gimbert et al. (2006) reported that different soil types have been fully characterized and that <1- μ m fraction is usually obtained by gravitational settling of 1% w/v soil suspensions. Comparing this technique and DLS results for sizes of Ag nanoparticles in soil solution resulted in a close agreement even if the NPs are coated (Koopmans et al., 2015).

FIFFF is applicable to macromolecules, particles and colloids ranging from 0.001 μ m (approximately 1000 molecular mass) to at least 50 μ m in diameter. FIFFF has flexibility in terms of sample type, carrier liquid

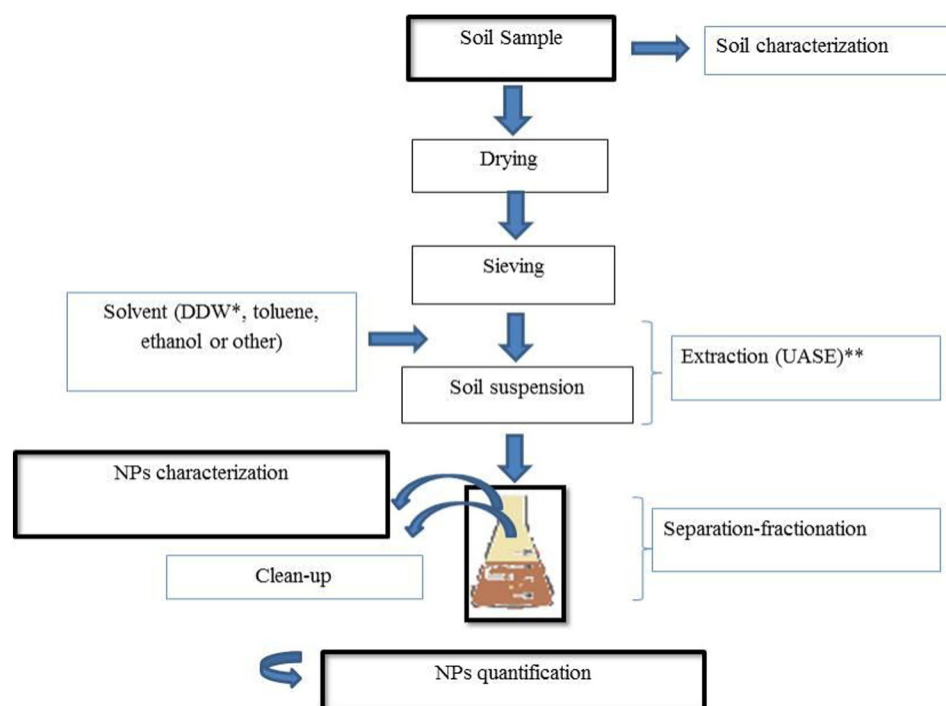


Fig. 4. General scheme for the characterization and quantification of ENPs from soil. *Deionized distilled water. **Ultrasound assisted extraction.

Table 3
Characterization of ENPs in soil with advantages and disadvantages of the analytical methods.

ENPs	Analytical method	Advantages	Disadvantages	Reference
C60 Fullerene	Accelerated solvent extraction (ASE) followed by LC-UV. <i>Separation</i> by gradient elution using methanol–toluene mobile phase. <i>Quantification</i> by ultrasound-assisted toluene extraction followed by liquid chromatography–electrospray ionization–tandem mass spectrometry	Minimization of the extraction step Good recovery in the range 84–107% C60 can be detected and quantified in 19% of the 58 samples of soils analyzed. Concentrations between 0.15 and 6.83 ng/g was quantified. First work that reports the presence of fullerenes in superficial soil.	Limit of quantitation (LOQ) = 20 µg kg ⁻¹ High cost After 5 h, a slight decrease in the efficiency, probably by the toluene heating and analyte degradation. Limits of detection ranged from 14 to 290 pg/g. Extraction in toluene could not reproduce the real conditions at which fullerenes are present in the soil environment.	Giergielewicz-Możajska et al. (2001), Shareef et al. (2010) Sanchis et al. (2013)
	<i>Quantification</i> by HPLC-UV. Consisted in a gradient elution starting with 75:25, toluene:acetonitrile (vol.%) and the gradual conversion after 6 min to 100% toluene to allow a faster elution of the more apolar compounds.	The peaks are fully resolved and elute in the end of the analysis after 17.0 min.	The analysis in environmental matrices can be problematic because of the presence of matrix components in the extracts that can absorb in the same range of wavelengths affecting the detection.	Carboni et al. (2014)
...Gold and silver	<i>Size fractionation</i>	Characterize particle size distributions (PSDs) in the <1-µm fraction of 'colloidal' soil suspensions.	NPs can change under environmental conditions and sample treatment. Sampling and sample preparation have to be optimized to prevent these change.	Gimbert et al. (2006)
TiO ₂	ICP-OES <i>Quantification</i> HPLC-photo array detector (binary mixture ethanol-water), wavelength of 336 nm.	Adequate determination of surface area and average particle size.	Evaluation in soil columns. Future work should study the transport of TiO ₂ in field soil columns.	Fang et al. (2009), Forouzangohar and Kookana (2011)

(solvent), pH and ionic strength. A possible limitation of Asymmetric FFFF is that the elution of coated Ag nanoparticles can be delayed by suspended clay particles, which has to be taken into account for comparisons (Koopmans et al., 2015). Also, FFFF Hyphenated ICP-MS was recently reported to achieve better results than cloud point extraction for quantification of nano silver at ng per kg, since the first concentrates the NPs, and then ICP-MS detects (Mudalige et al., 2015).

Carboni et al. (2014) also reported the use of UV–visible spectroscopic techniques in the characterization of ENPs in soils. These techniques provide information on NP size, aggregation, structure, stabilization, and surface chemistry through the surface plasmon resonance by collective oscillations of their conduction band electrons in response to electromagnetic waves. These techniques have been used jointly with other techniques for the ENPs quantification. Also nanoparticle tracking analysis (NTA) was reported to be useful in matrixes containing large amounts of liquid (Amini et al., 2015).

5.3. Quantification of ENPs

Although ENPs quantification is the third but decisive step to understand and study the processes in which they may be involved, there is a lack of validated analytical methods and standards. However, there seems to be a consensus in the election of ICP-MS to quantify metal and metal-oxide NPs. As a first step, it is recognized that pretreatment of the samples strongly modifies the results. In this sense, Fabricius et al. (2014) indicated that, aiming to establish a standard protocol for quantification of metallic NPs with ICP-MS, ultrafiltration combined with microwave digestion would be the best practice to maximize the measurements. This method delivered recoveries of 99.3%. In contrast Cruz et al. (2015) using acid extraction, reached less than 50%. Further Peters et al. (2014) reported a detection limit of 0.1 mg/kg when quantifying nano Ag in organic matrixes using ICP-MS. In this sense, single-particle inductively coupled plasma mass spectrometry (sp-ICPMS) was tested for a tentative protocol to quantify nano Ag. To do this 23 laboratories in Europe, USA and Canada performed measurements on simulations of food with nano Ag. Particle mass concentration and particle number concentrations were determined, but relative precision was good for Ag particle mass concentrations (78%) (Linsinger et al., 2014). Other techniques were also used for quantification of ENPs in

soils, inductively coupled plasma optical emission spectroscopy (ICP-OES) and high-performance liquid chromatography (HPLC).

For inductively coupled plasma optical emission spectroscopy (ICP-OES) the liquid and gas samples may be injected directly but solid samples require extraction or acid digestion so that the analytes will be present in a solution. Wang et al. (2014) utilized this technique to quantify the concentration of silver in solutions while Antisari et al. (2015) also used this technique to track the transport of Ag TiO₂ and other metals from soil to roots leaves and tomato fruits. Similarly, Servin et al. (2013) quantified TiO₂ uptake in cucumber fruit using µ-XRF, µ-XANES and ICP-OES, while Fan et al. (2014) used it to prove the negative effect of nano TiO₂ in *Rhizobium leguminosarum*. In contrast HPLC, when coupled with ICP-MS, was reported to have a detection limit of ng/L and recoveries over 80% for nano Ag (Soto-Alvaredo et al., 2013).

Adequate characterization of ENPs in soil requires a combination of different techniques based on extraction, size distribution, conditioning and quantification. Some of the ENPs with analytical methods used for extraction, separation and quantification along with advantages and disadvantages are discussed in Table 3. However, an adequate comparison of these techniques in the analysis of ENPs from soils was not possible due to the differences of the aim proposed in each analyzed report and also due to limits of analytical methods. Therefore, as stated above, ICP-MS seems to be currently the most easy and commonly used technique for quantification of Ag and TiO₂ NPs.

6. Future perspective on research in engineered nanoparticles in soil

There are several areas to investigate the presence, fate, transport, impact and characterization of ENPs and to contribute to monitoring, control or mitigating their adverse effects. A study on characterization of ENPs in real conditions represents a step forward towards integration of different research fields. Mapping the presence of ENPs in soils with higher intensity in relation to the hot spots of activities of production, elimination or uses around each site is the key for determining the local range of transport and possible implications. The correlation of the mapping of soils with the frequency of human exposure and toxicity studies could help in the evaluation of the hazard potential of these ENPs.

The development of social programs for the communication and awareness of their hazards could contribute in the responsible use,

treatment and disposal of ENPs in the coming years. Furthermore, studies of ENPs aggregation, deposition, and mobilization during their transport will help to better predict their behavior in soil systems simplifying the application of local regulations and controls. Development of methodologies for the precise and accurate characterization and differentiation of ENPs and their appropriate management is a growing research field. Comparative evaluation between the available techniques under same conditions of sampling and measurement is required for adequate characterization of ENPs. Finally, with all this data, it will be important to organize an international database of the conditions tested successfully in the characterization of ENPs to facilitate the identification of different nanoparticles present in an unknown sample. The implementation of international rules for the production, handling and release of ENPs considering their fate and behavior is still required.

7. Concluding remarks

The behavior of ENPs in soils is driven by their mutual interaction. The potential accumulation of ENPs in soils is mostly studied using simple porous media e.g. quartz and glass beads. However in complex natural soils, the organic matter increases aggregation and agglomeration. Furthermore, these interactions, mainly with humic acids, influence the bio-availability and mobility of ENPs. The toxicity of ENPs varies with soil type and also its transport and bio-availability varies according to soil chemical and physical properties. In addition, more realistic environmental studies using lower concentration over longer exposure periods, are needed, but their variables are difficult to control due to the dynamic changes that the NPs can undergo in a short time period. Other major limitations in ENPs research is the lack of data at environmentally realistic conditions since the background measurements can sometimes mask the results. Furthermore, detection and quantification of low concentrations of silver and TiO₂ NPs in natural soil is requires a large number of extraction and filtration steps, in comparison to standards. During these steps the NPs can further react affecting reliability of the results. Hence, characterization of silver and TiO₂ NPs in soil requires the development of methodologies that combine different techniques as ICP-OES, LC-MS/MS and FFFF to deal with the physico-chemical characteristics of soil. Even with the advanced technologies, major uncertainties do exist till date for the exact dose measurement, precise characterization and use of commercial ENPs for the studies. Because of these limitations, there are some unanswered questions related to ENPs stabilization mechanisms and their effect on the environment. Mobility of ENPs in natural soils under dynamic flow conditions, effect of soil properties on ENPs transport and also the kinetics of desorption under biological relevant conditions need to be further explored.

Nomenclature

ENPs	engineered nanoparticles
CNTs	carbon nanotubes
TiO ₂	titanium dioxide
FeO ₂	iron hydroxide
AgNPs	silver-nanoparticles
FFFF	flow field-flow fractionation
PSDs	particle size distributions
UV-visible spectroscopic	ultra-violet visible spectroscopic
ICP-OES	inductively coupled plasma optical emission spectroscopy;
LC-MS	liquid chromatography-mass spectrometry
HPLC	high-performance liquid chromatography
ESI-MS	electrospray ionization coupled to mass spectrometry

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References

- Antisari, L.V., Carbone, S., Gatti, A., Vianello, G., Nannipieri, P., 2015. Uptake and translocation of metals and nutrients in tomato grown in soil polluted with metal oxide (CeO₂, Fe₃O₄, SnO₂, TiO₂) or metallic (Ag, Co, Ni) engineered nanoparticles. *Environ. Sci. Pollut. Res.* 22 (3), 1841–1853.
- Amini, R., Brar, S.K., Cleon, M., Surampalli, R.Y., 2015. Intertechnique comparisons for nanoparticle size measurements and shape distribution. *Journal of Hazardous, Toxic, and Radioactive Waste (B4015004)*.
- Anne C, Kirsten R-H. Nanotechnology in a globalized world: strategic assessments of an emerging technology. PASC 2014; report number: 2014-006.
- Bakshi, S., He, Z.L., Harris, W.G., 2015. Natural nanoparticles: implications for environment and human health. *Crit. Rev. Environ. Sci. Technol.* 45, 861–904.
- Baláz, P., Buiňáková, Z., Kartachova, O., Fabián, M., Stalder, B., 2013. Properties and bioaccessibility of arsenic sulphide nanosuspensions. *Mater. Lett.* 104, 84–86.
- Bartłomiejczyk, T., Lankoff, A., Kruszewski, M., Szumiel, I., 2013. Silver nanoparticles— allies or adversaries? *Annals of Agricultural and Environmental Medicine* 20.
- Bindhu, M., Umadevi, M., 2015. Antibacterial and catalytic activities of green synthesized silver nanoparticles. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 135, 373–378.
- Calder, A.J., Dimkpa, C.O., McLean, J.E., Britt, D.W., Johnson, W., Anderson, A.J., 2012. Soil components mitigate the antimicrobial effects of silver nanoparticles towards a beneficial soil bacterium, *Pseudomonas chlororaphis* O6. *Sci. Total Environ.* 429, 215–222.
- Cañas, J.E., Qi, B., Li, S., Maul, J.D., Cox, S.B., Das, S., et al., 2011. Acute and reproductive toxicity of nano-sized metal oxides (ZnO and TiO₂) to earthworms (*Eisenia fetida*). *J. Environ. Monit.* 13, 3351–3357.
- Carboni, A., Emke, E., Parsons, J.R., Kalbitz, K., de Voogt, P., 2014. An analytical method for determination of fullerenes and functionalized fullerenes in soils with high performance liquid chromatography and UV detection. *Anal. Chim. Acta* 807, 159–165.
- Casals, E., Gonzalez, E., Puentes, V., 2012. Reactivity of inorganic nanoparticles in biological environments: insights into nanotoxicity mechanisms. *J. Phys. D: Appl. Phys.* 45, 443001.
- Chai, H., Yao, J., Sun, J., Zhang, C., Liu, W., Zhu, M., et al., 2015. The effect of metal oxide nanoparticles on functional bacteria and metabolic profiles in agricultural soil. *Bull. Environ. Contam. Toxicol.* 94, 490–495.
- Choi, O., Hu, Z., 2008. Size dependent and reactive oxygen species related nanosilver toxicity to nitrifying bacteria. *Environ. Sci. Technol.* 42, 4583–4588.
- Ciglenečki, I., Marguš, M., Bura-Nakić, E., Milanović, I., 2014. Electroanalytical methods in characterization of sulfur species in aqueous environment. *Journal of Electrochemical Science and Engineering* 4, 155–163.
- Cornelis, G., Pang, L., Doolette, C., Kirby, J.K., McLaughlin, M.J., 2013. Transport of silver nanoparticles in saturated columns of natural soils. *Sci. Total Environ.* 463, 120–130.
- Coutris, C., Joner, E.J., Oughton, D.H., 2012. Aging and soil organic matter content affect the fate of silver nanoparticles in soil. *Sci. Total Environ.* 420, 327–333.
- Cruz, N., Rodrigues, S., Tavares, D., Monteiro, R., Carvalho, L., Trindade, T., et al., 2015. Testing single extraction methods and in vitro tests to assess the geochemical reactivity and human bioaccessibility of silver in urban soils amended with silver nanoparticles. *Chemosphere* 135, 304–311.
- Cumberland, S.A., Lead, J.R., 2009. Particle size distributions of silver nanoparticles at environmentally relevant conditions. *J. Chromatogr. A* 1216, 9099–9105.
- Cupi, D., Hartmann, N.B., Baun, A., 2015. The influence of natural organic matter and aging on suspension stability in guideline toxicity testing of silver, zinc oxide, and titanium dioxide nanoparticles with *Daphnia magna*. *Environ. Toxicol. Chem.* 34, 497–506.
- Dale, A.L., Casman, E.A., Lowry, G.V., Lead, J.R., Viparelli, E., Baalousha, M., 2015. Modeling nanomaterial environmental fate in aquatic systems. *Environ. Sci. Technol.* 49, 2587–2593.
- Darlington, T.K., Neigh, A.M., Spencer, M.T., Guyen, O.T., Oldenburg, S.J., 2009. Nanoparticle characteristics affecting environmental fate and transport through soil. *Environ. Toxicol. Chem.* 28, 1191–1199.
- Dinesh, R., Anandraj, M., Srinivasan, V., Hamza, S., 2012. Engineered nanoparticles in the soil and their potential implications to microbial activity. *Geoderma* 173, 19–27.
- Dror, I., Yaron, B., Berkowitz, B., 2015. Abiotic soil changes induced by engineered nanomaterials: a critical review. *J. Contam. Hydrol.*
- Dumont, E., Johnson, A.C., Keller, V.D., Williams, R.J., 2015. Nano silver and nano zinc-oxide in surface waters—exposure estimation for Europe at high spatial and temporal resolution. *Environ. Pollut.* 196, 341–349.
- Dwivedi, A.D., Dubey, S.P., Sillanpää, M., Kwon, Y.-N., Lee, C., Varma, R.S., 2015. Fate of engineered nanoparticles: implications in the environment. *Coord. Chem. Rev.* 287, 64–78.
- Fabrizius, A.-L., Duester, L., Meermann, B., Ternes, T.A., 2014. ICP-MS-based characterization of inorganic nanoparticles—sample preparation and off-line fractionation strategies. *Anal. Bioanal. Chem.* 406 (2), 467–479.
- Fan, R., Huang, Y.C., Grusak, M.A., Huang, C.P., Janine Sherrier, D., 2014. Effects of nano-TiO₂ on the agronomically-relevant *Rhizobium-legume* symbiosis. *Sci. Total Environ.* 466, 503–512.
- Fang, J., X-q, S., Wen, B., Lin, J.-m., Owens, G., 2009. Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. *Environ. Pollut.* 157, 1101–1109.
- Farré, M., Sanchis, J., Barceló, D., 2011. Analysis and assessment of the occurrence, the fate and the behavior of nanomaterials in the environment. *TrAC Trends Anal. Chem.* 30, 517–527.
- Forouzangohar, M., Kookana, R.S., 2011. Sorption of nano-C 60 clusters in soil: hydrophilic or hydrophobic interactions? *J. Environ. Monit.* 13, 1190–1194.

- Furtado, L.M., Norman, B.C., Xenopoulos, M.A., Frost, P.C., Metcalfe, C.D., Hintelmann, H., 2015. Environmental fate of silver nanoparticles in boreal lake ecosystems. *Environ. Sci. Technol.* 49, 8441–8450.
- Ghosh, S., Mashayekhi, H., Bhowmik, P., Xing, B., 2009. Colloidal stability of Al₂O₃ nanoparticles as affected by coating of structurally different humic acids. *Langmuir* 26, 873–879.
- Giergielewicz-Możajska, H., Dąbrowski, Ł., Namieśnik, J., 2001. Accelerated solvent extraction (ASE) in the analysis of environmental solid samples—some aspects of theory and practice. *Crit. Rev. Anal. Chem.* 31, 149–165.
- Gimbert, L.J., Haygarth, P.M., Beckett, R., Worsfold, P.J., 2006. The influence of sample preparation on observed particle size distributions for contrasting soil suspensions using flow field-flow fractionation. *Environ. Chem.* 3, 184–191.
- Gomes, S.I., Hansen, D., Scott-Fordsmand, J.J., Amorim, M.J., 2015. Effects of silver nanoparticles to soil invertebrates: oxidative stress biomarkers in *Eisenia fetida*. *Environ. Pollut.* 199, 49–55.
- Gottschalk, F., Sonderer, T., Scholz, R.W., Nowack, B., 2009. Modeled environmental concentrations of engineered nanomaterials (TiO₂, ZnO, Ag, CNT, fullerenes) for different regions. *Environ. Sci. Technol.* 43, 9216–9222.
- Grand View Research, 2015. <http://www.grandviewresearch.com/press-release/global-silver-nanoparticles-market> (accessed November 10, 2015).
- Hagendorfer, H., Kaegi, R., Parlinska, M., Sinnet, B., Ludwig, C., Ulrich, A., 2012. Characterization of silver nanoparticle products using asymmetric flow field flow fractionation with a multidetector approach—a comparison to transmission electron microscopy and batch dynamic light scattering. *Anal. Chem.* 84, 2678–2685.
- Heck, P.R., Isheim, D., Pellin, M.J., Davis, A.M., Sumant, A.V., Auciello, O., et al., 2014. Atom-probe tomography of meteoritic nanodiamonds. *Microsc. Microanal.* 20, 1676–1677.
- Holden, P.A., Klaessig, F., Turco, R.F., Priester, J.H., Rico, C.M., Avila-Arias, H., et al., 2014. Evaluation of exposure concentrations used in assessing manufactured nanomaterial environmental hazards: are they relevant? *Environ. Sci. Technol.* 48, 10541–10551.
- Hooper, H.L., Jurkschat, K., Morgan, A.J., Bailey, J., Lawlor, A.J., Spurgeon, D.J., et al., 2011. Comparative chronic toxicity of nanoparticulate and ionic zinc to the earthworm *Eisenia veneta* in a soil matrix. *Environ. Int.* 37, 1111–1117.
- ICI, 2015. Asia TiO₂ prices likely to rise moderately in 2H 2015. By Gan, A. Independent Chemical Information Service <http://www.ici.com/resources/news/2015/03/03/9864574/asia-tio2-prices-likely-to-rise-moderately-in-2h-2015/>.
- Ito, A., Sun, X., Tateishi, T., 2001. In-vitro analysis of metallic particles, colloidal nanoparticles and ions in wear-corrosion products of SUS317L stainless steel. *Mater. Sci. Eng. C* 17, 161–166.
- Jaisi, D.P., Elimelech, M., 2009. Single-walled carbon nanotubes exhibit limited transport in soil columns. *Environ. Sci. Technol.* 43, 9161–9166.
- Jovanović, B., Guzmán, H.M., 2014. Effects of titanium dioxide (TiO₂) nanoparticles on caribbean reef-building coral (*Montastraea faveolata*). *Environ. Toxicol. Chem.* 33 (6), 1346–1353.
- Joo, S.H., Al-Abed, S.R., Luxton, T., 2009. Influence of carboxymethyl cellulose for the transport of titanium dioxide nanoparticles in clean silica and mineral-coated sands. *Environ. Sci. Technol.* 43, 4954–4959.
- Ju-Nam, Y., Lead, J.R., 2008. Manufactured nanoparticles: an overview of their chemistry, interactions and potential environmental implications. *Sci. Total Environ.* 400, 396–414.
- Kahru, A., Dubourguier, H.-C., 2010. From ecotoxicology to nanoecotoxicology. *Toxicology* 269, 105–119.
- Kim, I., Lee, B.-T., Kim, H.-A., Kim, K.-W., Kim, S.D., Hwang, Y.-S., 2015. Citrate coated silver nanoparticles change heavy metal toxicities and bioaccumulation of *Daphnia magna*. *Chemosphere* (in press).
- Klaine, S.J., Alvarez, P.J., Batley, G.E., Fernandes, T.F., Handy, R.D., Lyon, D.Y., et al., 2008. Nanomaterials in the environment: behavior, fate, bioavailability, and effects. *Environ. Toxicol. Chem.* 27, 1825–1851.
- Koopmans, G.F., Hiemstra, T., Regelink, I.C., Molleman, B., Comans, R.N.J., 2015. Asymmetric flow field-flow fractionation of manufactured silver nanoparticles spiked into soil solution. *J. Chromatogr. A* 1392, 100–109.
- Kumar, N., Shah, V., Walker, V.K., 2011. Perturbation of an arctic soil microbial community by metal nanoparticles. *J. Hazard. Mater.* 190, 816–822.
- Lin, D., Tian, X., Wu, F., Xing, B., 2010. Fate and transport of engineered nanomaterials in the environment. *J. Environ. Qual.* 39, 1896–1908.
- Linsinger, T.P.J., Peters, R., Weigel, S., 2014. International interlaboratory study for sizing and quantification of Ag nanoparticles in food simulants by single-particle ICP-MS. *Anal. Bioanal. Chem.* 406 (16), 3835–3843.
- Lopez-Serrano, A., Olivas, R.M., Landaluze, J.S., Camara, C., 2014. Nanoparticles: a global vision. Characterization, separation, and quantification methods. Potential environmental and health impact. *Anal. Methods* (6), 38.
- Mahdavi, S., Jalali, M., Afkhami, A., 2015. Heavy metals removal from aqueous solutions by Al₂O₃ nanoparticles modified with natural and chemical modifiers. *Clean Techn. Environ. Policy* 17, 85–102.
- Mansouri, F., Kalankesh, L.R., Hasankhani, H., 2015. Removal of humic acid from contaminated water by nano-sized TiO₂-SiO₂. *Advances in Biological Research* 9, 58–65.
- Martínez-Fernández, D., Vítková, M., Bernal, M.P., Komárek, M., 2015. Effects of nanomaghemite on trace element accumulation and drought response of *Helianthus annuus* L. in a contaminated mine soil. *Water Air Soil Pollut.* 226, 1–9.
- Milani, N., Hettiarachchi, G.M., Kirby, J.K., Beak, D.G., Stacey, S.P., McLaughlin, M.J., 2015. Fate of zinc oxide nanoparticles coated onto macronutrient fertilizers in an alkaline calcareous soil. *PLOS ONE* 10 (5), e0126275. <http://dx.doi.org/10.1371/journal.pone.0126275>.
- Mittelman, A.M., 2015. The Effects of Surface Aging on Nanoparticle Fate and Transport in Natural and Engineered Porous Media. Tufts University.
- Mudalige, T.K., Qu, H., Linder, S.W., 2015. Asymmetric flow-field flow fractionation hyphenated ICP-MS as an alternative to cloud point extraction for quantification of silver nanoparticles and silver speciation: application for nanoparticles with a protein corona. *Anal. Chem.* 87 (14), 7395–7401.
- Murata, T., Kanao-Koshikawa, M., Takamatsu, T., 2005. Effects of Pb, Cu, Sb, In and Ag contamination on the proliferation of soil bacterial colonies, soil dehydrogenase activity, and phospholipid fatty acid profiles of soil microbial communities. *Water Air Soil Pollut.* 164, 103–118.
- Neubauer, E., vd Kammer, F., Hofmann, T., 2011. Influence of carrier solution ionic strength and injected sample load on retention and recovery of natural nanoparticles using flow field-flow fractionation. *J. Chromatogr. A* 1218, 6763–6773.
- Nielsen, K., Kalmaykova, Y., Strömvall, A.-M., Baun, A., Eriksson, E., 2015. Particle phase distribution of polycyclic aromatic hydrocarbons in stormwater—using humic acid and iron nano-sized colloids as test particles. *Sci. Total Environ.* 532, 103–111.
- Osborne, O.J., Lin, S., Chang, C.H., Ji, Z., Yu, X., Wang, X., Nel, A.E., 2015. Organ-specific and size-dependent Ag nanoparticle toxicity in gills and intestines of adult zebrafish. *ACS Nano* 9 (10), 9573–9584.
- Peijnenburg, W.J., Zablotskaja, M., Vijver, M.G., 2007. Monitoring metals in terrestrial environments within a bioavailability framework and a focus on soil extraction. *Ecotoxicol. Environ. Saf.* 67, 163–179.
- Peralta-Videa, J.R., Zhao, L., Lopez-Moreno, M.L., de la Rosa, G., Hong, J., Gardea-Torresdey, J.L., 2011. Nanomaterials and the environment: a review for the biennium 2008–2010. *J. Hazard. Mater.* 186, 1–15.
- Peters, R.J.B., Herrera Rivera, Z., van Bommel, G., Marvin, H.J.P., Weigel, S., Bouwmeester, H., 2014. Development and validation of single particle ICP-MS for sizing and quantitative determination of nano-silver in chicken meat. *Anal. Bioanal. Chem.* 406 (16), 3875–3885.
- Pevrot, C., Wilkinson, K.J., Desrosiers, M., Sauvé, S., 2014. Effects of silver nanoparticles on soil enzyme activities with and without added organic matter. *Environ. Toxicol. Chem.* 33, 115–125.
- Philippe, A., 2015. Hydrodynamic Chromatography for Studying Interactions between Colloids and Dissolved Organic Matter in the Environment. Universität Duisburg, Germany.
- Prasad, A., Lead, J., Baalousha, M., 2015. An electron microscopy based method for the detection and quantification of nanomaterial number concentration in environmentally relevant media. *Sci. Total Environ.* 537, 479–486.
- Rana, S., Kalachelvan, P., 2013. Ecotoxicity of nanoparticles. *ISRN Toxicology* 2013.
- Read, D.S., Matzke, M., Gweon, H.S., Newbold, L.K., Heggelund, L., Ortiz, M.D., et al., 2015. Soil pH effects on the interactions between dissolved zinc, non-nano- and nano-ZnO with soil bacterial communities. *Environ. Sci. Pollut. Res.* 1–9.
- Riding, M., Martin, F., Jones, K., Semple, K., 2015. Carbon nanomaterials in clean and contaminated soils: environmental implications and applications. *Soil* 1, 1–21.
- Roco, M.C., Harthorn, B., Guston, D., Shapira, P., 2011. Innovative and responsible governance of nanotechnology for societal development. *Nanotechnology Research Directions for Societal Needs in 2020*. Springer, pp. 561–617.
- Sagee, O., Dror, I., Berkowitz, B., 2012. Transport of silver nanoparticles (AgNPs) in soil. *Chemosphere* 88, 670–675.
- Saleh, N.B., Aich, N., Plazas-Tuttle, J., Lead, J.R., Lowry, G.V., 2015. Research strategy to determine when novel nanohybrids pose unique environmental risks. *Environmental Science: Nano* 2, 11–18.
- Sanchís, J., Božović, D., Al-Harbi, N.A., Silva, L.F., Farré, M., Barceló, D., 2013. Quantitative trace analysis of fullerenes in river sediment from Spain and soils from Saudi Arabia. *Anal. Bioanal. Chem.* 405 (18), 5915–5923.
- Sciau, P., 2012. Nanoparticles in ancient materials. *The Metallic Lustre Decorations of Medieval Ceramics* vol. 115. INTECH Open Access Publisher.
- Servin, A.D., Morales, M.L., Castillo-Michel, H., Hernandez-Viezas, J.A., Munoz, B., Zhao, L., Nunez, J.E., Peralta-Videa, J.R., Gardea-Torresdey, J.L., 2013. Synchrotron verification of TiO₂ accumulation in cucumber fruit: a possible pathway of TiO₂ nanoparticle transfer from soil into the food chain. *Environ. Sci. Technol.* 47 (20), 11592–11598.
- Shareef, A.I., Guihua, Li, and Rai S. Kookana, 2010. Quantitative determination of fullerene (C60) in soils by high performance liquid chromatography and accelerated solvent extraction technique. *Environ. Chem.* 7 (3), 292–297.
- Sillen, W.M., Thijs, S., Abbamondi, G.R., Janssen, J., Wevens, N., White, J.C., Vangronsveld, J., 2015. Effects of silver nanoparticles on soil microorganisms and maize biomass are linked in the rhizosphere. *Soil Biol. Biochem.* 91, 14–22.
- Sohn, E.K., Johari, S.A., Kim, T.G., Kim, J.K., Kim, E., Lee, J.H., et al., 2015. Aquatic toxicity comparison of silver nanoparticles and silver nanowires. *BioMed Research International*, 893049 12 pages.
- Sokolov, S.V., Tschulik, K., Batchelor-McAuley, C., Jurkschat, K., Compton, R.G., 2015. Reversible or not? Distinguishing agglomeration and aggregation at the nanoscale. *Anal. Chem.* 87 (19), 10033–10039.
- Soni, D., Naoghare, P.K., Saravanadevi, S., Pandey, R.A., 2015. Release, transport and toxicity of engineered nanoparticles. *Reviews of Environmental Contamination and Toxicology*. Springer, pp. 1–47.
- Soto-Alvaredo, J., Montes-Bayón, M., Bettmer, J., 2013. Speciation of silver nanoparticles and silver (I) by reversed-phase liquid chromatography coupled to ICP-MS. *Anal. Chem.* 85 (3), 1316–1321.
- Stack, A.G., Raiteri, P., Gale, J.D., 2011. Accurate rates of the complex mechanisms for growth and dissolution of minerals using a combination of rare-event theories. *J. Am. Chem. Soc.* 134, 11–14.
- Sun, P., Shijirbaatar, A., Fang, J., Owens, G., Lin, D., Zhang, K., 2015a. Distinguishable transport behavior of zinc oxide nanoparticles in silica sand and soil columns. *Sci. Total Environ.* 505, 189–198.
- Sun, T.Y., Conroy, G., Donner, E., Hungerbühler, K., Lombi, E., Nowack, B., 2015b. Probabilistic modelling of engineered nanomaterial emissions to the environment: a spatio-temporal approach. *Environ. Sci.: Nano* 2, 340–351.
- Suresh, A.K., Pelletier, D.A., Doktycz, M.J., 2013. Relating nanomaterial properties and microbial toxicity. *Nanoscale* 5, 463–474.

- Tavares, D., Rodrigues, S., Cruz, N., Carvalho, C., Teixeira, T., Carvalho, L., et al., 2015. Soil-pore water distribution of silver and gold engineered nanoparticles in undisturbed soils under unsaturated conditions. *Chemosphere* 136, 86–94.
- Throbäck, I.N., Johansson, M., Rosenquist, M., Pell, M., Hansson, M., Hallin, S., 2007. Silver (Ag⁺) reduces denitrification and induces enrichment of novel nirK genotypes in soil. *FEMS Microbiol. Lett.* 270, 189–194.
- Tourinho, P.S., Van Gestel, C.A., Lofts, S., Svendsen, C., Soares, A.M., Loureiro, S., 2012. Metal-based nanoparticles in soil: fate, behavior, and effects on soil invertebrates. *Environ. Toxicol. Chem.* 31, 1679–1692.
- Wang, D., Jaisi, D.P., Yan, J., Jin, Y., Zhou, D., 2015. Transport and Retention of Polyvinylpyrrolidone-Coated Silver Nanoparticles in Natural Soils. *Vadose Zone J. Advancing Critical Zone Sci.* 1–13.
- Wang, X., Ji, Z., Chang, C.H., Zhang, H., Wang, M., Liao, Y.-P., Lin, S., et al., 2014. Use of coated silver nanoparticles to understand the relationship of particle dissolution and bioavailability to cell and lung toxicological potential. *Small* 10 (2), 385–398.
- Watson, J.-L., Fang, T., Dimkpa, C.O., Britt, D.W., McLean, J.E., Jacobson, A., et al., 2015. The phytotoxicity of ZnO nanoparticles on wheat varies with soil properties. *Biomaterials* 28, 101–112.
- Weir, A., Westerhoff, P., Fabricius, L., Hristovski, K., von Goetz, N., 2012. Titanium dioxide nanoparticles in food and personal care products. *Environ. Sci. Technol.* 46, 2242–2250.
- Wijnhoven, S.W., Peijnenburg, W.J., Herberts, C.A., Hagens, W.I., Oomen, A.G., Heugens, E.H., et al., 2009. Nano-silver—a review of available data and knowledge gaps in human and environmental risk assessment. *Nanotoxicology* 3, 109–138.
- Wilson, M.A., Tran, N.H., Milev, A.S., Kannangara, G.K., Volk, H., Lu, G.M., 2008. Nanomaterials in soils. *Geoderma* 146, 291–302.
- Wuithschick, M., Witte, S., Kettmann, F., Rademann, K., Polte, J., 2015. Illustrating the formation of metal nanoparticles with a growth concept based on colloidal stability. *Phys. Chem. Chem. Phys.* 17, 19895–19900.
- Yang, K., Lin, D., Xing, B., 2009. Interactions of humic acid with nanosized inorganic oxides. *Langmuir* 25, 3571–3576.
- Yin, Y., Yu, S., Shen, M., Liu, J., Jiang, G., 2015. Fate and transport of silver nanoparticles in the environment. *Silver Nanoparticles in the Environment*. Springer, pp. 73–108.
- Zahedi, F., Behpour, M., Ghoreishi, S.M., Khalilian, H., 2015. Photocatalytic degradation of paraquat herbicide in the presence TiO₂ nanostructure thin films under visible and sun light irradiation using continuous flow photoreactor. *Sol. Energy* 120, 287–295.