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REVIEW

Interaction of metal nanoparticles–plants–microorganisms in agriculture and soil remediation

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Abstract Design products or technologies that incorporate metal nanoparticles (NPs) in agriculture need to be safe for consumers, soil microorganisms, and environment friendly. This review analyzed application advances of metal NPs in crop production and soil remediation, which are two major challenges that are constraining world sustainability and food security. The use of NPs in agriculture is also explored as a tool to improve plant productivity, control phytopathogens and viruses, monitor the quality and health of plants and soil, and seed-priming. Concerning soil remediation, this review focuses on potentially toxic element pollution when NPs are used as an assisted phytoremediation alternative, combined with electrokinetic remediation, or for acid mining drainage remediation, as well as their role in photocatalysis. In addition, it addresses the pathways of interaction with soil properties, plants, and soil microorganisms, which are relevant factors influencing NPs fate and behavior in soil and their functions. Finally, this review aimed to explore the common purposes and challenges of nanotechnology in agriculture and remediation, which may be the basis for new technologies.

Keywords Environmental innovative technology · Environmental and agricultural issues · Nanoagrochemicals · Nano-enabled agriculture · Nanoremediation · Rhizosphere

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Introduction

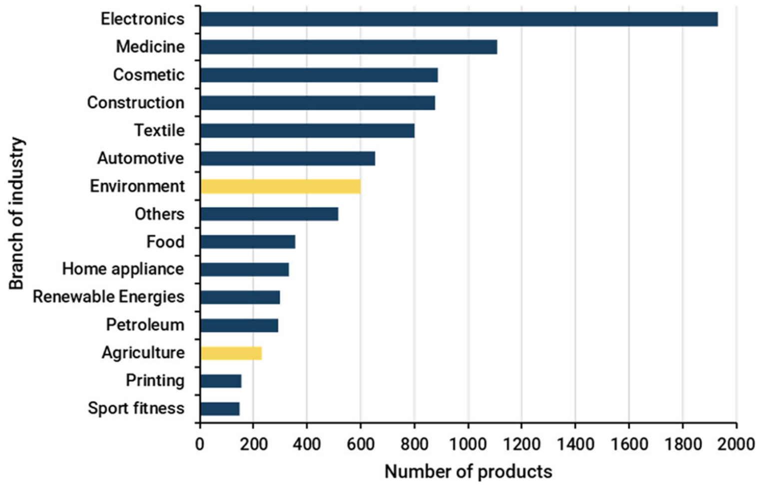
Fifty years ago, Richard Feynman suggested manipulating matter on an atomic scale by building machines at the nanoscale level allowing the arrangement of atoms (Toumey 2009). Afterward, what seemed to be science fiction became reality, originating nanoscience—the science of objects of size smaller than 100 nm—and nanotechnology—the design, synthesis, and use of nanomaterials (NMs) (Whitesides 2005).

NMs are materials with any external dimension or with surface or internal structures at the nanoscale (Santos et al. 2015). Some examples of synthesized NMs are nanoparticles (NPs), nanolayers, nanofibers, nanotubes, and quantum dots (Whitesides 2005). Matter of nanoscale has different properties than the same material at the macroscale size, for example, a high relative surface area, greater chemical reactivity, optical, electrical, and magnetic behavior (Ma et al. 2010; Raliya et al. 2018). Nowadays, NMs are mainly used in electronic, automobile, energy, chemical, health, cosmetic, and textile industries (Bundschuh et al. 2018; Sabourin and Ayande 2015) due to their properties. According to the nanotechnology products database (https://product.statnano.com/), more than 9000 products claim to contain NMs (StatNano 2018). Figure 1 shows the distribution of NMs used in different branch industries, and Fig. 2 shows the subdivisions of products for agronomic and environmental purposes.

When comparing the number of commercialized products in the agronomic and environmental sectors with other industrial branches, it results that nanotechnology is an emergent activity, with a large scale application in these sectors (Belal and El-Ramady 2016; Rajput et al. 2018). Moreover, the current market value in the agri-food sector was projected to increase to 160 billion dollars by 2020 because of the incorporation of nanotechnology in food production, processing, and packaging (Sabourin and Ayande 2015). The global nanopesticide market size is forecasted to grow at a compound annual growth rate of 14.6% from 2020 to 2027 (Bratovcic et al. 2021). The global market value for remediation using nanotechnology in 2010 was estimated to be 6 billion dollars (Bardos et al. 2018), and increase to $41.8 trillion by 2020, with a 10.2% average annual growth rate from 2015 to 2020 (Corsi et al. 2018). Besides the financial advantages, nanotechnology offers technological and environmental benefits in both sectors, agriculture, and remediation, which are circumstantially linked (Fig. 3). On the one hand, the use of nano-agrochemicals in agriculture can increase crop yield with lower amounts of substances applied, reduce the volume of spread chemicals, increase the capacity of plants to absorb nutrients, and minimize nutrient losses (Prasad et al. 2017), and consequently, reduce soil and water pollution. P.e. foliar-sprayed of nano-Fe (0.25 g L^{-1}) on cowpea plants (*Vigna unguiculata*) increased the yield 63% and 41% compared to plants treated with bulk $FeSO_4$ at 0.25 and 0.5 g L^{-1}, respectively (Delfani et al. 2014). The application of nanopesticides (including fungicides, bactericides, acaricides, nematicides, insecticides, herbicides, rodenticides, etc.) can also augment the efficiency of pest control with lower concentrations. On the other hand, a common world concern has been excessive and no reasonable use of agrochemicals such as fertilizers and pesticides for crop production. This uncontrolled use has propitiated soil, sediments, and water contamination, and has negatively influenced organisms across the food chain. Therefore, developing remediation alternatives to control contamination is a priority (Singh and Kumar 2020; Kumar et al. 2019). Nano-agrochemicals may be suitable in soil remediation; nano-remediation can reduce the reaction times compared to in situ conventional remediation techniques (Grieger et al. 2015), and be up to 80% cheaper (Corsi et al. 2018).

Even though NMs offer several benefits to food production and soil remediation, there remain gaps in knowledge to be studied that can be decisive to sooner and safer transfer of laboratory results on a large-scale application. The study of the interaction between nanosized materials and soil microorganisms is in the emerging stage. Microorganisms have crucial functions in biogeochemical cycles such as turnover organic matter, architecture soil formation, plant nutrition, and health. Moreover, they are strongly involved in the decomposition of xenobiotics, control of contamination, and soil remediation (Schloter et al. 2018). Especially, beneficial soil microorganisms are being recognized to play a paramount role in plant productivity and soil health, and they build an intricate bond between plants and soil. In plants, beneficial soil microorganisms improve nutrient uptake and enhance plant tolerance to different biotic or abiotic stresses (drought, heat, acidity, alkalinity, salinity, pathogens, and contaminants). In soils, microorganisms participate in aggregate formation, organic matter degradation, carbon sequestration, remediation, etc. (Jacoby et al. 2017). The use of NMs in agriculture and remediation compulsory requires analyzing their interaction with plants, soil, and beneficial microorganism, which has rarely been taken into account; therefore, it is addressed in this review. In the same way, unexplored effects of NMs on seed priming, soil quality, and environmental abiotic stresses such as salinity and drought need more attention. It is expected that arguments exposed here may contribute to propitiate sustainable agricultural production systems under environmentally friendly conditions, as the use of NPs without negative affectation of activity of beneficial soil microorganisms is highly desirable. Similarly, the interaction between NMs and soil microorganisms needs to be documented, including the fate of NMs after application, the residual effects, and the environmental and biological factors that affect their toxicity. These are some of the key points to predict the ecotoxicology of metal-based NMs and to formulate safe and wide public accepted technologies.

Fig. 1 Distribution of nanomaterials currently used in different industry branches according to the nanotechnology products database (StatNano 2018)



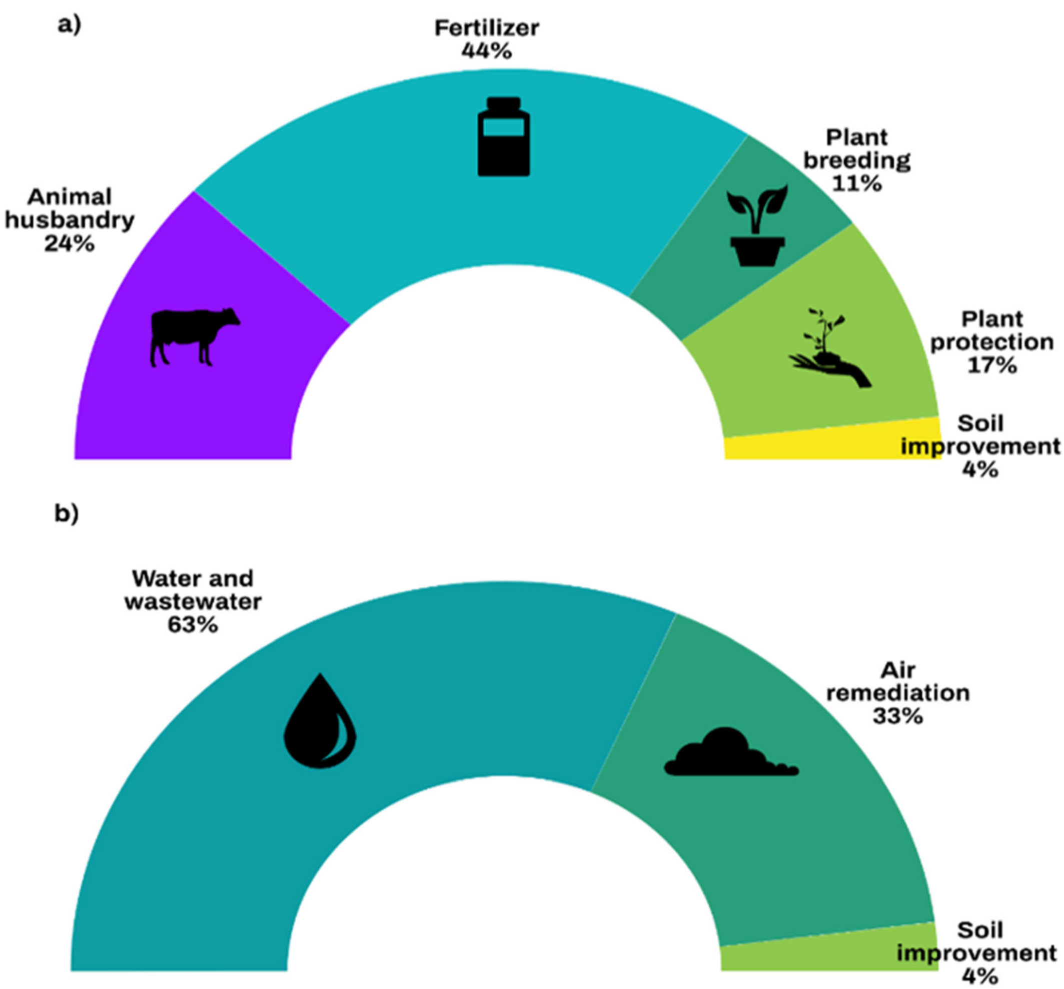


Fig. 2 Subdivisions of products for (a) agronomic and (b) environmental purposes according to the nanotechnology products database (StatNano 2018)

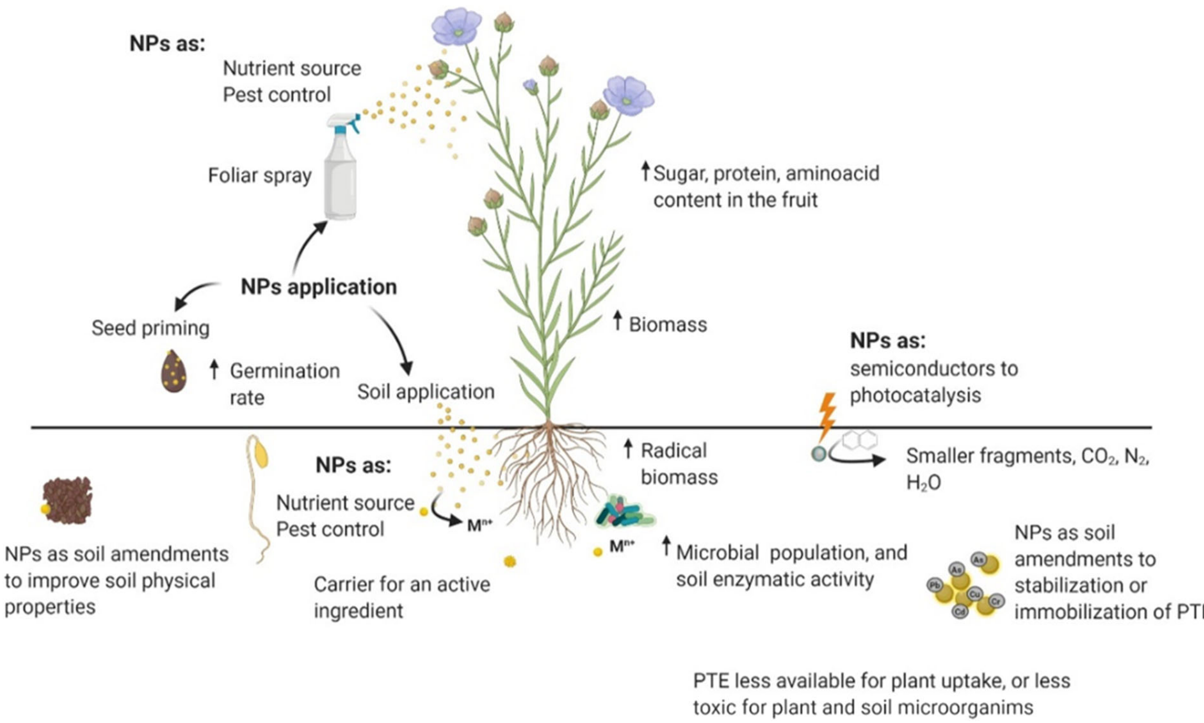


Fig. 3 Common applications of NPs in agriculture and soil remediation

Nanotechnology and NMs in agriculture

Agriculture is a sector that has a duality, on the one hand, it supplies food, and raw materials to produce consumer goods. That is to say, the agri-food industry can provide bioactive compounds (phenols, peptides, carotenoids, etc.) to produce drugs and cosmetics, fibers to the textile industry, lignocellulosic materials, and vegetable oils to produce ethanol and biodiesel (Boehlje and Broring 2011), and because of that Zulfiqar et al. (2019) pointed to agriculture as an economic sector that involves a "worldwide multitrillion dollars industry." Regarding its role in the economy, agriculture is one of the main sources of direct employment and incomes, e.g., in 2010, it was estimated that 2.6 billion people worldwide depended on agriculture for their livelihoods (Alston and Pardey 2014), and in 2018, agriculture accounted 4% of global gross domestic product (GDP). In some developing countries, it accounted for more than 25% of their GDP (The World Bank 2021). On the other hand, intensive agriculture has a negative environmental cost that ironically also endangers agriculture itself. For instance, agriculture is responsible for 15% of the total emission of methane and nitrous oxide; they both are greenhouse gases involved in global warming (Malhi et al. 2021; Park et al. 2012). Moreover, the immoderate use of agrochemicals (due to the low efficiency of some fertilizers) causes soil chemical contamination and low crop yields in the long term (Kothari and Wani 2019).

The global annual crop production (more than three billion tons) requires approximately 187 million tons of fertilizers and 4 million tons of pesticides (Usman et al. 2020). However, up to 75% of fertilizers applied to soil can be lost due to volatilization, leaching, or the runoff process (Trenkel 2010; Dimkpa et al. 2020). The range of loses from the soil are 40–70% of N, 80–90% of P, and 50–90% of K (Pitambara and Shukla 2019). This is also applicable to pesticides, where 90% of pesticides may escape during the application step (Kumar et al. 2019; Ghormade et al. 2011). So, annually 140 million tons of fertilizers and 3.6 million tons of pesticides are losing. This inefficient use makes agrochemical harmful to the environment and human beings.

Therefore, the efficient use of agrochemicals and conservation of soil quality are two of the main challenges in agriculture. They both affect food production, economy, and environmental quality. In this regard, nanotechnology is an emerging alternative that may revolutionize agriculture because of its diverse application (which will be discussed in more detail in the following section) as fertilizers, pesticides, plant growth promoters, seed treatments, opportune detection of plant diseases, monitoring soil and water quality, identification and detection of toxic agrochemical, and soil and water remediation (Prerna et al. 2021; do Espirito Santo Pereira et al. 2021; Acharya and Pal 2020). Singh et al. (2021) referred to the application of nanotechnology to agriculture production as phytonanotechnology, while Acharya and Pal (2020) mentioned the use of nanotechnology in agriculture in three specific areas: precision farming (by the application of nanosensors), crop productivity, and crop improvement (by the application of nanoagrochemicals). Furthermore, these authors discussed several qualities of NMs useful to agriculture: compact size, easy way to carry and handling, long-term storage, high effectiveness, and when used rationally, not toxic. Thus, these nanometric materials may be a favorite selection for farmers over conventional agrochemicals. Moreover, these may improve the efficiency of agricultural inputs, and achieve sustainable agroecosystems at a lower cost, energy, and waste production.

Nanoagrochemicals can improve the efficiency of applications, while reducing the loss of both nutrients and pesticides through the smart delivery and controlled release of an active ingredient (Seleiman et al. 2021). In this regard, tailored delivery systems can be designed based on the release time or environmental conditions (humidity, heat, light, pH, enzyme, redox state, and magnetic release) (Grillo et al. 2021; Huang et al. 2018). It will depend on the NMs properties and their interaction with the surrounding media. Moreover, nanoformulations may function in relation to not only time-control or spatial-target release, but also self or remote-regulation delivery to guarantee effective targeting (Kumar et al. 2019). In the case of fertilizers with high solubility and fixation in the soil, such as urea or iron, slow-release is desirable to avoid losses. Kottegoda et al. (2017) evaluated the slow release of N from urea-hydroxyapatite nanocomposites (6:1) in water. They found that the N release rate was approximately 12 times slower compared to pure urea. The urea released 99% of the nitrogen content in 5.3 min, whereas the nanocomposite released 86% of the nitrogen after 1.06 h. In this case, urea-hydroxyapatite nanocomposites may be an option to increase the efficiency of N application and to reduce the N volatilization as N_2O emissions. In contrast, when the effectiveness of a fertilizer mainly depends on the solubility of the nutrient source, nano-sized materials can improve their dissolution, because, in theory, the solubility of solids depends on the excess surface energy, which is correlated with the specific surface area and the particle size (Avramescu et al. 2017; Milani et al. 2012). To avoid undesirable effects or losses by the fast solubility of a NM, their release pattern can be improved through surface modification (by the addition of coating materials or nanoencapsulation) or by NMs coated onto granular macronutrient fertilizers (Milani et al. 2012). Under this point of view, Milani et al. (2012) synthesized urea and monoammonium phosphate-coated ZnO NPs, which had a higher fast dissolution degree and Zn solubility than bulk ZnO.

In the case of nanopesticides, the slow release may minimize crops' demand for pesticides (then, reduction of residues and environmental pollution), and achieve more effective, safe pesticide usage (Huang et al. 2018). Also, the controlled and slow release of an active ingredient is advantageous to treat specific pests or insects for longer duration without harm to non-specific targets (Nehra et al. 2021). The use of nanopesticides is in the early stage of development with safe environmental applications (Kumar et al. 2019). Gradually, the kinds of pesticide presentations are increasing, and new provisions are available: nanosuspensions, nanoemulsions, nanocapsules, nanospheres, nanogels, nanoliposomes, micelles, clay-based nanoformulations, and their function is the result of the physical and chemical properties at the nanoscale level (Table 1).

In synthesis, it is expected to maximize the crop yield with the minimum amount of fertilizers and pesticides, and to reduce the accumulation of organic and inorganic compounds in soils, as well as a decrement in greenhouse gas emissions (Raliya et al. 2018; Kah et al. 2018) by using nano-agrochemicals. It is expected that the action of external factors that cause the loss of agrochemicals will be reduced due to the properties of nanoformulations (Qureshi et al. 2018). Recently, the use of NPs as a tool for the fortification of plants was suggested (Elemike et al. 2019). In consequence, the use of nanoagrochemicals will improve crop yields, the nutrient value of crops, and may reduce the costs of production (Pestovsky and Martínez-Antonio 2017).

Nanofertilizers

Nanofertilizers are NMs or nano-enabled bulk materials used to improve plant nutrition (Raliya et al. 2018). Moreover, they have been mentioned as next generation fertilizers (Palchoudhury et al. 2018) that may help us to guarantee the world's food security (Usman et al. 2020), improve the nutritional value of food by Fe and Zn agronomic fortification (ZnO, Fe_3O_4) (Elemike et al. 2019), keep balanced nutrition to ameliorate biotic and abiotic stresses (Zulfiqar et al. 2019; Cai et al. 2020), reduce the ecological footprint due to lower amount of agrochemical used and low nutrient losses (Lal 2020). Regarding agricultural management, nanofertilizers offer some advantages: reduced transportation and application cost; the soil is not overloaded with salts; nutrient-delivered control may be synchronized to soil nutrient status, plant growth stage, and environmental conditions by using nanosensors (Zulfiqar et al. 2019; Cai et al. 2020).

Table 1 Types of nano-agrochemical formulations and their functions

Type of formulation	Function
Nanoemulsions, microemulsions of an active ingredient	Increase solubility in water of hydrophobic cargo, increase the absorption efficiency
Nanocatalyst-active ingredient conjugated in microcapsules	Rapid separation of the active ingredient in soil or plant
Nanocapsules with a conjugated catalyst with the active ingredient	Protection against premature degradation
Nanocapsules and nanospheres	Controlled release, guided delivery, protection against premature degradation, as carriers
Nanodispersions and nanosuspensions	Increase toxicity of an active ingredient in the target organism at low doses
Nanocrystals	Improve the bioavailability of water-insoluble compounds, and drug adhesiveness to surface cell membranes, enhance particle stability in suspension, and as a carrier
Dendrimers	Improve delivery, carriers for the active ingredient
Metal-nanoparticles and nano-clays	Active substance as NPs

Modified from Kookana et al. (2014)

Nanofertilizers currently available in the market are usually reformulations of active ingredients that already have a registration (Table 2, Fig. 2). There are several examples of nanofertilizers containing macro (N, P, K) or micronutrients (Cu, Fe, Mn, Mo, and Zn); however, some metal NPs such as Al, Zn, Ti, Ce, Cu, Ni, Ag, ZnO, AgO, MgO, TiO_2 and magnetic NPs as Fe_3O_4, Fe_2O_3, already used in the industry, also have versatile effects (Table 2) with potential use in agriculture (Rastogi et al. 2017). Also, carbon nanotubes and other NMs such as urea and monoamonniun phosphate coated ZnO NPs, Fe-pyrite, and nanocomposites of humic substances with Fe_2O_3 have shown their action also as fertilizers (Mastronardi et al. 2015; Lin et al. 2009).

One main advantage of nanofertilizers over bulk materials is boosting the crop yield (Kottegoda et al. 2017) even by applying lower amounts of the suggested nutrient dose. For example, P-nanofertilizers in *Glycine max* produced a 32% higher growth rate and 20% higher seed yield compared to plants treated with bulk P fertilizer (Liu and Lal 2014). In field experiments, the yield of rice after the application of urea-hydroxyapatite composites at 50% of the suggested dose (50 kg of N ha^{-1}) was 7.9 tons ha^{-1}, while applying 100 kg of N ha^{-1} as bulk urea, the yield was 7.3 tons ha^{-1}, and the nutrient absorption efficiency was 48% and 18% for urea-hydroxyapatite composites and pure urea, respectively (Kottegoda et al. 2017).

Micronutrient deficiencies in plants can result in a significant reduction of their yield attributes (Rahi et al. 2021) because micronutrients are essential to proper functioning in several processes such as plant growth regulation, chlorophyll formation, seed production, and regulation of enzyme systems. Moreover, there are important crops sensitive to micronutrient deficiency. In this regard, NPs also fix the micronutrient deficiencies and increase the crop yield. For instance, foliar application of Fe_3O_4- NPs was efficient to increase plant growth and improve Fe uptake in the order leaves>stem>roots in plants of *Nicotiana benthamiana*. Magnetita-NPs were an exceptional Fe supplement (Cai et al. 2020). Iron deficiencies in soils are a common problem that is difficult to fix due to the insolubility of Fe^{3+} in the soil and their quick fixation in soils after the application of iron-soluble fertilizers (Abbaspour et al. 2014). However, several types of Fe NMs as fertilizers and encapsulation methods have been tested. Khosroyar et al. (Khosroyar 2012) used Fe-saccharate

Table 2 Some nano-agrochemicals are currently available in the market

Product name	Composition	Formulation	Function	Properties	Use mode	Concentration	Country	Manufacturer	Reference
NanoK™	K_2O	Nanocapsule	Fertilizer	Crop yield enhancement, K delivery	Foliar spray	21%	USA	Aqua-Yield Hub	(Aqua-Yield® 2021)
NanoZn™	Zn	Nanocapsule	Fertilizer	Plant growth regulation and Zn delivery	Foliar spray	9%	USA	Aqua-Yield Hub	
NovaLand-Nano	NPs of microelements p.e. Mn, Cu, Fe, Zn, Mo, N	NPs	Fertilizer	Plant nutrition			Taiwan	Land Green and Technology Co	(Green and Co 2020)
Nano Zinc (chelated)	Zn	NPs	Fertilizer	Plant growth regulation	Foliar spray	12%	India	Alert Biotech	(Alert Biotech n.d.)
Nano Bor	B	NPs	Fertilizer	Plant growth	Foliar spray	20%	India	Alert Biotech	
Nano Cu	Cu NPs, adjuvants and chelating materials	NPs	Pesticide	Fungicide and bactericide properties		10%	Egypt	Bio-Nano Technology	(Bio Nano 2021)
Agro 2400	AgNPs, citric acid, trisodium citrate, polymerized organic compounds, and water	NPs	Pesticide	Permanent disinfection, disease prevention, extra crop growth	Soil and foliar application	2400 mg L^{-1}	Turkey	Silvertech Kimya Sanayi ve Ticared Ltd	(Silvertech Kimya Sanayi ve Ticaret Ltd., Products-Silvertech Kimya n.d.)
Agro 2475	AgNPs, CuNPs, citric acid, trisodium citrate, polymerized organic compounds, and citrate	NPs	Fertilizer and pesticide	Fungi control, and plant nutrition		2400, 7500 mg L^{-1}	Turkey	Silvertech Kimya Sanayi ve Ticared Ltd	
Agro 2490	AgNPs, CuNPs, nano chitosan, citric acid, polymerized organic compounds, and water	NPs	Fertilizer and pesticide	Fungi control, and plant nutrition	Soil and foliar application	2400, 7500, 1500 mg L^{-1}	Turkey	Silvertech Kimya Sanayi ve Ticared Ltd	
Argovit™	AgNPs	NPs	Pesticide	Huanglongbing disease	Trunk injection	2–300 mg	Mexico		(Stephano-Hornedo et al. 2020)

NPs, Nanoparticles

encapsulation with alginate coating and observed that the size of capsules influenced the Fe release time more than the doses inside of these, and the loading efficiency was higher than 90%. Iron released from these nanofertilizers is a key prospective Fe plant source. Rui et al. (2016) tested Fe_2O_3 NPs (20 nm) as iron fertilizer for peanut variety Kainong 15, a highly sensitive Fe deficiency crop. They observed increased iron shoot and root concentrations when using between 10 and 1000 mg kg^{-1} and comparable concentrations to the use of EDTA (45.8 mg kg^{-1}). The authors suggested that NPs are adsorbed on sandy soil, and are slowly dissolved, so the Fe availability increases. Also, humic substances may improve Fe solubility, plant uptake, Fe translocation, and corrected Fe deficiency in cucumber plants. The use of humic substances with nanofertilizer was considered an ecologically safe NM (Sorkina et al. 2014).

Nanofertilizers can also increase nutrient availability and absorption efficiency (between 18% to 29%) over traditional fertilizers (Usman et al. 2020), and thus increase the plant yield and nutrient value of some crops (Kah et al. 2018). Monreal et al. (2016) defined micronutrient use efficiency (MUE), according to soil fertility, as the quantity of added fertilizer-micronutrient that integrates into the crop (less than 5%). This term is related to transport, use, plant storage, and fate in the environment. To enhance MUE, foliar applications and protection of conventional micronutrients are suggested; however, the information regarding these approaches is still sparse. Interestingly, NMs can be an option to improve MUE because the small size of NMs allows them to cross biological barriers and diffuse into the vascular system of plants. Furthermore, the surface chemistry of NMs can be modified by coatings to provide new properties and functionalities to carry a target nutrient in the right place (Lowry et al. 2019). Examples of protected NM-micronutrients to improve the MUE are CuO NPs carried into mesoporous aluminosilicates with 1–10% of loading efficiency (Huo et al. 2014). Zn was nanoencapsulated on Mn carbonate-hollow core-shell with reduction of loss nutrient and improved rice Zn use efficiency (Yuvaraj and Subramanian 2015).

Similar to conventional fertilizers, nanofertilizers can be applied to roots or leaves, which influences their performance on these plant organs, bioavailability, and plant uptake. Nanofertilizers have longer and regulated nutrient release (40 to 50 days) compared to the short time availability (4 to 10 days) and less uptake efficiency (between 40% and 75%) of traditional fertilizers. For example, the concentration of Zn in leaves, fruit quality, and yield was increased 30% (number of fruits) by foliar application of commercial Zn-NM (636 mg $tree^{-1}$) in *Punica granatum* cv. Ardestani trees (Davarpanah et al. 2016). The tomato yield increased, in field and greenhouse experiments, by foliar application of CuO and MnO NPs (1000 mg L^{-1}) due to the better micronutrient plant absorption (Elmer and White 2016). Nanofertilizers obtained from green synthesis also have favorable results. Biosynthesized (*Rhizoctonia bataticola* TFR-6)-Zn NPs, size between 15 and 25 nm, were applied at 10 mg L^{-1} concentration at germination and 16 L ha^{-1} two weeks later in the field to pear millet plants (*Pennisetum americanum*). Plants treated with Zn NPs showed higher (37%) grain yield and (10%) plant Zn concentrations (Tarafdar et al. 2014).

NMs and plant diseases control

Nano-agrochemicals can be sorted as nanofertilizers and nanopesticides; however, some metal NPs have a dual function. Metal and metal oxides NMs have a role in plant protection, which has been tested under in vitro and in vivo experiments (Table 3). The foliar application of CuO and MnO NPs (1000 mg L^{-1}) reduced diseases caused by *Verticillium* and *Fusarium* in tomato and eggplants by 31% and 28%, respectively, compared to untreated plants (Elmer and White 2016). Similarly, Cu NPs were effective against *Curvularia lunata*, *Phoma destructiva*, and *Alternaria alternata*, and CuO NPs against *Saccharomyces cerevisiae* (Kanhed et al. 2014). Giannousi et al. (2013) tested diverse Cu-NPs (Cu/Cu_2O, Cu_2O, or CuO), which effectively controlled against *Phytophthora infestans* in field plants of tomato. Foliar application at low concentrations (150–340 mg L^{-1} of active ingredient) of NPs was more effective than four commercial products (540–2240 mg L^{-1} of active ingredient). Ag NPs exhibited antimicrobial activity against *Escherichia coli* and *Aeromonas hydrophila* (Aziz et al. 2016). Several examples presented before showed that different single metal NPs are useful to control phytopathogenic microorganisms; however, more complex NMs can protect from persistent organisms. Graphene oxide-Ag NPs were useful for crop disease prevention (*Fusarium graminearum*) in vitro and in vivo experiments (Chen et al. 2016), and Cu-chitosan NPs at low concentrations

(0.1%) against *A. alternata*, *Macrophomina phaseolina, Rhizoctonia solani* (Saharan et al. 2013). ZnO and nanocopper-loaded silica gel with antimicrobial activity were effective against plant fungal pathogens producing citrus canker disease and damage in grapefruit trees (Young et al. 2018). In comparison to the use of the standard fungicide captan at doses between 200 to 500 μg mL^{-1}, Sidhu et al. (2017) observed stronger antifungal in vitro activity against *A. alternata*, *Drechslera oryzae*, and *Curvularia lunata* in the range from 3 to 15 μg mL^{-1} of copper nitrate sodium sulfide (NCuS) NP aqua formulations. These authors tested naked CuS NPs and protected CuS NPs with three capping agents (polyvinyl pyrollidone, 4-aminobutyric acid, and tri-sodium citrate); the last one having the highest antifungal activity. Additionally, these authors observed enhanced rice seed germination, shoot and root length, and vigor index of seedlings at low concentrations (7 μg mL^{-1}). These Cu-derived NPs come from natural CuS, which is non-toxic and is used for human illnesses. CuS NPs have low production costs, and their synthesis is easy; therefore, their use should be further explored in agriculture.

Shenashen et al. (2017) also used cylindrically cubic mesoporous alumina NPs to control Fusarium root in tomato plants in in vitro and greenhouse experiments. Nano-sized ZnO also has antibacterial activity, Graham et al. (2016) observed an inhibitory effect of ZnO NPs on *Xanthomonas citri* subsp. *citri*, the cause of citrus canker. Additionally, ZnO was an effective bactericide against *E. coli* and *X. alfafae* subsp. *citrumelonis* at sevenfold less concentration than commercial Cu sources. Similarly, it also was an effective fungicide against *Elsinoe fawcetti* and *Diaporthe citri*, two fungal diseases causing citrus scab and melanoses on grapefruit, respectively. A commercial product with Ag NPs was highly effective in the field against Huanglongbing (yellow dragon) disease in *Citrus aurantifolia*, a devastating agro-industrial bacterial problem. When applied by foliar sprinkling or trunk-injection, this product was from 3 to 60 times and 75 to 750-fold more effective, respectively, than current antibiotic non-recommended for protection but used to control this disease (Stephano-Hornedo et al. 2020). Ag-doped TiO_2 NPs were also effective against *Fusarium solani* and *Venturia inaequalis* isolated from potato plants (Boxi et al. 2016). Foliar spray of CeO_2 NPs at 250 mg L^{-1} suppressed the symptoms of *Fusarium* disease and increased the fruit dry weight and lycopene content by 67% and 9%, respectively, compared to infested untreated plants. Plants growing in infested soil with *F. oxysporum* and treated with CeO_2 increased total sugar and Ca content by 60% and 140%, respectively, compared to plants growing in noninfested soil (Adisa et al. 2020). Satti et al. (2021) used *Moringa oleifera* leaf aqueous extract to synthesize TiO_2 NPs, which were effective at 40 mg L^{-1} against *Bipolaris sorokiniana*, the causal fungal agent of spot blotch of wheat plants. These authors observed increased water content, membrane stability, total chlorophyll concentration in fungal stressed wheat plants, higher spikes per plant, grains per spike, 100 g grain weight number. In contrast, less soluble sugar, proline, phenolic, and flavonoids concentrations were observed in fungal stressed plants. These stabilized physiological plant parameters develop wheat resistance to *B. sorokiniana*. Zn NPs (225 mg L^{-1}), after 96 h of plant treatment, also control (100%) the nematode *Meloidogyne incognita* (Kaushik and Dutta 2017). Similar effects were observed by Ag NPs, produced by green synthesis with *Cladophora glomerata*, a green macroalga, to control *M. javanica* in laboratory bioassay and when inoculated into tomato plants. These NPs had high negative impact on egg hatchability and juvenile mortality and were a potent nematicide that induced immune defense in tomato plants with significantly less galls number, egg males and females per root (Ghareeb et al. 2020). Recently, Cai et al. (2020) analyzed the influence of foliar spraying of Fe_3O_4 NPs in the *Nicotiana benthamiana* plants against *Tobacco mosaic virus* (TMV); regarded as a plant cancer and one of the most damaging plant viruses. These authors found that these NPs controlled virus spread and its proliferation due to enhanced reactive oxygen species in tobacco leaves, increased antioxidant enzymes participation against TMV (peroxidase and catalase), upregulation of salicylic acid, and expression of salicylic acid-responsive pathogenesis-related protein genes. Biogenic Ag NPs produced by *F. chlamydosporum* and *Penicillium chrysogenum* were effective to control fungal growth of *Aspergillus flavus* and *A. ochraceous*; and production of their mycotoxins, such as aflatoxin and ochratoxin A, respectively. Cytotoxic effects of Ag NPs on human melanocytes were not observed. This is an important application as mycotoxin contaminates diverse crops and is toxic at low concentrations to animals and humans causing hepatocarcinogenic diseases (Khalid et al. 2021). All these examples establish the basis of the use of NMs to control plant biotic

Table 3 Positive effects of metal NPs with potential use in agriculture

NPs	Concentration	Organism	Effect	Reference
Plant physiology				
α-Fe_2O_3	5.5×10^{-3} mg Fe L^{-1}	*Pisum sativum* *Vigna radiata* *Cicer arietinum*	The root growth increased from 88% to 366% in seedlings.	(Palchoudhury et al. 2018)
$CoFe_2O_4$	0–1000 mg L^{-1}	*Solanum Lycopersicon*	The absorption of Fe and Co improved as doses increase, but Mn and Ca absorption decreased by the presence of NPs. No negative effect on plant germination and development. Root length was greater at the 1000 mg L^{-1} dose.	(López-Moreno et al. 2016)
Fe_3O_4	20 mg L^{-1}	*Vigna radiata*	The germination percentage and bud growth improved.	(Ren et al. 2011)
	2–1000 mg kg^{-1}	*Arachis hypogaea*	The root length, biomass, and chlorophyll content augmented.	(Rui et al. 2016)
CuO	200 and 400 mg Cu kg^{-1}	Lettuce (var. ramosa Hort.)	The shoot biomass increased by 16% and 19%. Changes in the transpiration rate and stomatal conductance were observed.	(Wang et al. 2019)
ZnO	50–1000 mg kg^{-1}	*Triticum aestivum*	Biomass (63%), grain yield (53%), and Zn concentration in grain increased in comparison with plants treated with bulk $ZnSO_4$.	(Du et al. 2019)
	800 mg kg^{-1}	*Cucumis sativus*	The concentration of sugars and gluteine in the fruit was bigger than these in the control treatment.	(Zhao et al. 2014)
	1 mg kg^{-1} (foliar application)	*Cicer arietinum*	The aerial biomass, radical and root length increased 27%, 37%, and 53% respectively, compared to the control treatment.	(Mahajan et al. 2011)
	1.5 mg kg^{-1} (foliar application)		The dry weight of leaves increased.	(Burman et al. 2013)
	>10 mg kg^{-1}	*Cyamopsis tetragonoloba*	Leaves and roots growth stimulated. Photosynthetic pigments, proteins soluble in leaves, rhizospheric microbial population, and enzymatic activity of acid and alkaline phosphatase increased.	(Raliya and Tarafdar 2013)
	> 1000 mg kg^{-1}	*Arachis hypogaea*	The germination, seedling vigor, stem and root growth, as well as pod yield, were elevated comparing to the control treatment and the treatment with bulk $ZnSO_4$.	(Prasad et al. 2012)
	1.2 mM y 3 mM	*Solanum lycopersicum*	The germination rate, seedling vigor, the concentration of pigments, proteins, and sugar increased. The concentration of malondialdehyde and superoxide dismutase decreased.	(Singh et al. 2016)
TiO_2	2000 mg kg^{-1}	*Brassica napus*	The germination and seedling index increased, 75% and 1.6, respectively, in comparison with plants without the addition of NPs.	(Mahmoodzadeh 2013)
ZnO, CuSi dispersed in a silica gel matrix	0.22 kg ha^{-1} (foliar application)	*Citrus × paradise*	Antimicrobial in vitro activity against several model phytopathogenic bacteria. Control of citrus canker for two consecutive years in the field.	(Young et al. 2018)
Plant protection application				
Ag NPs	50 and 100 mg L^{-1} (Petri dish essay)	*Xanthomonas axonopodis* pv. *malvacearum,* and *Xanthomonas campestris* pv. *campestri*	Both concentrations showed antibacterial activity with zone diameters of 11 and 12 mm, respectively, for *X. axonopodis* pv. *malvacearum* and antibacterial activity zone diameters of 15 mm at 100 mg Ag NPs L^{-1}	(Vanti et al. 2019)

Table 3 (continued)

NPs	Concentration	Organism	Effect	Reference
			were observed for *X. campestris* pv. *campestris*.	
ZnO	3–12 mM (Petri dish essay)	*Botrytis cinerea* and *Penicillium expansum*	Fungal growth inhibition (63% to 80%) and hyphal malformations.	(He et al. 2011a)
	100 nM (Petri dish essay)	*Fusarium oxysporum*	Fungal growth inhibition.	(Rispail et al. 2014)
Soil effects				
nZVI	2–6 g kg^{-1}	–	The concentration of dissolved organic carbon and available NH_4^+ increased.	(Zhou et al. 2012)
SiO_2	100 mg of Si	–	The concentration of available P increased.	(Karunakaran et al. 2013)

nZVI, zero-valent iron nanoparticles

stress; they function as new weapons helping in plant protection (Cai et al. 2020). Future research should comprehensively analyze the molecular mechanisms and the toxicity of these materials.

NMs in plant pest control

Several metal NMs based on Ag, CuO, MnO, ZnO, CuSi, CeO_2, and CeAc NPs are also suitable for pest control (Kah et al. 2019; Du et al. 2019; Singh et al. 2018; Singla et al. 2019; Sun et al. 2021; Wang et al. 2019; Adisa et al. 2020). Awasthi et al. (2020) mentioned that common agricultural insect control alternatives have some constraints; such as, low efficiency, high input costs, not insect-specific, and cause environmental imbalance and negative effects to animals and humans. Therefore, NMs may provide healthy and resourceful alternatives and be environmental-friendly. Stadler et al. (2010) mentioned that nanostructured alumina is a cheap, reliable, and safe alternative in insect pest control. It was effective (95% mortality) and had quick action (3 days) against *Sitophilus oryzae* and *Rhyzopertha domina*, major insect pests in stored food supplies of wheat grains. Moreover, it was also effective in all concentrations tested (80, 125, 250, and 500 mg kg^{-1}) against *Acromyrmex lobicornis*; leaf-cutting ants affecting cacao, cassava, citrus, coffee, cotton, and corn crops (Buteler et al. 2018). Because of the strong adhesion of the nanostructured alumina to the insect's body surface, these authors suggested this NM as a particle carrier in insect control systems (insecticides, entomopathogens, or pheromones). Ag NPs have been tested for their toxicity against phytophagous mites; Pavela et al. (2017) used Ag nanocrystals synthesized with root extracts of *Saponaria officinalis* to control eggs, larvae, and adults of *Tetranychus urticae*. These authors suggested that demonstration of no phytotoxic effects of these NPs is needed for their safe use in integrated pest management strategies. Low concentrations of CuO NPs (10 mg L^{-1}) enhanced the expression of the *Bacillus thuringiensis* (Bt) toxin protein in transgenic cotton plants; however, at higher concentration (1000 mg L^{-1}) the expression was inhibited (Le van et al. 2016). These authors suggested the use of CuO NPs at low concentrations as a promising technology to improve the pest resistance of transgenic insecticide crops.

As observed, a diverse kind of NMs has potential for direct crop protection as active ingredients; however, they can also be nanocarriers of formulations. In most cases, NMs such as silica NPs, carbon nanotubes, and graphene oxides are vehicles to pesticide active ingredient to deliver in a controlled and intelligent form (Grieger et al. 2015; Pérez-de-Luque 2017; Qureshi et al. 2018; Wani et al. 2019). Nanocomposites, as plasmonically active nanorods of gold with Ag core-shell, were used as carriers of nutrients in tomato plants; moreover, to deliver bioactive agents such as the auxin growth regulator 2,4-D (Nima et al. 2014). Nano-materials may also be used to protect active compounds of biopesticides from plant or microbial origin, which have a short time span, suffer degradation by UV-rays, microbial activity, or other influencing factors (Khot et al. 2012). This protection occurs by nanoencapsulation that allows controlled dissolution kinetics as well as stability and solubility of active product. The thickness of encapsulation-wall material shells, composition, physical and chemical properties are factors to produce environmentally friendlier nanomaterials (Kumar et al. 2019). As the time of release from the nanocarrier can be modulated, the effectiveness of the biopesticide activity may be increased and prolonged for a longer time. For instance, zinc hydroxide nitrate at nanosize scale has high compatibility with anionic pesticides, and its surface functionalization is easy, which strongly influences the rate and equilibrium pesticide release (Kumar et al. 2019). Layered metal hydroxides, with magnetic and catalytic properties, offer a novel alternative as pesticide carriers (Rives et al. 2013). Kumar et al. (2019) mentioned that cyanobacteria powder may function as carriers of nanopesticides. The advantages to using these microorganisms are based on their cosmopolitan abundance, biocompatibility, and heterogeneous cell wall-functional groups able to load pesticides. Cyanobacteria powder and Carbopol coating functioned as an avermectin-nanocarrier under stimuli-controlled delivery; which was low and slow, and the photostability to UV radiations was enhanced compared to the use of free avermectin (Yang et al. 2013).

Nanosensors in agriculture

Nanosensors are next-generation sensors in a more compact presentation than traditional sensors (Usman et al. 2020). Nanosensors help improve agricultural practices: to identify soil contaminants and residues of their transformation, to detect nutrient soil deficiency and early plant diseases, to monitor soil temperature and humidity, and other environmental stressors (Baruah and Dutta 2009). Therefore, opportune corrections may be done and consequently positive effects on crop yield, plant health, and use inputs. Nanosensors are long-desired tools for precision farming (Acharya and Pal 2020); which may enhance productivity in agricultural systems maximizing output from plants while reducing the inputs (fertilizers, pesticides) with environmental monitoring and wise actions.

Any sensor used to bring information, combining biological and physical-chemical aspects, from nano to macroscopic scale is a nanosensor. The principle of operation of nanosensors is that they are based on the interaction of a particular characteristic of a NM with the surrounding environment at nanoscale level (Chakraborty et al. 2021). These smart devices are small, controllable, sensitive, accurate, and reproducible (Awasthi et al. 2020). Gold NPs, silica NPs, carbon nanotubes, graphene, quantum dots, and polymer nanocomposites have been used in the nanosensor production (Kwak et al. 2017). Developing simple methods to detect chemicals, indicators of organism, or process is a challenge due to the constraints. Organic dyes used for optical sensors may have poor photostability, easy photobleaching, small Stokes shifts, and short lifetimes. However, metal-NPs may be useful for this goal, semiconductor quantum dots, noble metals NPs can have the advantages of biocompatibility, low toxicity, resistance to photobleaching, and stable emission (Qian et al. 2014). Aptamers, short single-stranded DNA, or RNA are useful due to their ability to specifically bind the target (Taghdisi et al. 2015). Fluorescent nanoprobes of silica NPs were used for detecting *Xanthamonas axonopdis* that causes bacterial spot disease in Solanaceae plants (Yao et al. 2009). CuO NPs and nanolayers have been tested as a gas sensor to detect *A. niger* in bread (Etefagh et al. 2013). Alternatives such as this may be useful for detecting other phytopathogens in seeds or plants of agronomical interest. These nanodevices have high sensitivity for on-site detection at low concentrations such as parts per billion (ppb). P. e. Au NPs were used for simple, rapid, reliable, real-time, and highly sensible colorimetrically detection of organophosphorus pesticides such as diazinon (at 54 ppb), iprobenfos (54 ppb), and edifenphos (28 ppb), commonly used in agricultural production and highly toxic to human health (Kim et al. 2015).

Monreal et al. (2016) defined a nanodevice as a manufactured appliance to control and manipulate biomolecular constructs and assemblies such as proteins, cellular lipid layers, viruses, or nucleic acids. They suggested that these nanodevices may be useful to improve MUE and crops nutritional quality by controlling nanofertilizer delivery. Some examples are the incorporation of a fluorescent protein reporter gene (egfp) in a *P. putida*-genetically modified (GM) that detected 90% Zn content in soil:water extracts of Zn-amended soils. Similar results were observed with the *E. coli*-GM and the reporter gen pZNT-lux to quantification of soil bioavailable Zn concentration. Synthetic nucleic acids function to provide highly specific and sensitive detection of different chemical species in fluids or single living cells. These authors proposed that aptamer nanodevices may help to study metabolites in the alive cells involved in the rhizosphere and their interaction to nutrients cycling, control temporal and spatial nanofertilizers, identify and treat plant and soil nutrient deficiency. Therefore, a more complete understanding of in vivo plant–soil–microorganism systems and their influence on global crop production may be obtained.

NMs in seeds quality and protection

Seed priming is a traditional method practiced in agriculture to induce seed germination and seedling establishment that usually uses water or solutions with nutrients, hormones, plant regulators, or biopolymers. Seed priming using NMs is an innovative, easy, efficient process and convenient agricultural technique mainly for micronutrient application. Research shows that seed nano-priming not only improves seed germination and synchronization, vigor, and establishment of seedlings but also has a significant influence on the overall lifecycle of plants (crop resistance to biotic and abiotic stresses, storage, fortification). However, time imbibition and kind of NPs should be considered as effect on plant growth and yield may change (Rahman et al. 2020). Hence, it has important potential on food quality and production for agricultural applications (do Espirito Santo Pereira et al. 2021). Palchoudhury et al. (2018) suggested that seed priming with NMs functions as fertilization with lower amounts and avoids the need for soil fertilization. This represents a more environment-friendly fertilization alternative. These authors analyzed the use of low and high concentrations of two Fe NMs (Fe_2O_3 and Pt-decorated Fe_2O_3) on priming seeds of five legumes. Seedlings of green pea (*Pisum sativum*), chick pea (*Cicer arientinum*), and green gram (*Vigna radiate*) had better growth with low concentrations (5.54×10^{-3} mg Fe L^{-1}) of Fe_2O_3 NPs. The improvement growth rate of embryonic roots was also detected in these legume plants (88–366%). ZnO NPs applied to seeds of peanut (1000 mg kg^{-1}) also enhanced germination and vigor of seedlings (Prasad et al. 2012). Nano-iron pyrite (FeS_2) was used as seed priming from diverse vegetables, spice, fodder, and oilseed crops. Yield increment 47% in beetroot, 19% in carrot, 65% in mustard, 66% in sesame, and 217% in alfalfa (Das et al. 2016). Prerna et al. (2021) used α-Fe_2O_3 NPs on rice (*Oryza sativa*) and maize (*Zea mays*) seeds that were primed from 20 to 200 mg L^{-1}. These authors found that 25 mg L^{-1} enhanced germination and seedlings dry matter production of both plants in comparison to conventional hydro-priming. NPs also enhanced the levels of superoxide anions and hydrogen peroxide in seeds of rice and maize, and consequently higher concentrations of antioxidant enzymes (superoxide dismutase, catalase, and malondialdehyde) were observed in seeds of both plants imbibed for 24 h in NPs solution. They also found that foliar application of these NPs improved the yield of rice and maize measured by grain weight, and length, thickness, and width of seeds. Green synthesized FeO NPs (by *Cassia occidentalis* L. flower extract) at two concentrations (20 and 40 mg L^{-1}) were the priming treatment of *Pusa basmati* rice seeds. At both NP concentrations, seeds had higher germination and vigor than treatments with $FeSO_4$ and water. At lower NP concentrations, seedlings presented 50% induction of root length, dry weight and sugar, and amylase concentrations. Moreover, Fe uptake and reactive oxygen species (ROS) production also were stimulated (Afzal et al. 2021). Seed priming with metal NPs is a promising biotechnological alternative for saline conditions. Examples of Mn, Zn, and Fe NPs in pepper (*Capsicum annuum*), lupin (*Lupinus termis*), and sorghum (*Sorghum vulgare*) seeds, respectively, also showed improvement in germination, seedling and plant growth, photosynthetic pigments, phenols, organic molecules, antioxidant enzymes, and root and shoot distribution of Na (reviewed by Do Espiritu Santo Pereira et al. 2021).

The use of Cu^0 NPs (65 μm) in seed priming resulted in developed drought resistance in corn plants. Higher chlorophyll and carotenoid concentrations were observed, and regulation of protective mechanisms as enzymes scavenging ROS and antioxidants (Van Nguyen et al. 2021). Similarly, Cu^{2+}-loaded chitosan NPs at 0.0625 mmol L^{-1} favorably activated enzymes related to antioxidant response in corn seeds under high temperature (42 °C) and relative air humidity, near 100% (Gomes et al. 2021).

Materials at nanoscale size are also useful to protect seeds from seed-borne diseases (Acharya and Pal 2020), which may be a valuable alternative in agriculture as crop productivity depends on seed quality. Arumugam et al. (2016) observed no effect on seed germination, the growth rate of root and shoots when using hydrophobic silica NPs in several seeds (*Vigna ungiculata*, *V. mungo*, *V. radiata*, *Cajanus cajan*, *Macrotyloma uniflorum,* and *Cicer arietinum*). However, these authors found a protective effect of seeds of these plants against beetle infestation (*Callosobruchus maculatus*) by significant oviposition reduction, emergence of adults, and seed damage. The physical seed characteristics influenced maximum surface area covering or not by NPs. These results show the use of NMs in postharvest management. Another example in this aspect is the use of plant-extract biosynthesized Ag NPs (2000 μg mL^{-1}) to effectively protect banana fruits against *Colletotrichum musae*. Jagana et al. (2017) observed 6% of disease severity in comparison to 76% in non-treated fruits.

Choudhary et al. (2019) tested Zn-coating chitosan NPs in maize seeds priming and observed increased antioxidant enzymes and lignin concentrations, which was related to increased resistance to pathogens. Similarly, low concentrations of mesoporous Si NPs loaded with cinnamon essential oil in pea (*Pisum sativum*) primed seeds increased 90,000 times the bactericide action against *P. syringae* (Li et al. 2021). Moreover, the effects observed in NMs-primed seed were not only on seed growth and biotic stresses but also had a positive influence on abiotic plant stress. Li et al. (2021), under Cd stress (0 and 100 mg L^{-1}), observed significant plant growth improvement and a modified metabolomics analysis in two fragrant rice varieties treated with ZnO NPs (0, 25, 50, and 100 mg L^{-1}). The concentration of Zn in seedlings increased by ZnO NPs, but seedlings had significantly fewer Cd concentrations. As seed priming using NMs is a novel agronomical tool, more benefits by their use are expected.

Other benefits of metal NPs in agricultural soils

Scarce information is available on NMs influence in agricultural soils, especially on their physical and chemical properties (Table 3), and their use to solve other soil limitations besides soil remediation (Zhuo et al. 2012). There are several soil constraints strongly influenced by global climate change that threaten sustainable agriculture by decreasing crop productivity. For example, soil salinity is a major world environmental concern, involving nearly 800 million hectares of arable land worldwide. Some authors have demonstrated that TiO_2 NPs ameliorate negative effects of soil salinity on agricultural or medicinal crops such as broad bean (*Vicia faba*), tomato (*Solanum lycopersicum*), or Moldavian balm (*Dracocephalum moldavica*) (Khan 2016; Abdel Latef et al. 2018; Gohari et al. 2020). Abdel Latef et al. (2018)-observed that the application of 0.01% TiO_2 NPs influenced plant growth and reduced soil salinity stress in broad bean, a widely growing leguminous crop. Proline, soluble sugars, amino acid concentrations, and antioxidant enzyme activity were increased. Gohari et al. (2020) showed that 100 mg L^{-1} of TiO_2 NPs under saline conditions (50 mM NaCl) enhanced agronomic traits (plant height, fresh and dry shoot weight, leaf number, and fresh and dry leaf weight) and antioxidant enzyme (catalase, ascorbate peroxidase, superoxide dismutase, and guaiacol peroxidase), and lowered hydrogen peroxide concentration. The amounts of geranial, geraniol, and z-citral, the dominant essential oil components of the medicinal plant *D. moldavica*, used as a painkiller for kidney complaints, toothache, and colds, increased by application of TiO_2 NPs in the control treatments but decreased under salinity conditions.

Nanomaterials have applications for soil improvement from geotechnical and geological engineering and design point of view. For example, low concentrations (0.2%) of multiwall carbon nanotubes and carbon nanofiber enhanced hydraulic conductivity and reduced soil cracks of clayey sand soils. Similarly, mixtures of nanoalumina positively influenced compaction, crack intensity, and particle arrangement of soils (Alsharef et al. 2016). Metallic NPs used as soil amendments may improve soil properties. Iron oxides NPs can induce changes in the physical and chemical soil properties (Mukhopadhyay 2014), bulk density, and porosity (Bayat et al. 2018); Sun et al. 2021; Pérez-Hernández et al. 2020; Zhang and Zhang 2020). The bulk density of agricultural soil, classified as Hypocalcic Cambisols, increased from 1.05 to 1.1 g cm^{-3} with the addition of Fe_3O_4 NPs at 3% (*w*/w). In contrast, MgO NPs at 3% (w/w) decreased soil bulk density from 1.05 to 0.97 g cm^{-3}. Moreover, Fe_3O_4 increased the tensile strength of the soil aggregates by the establishment of bonds between Fe and soil particles (Bayat et al. 2018). Interestingly, alfalfa seed priming FeS_2 treatment not only influenced plant growth and yield but also had an influence on the soil. This treatment resulted in plants that increased soil cover, anchorage of the soil, and consequently reduced soil erosion (Das et al. 2016). These authors suggested this approach as sustainable in a fragile ecosystem to decrease soil erosion. Zhou et al. (2012) studied the influence of different doses (2 to 6 g kg^{-1}) of three iron-based NPs such as Fe^0, Fe_3O_4, and Fe_2O_3 on pH, dissolved organic carbon (DOC), NH_4^+ and P availability, and enzymatic activities (key components of biogeochemical cycles and soil quality) in two soils. Responses were dependent on soil type and kind and doses of NPs. Fe^0 increased DOC and NH_4^+ availability but decreased P availability. Both NP, Fe_3O_4 and Fe_2O_3 lowered pH and nutrient availabilities. Summarizing, the information shows that NMs may influence soil quality; however, more research is needed to apply this knowledge in agricultural soils to improve their quality, physical and chemical properties, and sustainability.

Interaction NMs and plants

There are several examples of the beneficial impacts of metal NPs on plants (Table 3); however, undesirable effects on plants have also been described (Table 4). This intricate impact is due to the fact the effects of metal NMs on plant morphology, physiology, and biochemistry depend on several interacting factors: shape, type, and size of NPs, concentration, agglomeration, application form, kind of metal, and their properties, etc. (Batsmanova et al. 2020). Plant species (Elemike et al. 2019), environmental conditions (Morales-Díaz et al. 2017), and nature of growth media (soil, hydroponics, in vitro conditions, etc.) are also key elements influencing the result of this interaction (Singla et al. 2019). Although these factors are key aspects to assess the plant response, and their analysis is partial, the type, size, and concentration are the NMs features more often studied. More information is also available in less natural experimental conditions such as laboratory tests and soilless experiments. Therefore, generalization on the interaction NMs-plant is not possible and proper comparison from results obtained is difficult.

On the one hand, the positive effects of metal NPs on plants may be observable at different plant stages and growth conditions (Table 3). Metal NPs can accelerate germination (Ag NPs, nZVI, ZnO, TiO_2, $nSiO_2$), stimulate aerial and radical biomass (Ag NPs, Al NPs, CeO_2, ZnO, Fe_2O_3, $CoFe_2O_4$, CuO), and increase crop yield (Fe, Co, Cu, Au NPs). In regenerated shoots of *Vanilla planifolia* obtained by a temporary immersion bioreactor system, Ag NPs stimulated shoot multiplication and elongation; however, at high concentrations, there was inhibition of these two processes (Spinoso-Castillo et al. 2017). In a greenhouse experiment, Antisari et al. (2015) evaluated the effect of CeO_2, Fe_3O_4, SnO_2, TiO_2, Ag, Co, and Ni NPs at 20 mg L^{-1} on the morphology and nutrition of tomato plants growing in soil. The authors found that plant yield and nutrient content depended on the type of NP. For instance, SnO_2 NPs reduced root biomass by 63% compared to control plants (without the addition of NPs). While Fe_3O_4 NPs increased root biomass by 153%. Palchoudhury et al. (2018) observed a positive effect on the plant growth of three legumes when low iron oxide NPs concentration (5.54×10^{-3} mg L^{-1} Fe) was used; however, these authors found contrary effects at high NPs concentrations (27.7 mg L^{-1} Fe). Jahani et al. (2019) assessed the effect of different concentrations, from 0 to 4000 mg L^{-1}, of Co_3O_4 NPs foliar sprayed in *Brassica napus* L. The results showed that at concentrations of 50 and 100 mg L^{-1} stimulated plant height, biomass, and chlorophyll concentration. Doses of 250 to 4000 mg L^{-1} increased plant height, fresh and dry weight, leaf area, but the membrane stability index decreased due to the high concentration of oxidative stress markers such as peroxide, malonaldehyde, and other aldehydes. Similar results have been observed in *Calendula officinalis* L. treated with CeO_2 NPs (Jahani et al. 2018). Askary et al. (2017) applied Fe_2O_3 NPs (0 to 40 mM) to *Catharanthus roseus*, which resulted in increased plant growth variables, photosynthetic pigments, and concentration of proteins. Prerna et al. (2021) using α-Fe_2O_3 NPs found significant yield increase in wheat and corn under field conditions; similarly, in wheat with ZnO NPs (Kah et al. 2019) and in *Arachis hypogaea* (Das et al. 2016). More examples of the positive effect of NMs in agricultural plants were presented previously, in the "Nanofertilizer" section. Furthermore, several specific reviews have been published recently (Usman et al. 2020; do Espirito Santo Pereira et al. 2021; Acharya and Pal 2020; Singh et al. 2021; Awasthi et al. 2020).

On the other hand, metal NPs in plants can inhibit several plant processes and several factors as mentioned before may be involved (Table 4). For example, root length (Ag NPs, Al_2O_3, CuO, ZnO), leaf expansion (Ag NPs and TiO_2, ZnO), growth (Ag NPs, CuO, TiO_2, ZnO), and nutrient uptake (Ag NPs); in addition to reduction of biomass (Ag NPs, Ag_2S, CuO, SiO_2), photosynthetic rate (CeO_2, Co_3O_4, ZnO, TiO_2), chlorophyll content (CuO, ZnO, Ag NPs), and germination rate (Si, Pd, Au, Cu, Ag NPs, ZnO, CuO, Al_2O_3). High concentration of NPs may damage vacuoles (Ag NPs), induce cell wall rupture (Ag NPs, CeO_2), lipid peroxidation (ZnO, CuO, NiO, CeO_2), and increase the concentration of ROS (CuO, ZnO, Fe_3O_4, TiO_2, CeO_2), abscisic and jasmonic acid (TiO_2). Even DNA damage (Al_2O_3), chromosomal aberrations (ZnO, NiO), and different pattern expression of some proteins involved in cell defense (Ag NPs) have been observed (Zuverza-Mena et al. 2016; Singla et al. 2019; Youssef and Elamawi 2020; Liu et al. 2020; Raffi and Husen 2019;

Table 4 Some negative effects of metal NPs on plants and soil microorganisms

NP	Effect	NP size (nm)	Concentration (mg L^{-1} or mg kg^{-1})	Medium	Organisms	Reference
Plants						
Ag	Oxidative stress and DNA damage.	<100	Effect dose-depend (5–80)	Solution	*Allium cepa*	(Pand et al. 2011)
Ag	Low biomass and chlorophyll content.	10–15	50–5000	Solution	*Lycopersicon esculentum*	(Song et al. 2013)
Ag	Low water content, the root, and shoot length were reduced by 48%, and 40% compared without NP addition. Less concentration of Ca, Mg, B, Cu, Mn, and Zn compared to the control plants.	2	500	Solution	*Raphanus sativus*	(Zuverza-Mena et al. 2016)
ZnO	Low biomass and root length.	20±5	> 1000	Hoagland nutrient solution	*Lolium perenne*	(Lin and Xing 2008)
ZnO	Reduced germination rate. Root cells denoted chromosomal aberrations and alterations in the cell cycle were observed. Enzyme systems showed an altered expressed pattern.	80	100–200	Solution	*Vicia faba*	(Youssef and Elamawi 2020)
Al_2O_3, TiO_2, ZnO	TiO_2 reduced the mitotic index by 60% at 0.1 mg L^{-1}. Disturbed metaphase was observed in roots treated with Al_2O_3 at 10 and 100 mg L^{-1}. Oxidative stress increased with the increasing concentration of NPs.	>50	0.1, 10 and 100	Solution	*Allium cepa*	(Debnath et al. 2020)
ZnO	At low NPs concentration higher nitrogenase activity in the four legumes tested. At 10 mg kg^{-1} negative effects were observed.	16–30	1.5–10 mg L^{-1}	Hogland Nutrient solution	*Vigna unguiculata*, *V. radiata*, *V. aconitifolia* and *Cyamopsis tetragonoloba*	(Kumar et al. 2015)
CuO	Reduced percentage of germination, loss of viability of root cells, oxidative stress.	<50	0.080 and 0.12	Solution	*Oryza sativa*	(Shaw and Hossain 2013)
ZnO	Growth inhibition, low chlorophyll content, reduction of photosynthetic rate, stomatal conductance, and intracellular CO_2.	<50	200–300	Soil	*Arabidopsis thaliana*	(Wang et al. 2016a)
TiO_2, ZnO	Both NPs reduced the biomass of wheat plants. Soil protease, catalase, and peroxidase activities were inhibited.	<100	10 5	Soil	*Triticum aestivum* L.	(Du et al. 2011)

Table 4 (continued)

NP	Effect	NP size (nm)	Concentration (mg L^{-1} or mg kg^{-1})	Medium	Organisms	Reference
Soil microorganisms						
Carbon-coated Ag	Concentrations >0.25 mg kg^{-1} had negative effect on several genes involved in denitrification (DN), nitrogen fixation (NF) and nitrification (N). Concentrations between 0.025 to 0.05 mg kg^{-1} the genes involved in DN and NF were not affected, but the genes expression in N (*amoA1* and *amoC2*) was upregulated between 2 to 3 times.	35	Several concentrations according to their minimal inhibitory concentration to Ag NPs	Pure culture	*Azotobacter vinelandii* (NF) *Nitrosomonas europaea* (N) *Pseudomonas stutzeri* (DN)	(Yang et al. 2013)
Ag	Inhibition of microorganisms involved in nitrogen cycle (nitrite and ammonia-oxidizers).	27	5, 50 mg L^{-1}	Pure culture	*Nitrospira multiformis*, *Nitrosomonas europea* and *Nitrosococcus oceani*	(Beddow et al. 2014)
ZnO	Modified morphology of *R. leguminosarum*, diminished root nodulation and biological nitrogen fixation.		250–750 mg L^{-1}	Liquid medium	*Vicia faba/Rhizobium leguminosarum*	(Huang et al. 2014)
Ag	The abundance of Acidobacteria, Actinobacteria, Cyanobacteria, Nitrospirae, and Firmicutes decreased significantly in comparison with control treatment. Cell damage in the cell wall of *Nitrosomonas europaea* was observed.	50	50, 100	Soil	Soil microorganisms	(Wang et al. 2017)
Ag	The number of nodules and spores, nitrogenase activity, rate of mycorrhizal colonization, plant dry weight, and plant height decreased in comparison to control treatment. Delayed nodulation processes and alterations in the number of bacteroids.	5–50	0.8	Soil	*Rhizobium leguminosarum bv. viciae ASU (KF670819), Glomus aggregatum, Vicia faba*	(Abd-alla et al. 2016)
ZnO	Inhibition of root elongation. Two hours after NPs exposure the activity of glucosidase was reduced. 30 d after NPs exposure the abundance of *Actinobacteria, Proteobacteria,* and	50	200–1000	Soil	Soil microorganisms and *Phytolacca americana*	(Shi et al. 2020)

Table 4 (continued)

NP	Effect	NP size (nm)	Concentration (mg L^{-1} or mg kg^{-1})	Medium	Organisms	Reference
	Acidobacteria decreased by 76%, 40%, and 11%, respectively.					
ZnO	The number of nodules and plant biomass was reduced in non-inoculated plants (AMF) and treated with NPs. While in plants inoculated with AMF, the colonization rate decreased in comparison to control plants.	18	375 and 500	Sand:Perlite (1:1)	*Trigonella foenumgraecum*, *Rhizobium mellilot*i, *Glomus intraradices*	(Siani et al. 2017)
ZnO	Plant growth and soil enzyme activity were inhibited.	30	250–500	Soil	*Sorghum bicolor* L., *Funneliformis caledonium* (*Glomus caledonium)*	(Wang et al. 2018a)
ZnO	The rate of root colonization was inhibited.	30	500	Soil: Sand (3:2)	*Zea mays* L. var. Zhengdan958, *Funneliformis mosseae*	*(Wang et al.* 2018b*)*
ZnO	The plant growth and the rate of AMF colonization were inhibited.	90	>800	Soil	*Zea mays* L. var. Zhengdan958, *Glomus versiforme, Glomus caledonium,*	*(Wang et al.* 2016b*)*
ZnO s-ZnO	After 90 d, the richness and alpha diversity of the bacterial community was significantly reduced compared to the control treatment.	25	500	Soil	Soil microorganisms	(Chen et al. 2020)
Ag, Ti	The colonization of AMF decreased, as well as the uptake of ^{134}Cs by mycorrhizal plants.		154	Soil	*Helianthus annus, Glomus intraradices*	(Dubchak et al. 2010)
CuO	Inhibitory effects on the dehydrogenase and phosphatase enzyme activity.	<50	68 and 332	Biosolids-amended soil	Soil microorganisms	(Samarajeewa et al. 2020)
CuO	A decreased abundance of the denitrification genes *nirS* and *narG* was observed.	28	0.63 and 63	Soil	*Triticum aestivum* cv. Cumberland and rhizospheric bacteria	(Guan et al. 2020)
FeO	Glomalin content was reduced. An inhibitory effect on the plant uptake nutrients.	10	3	Sand: Perlite (1:1)	*Trifolium repens, Glomus caledonium*	(Feng et al. 2013)
Fe_3O_4	The decrease in bacterial abundance and AMF diversity of corn plant rhizosphere.	10	10	Soil	*Zea mays*	(Cao et al. 2016)

Table 4 (continued)

NP	Effect	NP size (nm)	Concentration (mg L^{-1} or mg kg^{-1})	Medium	Organisms	Reference
Fe^{o}	Adsorption of nZVi onto outer cell membranes may affect membrane permeability or to disruption of the membrane lipid bilayer. It may increase the generation of the free radicals.	320	70–700	Ultra-pure water pH adjusted at 5–5.5	*Escherichia coli*	(Auffan et al. 2008)

Rasouli et al. 2020; Zuverza-Mena et al. 2017). However, the effect of NP depends on the doses and type of particle and plant species.

Nano-biotechnology is an interesting research field in which some authors have analyzed the use of NMs in transgenic plants. Le Van et al. (2016) investigated the effect of CuO NPs on conventional and transgenic cotton plants. These authors observed that at low concentrations (10 mg L^{-1}), CuO NPs did not influence plant height, root length, root hairs, shoot, and root biomasses in both cotton genotypes; however, at higher concentrations (200 or 1000 mg L^{-1}) both genotypes were negatively affected. They also observed modifications in hormone (IAA and ABA) and nutrients concentrations by adding CuO NPs. The responses were dependent on NPs concentration, part of the plant (root or shoots), and cotton genotype. Li et al. (2014) concluded that transgenic cotton plants are less tolerant than conventional cotton plants to CeO_2 NPs. Shoot biomass, Zn shoot, and Fe root concentrations significantly decreased at 500 and 1000 mg L^{-1} of CeO_2 NPs in Bt-transgenic cotton plants. These authors observed significantly lower Ce shoot and root concentrations in transgenic cotton plants than the conventional ones at the three Ce NPs concentrations tested (100, 500, and 2000 mg L^{-1}). Bt-transgenic cotton plants have low transportation ability due to the consumption of energy to produce the toxic protein Lepidoptera larvae species.

Interaction metal NMs and soil

The interactions between NPs and soil control the fate and behavior of NPs. Thus, these interactions and the variables involved are relevant to make sure that NMs fulfill their function. Similar to the bulk metallic compounds transport, it is recognized that soil properties affect the mobility, size, dissolution, and toxicity of metal NPs, in addition to the NPs properties (Bruemmer et al. 1986; Dimkpa and Bindraban 2018). The interactions between metal NPs and soil are complex, due to the effects on the organisms living in the site, chemical reactions, transport, and the soil variables involved in these reactions (Fig. 4).

The mobility of NPs in soil determines their bioavailability to the plants and their fate (Singh and Kumar 2020). Some studies highlighted that ionic strength, soil humic acids, organic matter, soil texture, and pH may influence the mobility of Fe_3O_4, TiO_2, CuO, and ZnO NPs (Belal and El-Ramady 2016; Singh and Kumar 2020; Ermolin et al. 2019). Soil column experiments showed that ionic strength affects the mobility of NPs in soil and porous media (Singh and Kumar 2020). Because ionic strength affects different forces acting on NPs, such as the van der Waals, electrical double layer, and electrostatic forces potential differences, a high ionic strength limits the mobility of NPs by promoting the agglomeration (reversible) and aggregation (irreversible) of NPs and their deposition on the surface of soil colloids (Mondal et al. 2021; Ben-Moshe et al. 2010), linking ions are relevant in these changes.

Some NPs properties influence the behavior and mobility in soil, including changes in particle aggregation or disaggregation, the surface structure, and charge. The NPs can move in porous material as individual particles, agglomerates, or micro-aggregates. As individual particles, NPs move in soils by diffusion, and mass flow, particle transport is controlled by the NPs filtration rate by the porous media (Chen 2018). In contrast, when agglomeration or aggregation occurs, NPs can be immobilized by physical straining (Conway and Keller 2016). The physical straining means that NP aggregates are retained in a soil pore that

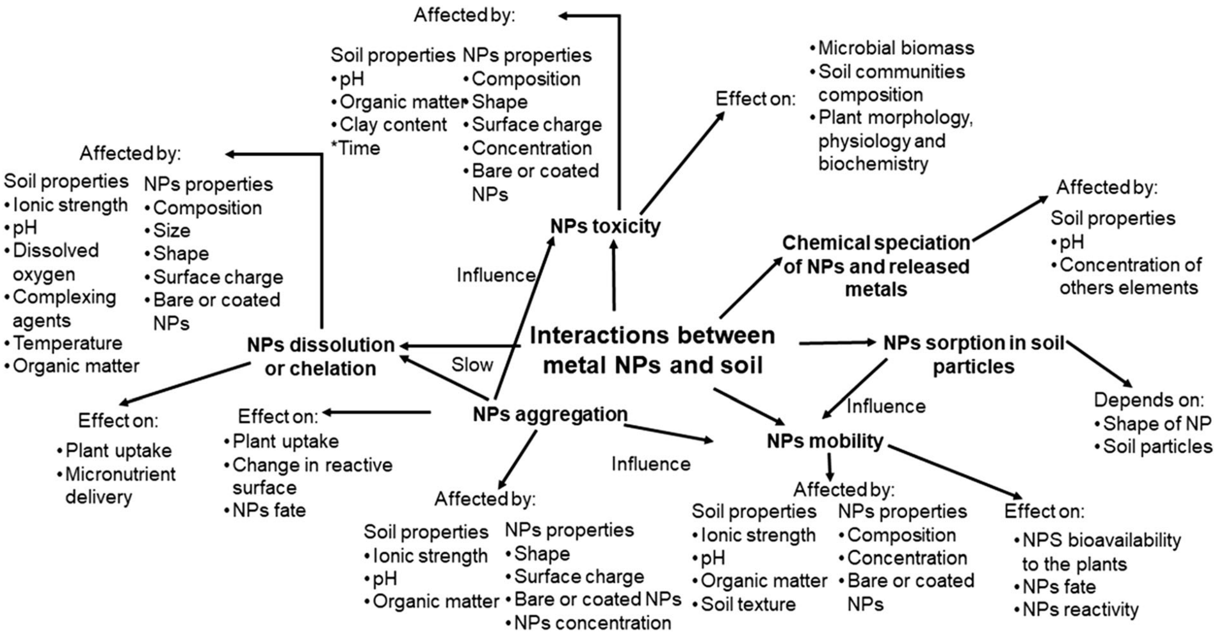


Fig. 4 Main interactions between metal NPs and soil and their effects

is smaller than them (Díaz et al. 2010). Results show that after 72 h of application of TiO_2, CeO_2, and $Cu(OH)_2$ NPs, their mobility in agricultural and grassland soils was limited to the upper 3 cm soil depth. The formation of micro-aggregates with the organic matter was the cause of the immobilization of these NPs, and the higher retention occurred in less porous soil columns. Therefore, physical straining was the primary mechanism of retention (Conway and Keller 2016). Soil minerals can enhance or inhibit the mobility of NPs aggregates. It depends on the NPs adsorption on mobile colloids or non-mobile soil particles (Belal and El-Ramady 2016; Ermolin et al. 2019). Ermolin et al. (2019) measured the mobility of CeO_2 NPs in agricultural soil under wetting–drying cycles. The mobility of CeO_2 NPs decreased from 0.11% to 0.07% by water-stable soil aggregates formed between the NPs and soil particles. However, the authors also observed through micrographs, ensembles of CeO_2 NPs with soil minerals in the soil leachate. Soil mineralogy affects the transport of aggregates because clay minerals can serve as a carrier of NPs.

The NPs agglomeration depends on both NPs and soil properties (Singh and Kumar 2020). Some authors pointed out that NPs concentration in a liquid medium is a critical variable in the NPs agglomeration (Singh and Kumar 2020; Shrestha et al. 2020; Wang et al. 2020) because NPs concentration determines the interparticle distance and the collision frequency between particles. If the interparticle separation is lower than the maximum repulsive potential, the agglomeration of NPs occurs. NPs remain in suspension if the interparticle gap exceeds the maximum repulsive potential (Shrestha et al. 2020). This point is relevant in the formulation of stable suspensions of nano-agrochemicals and their application.

The particle size and surface charge are other NP features that play a role in the interaction of NPs with their medium and their agglomeration or aggregation (Singh and Kumar 2020; Chen 2018; Gatoo et al. 2014). From the kinetic stability studies with NPs, it has been observed that NPs smaller than 50 nm agglomerate and form aggregates bigger than those formed by large size NPs (Ben-Moshe et al. 2010; Chen 2018). In this case, the size of agglomerates in an aqueous solution of TiO_2 NPs with a size smaller than 100 nm and zeta potential −33.53 mV was 190 nm. The NPs of Fe_3O_4 and CuO smaller than 50 nm and zeta potential of −8.51 and 17.13 mV formed agglomerates of 1281 nm and 342 nm, respectively. This behavior is related to the surface charge of NPs, which determinates the type of forces (attractive or repulsive) between particles (Chen 2018; Shrestha et al. 2020). NPs size and surface charge are related to each other by a fixed background (ionic strength and pH), the magnitude of the surface charge of a NP decreases with an increase in the particle size and reaches a constant when the particle exceeds a critical value (Barisik et al. 2014). According to DLVO theory, the van der Waals and electrical double layer interactions depend on particle diameter (Zehlike et al. 2019). Moreover, in the case of bare metal NPs and given the same solution chemistry, NPs with a high absolute value of zeta potential have a lower agglomeration tendency compared with NPs with a low absolute value of zeta potential because electrostatic repulsive forces between NPs are dominant at a higher absolute value of zeta potential (Mondal et al. 2021; Chen 2018).

Considering the soil solution conditions, the NPs agglomeration is also affected by the presence of organic matter, pH, and ionic strength (Kookana et al. 2014). Among environmental conditions, ionic force is the most relevant variable for NPs agglomeration (Dimkpa 2018). The ionic strength of the soil solution affects the force of the electrical double layer, which is related to the repulsive forces between particles. Then, when the ionic strength increases, the double layer is compressed; therefore, the attractive forces (van der Waals) will be dominant and induce NPs agglomeration (Shrestha et al. 2020; Elhaj et al. 2019). High Ca^{2+} concentration in the soil solution not only affects the ionic strength but also plays an important role in the mobility of NPs in porous media because Ca^{2+} leads to an increase in the adhesion of NPs to sediment surfaces (Degenkolb 2021). Moreover, when ions from the soil solution are adsorbed on the NP surface, the magnitude and sign of the zeta potential can change (Shrestha et al. 2020).

Dissolved organic matter (DOM) has a dual effect on NPs mobility. On the one hand, DOM can reduce NPs mobility. The mechanisms involved in the increment of NPs agglomeration are the augment of hydrophobicity, electrostatic forces between particles, or modification of the charge of the NPs surface. On the other hand, DOM can promote the stabilization of NPs in soil solution by steric stabilization. In this case, DOM acts as a coating (it will be attached to the NP surface), which influences the van der Waal attraction forces by impending the approximation of NPs and leads to entropic repulsion by the overlapping of coating molecules of different particles (Degenkolb 2021; Worthen et al. 2016; Hoppe et al. 2014). It has been observed that high molecular weight organic matter has a stronger stabilizing effect against NPs aggregation than low molecular weight organic matter (Degenkolb et al. 2019; Louie et al. 2015). The effect of DOM on NPs is relevant when the solution has higher ionic strength and the electrostatic forces play a minor role in the NPs stabilization (Degenkolb et al. 2019). However, the effect of DOM on NPs agglomeration and stabilization depends on its characteristics, its concentration, ionic strength, and the type of cations present in soil solution, as well as the NPs features (Chen 2018; Zehlike et al. 2019). Ben-Moshe et al. (2010) using columns with Fe_3O_4 NPs assessed the effect of ionic strength and organic matter on NPs mobility. The NPs were introduced into the column as a suspended solution at 1000 mg L^{-1}. The authors found that increasing the ionic strength from 0.001 to 0.1 M enhanced the deposition of NPs in the porous medium. The addition of humic acids increased the stability of the NPs suspension and prevented the NPs agglomeration. The concentration of eluted NPs increased from 1.5% to 75% after the addition of humic acids from 10 to 60 mg L^{-1}. Through batch experiments with TiO_2 (particle size of 79 and 180 nm), citrate-stabilized Ag NPs (particle size of 73 and 180 nm), and soil solutions with hydrophobic and hydrophilic features from farmland and floodplain soils, Zehlike et al. (2019) found that the composition of DOM affected the size of NPs aggregates. The Ag NPs of 73 nm size formed larger agglomerates (1179 nm) in the presence of hydrophilic DOM compared to the hydrophobic one (832 nm). In contrast, the hydrophilic DOM maintained in suspension the NPs of 180 nm. Moreover, small agglomerates (192 nm) were formed compared to those formed (406 nm) in the presence of hydrophobic DOM. The authors pointed out that the stabilized effect of organic matter in Ag NPs was due to sterical hindrance rather than electrostatic stabilization because of the zeta potential of NPs in soil solutions and their control (2 mM Ca^{2+} solution) was similar. In the case of TiO_2 NPs in both soil solutions, the NPs remain stabilized and formed small agglomerates, but the stabilization of NPs in the soil solution was due to a change in their zeta potential from 0 until −25 mV.

The soil pH can regulate the surface charge of NPs, and therefore the value of their zeta potential, through surface de-protonation or protonation (Wang et al. 2020). When approaching the zero charge point, the particles can agglomerate because the NPs surface is neutral (Shrestha et al. 2020). On the other hand, soil pH influences the rate at which NPs are dissolved into their constituent metal and dictates the speciation of released metals within the soil (Cartwright et al. 2020). Furthermore, the NPs dissolution rate increases as the particle size decreases in the same solution matrix (Chen 2018).

In contrast, it can be slowed by the agglomeration of NPs due to a reduction in the exposed surface. Consequently, the delivery and bioavailability of a target nutrient or active ingredient are reduced (Cartwright et al. 2020). Sekine et al. (2017) analyzed the dissolution of CuO NPs in five types of soils with pH from 5 to 8. Their results showed that pH affected the NPs dissolution in the short term. After 3 d of NPs addition, a rapid dissolution occurred in acidic soils, whereas the opposite effect occurred in alkaline soils. After 5 d, the Cu released from the NPs was redistributed to the iron oxyhydroxides and soil organic matter, and Cu chemical species remained after 135 d of application.

One form to overcome the problems related to the NPs agglomeration and aggregation is through their surface functionalization. Coatings can alter the NPs surface charge, reduce the particle attraction by steric stabilization, preserve smaller agglomerates, regulate the NPs dissolution, mitigate NPs runoff into the soil, enhance the particle binding to plants and soil minerals, and provide an additional source of nutrients for plants and microorganisms (Shrestha et al. 2020; Cartwright et al. 2020; Kim et al. 2020). To avoid the agglomeration of nZVI and increase their dispersion, Xue et al. (2018) coated the nZVI with rhamnolipid. Moreover, the authors assessed changes in the Cd and Pb distribution in contaminated sediment after the application of nZVI or rhamnolipid-coated nZVI. After the application of 0.05% (*w*/w), rhamnolipid coated nZVI, and nZVI, the acid-soluble Cd fraction reduced by 47% and 26% after 42 d, respectively. The rhamnolipid application increased the residual fractions of Cd and Pb increased by 56% and 43% after 42 d. In addition, the urease and catalase activities were enhanced. These authors suggested that coated nZVI contributed to recover sediment metabolic function.

On the other hand, some organic coatings for NMs may have a low toxic impact on soil microorganisms due to their biocompatibility (de Oliveira Pereira et al. 2020). However, soil properties such as pH, organic matter, and clay content influence the toxicity of NPs (Raffi and Husen 2019). Simonin et al. (2015) assessed the influence of soil properties on the toxicity of TiO_2 NPs. For this purpose, the authors used six soils with three textural classes: a sandy-loam, a loam, and a silty-clay, with high or low organic matter content (2% to 8%) and different pH (6.3 to 7.7). They evaluated two scenarios: a low concentration of NPs, 1 mg TiO_2 kg^{-1}; and a high concentration of NPs, 500 mg TiO_2 kg^{-1}. In the silty-clay soil with 8% of organic matter and treated with 500 mg TiO_2 NPs kg^{-1}, a decrease in the C mineralization over the monitored time was observed. After 90 d of NPs application, the C mineralization decreased 16% compared with control treatment. In contrast, a low concentration of TiO_2 NPs applied in loam soil with poor organic matter decreased 23% C mineralization after 7 d, but the effect seemed to be transitory over time. Similarly, in the silty-clay soil with a high organic matter content, the abundance of microbial communities decreased by 24% and 37% with doses of 1 and 500 mg kg^{-1}, respectively. The authors found a significant relationship between NPs effects, pH, and organic matter content; both factors might be related to the NPs toxicity in soil. García-Gómez et al. (2018) assessed the toxicity of aged ZnO NPs at 3, 20, and 225 mg kg^{-1} on *Pisum sativum* growth in acidic or calcareous soil. The authors found that the concentration of ROS increased from 47% to 130% in plants grown in acidic soils with doses of 3 and 20 mg kg^{-1} of NPs after 30 d exposure, compared with control plants. In contrast, no significant changes were observed in the plants from the calcareous soil regarding the control. The concentration of photosynthetic pigments decreased by 20% to 42% in the plants that grew in the acidic soil after 30 d. Meanwhile, plants that grew in acidic soil treated with 225 mg kg^{-1} of NPs did not survive. The authors related the toxic effects to the available Zn concentration because, in acid soil, the available Zn fraction increased from 2 to 64 mg kg^{-1} and from 0.10 to 0.70 mg kg^{-1} in calcareous soil. The soil pH had an impact on Zn availability. Moreover, the authors highlight that the clay content in calcareous soil was higher than in acidic soil, which can contribute to the immobilization of Zn released from the NPs.

Interaction metal NMs, plants, and soil microorganisms

Exposure models suggest that NMs concentrations are higher in soil than in other systems as water or air. Therefore, the soil becomes the main sink of NMs in the environment (Bundschuh et al. 2018). Plants and microorganisms are the major co-receptors of NPs introduced to the environment by agricultural use or unintentional release (García-Gómez et al. 2018). Therefore, to lead sustainable and environmentally safe agriculture taking into account the many potential benefits of metal NMs, it is important to understand the influence of NMs applied to soil and their effect on microbial structure, diversity, and activity (Usman et al. 2020). The interaction of plant–microorganism is fundamental for agriculture as soil microbial communities maintain a balanced process in the soil–plant system and provide ecosystemic services, especially the microorganisms establishing beneficial associations with plants, such as nitrogen-fixing bacteria, plant growth-promoting bacteria, and arbuscular mycorrhizal (AM) fungi (with more than 400 million years of evolution with plants), are important for efficient absorption of macro and micronutrients, plant nutrition and growth. Moreover, they are involved in carbon sequestration, effective plant protection against pests and pathogens, plant quality and productivity, plant tolerance against abiotic stresses as well as soil quality and health (Jacoby et al. 2017; Hedge and Wilson 2016; Compant et al. 2019). Soil microbial communities also participate in the degradation of soil organic matter, improvement on soil fertility through nutrient bioavailability and soil biodiversity, and bioremediation of different pollutants (Jacoby et al. 2017; Mahawar and Prasanna 2018; Thijs et al. 2016; Sánchez-López et al. 2018a). However, the deep analysis of the complex interactions between NPs and soil microorganisms (Fig. 5), the methodology to identify the influence of NMs, and the molecular and cellular mechanisms of these interactions are largely ignored (Hedge and Wilson 2016).

There is an extensive toxicology analysis of metal NMs on soil microorganisms. Resumed from several authors, the negative observed effects, of metal NMs on soil microorganisms (Table 4) are antimicrobial activity (AlO_3, CuO, Ag NPs); alteration of the microbial community (TiO_2, CuO, Fe_3O_4, Cu NPs); reduction of soil enzymatic activity (CuO); soil microbial biomass (CuO, TiO_2); N-fixation (Ag NPs, WO_3); alterations in gene expression (Ag NPs); inhibition of plant growth-promoting rhizobacteria (TiO_2, AlO_3); and induction of morphological changes (TiO_2). On the other hand, positive effects of NMs on soil microorganisms (Table 5) may be observed. These are an enhancement of soil enzymatic activity (ZnO, Fe_3O_4, Fe_2O_3, CuO, ZnO); microbial population (ZnO, Ag, Fe_3O_4, and γ-Fe_2O_3); bacterial growth (Fe_3O_4, Fe_2O_3); microbial diversity and richness (Ag); AM fungal metabolites and mycorrhizal colonization (Ag, Feo); denitrification (PVP-coated Ag NP); genes involved in N cycling (CuO). The stimulating effect of NPs comes from the role of metal ions in the structure and function of microbial enzymes (Jośko et al. 2019).

Similar to the plants, results on the effect of NMs on microorganisms range from biostimulation to toxicity (Juárez-Maldonado et al. 2021). Traits of NPs (nature, exposure time, concentration, type, form, and size), plants (presence or not, type, age), soil (type, chemical, and physical characteristics), microorganisms (type and function), and environmental conditions (biotic stress conditions) determine the response to NMs (Usman et al. 2020; Kumar et al. 2015; Juárez-Maldonado et al. 2021). For example, numerous studies mentioning the high toxicity of NMs to soil microorganisms were conducted under pure culture media; however, extrapolation to natural environments such as soil is difficult.

Figure 5 resumes the interactions between NMs, soil microorganisms, and plants, where soils may regulate the effect of NPs on these two organisms. Complex interactions between NPs and soil surfaces are intractably involved and result in less microbial toxicity caused by NPs (as mentioned in the previous section and shown in Fig. 4). Moll et al. (2016) observed no effect of TiO_2 NPs (10–1000 mg kg^{-1}) on nutrient uptake and biological nitrogen fixation on red clover inoculated plants and grown in soil. In contrast, under hydroponic conditions, TiO NPs (250, 500, and 750 mg L^{-1}) caused a delay in the root nodule development and biological nitrogen fixation in peas (Fan et al. 2014). Masrahi et al. (2014) also detected much lower microbial toxicity of Ag^+ and Ag NPs in soil than trials performed in pure culture media.

Concerning NPs concentrations, Juárez-Maldonado et al. (2021) and Iavicoli et al. (2018) explained that while an initial stimulus can result in a positive reaction and gene expression in microbial or plant metabolism (biostimulation), the contrary effect can occur and cause toxicity. Therefore, response to concentration is of a biphasic or hormetic nature. This boundary between biostimulation–toxicity is variable, even for NMs with similar composition, but highly dependent on several already mentioned NMs characteristic as well as surface energy, surface charge, hydrophobicity, roughness, surface functionalization, and components of the corona (organic molecules or biomolecules adsorbed to the NMs surface from the media where NM is found). High consideration of this hormetic dose-response should help for a safe application of innovative materials (Iavicoli et al. 2018). Kumar et al. (2015) observed less nitrogen fixation in *Rhizobium* strains when Ag NPs concentration was between 0.6 to 6.6%; however, at a low concentration, no effect was found. Judy et al.

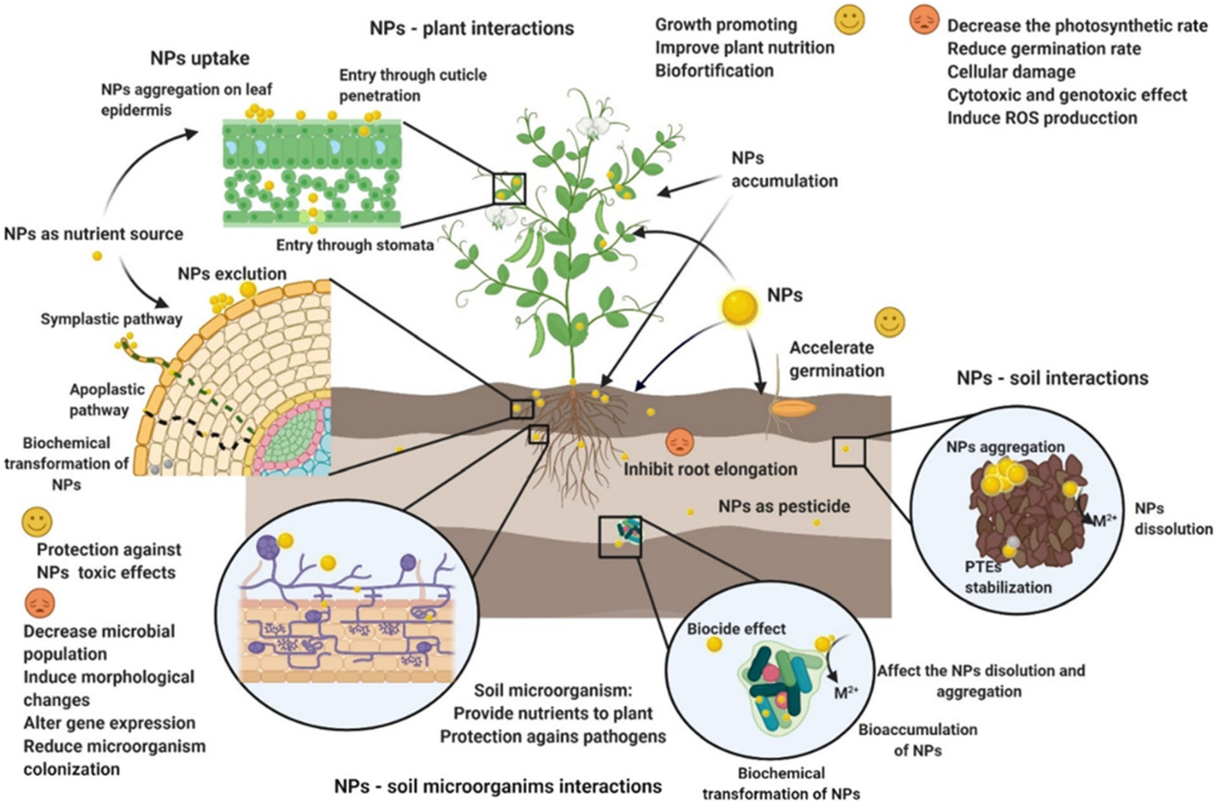


Fig. 5 Interactions and effects of metallic NPs with plants and soil microorganisms

(2016) did not observe the negative effect of Ag NPs (1, 10, and 100 mg kg^{-1}) on *Sinorhizobium meliloti* associated with *Medicago truncatula*. These authors emphasized that the highest Ag NPs concentration was analogous to a worst-case scenario; moreover, tested as long-term repeated soil addition with biosolids amendments.

The response of NMs to the microbial community is also dependent on the presence or not of plants and type of soil microorganisms. Ge et al. (2014) observed that plants and kind of NP alter the response of NMs on soil bacterial communities. CeO_2 NPs (100 to 1000 mg kg^{-1}) did not affect soil bacterial communities in unplanted soils. However, 100 mg kg^{-1} enhanced soil bacterial communities in soil with soybean. While 500 mg kg^{-1} of ZnO increased *Rhizobium* and *Sphingomonas* communities, but decreased *Enfiser*, Rhodospirillaceae, *Clostridium*, and *Azotobacter*. A higher decrement of bacterial communities was observed in unplanted than in planted soils, which indicated that soybean plants reduced the negative effects of ZnO on bacterial soil communities.

Toxicity response to NPs is also dependent on soil microbial species. The minimum inhibitory concentration of coated Ag NPs was different in three bacteria involved in the N cycle; for *Nitrosomonas europaea* (involved in nitrification) it was 500 μg L^{-1}, for *P. stutzeri* (a denitrificant-bacteria) it was 4000 μg L^{-1}, and for *Azotobacter vinelandii* (a nitrogen fixing bacteria) it was 12,000 μg L^{-1}. In all bacteria, ionic Ag was more toxic than Ag NPs (25, 200, and 250 μg L^{-1}, respectively). Judy et al. (2015) observed that Ag_2S NPs were less toxic to plants, AM symbiosis and soil microbial community than polyvinylpyrrolidone (PVP) coated Ag NPs and Ag^+. However, low concentration of Ag_2S NPs (1 mg kg^{-1}) still negatively influenced the soil microbial community, but higher concentrations (100 mg kg^{-1}) did not influence the colonization by AM fungi. Differences in toxicity to metal NPs were observed in plant growth promoting bacteria (*Bacillus thuringiensis*, *P. mosselii*, *Azotobacter chroococcum,* and *Sinorhizobium meliloti*). Concentration up to 3000 mg L^{-1} of CuO, TiO_2, and Al_2O_3 NPs did not inhibit bacterial growth. In contrast, these

Table 5 Some positive effects of metal NPs soil microorganisms

NP	Effect	NP size (nm)	Concentration (mg L^{-1} or mg kg^{-1})	Medium	Exposure duration (d)	Reference
ZnO	Phosphatase and phytase enzyme activity increased (84%–108%)	1–7	0.025	Soil	28	(Raliya et al. 2016)
Fe_3O_4, γ-Fe_2O_3	NPs stimulate the growth of *Streptomyces*, *Duganella*, and *Nocardioides* bacteria; and soil activity of invertase and urease	10 10	840, 1260	Soil	30	(He et al. 2011b)
CuO, ZnO	NPs enhance the dehydrogenase activity 1 d after NPs application. Cu NPs increase the dehydrogenase activity in silt-loam soil after 90 and 730 d exposure compared to the control soil. No changes in the number of bacteria were observed after 730 d	50	10	Soil	1–730	(Jośko et al. 2019)
Ag	The alpha diversity estimates of operational taxonomic unit abundance (5286 to 6077), the Chao richness (6153 to 6667), and the phylogenetic diversity (133 to 149) increased compared to control soil. The abundance of sequences of Proteobacteria increased from 44% to 62%	12	15	Soil	4	(Chavan and Nadanathangam 2019)
Ag	Increment of total and easily extractable glomalin. Less Ag shoot and root content (%) in faba bean plants inoculated with *Glomus aggregatum*.	5–50	800	Autoclaved loam and sandy soil (21 w/w)	35	(Abd-alla et al. 2016)
Ag	Biomass, P plant uptake and mycorhizal colonization by *G. caledonium* was increased. Less Ag uptake and soil soluble Ag concentration in maize-mycorrhizal plants	20	0.025	soil	20	(Cao et al. 2020)
Ag	Higher root colonization by *G. caledonium* in clover plants as dose increased. AM fungi alleviate Ag NPs stress in its host plant. At high Ag concentration, extractable glomalin content and root P uptake increased at high Ag NPs concentration	21	0.01, 0.1, 1	Sand:perlite	80	(Feng et al. 2013)
FeO	Increased root colonization by *G. caledonium*	10	0.032	Sand:perlite	80	(Feng et al. 2013)
CuO	The gene *nifH* was significantly more abundant than the control treatment, then the fixation capacities were increased by the addition of NPs. Also, the abundance of gene *amoA* (involved in nitrification) increased in treatments with NPs compared to the control treatment.	28	0.63 and 63	Soil	28	(Guan et al. 2020)
Au:PVP, Ag:PVP	Poly(vinylpyrrolidone) stabilized Au and Ag NPs did not decrease colonization by AM fungi and *Rhizobium*.	2.6 and 3.6	1 mM	Seed priming	0.04–0.081 (1–3 h)	(Rahman et al. 2020)

bacteria were sensitive to concentrations less than 1500 mg L^{-1} of Ag and ZnO NPs (Ahmed et al. 2020). A high concentration of Ag NPs (800 μg kg^{-1}) significantly decreased the structure, nitrogen fixation, number, and dry weight of nodules produced in faba plants inoculated with *Rhizobium leguminosarum* bv. *viciae*. Therefore, root nodules showed autophagy (internal degradation of bacilli) as an Ag detoxification mechanism (Abd-alla et al. 2016).

Most of the studies related to the interaction between metal NPs and agricultural soil beneficial microorganisms show negative effects of NPs because of their antimicrobial effect (Table 4). Metal and metal oxide appears to have higher toxicity than organic NPs such as fullerenes and carbon nanotubes (Rajput et al. 2018; Rajput et al. 2020). Michels et al. (2017) showed Ag and magnetite NPs were attached to the bacterial surface and reduced membrane permeability; however, Ag NPs were 45-fold more toxic than magnetite NPs. The EC_{50} to decrease ammonia oxidizing bacteria for Ag NPs was 10.75 mg L^{-1}, while for magnetite it was 483.01 mg L^{-1}. The highest doses on Ag NPs (30 mg L^{-1}) and magnetite (1000 mg L^{-1}) decreased 90% and 71% the nitrite production of this kind of bacteria, respectively. Ti_2O and ZnO NPs decreased microbial biomass carbon and the Gram-negative bacterial community (Rashid et al. 2017).

Hedge and Wilson (2016) resumed that NMs may influence soil microbial communities through four mechanisms: (a) direct particle-cell interaction, (b) indirectly by NMs interaction with natural organic compounds, (c) interaction with recalcitrant organic pollutants and enhancing toxicity, and (d) modifying toxin or nutrients bioavailability. Similar to in plants and with metal bulk-size compounds, the general toxicity mechanisms to NMs known in microorganisms are related to cellular level response: cell membrane damage, proteins denaturalization, respiratory chain alteration, oxidative damage, and genotoxicity (Wang et al. 2017; Jośko et al. 2019; Ševců et al. 2011; Dinesh et al. 2012). However, scarce information is available related to molecular mechanisms to deal NMs in soil microorganisms.

Noori et al. (2017) analyzed the impact of Ag NPs (2 and 15 nm) in concentrations 0, 12, 24, and 36 mg kg^{-1} on colonization by the AM fungus (*Rhizophagus intraradices*) on the growth and accumulation of Ag in tomato plants, and the expression of gene-related with uptake pathways (potassium channel proteins: KC; aquaporins proteins such as plasma membrane intrinsic protein: PIP and tonoplast membrane intrinsic protein: TIP). These authors observed that mycorrhizal colonization was reduced at the higher Ag NPs concentration and that smaller-sized NPs had not only the highest impact on colonization but also on plant biomass. Moreover, mycorrhizal colonization moderates plant Ag uptake (14% less accumulation) and changes in the expression level of membrane transport proteins. The expression of KC, PIP, and TIP in mycorrhizal tomato plants was 5.8, 3.5, and 2 higher than in control plants (without the addition of NPs), respectively. In contrast, the expression in non-mycorrhizal plants the expression was 8, 5 and 9 times higher than in control plants. Cao et al. (2020) also observed modification of genes putatively related to Ag/Ag NPs transport in maize-mycorrhizal plants inoculated with *Glomus caledonium* (current name *Funneliformis caledonium*), which were involved in the mitigation of Ag NPs phytotoxicity. At high Ag NPs concentration (2.5 mg kg^{-1}), the expression of *Pht1;6* (related to P uptake) was higher in mycorrhizal plants but lower in the expression of *PIP1;2*, *TIP2;1*, and *Mt2* (related to metal homeostasis and cell detoxification). Furthermore, these fungi ameliorated the negative effects of Ag NPs on the metabolic activity of other soil microorganisms, enhanced soil bacterial diversity, and altered the bacterial community composition at the mycorrhizosphere/rhizosphere of corn plants.

Fajardo et al. (2014) analyzed the cellular response of *P. stutzeri* and *Bacillus cereus* to two types of NPs. These authors tested Al_2O_3 NPs (50 nm) in concentrations 1, 5, and 10 g L^{-1}, and Ag NPs (40 nm) in concentrations 0.5, 1, and 5 mg L^{-1}. These bacteria responded differently to NPs exposure. While no modification was observed of the transcriptional response of four genes involved with cellular activity in *B. cereus*, in *P. stutzeri* exposed to Al_2O_3 NPs, the gene related to catalase enzyme (KatB) was overexpressed, resulting in less cellular oxidative stress. Ag NPs (35 nm) did not modify the expression of denitrifying genes or nitrogen-fixing genes of *P. stutzeri* (20 μg L^{-1}) and *A. vinelandii* (25 μg L^{-1}). In *N. europaea*, up-regulation of ammonia mono-oxygenase genes at low concentrations of 2.5 μg L^{-1} occurred (Yang et al. 2013). ZnO NPs applied at high concentrations (500 mg kg^{-1}) negatively influenced AM fungi species diversity, and altered their community composition. *Ambispora* genus was decreased, but *Paraglomus* increased (Yang et al. 2021).

Iavicoli et al. (2018) concluded that suitable assessment of NMs, in vitro or in vivo conditions, should be done in long-term experimental studies and with low-dose realistic environmental exposure scenarios; moreover, in the presence of other co-exposed substances. These authors showed hormetic dose-response in several biological models: microorganisms, algae, nematodes, plants, and superior aquatic organisms. It is also suggested that a low concentration of NPs induces a beneficial defense response in organisms (Juárez-

Maldonado et al. 2021). Wheat plants exposed to TiO_2 NPs enhanced their growth when inoculated with *Paenibacillus polymyxa*, *Alcaligenes faecalis*, *Bacillus thuringiensis,* and a mutant strain of *P. polymixa* A26Dsfp (Timmusk et al. 2018).

Wang et al. (2016a) observed that ZnO NPs did not have negative effects on maize mycorrhizal plants at 400 mg kg^{-1}; however, when NPs concentration was higher (800 mg kg^{-1}), inhibition of plant growth and mycorrhizal colonization were found. AM fungi putatively mitigate the negative effects of ZnO NPs in plants as increased growth, nutrients absorption, photosynthetic pigment concentration, and leaves SOD activity. The mycorrhizal plants also presented less ROS accumulation, Zn shoot concentrations, and DTPA-extractable Zn concentrations. Similar results have been observed by other authors (Abd-alla et al. 2016; Wang et al. 2018b; Noori et al. 2017; Cao et al. 2017). Joseph et al. (2015) used biochar rich in magnetic Fe NPs during the growth of wheat. These authors concluded that the use of biochar (100 kg ha^{-1}) increased P and N plant nutrition, mycorrhizal colonization, and soil microorganisms. This is because of high concentrations of Fe NPs within the biochar that are involved in nutrient availability due to acidic functional groups and soil organic matter decomposition, and labile organic molecules stimulating soil microorganisms.

The effect of NPs used in seed priming on soil microorganisms is a novel area demanding more efforts to avoid negative effects on soil, but more specifically on beneficial microorganisms. The effects are depend on type, size, and concentration of NPs, and the time of imbibition among other factors. Rahman et al. (2020) observed that seed priming (1–2 h) with 1 mM Pt NPs stabilized with poly(vinylpyrrolidone) (PVP) hurt colonization by AM fungi and *Rhizobium* in *Pisum sativum* plants. After 3 h imbibition, microbial colonization was absent. However, with Au- and Ag-PVP NPs the effect was negligent, independently of imbibition time.

Information already presented showed research on the effect of NMs on soil microorganisms, but still unexplored is the interaction of NMs with microorganisms associated with other plant niches, which may influence response to next generation fertilizers, pesticides, and other products at nanometric scale, useful for agriculture and phytoremediation. Currently, plants are recognized as meta-organisms. This refers to plants by themselves and their associated microorganisms from roots, leaves, seeds, fruits, flowers, etc. Hence forming specific microbial-plant interactions located at the rhizosphere, phyllosphere, spermosphere, anthosphera, and carphosphere, respectively; all of them influencing plant performance in agricultural and natural ecosystems (Compant et al. 2019; Mendes et al. 2013; Vryzas 2016; Jaspers et al. 2019). In consequence, in-depth research is urgent to explore the risk assessment of NMs on non-target toxicity of beneficial microbe communities from several plant niches that are key actors directing health, quality and productivity.

Metal NPs for remediation of polluted soils with potentially toxic elements

Raj and Maiti (2020) reviewed that potential toxic elements (PTE) such as As, Cd, Cr, Pb, Ni, Zn, and Hg are recognized as the utmost hazardous and persistent elements in the environment. Several agrochemicals contain PTE in their formulations. Continued use for long periods enrich soil and water. These elements also accumulate in the tissues of organisms and increase their concentration through the food chain (biomagnification). Thus, PTE contamination is a serious concern to human health, and in the case of agricultural, lands may be in jeopardy regarding productivity and the living soil organisms. Therefore, diverse remediation alternatives have been developed to remediate contamination by PTE, and one of them is the application of nanotechnology.

Nanotechnology for soil remediation, also called nano-remediation, nano-enabled remediation, or NMs-assisted remediation, uses NMs to detect, degrade, or stabilize contaminants (Pulimi and Subramanian 2016). In the case of soils polluted with PTE, NMs are used as amendments to immobilize or stabilize PTE by some of the processes shown in Fig. 6 (Souza et al. 2020; Bardos et al. 2018). The application of NMs aims to reduce the ability of PTE to partition to water or biota, potential transport, and toxicity (O'Day and Vlassopoulos 2010), by forming less toxic chemical species. Moreover, when soil pollution is due to organic compounds, several NMs (TiO_2, ZnO, Fe_2O_3, ZnS, and CdS) are useful as semiconductors to photocatalysis. The NPs absorb light energy to break down organic molecules into smaller fragments and turn them into minerals; acids, CO_2, N_2, H_2O (Baruah and Dutta 2009). Mourão et al. (2010) evaluated the photocatalytic potential of TiO_2 coated with $CoFe_2O_4$ NPs. These authors observed that $TiO_2/CoFe_2O_4$ nanocomposites were more effective than pure TiO_2 for atrazine degradation. The application of nanocomposites of $TiO_2/CoFe_2O_4$ can be an alternative for pesticide degradation in soil. Furthermore, the recovery and reuse of magnetic nanocomposites are possible due to their magnetic features (Zuverza-Mena et al. 2017). More recently, Mazarji et al. (2021) reviewed the use of nZVi (single or in combination with biochar), metal oxides (TiO_2, Fe_2O_3, green synthetized-potassium zinc hexacyanoferrate nanocubes or NPs, magnetite NPs modified graphite), and several carbon- and polymer-based NMs for remediation of toxic polycyclic aromatic hydrocarbons. Nehra et al. (2021) provide a comprehensive review on the management of pesticide residues in soils that can be consulted, while this paper focuses on the applications of nanotechnology for the remediation of soils polluted with PTE.

The use of NMs as amendments has an advantage over bulk materials because they have a higher reactive surface and area/volume ratio than bulk materials. These properties enhance the NMs' capacity to adsorb, reduce, or oxidize PTE (Bardos et al. 2018; Pulimi and Subramanian 2016; Guerra et al. 2018). For instance, zero-valent iron (Fe^o) and $CoFe_2O_4$ NPs have a total specific surface area of 20–40 $m^2\ g^{-1}$ and 1243 $m^2\ g^{-1}$, respectively. In contrast, the total specific surface area for granular Fe is <1 $m^2\ g^{-1}$. Reactivity is also from 10 to 1000 times more in NPs of these compounds (Karn et al. 2009; Qiu et al. 2016).

Many of the NMs recommended for soil remediation (Table 6) have been adapted from technologies for water treatment, and the results were observed in sorption kinetic assays in aqueous media (Kefeni et al. 2017; Zhang et al. 2010; Zhao et al. 2016). Nevertheless, Fe NPs seem to be the best material (Souza et al. 2020; Kefeni et al. 2017; Caroline and Antônio 2019) due to their magnetic properties. This feature facilitates their recovery (Zuverza-Mena et al. 2017; Martinez-Vargas et al. 2017). The high chemical reactivity (Kefeni et al. 2017) increases the efficiency and fast kinetic adsorption of ions such as Ni^{2+}, Cu^{2+}, Co^{2+} Cd^{2+}, and Cr (IV) (Guerra et al. 2018). Moreover, iron NPs are considered non-toxic for the environment or plants (Zuverza-Mena et al. 2017). These particles can be modified to improve their performance by including a catalytic element such as Ti or Pd, using coatings such as citrate or polymers, or soaking other materials such as active carbon or zeolites with NPs (Gens et al. 2016).

Zero-valent iron is one of the iron-NPs most studied for in situ soil remediation because it can reach sites that are inaccessible by other methods in a less destructive form and less time-consuming. Additionally, they can reduce and immobilize several redox-active PTE (Zhao et al. 2016). For instance, Gil-Díaz et al. (2016) evaluated the immobilizing effect of nZVI NPs to assist the phytoremediation of As polluted soils, from a metallurgical industrial site at Asturias, Spain. The authors carried out a growth chamber experiment with barley plants and nZVI at 1% and 10% (*w*/w). The results showed that the available As concentration decreased from 83 to 12 mg kg^{-1} with 10% nZVI treatment compared to the untreated soil. While the concentration in the residual fraction increased from 4139 to 5321 mg kg^{-1}, the leaching of As was significantly reduced. Posteriorly, Gil-Díaz et al. (2019) in field experiments tested the application of 2.5% of nZVI to a highly polluted soil with As (43,300 mg kg^{-1}) and Hg (2200 mg kg^{-1}).

These authors found that 72 h after nZVI application, the exchangeable As fraction decreased by 40% and in the leaching extract by 54%. Similarly, the Hg concentration in the leaching extract decreased by 39% regarding the Hg initial concentration. The immobilization of As and Hg remained stable after 24 months. A second application was required eight months after the first one. These authors also tested the application of nZVI in soils containing 7280 mg kg^{-1} of As and 1300 mg kg^{-1} of Hg. In this case, the As and Hg concentrations in the leachable extract were 70% and 80%, respectively, lower than the initial concentrations; conditions that remained stable 24 months after the nZVI application.

NMs-assisted phytoremediation

Phytoremediation is one of the cheap soil recovery technologies and is non-intrusive compared with the physical and chemical methods (Thijs et al. 2017; González-Chávez et al. 2017). Plants useful for phytoremediation encourage fixation of atmospheric CO_2, increase soil biodiversity, and their biomass may have application in bioenergy production. Moreover, plant surfaces avoid the air dispersion of soil particles containing PTE (Thijs et al. 2017; González-Chávez et al. 2017; Sánchez-López et al. 2018b). However, their efficiency and success depend on the plants' ability to take up, tolerate, and accumulate PTE (Thijs et al. 2017). To overcome the limitations of phytoremediation, biotechnology can be combined with other approaches as the use of NMs as soil amendments or soil pretreatment (Zhu et al. 2019).

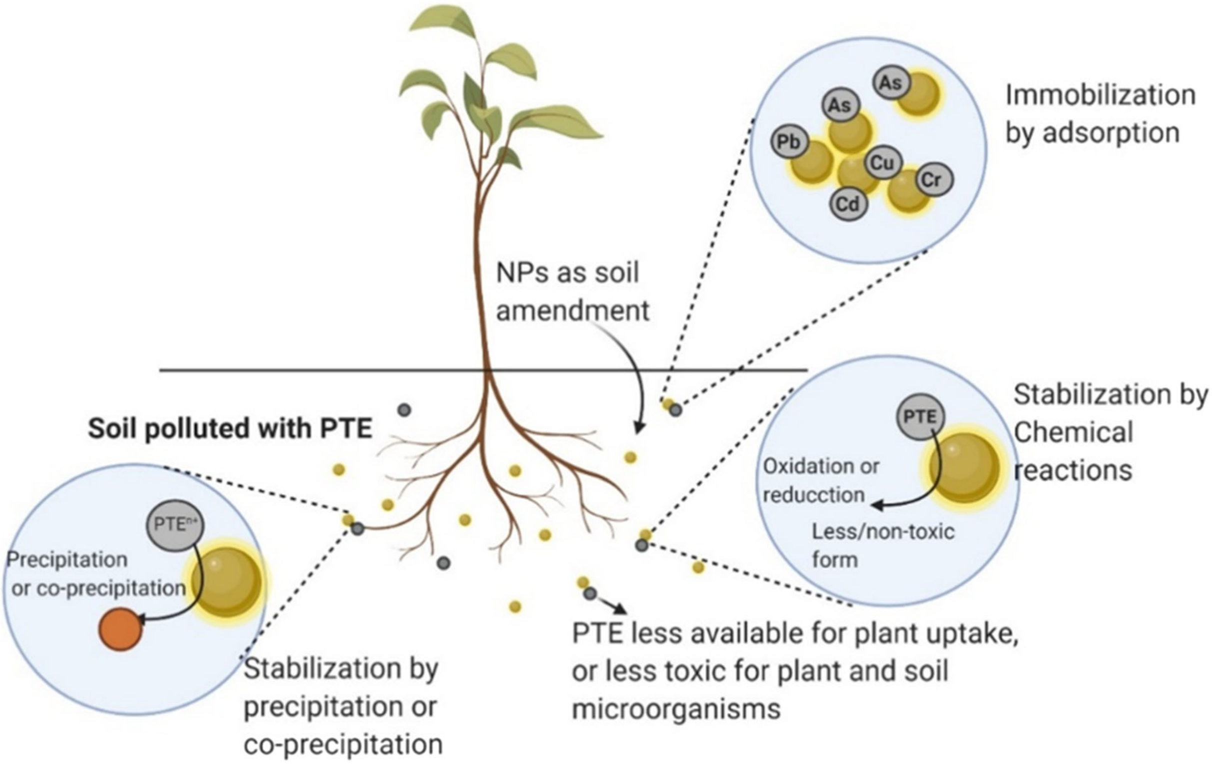


Fig. 6 Pathways in which nanoparticles can assist soil remediation and phytoremediation

Metal NPs may enhance phytoremediation efficiency (Zhu et al. 2019; Gong et al. 2018) by reducing the availability of PTE (Fig. 6). However, the excessive use of NMs may also produce contamination of soil and water resources. The addition of NMs to PTE-contaminated soil may be insufficient to help plant establishment because these altered soils often lack nutrients, organic matter, and have a poor structure (Thijs et al. 2017). Hence, NMs assisted phytoremediation can be combined with organic amendments to provide nutrients for plants and stimulate soil microbial communities, or with beneficial soil microorganisms to promote plant growth (Mokarram-Kashtiban et al. 2019; Baragaño et al. 2020b; Lacalle et al. 2020). For instance, mature compost, from olive mill waste and cow manure, at a rate of 14 g kg^{-1} combined with 1% of ϒ-Fe_2O_3 NPs assisted phytoremediation with *Helianthus annuus* plants of a mine tailing from Murcia, Spain. After 50 d, the reduction of the Zn concentration in soil solution was 22% in comparison to the treatment without compost and NPs. Moreover, the foliar concentration of Zn, Cd, Cu, and Co significantly decreased, while the root concentration of Al, Cu, and Pb were lower than this in the control plants. The plant dry aerial biomass increased due to the synergistic effect of compost and NPs (Martínez-Fernández et al. 2015).

Biochar is another organic amendment that may be mixed with NMs. For example, through a greenhouse experiment, Baragaño et al. (2020b) assessed the effect of nZVI, compost-biochar, or a combination of these amendments to assist the phytoremediation with *Brassica juncea* L. of a PTE polluted soil. After 75 d of amendments application, the mix of compost-biochar-nZVI, at a proportion of 15%, 5%, and 2% (*w*/w), respectively, lowered significantly the Cu, Pb, and Zn available concentrations compared with soil treated with nZVI and the control (without amendments).

Foliar spray of NMs may be used to promote structural stability, improve yield, and enhance the resistance of plants under PTE stress (Cui et al. 2020). Foliar spray of Si NPs in plants as *Brassica chinensis* L., *Coriandrum sativum* L., and *Oryza sativa* L. reduced the accumulation of Pb and As in the aerial biomass of plants, stimulated the production of antioxidant enzymes in the plant, and also the soil microbial activity (Cui et al. 2020; Fatemi et al. 2020; Tian et al. 2020; Liu et al. 2015b). The reduced As rice plant accumulation

Table 6 Nanoparticles tested for soil remediation under different conditions

NP	PTE	Action mode	Effect	Reference
Apatite with carboxymethyl cellulose stabilizer	Pb	Immobilization	Ratio 2:1 NPs: soil reduced the leachable Pb fraction from 66% to 10% after one month of NPs application.	(Liu and Zhao 2013)
Hydroxyapatite	Pb	Immobilization	2 g kg^{-1} reduced the accumulation of Pb in *Brassica napus*.	(Shaheen and Rinklebe 2015)
	Cd, Zn, Pb, Cu	Adsorption	0.2 g of NPs inhibited soil PTE desorption.	(Chen et al. 2010)
Nano silicone	Pb	Stabilization	2.5 mmol L^{-1} increased the biomass of two rice cultivars and decreased foliar and grain Pb concentration.	(Liu et al. 2015a)
Carbon Black	Cu, Zn	Immobilization	Soil Cu and Zn availability decreased between 47% to 80% and 17% to 43%, respectively when using 1, 3, and 5% NPs compared with no NPs addition. Zn and Cu proportion in the organic and sulfide soil fraction increased. Higher biomass of *Lolium multiflorum* and less plant Cu and Zn accumulation.	(Wang et al. 2009)
Ca/CaO and Ca/PO_4	^{137}Cs	Immobilization	96% ^{137}Cs was immobilized.	(Mallampati et al. 2012)
nZVI	Cr(VI)	Reagent material in a permeable reactive barrier for electro remediation	It was achieved to reduce 75–90% of the Cr(VI) in the soil. The total Cr removal efficiency rose to 42% compared with conventional electrokinetic treatment.	(Shariatmadari et al. 2009)
	As, Hg	Immobilization	5% nZVI dose decreased 70% exchangeable As concentration. 10% nZVI dose reduced the exchangeable Hg between 635 to 90%.	(Gil-Díaz et al. 2017)
	Cd	Immobilization	150 mg nZVI kg^{-1}, *Salix alba*, and inoculation with *Pseudomonas fluorescens* and *Rhizophagus irregularis* increased the bioconcentration factor of Cd. 300 mg nZVI kg^{-1} inhibited *Salix alba* growth.	(Mokarram-Kashtiban et al. 2019)
			The Cd concentration in the residual fraction increased from 15% to 57% after 30 d incubation of river sediments with sodium alginate modified nZVI at 0.1% (*w*/w).	(Huang et al. 2016)
	Zn	Sorption	Extractable Zn concentration reduced when used from 0.5 to 4 mg kg^{-1}. No negative effects on soil microorganisms were found.	(Anza et al. 2019)
	Pb, Zn, Cd	Immobilization	120 d after NPs application, 20% of Pb, and 8% of Zn were immobilized. The maximum immobilization reached was 15 d after NPs application.	(Fajardo et al. 2020)
nZVI, FeS Fe_3O_4	As	Immobilization	The soil bioaccessible concentration of As decreased from 71% to 31%, 37%, 30% when the soil was treated with nZVI, FeS, and Fe_3O_4 at a Fe/As molar ratio of 100:1, respectively.	(Zhang et al. 2010)
nZVI, goethite	As	Immobilization and reduction	nZVI at dose 2% decreased 90% the As availability, while nGeothite at 0.2% dose decreased 83% the As available nZVI at dose 10% increased 1.4% the As^{3+} concentration.	(Baragaño et al. 2020a)
ϒ-Fe_2O_3	Zn	Immobilization	NPs and compost decreased 22% of the soluble Zn concentration and Zn accumulation in *Helianthus annuus*. Higher plant biomass was observed.	(Martínez-Fernández et al. 2015)

Table 6 (continued)

NP	PTE	Action mode	Effect	Reference
Fe_3O_4 coated with polyethyleneimine	Cs	Adsorption	Coated magnetic NPs at a dose of 0.05 g g^{-1} removed 82% of Cs.	(Kim et al. 2020)
WO_3 coated with EDTA	Cd, Pb	Complexation	The dose of 10 mg NPs g^{-1} soil removed from 60% to 80% of Cd and Pb in two different soil matrices.	(Huang and Keller 2020)
TiO_2, CeO_2	Cu (II)	Adsorption	Soluble Cu soil concentration and toxic effects on rice plants decreased.	(Wang et al. 2015)
Amorphous manganese oxide	Cd, Cu, Pb	Stabilization	Exchangeable soil fraction of Cd, Cu, and Pb decreased around 92%.	(Michálková et al. 2014)
	Fe, Al, Pb, Zn, Cu, y Cd	Immobilization	Soil neutralization reactions accelerated. Fe, Mn, and Al precipitated as secondary oxyhydroxides.	(Vítková et al. 2015)
ZnO, Al_2O_3 (bare and modified with humic acids NPs)	Cd, Cu, Ni	Sorption	Leaching and bioavailability decreased after 56 d NPs addition. Order of metal removal Cu>Cd> Ni.	(Mahdavi et al. 2015)
Hydroxyapatite, hematite, and magnetite	As, Pb, Sb	Sorption	Available As, Pb, and Sb soil concentrations decreased.	(Arenas-Lago et al. 2019)

Modified from Pulimi and Subramanian (2016)

was due to improvement of pectin synthesis that chelated As and the mechanical force of the cell walls enhanced by a higher thickness that maintained the integrity of the cell and then ameliorated oxidative stress upon As exposure (Cui et al. 2020). While less Pb concentration by Si NPs was explained because Si induces root exudates that chelate metals and also due to silicates Pb complexes formation; therefore, reduced metal uptake was observed in coriander plants (Fatemi et al. 2020).

NMs and electrokinetic remediation

Another form to use NMs for soil treatment is to manufacture permeable reactive barriers (PRB) for electrokinetic remediation (EKR). The EKR-PRB is an attractive technique because it avoids the secondary contaminants synthesis, in contrast with conventional EKR (Wang et al. 2021). It is also potentially applicable to several organic and inorganic pollutants. Moreover, it has a high removal efficiency and time-effectiveness in soils with low permeability (Souza et al. 2020). Figure 7 shows the mode of action of EKR-PBR.

Permeable reactive barriers aim to intercept a contaminant plume and transform it into environmentally acceptable forms to attain the concentrations of chemical species safe for both environment and organisms (Andrade and dos Santos 2020). The PRB can be filled with NPs as reactive material (Souza et al. 2020; Wang et al. 2021) or manufactured with nanofibers (Wang et al. 2021). Iron NPs such as nZVI have been used in the EKR-PRB to remove Cr(VI). Shariatmadari et al. (2009) found that EKR-PRB can increase the removal efficiency of total Cr from 15% to 42% compared with EKR application in clayey soil. Nasiri et al. (2020) used Fe_3O_4 NPs as reactive material in PRB and assessed the use of chelating agents to remediate a Cr contaminated soil by EKR. The combination of EDTA and placing the PRB in the middle of the ER reactor removed approximately 70% of the initial Cr concentration (150 mg kg^{-1}). These authors found that Cr(VI) ions were reduced to Cr(III) when they passed through the PRB, and therefore the NPs play a role in the Cr reduction. The Cr accumulation observed near the cathode section suggested that the mechanism of Cr removal was electromigration. Despite the high rate of Cr removal of EKR-PRB compared with EKR, the authors concluded that EKR-PRB may consume more energy than the traditional EKR process. Therefore, more experimental evidence to determine its cost-effectiveness in the long-term is necessary.

NMs for acid mine drainage treatment

In mining areas, both active or abandoned, the acid mine drainage (AMD) is a source of PTE-soil and water pollution in addition to the mining wastes (Atrei et al. 2019). Sulfide minerals oxidize when exposed to environmental conditions, particularly rain and atmospheric oxygen. As a result, protons are released, and AMD occurs. When sulfide minerals are oxidized, they produce acid iron and sulfate-rich waters that can dissolve other minerals that contain PTE, and release them to the environment (Kefeni et al. 2017; Atrei et al. 2019).

Once AMD occurs, its treatment can be expensive. To treat one ton of AMD with limestone can cost 60 dollars, while the treatment with caustic soda costs 1240 dollars (Skousen 2014). The neutralization treatments of AMD are useful to remove PTE; however, they need to reach a pH above 10, and the proper disposal of the sludge that is generated after ADM neutralization (Kefeni et al. 2018). In contrast, treatments with NPs offer the opportunity to recover valuable resources that are impossible to recuperate with conventional treatments. Furthermore, treatment with NMs reduces secondary waste products as part of the AMD treatment process (Kefeni et al. 2018; Wei and Viadero 2007). For instance, $CoFe_2O_4$ and Fe_3O_4 NPs can remove 100% of Al, Mg, and Mn; and up to 90% of Fe, Ni, and Zn from samples of AMD (pH adjusted to 7.05 ± 0.35) from coal mines of Emalahleni and Randfontein in South Africa (Kefeni et al. 2017). α-Fe_2O_3 NPs can completely remove Al, Mg, and Mn; up to 80% of Zn and Ni; and between 47% and 72% of Ca and Na (Kefeni et al. 2018). nZVI was used for the treatment of AMD from a uranium gold mine in Gauteng, South Africa. AMD-pH increased from 3.49 to 6.01, diminished the electrical conductivity from 0.59 Ohm m^{-1} to 0.13 Ohm m^{-1}, and decreased the total dissolved solids from 1683 mg L^{-1} to 384 mg L^{-1}. The removal capacity of PTE of nZVI followed this trend: Li, Sr, Ba, B, Al, Na, and Co (Gilbert et al. 2019).

Some considerations for nanoremediation

Previous information resumes that NMs are a useful and effective alternative for the remediation of soils polluted with PTE. However, similar to the use of other soil amendments recommended for soil remediation (Carrillo-González et al. 2017), it is suggested that before the use of metal NPs, it is desirable to make an adequate characterization of the site. This includes geological conditions, types of contaminants and concentration, hydrology, soil composition, porosity, hydraulic conductivity, groundwater gradient, flow velocity, depth of the water table, and geochemical properties. All this information aims to make the action of the NPs efficient and prevent undesired effects after their application (Karn et al. 2009). For a successful application in the field, particulate agglomeration control, mobility in porous environments, reactivity, and longevity in the subsurface environment are all major controlling factors for the efficient remediation of contaminated sites under field conditions (Cecchin et al. 2017). Fulling mixing between NPs and soil is an important management step to guarantee successful remediation. In greenhouse experiments, Fajardo et al. (2020) and Gil-Diaz et al. (2016) used a commercial 5% nZVI *w*/w suspension applied to the soil, and mixed carefully obtained metal immobilization, which was dependent on soil properties and level of soil contamination. In a field experiment, Gil-Diaz et al. (2019) referred to the use of a commercial 2.5% nZVI suspension, which was diluted with water in equal proportions and uniformly dispersed on the soil surface. Then, NPs were incorporated with the topsoil surface layer to guaranty the depletion of As and Hg availability after only 72 h, which was stable during 32 months of monitoring. Liu et al. (2015a) concluded that stabilized NPs with low-cost materials, such as starch, chitosan and carboxymethyl cellulose improves the dispersion in soils. Moreover, affinity, reactivity, and sorption capacity to target metals are improved for soil metal immobilization. To improve the combination of NP with soil, Moll et al. (2016) combined 300 g of soil–sand mixture (1:1 w/w) with NPs on an overhead mixer in Schott bottles. Then, each pre-mixture was diluted with the mixture to a final volume of 30 kg and homogenized in a cement mixer for 6 h. This mixture with NPs was used for greenhouse experiments testing three types of NPs in pots.

Interaction metal NMs, plant and soil beneficial microorganism in remediation

Beneficial soil microorganisms improve several functions in the plant–soil system, such as plant protection, stability, productivity, growth, and

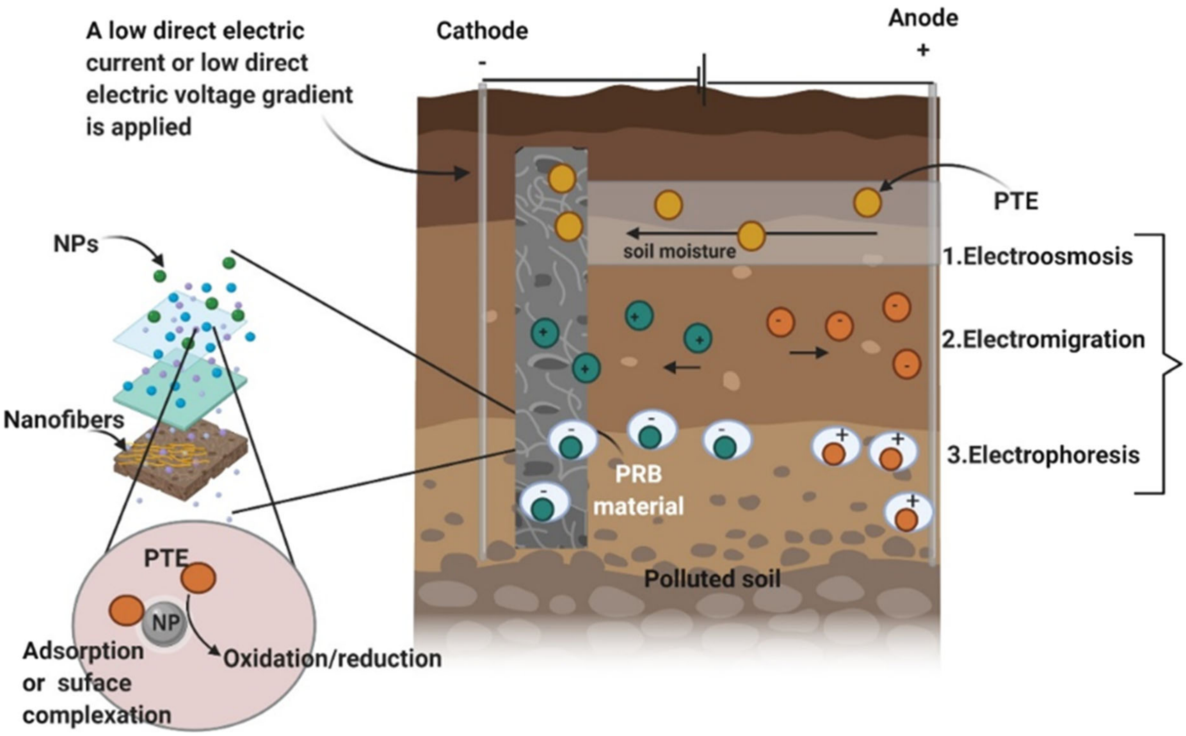


Fig. 7 Fundamental mechanisms of permeable reactive barriers for electrokinetic remediation

phytoremediation (Khalid et al. 2021). Understanding the interactions between NPs, plants, and soil microorganisms are key to designing efficient NPs application methods for plant nutrition, soil remediation, and predicting the effect of NPs on ecosystems (Ma et al. 2010). Figure 5 summarizes the possible NPs interactions with microbial components of the plant–soil system and effects for which there is evidence so far. The irrational use of NMs and their potential negative impact make them emergent contaminants, which may affect different organization levels in the environment.

Owing to the widespread and ecologically relevance of AM fungi as plant symbionts and key participants in the global plant diversity, there is a significant interest to analyze their interaction with metal NMs. Results demonstrate that these fungi have an intricate interaction with bulk-sized metals and alleviate phytotoxicity in their host plant. Therefore, they may influence the fate, transformation, accumulation, and toxicity of NMs. Feng et al. (2013) observed that *G. caledonium* (*F. caledonium*) effectively ameliorated the effect of Ag NPs (20 nm) in a concentration-dependent manner. This is as Ag NP concentration enhanced (0.01, 0.1 and 1 mg kg^{-1}). Similarly, plants had higher root fungal colonization and P root absorption, but lower Ag shoots concentration. Siani et al. (2017) evaluated the effect of inoculation of *R. irregularis* on *Trigonella foenumgrecum* plants when exposed to increasing concentrations of ZnO NPs (0, 125, 250, 375, and 500 mg kg^{-1}). The results showed that *R. irregularis* protected its host plant from the toxic effects of ZnO NPs at the dose of 500 mg kg^{-1}. The authors suggested that plant protection was due to the secretion of glomalin, a glycoprotein produced mainly by AM fungi. Glomalin increased 15% in comparison to the control treatment (without inoculation of *R. irregularis*). Similar results were found in *Zea mays* plants inoculated with *F. mosseae* and the addition of ZnO-NPs at 500 mg kg^{-1}. *F. mosseae* inoculation reduced the Zn bioavailability released from NPs, but increased available P, which depleted the toxic effect of the NPs (Wang et al. 2018b). Jing et al. (2016) also found the proper combination of P with AM fungi may lessen the effect of high NP toxicity.

Abundant information is available about the influence of beneficial soil microorganisms ameliorating toxic effects of bulk metals, and their relevance on phytoremediation, one of the utmost cost and environmentally friendly strategies, is now highly recognized. However, the interaction between these soil microorganisms and metal NMs and their participation in soil remediation remains very limited (Khalid et al. 2021; Feng et al. 2013; Cao et al. 2020; Ogunkunle et al. 2020). Research suggests that these microorganisms can protect plants from metallic NPs toxicity through regulation of NPs absorption, secretion of substances that act as chelating agents, providing nutrients to the plant, and protecting plants against toxicity and stress caused by metals.

Metal soil contamination, caused by common sources (fertilizers, pesticides, mining, etc.), may be solved by using NMs and beneficial soil microorganisms as a sophisticated assisted phytoremediation strategy. A cellular metal tolerance mechanism in plants and microorganisms may be convenient to deal with metal soil contamination, for example, structural-functional cell wall compounds, intercellular metal accumulation as electron-dense particles or granules, efflux pumps of metal ions. In the case of plant growth-promoting bacteria, some microbial products (extracellular polymeric substances, hormones, organic acids, and enzymes) may interact with NMs modifying surface, bioavailability, and speciation (Ameen et al. 2021). Similarly, the fungal structures and glomalin (a glycoprotein produced by hypha under active growth) from AM fungi can sequester significant concentrations of metals, such as Cu, Cd, Pb, Mn, etc. (González-Chávez et al. 2004).

Ogunkunle et al. (2020) studied the interaction of an unidentified native fungal consortium of AM fungi with TiO_2 NPs, with particle size between 43 to 55 nm and 200 mg kg^{-1} of concentration, in a soil spiked with $CdCl_2$ (10 mg kg^{-1}) in the remediation of cowpea plants (*Vigna unguiculata*). These authors concluded that AM colonization promoted plant growth, chlorophyll pigments, antioxidative defense to plants stressed by Cd contamination, and lower Cd plant uptake (roots and shoots). TiO_2 NPs synergistically potentiated these effects; therefore, both alternatives may ameliorate the negative effects of Cd toxicity and improve plant fitness in contaminated soils. More efficient phytoremediation may be obtained when the synergistic contribution of NMs and AM fungi is achieved. Low NPs concentrations and a metal tolerant fungal inoculum can facilitate phytoremediation and have prospective application. Cheng et al. (2021) observed that the use of 100 mg kg^{-1} of nZVI (bare = B-nZVI or starch-stabilized = S-nZVI) and inoculation of sweet sorghum (*Sorghum bicolor*) with *Acaulospora mellea* was efficient in the nanoremediation of an acidic (pH = 5) and multipollutant soil (DTPA-Cd = 1.9, -Pb = 413 and -Zn = 239 mg kg^{-1}). Both types of NMs were not phytotoxic to sweet sorghum although decreased fungal root colonization; however, *A. mellea* still reduced soil Cd-, Pb-, and Zn-availability, their accumulation in plants, and contributed to phytostabilization of these elements. These NMs immobilized Pb on their surface as well as Cd and Zn, especially when using S-nZVI there were several Pb minerals ($PbZnP_2O_4$, $PbFe_3(P_2O_7)_2$ explaining soil precipitation of this element; however, with B-nZVI these compounds were not observed. Moreover, *A. mellea* modified speciation of Fe, decreased occurrence of Pb, Cd, and Zn on the surface of S-nZVI, but a contrary effect with Cd and Pb was observed on B-nZVI.

Plant growth-promoting bacteria under metal polluted soil conditions may improve growth and metal stress tolerance in plants. Shah et al. (2021) analyzed the mitigation effect of *Bacillus fortis* and ZnO NPs (20 mg kg^{-1}), single or combined application, on Cd toxicity (75 mg kg^{-1}) in *Cucumis melo*. These authors found that the independent use of *B. fortis* or ZnO NPs improves antioxidant enzyme activity (catalase, superoxide dismutase, and peroxidase). However, the combined application was more effective to enhance plant growth and decrease Cd plant concentration. Mokarram-Kashtiban et al. (2019) tested the white willow (*Salix alba*) assisted by *P. fluorescens*, *R. irregularis*, and nZVI at doses of 0, 150, and 300 mg kg^{-1}. The results showed that the treatment of 150 mg kg^{-1} of nZVI in combination with the inoculation of microorganisms increased root length, leaf area, and root Cd concentration of white willow seedlings compared to plants without inoculation or addition of NPs. Although molecular mechanisms involved in metal tolerance were not analyzed and need to be understood, the synergistic use of NMs and beneficial soil microorganisms in phytoremediation of metal-polluted soils is an unexplored research topic that promises to encourage environmental applications.

Currently, the potential co-occurrence of NPs and microplastics is another environmental concern. Yang et al. (2021) analyzed the effect of two kinds of microplastics (HDPE and PLA) and ZnO NPs (500 mg kg^{-1}) on AM fungi population and maize plant growth. Both contaminants greatly influenced the community composition and relative abundance of AM fungi and the effects were type and dose-dependent. Microplastics exerted a protective effect against ZnO

NPs plant growth. These authors suggested that these contaminants have an intense ecological influence with undefined significance for agroecosystems.

Applications and challenges of nanotechnology in agriculture and soil remediation

Applications of NMs in agriculture and NMs-assisted phytoremediation soil are illustrated in Fig. 3. In summary, NMs can release nutrients for plants, carry pesticides, be amendments to improve soil quality and degrade or stabilize soil pollutants. Despite the potential benefit of NPs application in agriculture and soil remediation, the NMs are not used on a large scale. There are no clear reasons for the slow development and use of NMs in agriculture. We need to find the limiting factor for technology transference from the laboratory to the field. The identification of restrictive factors is difficult due to myriad aspects that must be considered (Fig. 8), from different focuses: technological, environmental, economic, social, and political (Kah 2015; Dimkpa et al. 2018).

Essentially, to scale laboratory results to widespread field applications requires the design of processes and policies to transfer technology (Kim et al. 2018), safely and cheaply; p.e. to develop analytical methods to validate the chemical quality of nano-agrochemicals. Monitoring transformation and quantifying their concentrations in the environment is relevant (Dimkpa and Bindraban 2018), and to ensure that NMs do not represent a danger to environmental and human health. Hence, one of the technical challenges is related to experimentation (Sharma et al. 2020).

There is a need to carry out field and laboratory experiments to find safe NMs doses to reach sustainable crop production, to mitigate soil pollution without damaging the soil quality and users' health (Sharma et al. 2020). Many of the reported studies were designed using high doses of NPs, short exposure times, and different media; therefore, the results may not be comparable. Moreover, experimental conditions do not reflect agricultural soil reality and complexity (Dimkpa and Bindraban 2018; Cao et al. 2017). Field-based studies to understand the life of NMs in agriculture systems are a critical requirement (Chen 2018).

To apply NMs at a wider scale and the transfer of nanotechnology, we should address social concerns, regulation, and legislative support (Corsi et al. 2018). There is an urgent need for policies for production and use to guaranty a low impact on the environment and safety to human health. Acceptation of the NMs by the potential consumers is transcendent. The NP interaction and transformation in the environment should be understood. Nanotechnology may have outstanding implications for sustainable development.

Conclusions

The metal NPs application for food production and soil remediation offers technological advantages. In the case of agriculture, MNs through precision farming

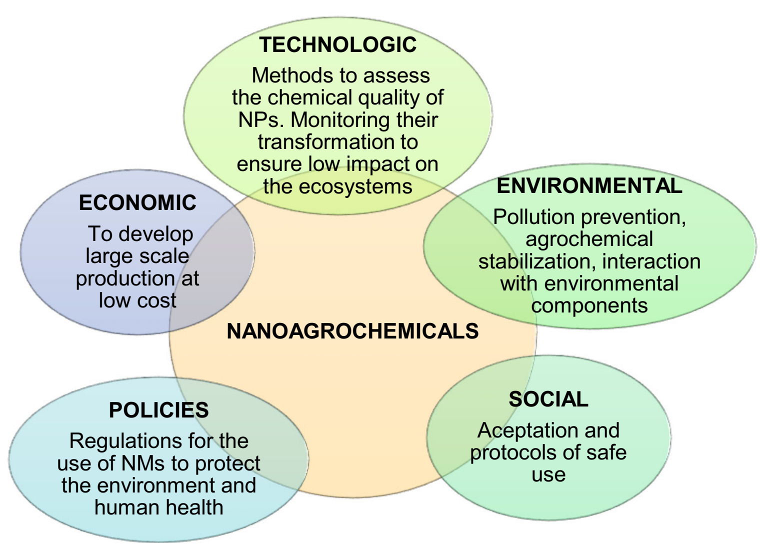


Fig. 8 Concern related to the use and commercialization of nanoagrochemicals on a large-scale

techniques may promote efficiency in nutrients absorption, enhance crop yields, and pest control avoiding environmental impact to soil and water resources. Furthermore, the agro-chemicals losses would decrease due to the properties of NMs and the slow release of an active ingredient. For soil remediation, metallic NPs act positively in combination with microorganisms and plants for immobilization or stabilization of PTE. Moreover, these particles may solve the problems of both organic and inorganic pollutants. There are applications of nanotechnology to face agriculture and environmental issues. Nevertheless, it remains to select safe nanotechnologies for the environment and living organisms. In this regard, it is required to do convincing studies, using concentrations and conditions as realistic as possible, and evaluate long-term effects. The goal is to understand the complex networks of interactions between plants, soil microorganisms, the soil, and the NMs. Thus, we determine the variables that influence the toxicity of NMs, predict their fate after application, and design methods for their correct use.

Abbreviations *AM,* arbuscular mycorrhizal; *DOM,* dissolved organic matter; *NMs,* nanomaterials; *NP,* nanoparticle; *NPs,* nanoparticles; *GDP,* gross domestic product; *MUE,* micronutrient efficiency; *TMV, Tobacco mosaic virus*; *DOC,* dissolved organic carbon; *PTE,* potentially toxic elements; *nZVI,* zero-valent iron nanoparticles; *PRB,* permeable reactive barrier; *EKR,* electrokinetic remediation; *EKR-PRB,* electrokinetic remediation with permeable reactive barriers; *AMD,* acid mining drainage

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Declarations

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