Engineered Nanoparticles in Agro-ecosystems: Implications on the Soil Health

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Abstract

Soil health has been considered as one of the important factors for maintaining ecosystem boundaries, balanced biogeocycles, sustaining plant growth, support habitat, and balanced environmental functions. However, along with the presence of persistence xenobiotics, the entry of newer engineered nanoparticles (ENPs) to the agro-ecosystem has directly influenced the soil health. ENPs are now having tremendous potential to shape the global economy and thus their production has increased deliberately. They are refined from bulk materials to offer unprecedented interactions with small-scale molecules or naturally occurring compounds that are produced on a scale of ∼1–100 nm. These nano-architects are chiefly employed for controlled delivery of fertilizers, pesticides, hormones, genetic material, nano-sensors, and rebuilding of soil structure in agro-ecosystem. However, they undergo various transformations like aggregation, sorption, dissolution, decomposition, dispersion, and transportation in soil environment which directly affects the soil health. Thus, their exposure has resulted in various implications like disturbed soil microflora, impeded decomposition of organic matter, lowered nutrient and carbon reserves, and additionally toxicity to soil microbial communities. The scientific communities have widely reviewed major concerns about their origin, interaction, distribution, toxicity, and mitigation in the soil ecosystem. However, the unethical and uncontrolled liberation of ENPs to the environment always made it a matter of concern. Therefore, strong regulation, risk assessment, and mitigation strategies are required for the sustainable use of ENPs. Here, we have attempted to review the structures, properties, mobility, interaction with soil components, impact on soil health, toxicological profile, effects on soil microbial communities, and assessment methods. This will provide valuable approaches to tackle the challenges associated with ENPs and directions for future research.

Keywords

Nutrient content • Persistent • Risk assessment • Soil microflora • Toxicity

1 Introduction

Engineered nanoparticles (ENPs) are the artificially derived nanometer-scale components (1–100 nm in dimension) which are produced for advanced nanomaterial construction in smart applications (Auffan et al. 2009). ENPs are composed of two-layer, i.e., the surface layer having small doped molecules like metal ions, polymer, surfactants, and the inner core referring nanoparticle itself (Raliya 2019). Currently, many smart application of ENPs in soil nanotechnology has been documented, including as nanobiosensors, delivery of nutrients, growth hormones, pesticides, food additives, and genetic improvement of plants (Jampílek and Kráľová 2017; Dar et al. 2020; Saxena et al. 2020). Therefore, to keep harmony in the soil functioning such as sustained growth of microbial species, nutrient bioavailability, plant growth, crop yield, and application of engineered nanoparticles (ENPs) have been considered as an emerging and potentially viable technique for agricultural practices. An increasing number of studies have suggested massive production and liberation of ENPs in the ecosystem has raised the question about their transformation, toxicity, risk, and uncertainty during application. They are widely accepted by the scientific community for the application in agricultural purposes; however, accidentally soil becomes a major sink of ENPs through different exposure routes (Kumar et al. 2012).

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Modeling studies have suggested that soil receives a higher amount of ENPs than air or water. They easily adapt different electrical, magnetic, optical, properties than its bulk material and influence soil physico-chemical properties which manipulates soil texture, particle size, soil pH, microbial population, and simultaneously causes potential toxicity. The release of ENPs to the soil could be from a point or diffuse sources including liberation directly through primary particles, or transformation after reactions like agglomeration, aggregation, association with soil matrix, or dissociation. Direct exposure pathways of ENPs to soils occur when ENPs are used for delivery of fertilizer, pesticides, for remediation purposes, or via an accidental release. However, the deliberate entry of ENPs to the soil environment may lead to bioaccumulation, expanded toxicity, loss of organic matter, alteration in soil biodiversity, and altered soil physico-chemical structures. The application of ENPs to soil has varied according to application and includes two major categories, i.e., (1) In the organic forms (carbon nanotubes, fullerenes) and (2) inorganic forms (metal nanoparticles, silica-based, and quantum dots). However, the absence of proper monitoring methods and complex heterogeneous environment of soil turns it difficult to measure than in any other environment. The fate and travel of ENPs are usually governed by soil properties, like pH, texture, organic matter, water regime, and ionic strength. It is often argued that during travel into soil components the transformation of ENPs occurs which makes it difficult to extrapolate in a realistic scenario.

The detailed study about the effect of ENPs in soil ecosystem has outlined a clear sketch about modification in microbial enzymatic activities due to metals and metal oxides, alteration in soil pollutant mobility, toxicity in the plant (De La Rosa et al. 2011), accumulation in plant tissues, soil and sediments (Cornelis et al. 2014), control of plant insects (Debnath et al. 2012). However, the behavior and fate of the ENPs in the soil will be determined by a complex set of factors of both ENPs and soil. The chapter will provide an overview of the ENPs in the agro-ecosystem considering their synthesis, mobility, transformation, interaction, accumulation, toxicity, assessment methods, and impact on soil health briefly. This would further be designed as a framework and provide relevant information for futuristic studies regarding ENPs in soil environment.

2 Synthesis and Types of Engineered Nanoparticles

Generally, two different synthesis approaches have been employed for the construction of ENPs namely top-down and bottom-up methods. The top-down is a destructive approach, which involves the division of larger particles into smaller particles ENPs. The top-down methods are usually destructive methods that are costly, time-consuming, and not suitable for large-scale production. Various methods like mechanical milling, nanolithography, laser ablation, sputtering, and thermal decomposition chemical methods, photo-lithography are suggested for this purpose (Dhand et al. 2015). While in bottom-up known as building up approach, the ENPs are formed from relatively simpler substances. The bottom-up or constructive method is made of material from atom to clusters to ENPs through sol–gel, spinning, chemical vapor deposition, and pyrolysis processes (Khan et al. 2019).

Between organic and inorganic types they are mainly applied in the form of metal/metal oxides, carbon-based, silica-based, quantum dots, and dendrimers. Their application in the form of metal oxides such as ZnO, TiO_2, CeO_2, CrO_2, Fe_3O_4, and binary oxides was frequently noticed (Bhatt and Tripathi 2011).

To create silica ENPs, the covalent grafting of polymers was carried out through the use of various polymers such as polystyrene and polyacrylamide (Adams 2018). Nano-SiO_2 was reported to promote seed germination and stimulated the antioxidant system, promote plant, and root growth (Gul et al. 2014). Mesoporous silica was also used for delivery of nutrients, fertilizers, drugs, gene, and DNA to the plant cell due to their high surface area, pore-volume, stability, and tunable structure. Thus, various nanodevices with tremendous effects could offer novel insights for the safer use of these nanoparticles.

Carbon nanotubes (CNT) are cylindrical layers of graphene with single or multiwalled designed as open and closed ends. Various nanodevices for application in agricultural purpose and pollutant remediation were constructed due to their unique conductive, optical, and thermal properties. CNT can also make soil nutrient-rich and enhance its biota as well as chemical and physical properties. CNT provides adsorption sites due to the cylindrical structure and a wide range of toxic compounds can easily absorb on it. While the use of CNT-based nanosponges was identified as a great tool for remediation of xenobiotics from soil (Manjunatha et al. 2016). Unfortunately, CNTs have shown potential toxicity in human cells due to their penetrability and accumulation in the cytoplasm (Prasad et al. 2017).

Nanocrystal quantum dots are semiconducting heterostructured materials such as cadmium selenide (CdSe), indium phosphide (InP), or zinc selenide (ZnSe) with controlled optical and electrical properties (Xiaoli et al. 2020). Quantum dots (QDs) can be employed for live imaging in plant tissue for retrieving information about physiological processes. Sometimes, ENPs were made by dendrimers, and these are normally organic-based ENPs which are complex, multifunctional polymers with their size range between 1 and 10 nm diameters. They are having branched asymmetric structures with nanospheres or nanocapsules shape (Ishtiaq et al. 2020). The unique structures with a solid center and surrounded spherical surface of dendrimers have shown tremendous capability in the field of sensors development and also as a sorbent for contaminants (Zhang et al. 2017). In the future, more focused research toward the development of application-specific nanoparticles through controlling reaction parameters, shape, size, and morphology should be done.

3 Exposure of Engineered Nanoparticles in Soil

The rapidly evolving synthesis of ENPs has provided maximum chances of ENPs to enter in soil compartment during traveling. As far as the concern of their entry to the soil ecosystem, they can enter through point or nonpoint sources. The direct exposure route consists mainly of the application of nanofertilizers, nanopesticides, seed treatment preparation, agrofilms, or for remediation of contaminated land or groundwater. However, the accidental liberation was primarily from diffuse emission, ENPs containing products, solid waste disposal, landfilling, and incineration or mishandling of those during transportation (Walden and Zhang 2016). The product matrix has severely affected the ENPs physical and chemical characteristics and thus long-term application of ENPs resulted in bioaccumulation in soil. Nonetheless, after liberation, they get interacted with the heterogeneous structure of the soil. Soil provides a suitable habitat for the retention of ENPs, as they can adsorb on the soil pores, forms aggregates with organic matter, or establish electrostatic interaction, ligand exchanges networking with the soil-solid matrix. The surface chemistry of ENPs plays an important role in deciding its mobility, stability with inorganic and organic soil colloidal suspension (Alimi et al. 2018). The release of silver nanoparticles was found more in presence of natural organic matter as without that in the soil the reduction in negative surface potential of ENPs would cause more aggregation in soil (Li et al. 2013).

Application of wastewater sludge enriched with Zn and Ag nanoparticles in soil final concentration of 1400 and 140 mg/kg for Zn and Ag, respectively, has shown a reduction in the fungal community in soil (Durenkamp et al. 2016). The calculated risk assessment of ENPs released through personal care products has suggested that about 43% of it ends up in landfills, 0.8% directly goes to the soil, and 32% in water bodies. The uprising concentration of ENPs was mainly due to the usage of sunscreen, facial moisturizer, hair coloring agents, body wash, toothpaste, and shampoo (Keller et al. 2014). After entering the ecosystem, it is very easy to enter the soil either via wastewater sludge, landfilling, or atmospheric deposition. However, the fate of ENPs after liberation has been described in detail in the later section. The impetus of the application of ENPs in the soil through key drivers is being summarized in Table 1. This would provide insight into their application in various forms and possible impacts on the soil ecosystem.

4 The Fate of Engineered Nanoparticles in the Soil

The modification in the physico-chemical characteristics took place due to major transformation reactions occurring between soil matrix and ENPs. The soil reaction occurring inside soil pore or soil solution resulted in either their retention or mobilization. The surface area, size, charge, density, and shape of ENPs play a major role in determining their fate in the soil matrix. The complex and heterogeneous environment of soil leads to aggregation, sedimentation, dissolution, the transformation of ENPs. Furthermore, their bioavailability in the soil is mainly influenced by soil chemistry and soil microorganism (Dwivedi et al. 2015). It is well predicted that the residence time of ENPs is more in soil and sediments than in aquatic system. Based on their biodegradation potential, they eventually build up in the soil and thus become bioavailable for plants and terrestrial organisms. Although many theories have been suggested to the fate of ENPs in soil, however, clear mechanisms of fate remain unclear due to the heterogeneous surface of the soil. The interaction between these processes and the ENPs transfer determines the fate and finally the ecotoxicological potential of ENPs in the soil matrix. The upcoming section will summarize the different fate behavior of ENPs according to the consensus of various scientific theories.

4.1 Engineered Nanoparticles and Colloids

Many processes inside the soil matrix are generally governing their fate in soil. Regarding this, colloids of the soil (diameter <1 μm) play a magnificent role in the interaction chemistry of ENPs. These fractions of soil are very mobile and active components with high surface area and often turn as carriers for different contaminants and nutrients in the soil. These colloid particles govern the transport of various engineered nanoparticles and then impart to environmental pollution (Pan and Xing 2012). The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and the colloid filtration theory both have explained their transport in the soil porous media due to the structural similarities between natural

Table 1 Application mode of different types of engineered nanoparticles

Classes	Types	Application	References
Metallic	Manganese and copper nanoparticle	Act as micronutrient nanofertilizer, reduction in the rate of release of micronutrients to plants and help in N-fixation	Kopittke et al. (2019), Zahra et al. (2015)
	Iron and magnesium nanoparticle	Reduce the concentration of polychlorinated biphenyls in soils up to 56%	Olson et al. (2014)
	Iron sulfide nanoparticles with carboxymethylcellulose	Immobilizes Hg in soils up to 65–91%	Gao et al. (2013)
	Zero-valent iron nanoparticle	Act as excellent phosphate ion absorbent (90–98%)	Lin and Xing (2007)
		Degrade polybrominated diphenyl ethers up to 67%	Qiu et al. (2011), Xie et al. (2016)
		Removal of Cr (VI) up to 56–98%	Yang et al. (2019)
		Removes nitrates from soils, water, and sediments	Liu and Wang (2019)
		Degraded molinate (a carbothionate herbicide)	Joo et al. (2005)
Metallic oxide	Nano-titanium oxide, iron oxide	Enhances rhizopheric phosphorus content when applied on *Lactua sativa*	Zahra et al. (2015)
	TiO_2	Helps in the bioremediation of various organic compounds such as phenol, p-nitrophenol, salicylic acid, and benzene	Zhang et al. (2010)
		Extensively used as photocatalyst for waste treatment	Li et al. (2008)
	CeO_2	Improved plant growth, biomass yield, grain yield in *Triticum aestivum* L	Rico et al. (2014)
	ZnO	Act as nanofertilizer to boost the yield and growth of food crops	Sabir et al. (2014)
		Removal of Cr by 45–53%	Ahmed and Yusuf (2015)
Carbon	Graphene oxide	Act as suitable amendment to immobilize copper in polluted soil 65%	Baragaño et al. (2020)
		Sorption of volatile organic compounds, pesticides, heavy metals, and pharmaceuticals	Gao et al. (2013), Deng et al. (2017)
	Carbon nanotubes	Sorption of metals (Cu, Ni, Cd, Pb, Ag, Zn)	Khin et al. (2012)
		Adsorbed cationic dyes up to 97.2%	Li et al. (2003)
	Fullerenes	Sorption of organic compounds (e.g., naphthalene)	Cheng et al. (2004)
		Used for remediation of organometallic compounds	Ballesteros et al. (2000)
Silica	SiO_2 nanoparticle	Used for bioremediation of polycyclic aromatic hydrocarbons pyrene efficiency of 75–102%	Topuz et al. (2011)
	Silica nanoparticles	Removal of cationic dyes (86%)	Tsai et al. (2016)
Polymeric nanoparticles		Helps in removal of hydrophobic pollutants from soils (e.g., phenanthrene) by 85.2%	Tungittiplakorn et al. (2005)
Dendrimers		Removal of copper (II) from sandy soil up to 85%	Xu and Zhao (2005), Zou et al. (2016)

colloids and ENPs. The organic (<30 nm) and inorganic particles (>20–30 nm) of iron or aluminum oxide or clay oxides, larger colloids of soil minerals (>100 nm) play important role in adhering and act as the carrier of ENPs. Wang et al. (2015) have described the main key factors governing the transport of ENPs in soil porous media. The interaction between silver nanoparticles and natural soil colloids has shown deposition of nanoparticles followed by hetero-aggregation and hence confirming their reduced mobility in soil solution (Cornelis et al. 2013). The transport of nanoscale zero-valent iron (nZVI) was also promoted by soil-colloids interaction behavior suggesting the highest mobility in quartz while least in diatomite (Zhang et al. 2019). The transport of ENPs in the soil column was mainly affected by texture, charge, porosity, and adsorption capacity of colloids fraction.

4.2 Aggregations

The word "aggregate" is known as the clusters of ENPs in different shapes. This phrasing is aggravated passing through the potency of adhesion of the majority of ENPs to both and other particles, by which ENPs frequently agglomerates to form particle clusters (Cornelis et al. 2014). Aggregation reduces the specific exterior area of particles and interfacial energy. In aggregation presence of the natural organic matter commonly limits their movement in the soil. The actions of soil organisms manipulate carbon maintenance time and return in soil, which revolves change carbon stabilization, aggregation, and yield. Aggregation favors the movement and deposition of ENPs in soil solution. It can be homoaggregation (between ENPs) or hetroaggregation (between ENPs and other soil components such as clay, minerals, or oxides). The collision among the ENPs resulted in the formation of aggregates and thus the establishment of weaker van der Walls forces or strong chemical bonds takes place. The presence of natural organic nanoparticles in the soil porous media further facilitates the hetero-aggregation among them, thus, severely affects their bioavailability, toxicity, and transport across porous media. Aggregation of metal-based ENPs (Ti, Cu, Au, Ag, Ni) was already noted in soil (Cornelis et al. 2014). Hetero-aggregation most likely occurs than homoaggregation rates in soil pores and appears to vary depending on the soil colloid and ENPs nature. The formation of large hetero-aggregates may also reduce the translocation and uptake of ENPs through plant cells and membranes, and thus decreasing their biological availability (Gogos 2015). The loss of ENPs polymeric coatings under sunlight catalyzed redox reactions may stimulate instability and favors hetero-aggregation. The soil pH, clay content, organic matter, and particle characteristics play an important role in ENPs transport and retention (Abbas et al. 2020). The movement of ENPs across the soil solution was likely to be influenced by zeta potential, surface coating of ENPs, however, the use of emulsifier during processing helps in stabilizing while capping agents prevent degradation and transformation (Sajid et al. 2015).

4.3 Deposition

Engineered nanoparticles (ENPs) undergo deposition in the soil as a result of collisions and bonding with the surface. The Brownian diffusion, interception, or gravitational settling inside soil pore wall are responsible and thus deposition took at a place (Cornelis et al. 2014), while hydrodynamic drag forces further allow their travel to the collector sites (Torkzaban et al. 2007). The absence of repulsion due to the presence of similar charges on the surface and high collision efficiency always promotes their deposition. The large aspect ratio of CNT has resulted in higher deposition than other colloids or ENPs (Lin et al. 2010), due to the coiling features of CNT around soil particles (Canady and Kuhlbusch 2014). The deposition can be considered as analogous to the aggregation of relatively small ENPs with a much larger colloid, and as dominates as aggregation in the soil matrix. Li et al. (2020) have demonstrated relatively high mobility of silver nanoparticles (Ag NPs) in the loamy sand than in silty soil under low ionic strength and higher flow rates. Further, the transport of the Ag NPs in loamy sand was slowed at a low flow rate, due to the dominance of diffusion and depositions after compression of the electrical double layer of Ag NPs and soil surface (Braun et al. 2015). The effect of input concentration, size, and surface coating of Ag NPs for the transport was also studied and it was stated that migration was less in ultisols due to high surface area and retention sites. The increased concentration, lower particle size, and surface coating of Ag NPs have promoted the transport (He et al. 2019). However, the transport and deposition of ENPs are a complex process that is jointly affected by several factors such as physico-chemical properties of soil, pore-water solution, ENPs features as well as hydrodynamic behavior. The transport and retention of CuO nanoparticles in soil subsurface environment was also affected by soil pH, ionic strength, and humic acid (Fig. 1).

However, the establishment of van der Walls forces between nanoparticles and collector surface was repulsive, promoting an unfavorable deposition due to interaction energy, collision, and aggregation in soil (Ma et al. 2018; Wu et al. 2020).

4.4 Oxidation/dissolution

The ENPs generally undergoes different oxidation process, followed by their complexation with organic matter and chelating agents and finally adsorbs on the colloidal surface. The dissolution, oxidation–reduction reactions largely depend upon the structure of ENPs such as soft metal cations Mg, Ag, Zn, and Cu are susceptible to these reactions (Boxall et al. 2007). However, the reason for the increasing trend of ENPs use has exposed the soil with a rising concentration of ENPs. The speed of dissolution of ENPs in soils can be explained by the type, texture, and source material of ENPs (Rodrigues et al. 2016). The dissolution of metal-based ENPs is affected by their chemical properties and soil conditions like pH, organic carbon, texture, and size (Arora et al. 2012). Still, the kinetics of oxidation of the different ENPs in a complex soil matrix, and the relevant controlling factors are unexplained. According to the reports in soil systems, the dissolution of ENPs allows the liberation of free ions in soil solution which further transforms by reacting with organic matter, soil chelators, or adsorb on soil particles/minerals followed by precipitation of non-soluble reactive counterparts. In non-saturated aerated soil, i.e., low pH and high oxygen contents and the rate of oxidation enhances. In contrast, the presence of organic coatings

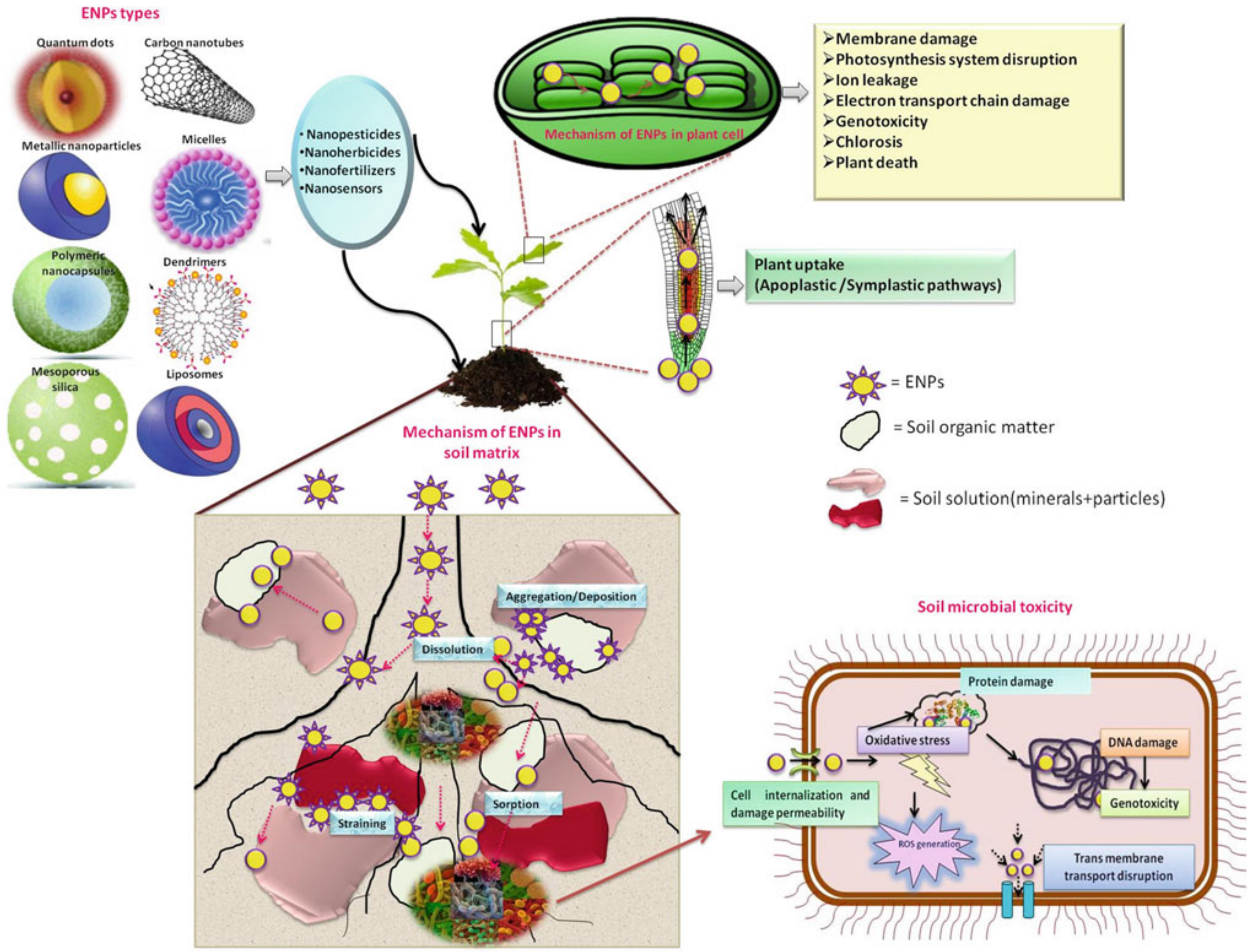

Fig. 1 Fate of engineered nanoparticles (ENPs) in the soil matrix and associated toxicity (modified from Santiago et al. 2016)

impedes dissolution while sometimes their quick degradation promotes dissolution (Chen 2018). The dissolution of Ag NPs was reported due to chemical reactions in the soil (Benoit et al. 2013) while Au nanoparticles were impervious to oxidative dissolution due to its instability of oxidized Au (Au^{+3}) hence readily reduced in soil.

The oxidation and dissolution of CeO_2 nanoparticles were enhanced by complex formation between chelating agents and Ce^{+3} in soil, thus, lowering the bioavailability and transport of nanoparticles (Zhang et al. 2017; Rodrigues et al. 2016). In contrast, sometimes, the dissolution process is inhibited by certain factors in soil subsurface likewise the dissolution of Ag NPs was hampered by iron oxides due to the formation of electrostatic attraction followed by hetero-aggregation (Wang et al. 2019). Thus, the dissolution kinetics of nanoparticles is a very complex process and therefore the factors affecting the dissolution should be critically evaluated. Overall future study should incorporate detailed inspection of the in vitro fate behavior of ENPs for better identification of risk associated with ENPs application in soil.

5 Factors Affecting Transport of Engineered Nanoparticles in Soil

As discussed above, the aggregation, transport, and deposition of ENPs have been affected by several parameters like size, surface area, zeta potential, hydrophobicity, structure, and synthesis route. These properties may interact with soil solution and it was proposed that ENP size between 1 and 30 nm behave differently for the aforementioned processes (Santiago-Martín et al. 2016). Due to their smaller size, they start to aggregate in soil, however, they can keep on changing the properties in soil solution depend on the particle size. The high surface area further boosts its activity and therefore the aggregation with soil particles amplified. However, the particle size becomes a major parameter as surface atoms increase with a decrease in particle size (Alan et al. 2020). Ag NPs of diameters around 10 nm showed higher penetration capacity into the cell than of particle size of 20–100 nm (Ivask et al. 2014; Goswami et al. 2017). The surface charge of ENPs often governs their binding pattern with clay or minerals in soil solution likewise the electrostatic interaction of negatively charge cerium oxide nanoparticles was increased with clay edges. Similarly, the low affinity of cerium oxide nanoparticles with the surface of kaolinite suggested strong electrostatic interactions between them. The charge-dependent aggregation was due to the variation in hydrodynamic size and surface charge (Guo et al. 2019). Further, the coarse surface of some clay minerals also provides binding sites for positively charged ENPs (Ghorbanpour et al. 2020).

The retention of functionally stabilized Ag NPs was increased with the interaction of iron and clay minerals (Hoppe et al. 2014). Furthermore, the retention in the soil largely depends on the ionic strength, mass concentration, and particle numbers which contributes to the filling of retention site and concentration-dependent mass transfer in soil solution (Alan et al. 2020). However, the increase in the magnitude of electrical double layer forces between the charged colloids and minerals leads to the release of ENPs. Likewise, Zn nanoparticles and carbon nanotubes have shown low mobility in different ionic strength of clay minerals soil and natural soil, respectively (Zhao et al. 2012). It might be related to their shape, aspect ratio, surface charge, size distribution, and interconnected soil pores. In addition to this, the surface coating also responsible for their fate in the soil like a coating of polyvinylpyrrolidone and citrate has boosted the transport and reduced the retention of Ag NPs in soil, which related to obstruction in the solid phase retention sites in soil (Kanel et al. 2015). Consequently, ENPs surface modification generates electrostatic, steric, or repulsive forces which more likely to reduce the aggregation and thus enhance their transport and bioavailability (Goswami et al. 2017). Similarly, the uncoated Ag NPs were more bioavailable than citrate-coated nanoparticles due to a rise in their stabilization after coating (Cornelis et al. 2014). The transport of sodium dodecylbenzene sulfonate surfactant on the transport of Ag NPs and CNTs in saturated porous media has shown high mobility in soil column and they exhibited similar transport patterns as of natural clay soil (Tian et al. 2010).

Soil is the complex mixture with heterogeneous features thus extrapolation of the effect of any one characteristic of the ENPs cannot be described perspicuously. Nevertheless, the complex mechanism simultaneously occurring in the soil system helps to solve the question related to their abundance, mobility, bioavailability, transformation, and toxicity.

6 Effect of Engineered Nanoparticles on the Soil Properties

Being the natural sink of ENPs, the soil environment has been critically affected by their presence. Most of the studies have suggested the complex reactions occurring in soil media have been actively mediated by both soil components and ENPs (Pradhan and Mailapalli 2017; Abbas 2020). In this view, the discussion about the effect of the ENPs on the soil properties and edaphic biota has been elaborated here.

6.1 Effect on Physico-Chemical Properties

Soil pH is a major governing parameter that directly influences soil health, indicates its nutrient status, and also about ionic strength of soil solution. Somehow, it plays a major role in the ionization of various organic/inorganic compounds and changes their solubility and responsible for the sorption of many compounds. It is pragmatic that variation in the pH of the soil is sometimes mediated through the accumulation of the different ENPs mentioned above (Schultz et al. 2015). These variations in pH further lead to toxicity in soil fauna and led to metal ion solubility, nutrient availability, plant growth, and clay dispersion (Zhang et al. 2018; Tarafdar and Adhikari 2015). In another study, the change in soil pH from 5.9 to 6.8 has shown no changes in solubility of copper nanoparticles, however, it was positively correlated with the change in the organic matter content of soil (Gao et al. 2019). In contrast, the solubility of Zn was related to negatively correlate with soil pH, due to its retention and adsorption on the clay particles (García-Gómez et al. 2018). In addition to this the agglomeration, discharge, oxidation, and release of nanoparticles are highly dependent on soil pH (Nowack et al. 2012). Likewise, the impact of pH on ZnO ENPs breakdown has caused danger on the population of *Folsomia candida* and *Eisenia fetida* in soil (Kool et al. 2011). The gravity-driven transport of ENPs like TiO_2, CeO_2, and $Cu(OH)_2$ owing to their effect on soil pH and nutrient release in unsaturated soils has determined and small changes in the soil pH were detected due to the release of natural ions (Mg^{2+}, H^+) through substitution suggesting the high retention of ENPs in soil (Conway and Keller, 2016). Furthermore, the interaction of ENPs with dissolved organic matter would greatly alter the magnitude of fate, transport, binding, and bioavailability of ENPs in soil.

The ubiquitous organic matter is generally composed of heterogeneous and different molecular compounds and thus multiple interaction mechanisms such as hydrogen bonding, electrostatic interaction, hydrophobic binding, π-π interaction, cation bridging, and adsorption take place between ENPs and organic matter surface. These interaction leads to

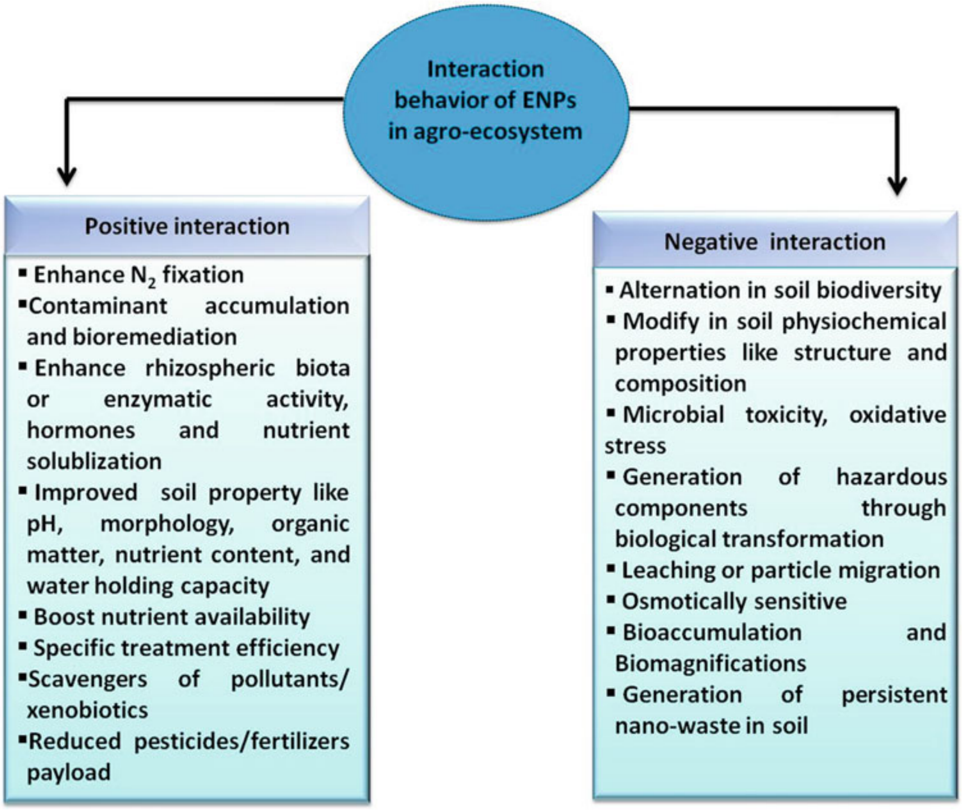

Fig. 2 Interaction of engineered nanoparticles (ENPs) in agro-ecosystem

aggregation, sedimentation, dissolution, oxidation, reduction, and deposition of ENPs and eventually modify the bioavailability and toxicity for soil environment. The release of metal ions from certain ENPs and metal ion complexes causes toxicity to microorganism and the dissolved organic matter could significantly alter their release by blocking ENPs oxidation sites. Recent research about this has clearly stated that the reduction of Ag$^+$ through dissolved organic matter has diminished the acute toxicity in *Daphnia magna* (Zhang et al. 2016). Also, in different natural organic macromolecules types, such as humic acid, fulvic acid, alginic acid, and tannic acid have collectively alleviated the ZnO induced antimicrobial activity in *Bacillus subtilis* due to their binding of Zn^{+2} with natural organic matter (Ma et al. 2013). Similar findings were also observed by Nie et al. (2020) who showed that soil organic matter reduces Ag$^+$ to Ag NPs which was mediated through free organic radicals and reducing surface groups of organic matter. The interaction of Ag$^+$ with soil organic matter has helped in elucidating the formation of silver nanoparticles (Nie et al. 2020). Different interaction behaviors of ENPs are presented in Fig. 2.

The natural organic matter often used as a stabilizer for ENPs production (Grillo et al. 2015), as a controlling agent for the stability of nanoparticles in the environment for control of toxicity (Omar et al. 2014) and remediation of media contaminated with heavy metals (Karnib et al. 2014) or organic compounds (Tang et al. 2014; Grillo et al. 2015) has critically reviewed the emphasis of natural organic matter for the interaction and stability of nanoparticles. The effect of C60 on soil microbial activity was also suggested due to the strong binding of C60 to soil organic matter (Patra et al. 2016). The adsorption of ENPs on the surface of soil organic matter has curtailed their mobility which ultimately changed their impact on soil properties.

The impact of Ag ENPs on the five different soils with varying physico-chemical properties has demonstrated that its toxicity was positively correlated with clay content and pH of the soil while the organic matter has not shown any relation with toxicity (Schlich and Hund-Rinke 2015). Surface adsorption and diminished actions of humic and fulvic acid in soil were responsible for the restraining of Ag ENPs disintegration (Javed et al. 2019).

Including these properties, the physical structure and hydraulic properties of soil were also affected upon exposure with ENPs. Besides soil texture, nutrient content, soil ionic strength, and pH of the soil solution also significantly impact ENPs transfer in soil (Patra et al. 2016). It was found that the concentration of valence of soil salt cation was also changed providing greater stability of divalent cation calcium (Ca$^{2+)}$ than monovalent cation potassium (K$^+$) (Makselon et al. 2018). It has been observed that there is 30%, 45%, and 2%

reduction in hydraulic conductivity when the soil is treated with 2% Al_2O_3, ZnO, and CuO ENPs, respectively as compared to untreated clay owing to pore-clogging (Tan 2017). In support of this study, it was found that reduction in hydraulic conductivity by clogging soil pores when there is an addition of nanosized material (montmorillonite) to fine-grained soil. Similar results also observed when metal oxide ENPs are added to sands (Braun et al. 2015). The application of nZVI in the soil at concentrations of 1 and 4 g l^{-1} showed no consequences on the hydraulic conductivity of natural soil (Reginatto et al. 2020).

6.2 Effect on Biological Properties of Soil and Phytotoxicity

The increased liberation of ENPs in soil has resulted in inevitable accumulation in soil and thus becomes a serious threat to the soil microbial community. Due to the dynamic nature of ENPs, they produce certain toxicity to soil microorganisms either directly or indirectly through interacting with other organic compounds. But due to the dynamic features of ENPs, it is always under discussion and newer theories have been developed day by day. The chemicals present in the root exudates in the rhizosphere greatly affect the physical properties of soil such as pH, cation exchange capacity (CEC), and salinity which ultimately influence ENPs aggregation and dissolution. Moreover, the rhizospheric microbiome also produces biomolecules which affect the ENPs fate. For instance, amino acids such as cysteine have shown to fasten ENPs aggregation rates but not long-term aggregation to a larger size (Hsieh 2010).

The impact of ENPs on the plant growth-promoting rhizobacteria (PGPR) like *P. aeruginosa, P. putida, P. fluorescens, B. subtilis*, soil nitrifying bacteria, and phosphate solubilizing bacteria was visible with retarded growth in culture conditions (Kumar 2018). Metal ENPs are generally toxic to microorganisms thus these ENPs damages plant-fungi and plant-bacteria association. Nano-ZnO and nano-TiO_2 were reported toxic against *B. subtilis*, *E. coli*, and *V. fischeri* (Li et al. 2011). Metal oxide ENPs of Cu is found to be toxic against PGPR such as *K. pneumoniae*, *P. aeruginosa*, *S. paratyphi,* and *Shigella* strains due to antibacterial property of Cu (Mahapatra et al. 2008). Iron and copper-based ENPs are observed to react with peroxides present in the soil, releasing free radicals which have a toxic effect on microorganisms (Saliba et al. 2006). Javed et al. (2019) showed that TiO_2 and CuO ENPs reduced the microbial biomass of the paddy soil due to their chemical characteristics. Similar outcomes were contemplated for the impact of ZnO, TiO_2, CeO_2, and Fe_3O_4 ENPs for lowering bacterial communities in saline/black soil and it was possibly responsible for the decreased enzymatic activities of invertase, urease, catalase, and phosphatase in the soil (You et al. 2018). Pérez-Hernández et al. (2020) have also summarized the impact of various ENPs on the soil microbiota and suggested that they were responsible for the reduction in the population of mesofauna and microfauna in soil.

Arbuscular mycorrhizal fungi (AMF) are known to show symbiotic association with plants and thus largely affect plant growth. However, it has been reported that AMF diversity decreased after exposure to Fe_3O_4 NPs at the concentration of 10 mg kg^{-1} (Cao et al. 2017). On the other hand, AMF remediates the toxicity when ENPs are exposed to plants. A study revealed the AMF inoculation eliminated the negative effect of ZnO ENPs on maize by increasing plant growth and nutrient uptake. Similar effects were reported in tomato plants when inoculated with AMF, the plant showed a reduction in Ag uptake up to 12% after exposure of Ag NPs (Noori et al. 2017). AMF restricts the uptake of ENPs by plants through the discharge of glycoprotein known as glomalin which acts as a chelator in the rhizospheric region (Siani et al. 2017).

The exposure of copper oxide nanoparticles (1000 mg/kg) prevail suppressed immune response followed by the mortality of the earthworm species (*Metaphire posthuma*) which was related to phagocytosis, production of cytotoxic molecules, stress enzymes, and loss of total protein of coelomocytes (Gautam et al. 2018). In another study, CuO ENPs were found to limit the life span of another invertebrate species *Enchytraeus crypticus* (Gonçalves et al. 2017). More susceptibility of ENPs was recorded in the case of juvenile species of *Lumbricus rubellus* than adult populations after exposure with C-60 ENPs (Van Der Ploeg et al. 2013). The ENPs remain attached to soil colloids, invertebrates internalize the ENPs by ingestion and eventually get transferred to the gut epithelium. The ENPs toxicity toward soil invertebrates through hindering ribosomal and histone activity, by disrupting sugar, protein, and lipid metabolism (Novo et al. 2015). Moreover, NMR studies have shown the amino acid such as leucine, valine, isoleucine, and sugars such as glucose and maltose are potential bioindicators of ENPs toxicity in invertebrates (Liang et al. 2017). The negative impact of Ag ENPs on reproduction ability in *E. andrei* (Velicogna et al. 2017) and multiwalled carbon nanotubes (MWCNTs) on *E. fetida* population were also reported (Zhang et al. 2014) and it might be due to the inhibition of antioxidant enzymes and restriction on metabolic pathways.

The phytotoxicity of ENPs mainly depends on its size, shape, chemical properties, and chemical subcellular sites where it is accumulated. Depending upon the chemical and physical nature of plant cell wall, ENPs act as a carrier or modulator which interacts with cellular processes. ENPs when interacts physically with plant cells, it mainly clogs the cellular structures mechanically while chemically it influences specific groups such as sulfhydryl and carbonyl groups, thereby imparting oxidative stress by hindering the cellular homeostasis. Particle size and surface properties greatly influence the plant-ENPs interaction. Depending upon the physical properties of ENPs, these can either act as nanofertilizers or as phytotoxic agents (Pradhan and Mailapalli 2017). The metal ENPs impart toxic effects in plants through three mechanisms; first: the ENPs release specific ions which might be toxic to plants. For instance, Ag^+ ions released from Ag ENPs transport through the plasma membrane hinder cellular respiration which ultimately results in cell death. Second, their chemical interactions with cellular components may produce chemical radicals to generate oxidative stress in plants. Thirdly, ENPs can directly interact with plant cells and disrupt membrane integrity. Since metal-based ENPs are sparingly soluble, impart a detrimental effect on plants (Verma et al. 2018). The outcomes of toxicity are recorded as inhibition in seed germination, lowered photosynthetic rate, plant growth, and development, fruit production, followed by reactive oxygen species (ROS) generation, and hampering in the synthesis of major biomolecules for cell growth (Pullagurala et al. 2019). The co-exposure of TiO_2 NPs (0, 100, 250 mg l^{-1}) and Cd (0, 50 mM) determined that root exposure has shown a more prominent effect rather than foliar exposure on hydroponic culture study in maize (*Zea mays* L.). In addition to this, the accumulation of TiO_2 was also reported (increased by 1.61 and 4.29 times) upon root exposure and foliar spray of TiO_2 nanoparticles helped in reducing Cd accumulation and further lowering Cd-induced phytotoxicity in maize than root exposure (Lian et al. 2020).

A similar type of study was also performed to evaluate the effect of TiO_2 on the phytotoxicity of Cd in *Oryza sativa* L. and TiO_2 was found to lower the toxicity and accumulation of Cd in booting and tillering stages of plants (Zhang et al. 2020). Furthermore, the impact of PbS nanoparticles on the *Zea mays* L. was also studied at various hydroponic treatments and it was concluded that it exerts potential toxicity to plant, seed germination, and root elongation. The STEM-EDS mapping has suggested the presence of PbS inside cortical cells, cytoplasm, and intracellular space suggesting its translocation and accumulation (Ullah et al. 2020). In this view, Tripathi et al. (2017) have summarized the potential mechanism of phytotoxicity, anatomical, physiological, biochemical, and molecular damages due to ENPs. They have also pointed out the defense and detoxification mechanism led by plants owing to the accumulation of ENPs inside plant cells (Tripathi et al. 2017). Another study has highlighted the Ag NPs-driven changes in photochemical efficiency of *Vicia faba* through leaves injection at the concentration of 100 ppm and it has the prominent repercussion of decreasing photosystem II efficiency and increases non-photochemical quenching, affecting stomatal conductance, and assimilation of carbon dioxide (Falco et al. 2020).

7 Monitoring Methods for Engineered Nanoparticles

The exposure of ENPs results in adsorption, aggregation, deposition, or accumulation in the soil–plant system, and thus valid analytical methods are required to monitor their quantification, traveling, imaging in the ecosystem. To address the characteristic features of ENPs which mainly influence their interaction in the environment, the broad range of methods are available for their recognition and categorization, jointly with microscopy, spectroscopy, chromatography, synchrotron radiation-based methods, and also including dynamic light scattering (DLS), voltammetry, isotopic methods, size partition, and sensor-based methods.

The shape, morphology, particle size, size distribution, and aggregation, accumulation can easily be acquired by using different microscopy-based techniques. For this scanning/transmission electron microscopy (SEM/TEM), scanning transmission electron microscopy (STEM), X-ray fluorescence microscopy (XRF), atomic force microscopy (AFM), transmission X-ray microscopy (TXM), confocal laser scanning microscopy (CLSM), and hyperspectral microscopy are currently available modern spectroscopy techniques. They can easily imaging the ENPs up to nanometer size, helps to acquire 2D/3D images, in the detection limit μg-ng/g without using any external standard in imaging. Many researchers have previously used these kinds of imaging techniques to obtain different monographs of ENPs which are useful to their kinetic investigation, in vivo toxicity, translocation, accumulation, and particle behavior (Jampílek and Kráľová 2017). However, these methods have certain limitations like tedious sample preparation, whole sample representation, geometry, mechanical tips, and loss of material during staining which counteracts for inaccuracy in data acquisition.

Furthermore, spectroscopy methods like UV–Vis spectroscopy, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and energy-dispersive X-ray spectroscopy (EDX) are frequently used due to their easy handling, fast sample preparation, user-friendly, minimum aggregation, direct analysis, and economically viable. To investigate the fluorescent-labeled ENPs matrix-assisted laser desorption/ionization (MALDI), laser-induced fluorescence (LIF), or iron-trap (IT) mass spectrometry has been previously conducted (Shrivastava et al. 2019). In this view, the information about the particular nanoparticle, nanoparticle aggregation state, and average particle size, functional characteristics, and presence of outer coating can be obtained through these methods. Both NMR and IR spectroscopy were employed to detect the surface functionality of ENPs (Jiang et al. 2012). Mostly, FT-IR data was utilized to study humic substance adsorption onto silica and magnetite ENPs (Ma et al. 2018). These types of analysis are quite helpful in quantifying the quality of ENPs and also which type of functional group are present. It also detect surface charge present on ENPs and address different types of ENPs and their suitability to various type of soil for nutrient arability and deficiency to enhance soil quality. Mostly, XRD techniques are acquired to determine the crystalline nature, phase, and grain size of the nanoparticles (Jorge et al. 2013).

Dynamic light scattering (DLS) is the most commonly used technique to measure the aggregation rate/kinetics of ENPs through the measurement of zeta potential (Peijnenburg et al. 2015). Zeta potential helps to study particle aggregation or particle behavior of ENPs in the environment. Another is the mass spectrometry techniques, which generally consist of inductively coupled plasma-mass spectroscopy (ICP-MS), matrix-assisted laser desorption/ionization (MALDI), laser-induced fluorescence (LIF), or iron-trap (IT) mass spectrometry. Total metal concentrations in metallic nanoparticles can easily analyzed by aqua regia digestion followed by ICP–OES and ICP-MS measurements. Commonly used separation methods based on filtration, centrifugation, chromatography, and electrophoresis techniques are the conventional available strategies for the detection of size, shape, and charge of ENPs. Among that the most popularly high-performance liquid chromatography (HPLC), field-flow fractionation (FFF), size-exclusion chromatography (SEC), and capillary electrophoresis (CE) are used (Luo et al. 2014). They were well applied to study the various features of multiwalled carbon nanotubes, silica nanoparticles, and metal nanoparticles due to faster separation, high efficiency, low sample volume, and high sensitivity (Navratilova et al. 2015). Their combination with appropriate techniques like ICP-MS, UV–visible spectroscopy, nephelometry, and static light scattering (SLS) can extend their applications due to their broad size separation ranges and relatively moderate sample disruption (Choi et al. 2007). While the size-exclusion chromatography has higher partition efficiency, it can undergo as of fixed-phase interactions. FFF and HDC are having high detection limits (as per detector) but non-ideal samples of ENPs require additional pre-fractionation steps during sample preparation (Pornwilard and Siripinyanond 2014).

In the advancement of techniques, few methods like small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), X-ray reflectometry (XR), and neutron reflectometry (NR) are advantageous due to fast sample analysis and data extraction. The knowledge about the surface properties, organic coatings, and crystallographic behavior can excogitate by application of X-ray-based methods such as X-ray absorption (XAS), fluorescence (XRF), and photoelectron spectroscopy (XPS) as well as diffraction (XRD) as they are non-destructive, flexible, and relatively less expensive (Nurmi et al. 2005). Extensive applications of these techniques include the measurement of percentage crystallinity, detection of fine-grained minerals such as nanoparticles, nano-clays, and mix layer identifications. The XAS technique is often preferred due to its non-destructive nature, collection of wet samples (soil, sediments, and tissue) with absorption spectra but high metal concentration often creates hindrances in measurement (Tiede et al. 2008).

As emerging techniques currently small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), and static light scattering (SLS) are utilized to study the presence of ENPs in the solid and liquid phase (Polte et al. 2010). To study the atomic, molecular, and structural features mostly RAMAN and laser-induced fluorescent spectroscopy were utilized. As an advanced mechanism, synchrotron radiation-based techniques were being adapted for localization and speciation of ENPs as they are non-destructive, higher spatial resolution, and higher detection limits (Castillo-Michel et al. 2017). These are often combined with XAS, photothermal flow cytometry (PTFC), and photoacoustic flow cytometry PAFC to study the ENPs in live plant tissue (Nedosekin et al. 2010). Also, the radioactive stable isotopes based methods such as autoradiography and positron emission tomography are combined with SEM and TEM to track and visualize ENPs in the in vivo soil–plant system. Stable isotopes provide as a tracer with no harm to radiation and have a long half-life. Although rapidly evolving sophisticated analytical techniques have shown its immense potential in testing the localization, speciation, uptake, availability, biotransformation, and toxicity in the soil–plant system. But in the future, the focus should be more on isotopic and sensors based methods with the right synchronization of technologies to understand the exposure risk of ENPs.

8 Conclusions and Future Directions

The exposure, transfer, accumulation, and transformation of ENPs in the agro-ecosystem have now become an imperative subject to address their environmental fate and risk. Engineered nanoparticles (ENPs) have been enacted as sophisticated technology with conceivable consequences for sustainable agriculture. A significant contribution of ENPs for crop management, delivery agents, sensing material, disease control, and soil conservation is well known. But the unregulated exposure of ENPs in soil has shown serious implications on soil health like damage of soil structure, loss of soil fertility, and toxicity in soil microflora. Therefore, the key focus should be on the development of biodegradable nanoparticles to avoid the nano-waste-related toxicity in specific soil microorganism, plant, and long-term persistent in soil. The risk assessment with a systematic study of their production, acceptable limit, degradation, and multicentre field trial should not be overlooked in foreseeable future.

Considering all the points, a more comprehensive in vivo, in vitro study, elaborated ENPs interaction mechanism, database modeling for their bioavailability, biomagnifications, on-field monitoring through highly sophisticated techniques are the crucial points of care. Also, the strict implementation of regulatory affairs regarding their production, application exposure, and disposal, identification of exposure source, and fate pathways should be implemented to overcome the challenges and risk of ENPs. Moreover, the developing nano-era of ENPs has created a revolution in sustainable agriculture; nonetheless, the hazards associated with their continuous application cannot be ignored. Thus, the knowledge of ENPs presented here could pave a way for future research to minimize the detrimental impacts of ENPs in the soil environment through designing sustainable, green, and more efficient ENPs.

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