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To cite this article: Hao Chen (2018) Metal based nanoparticles in agricultural system: behavior, transport, and interaction with plants, Chemical Speciation & Bioavailability, 30:1, 123-134, DOI: [10.1080/09542299.2018.1520050](https://doi.org/10.1080/09542299.2018.1520050)

To link to this article: <https://doi.org/10.1080/09542299.2018.1520050>



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Published online: 14 Sep 2018.



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Metal based nanoparticles in agricultural system: behavior, transport, and interaction with plants

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ABSTRACT

With the fast-developing nanotechnology, metal based nanoparticles (NPs) production and application are increased significantly. These metal based NPs can enter agricultural land through both direct and indirect pathways. This review presents an overview of the fate and transport of metal based NPs and their interactions with plants in agricultural ecosystem system. The physical chemical properties of both metal based NPs (e.g. size, surface charge, surface coating) and soil matrix (e.g. pH, ionic strength, mineral composition, dissolved organic matter) all play important roles in determining the mobility, transformation and potential risks of metal based NPs in plant and soil system. NPs can be accumulated to plant roots and translocated to other parts of the plants. The properties of both plant and metal based NPs are playing critical roles to this process. Systematic research of metal based NPs in environmentally relevant concentrations and conditions is needed for the future study.

ARTICLE HISTORY

Received 24 December 2017
Accepted 30 July 2018

KEYWORDS

Metal based nanoparticles;
fate and transport;
phytotoxicity; nano toxicity

1. Introduction

Nanoparticles (NPs) are defined as materials with at least two dimensions between 1 and 100 nm^[1]. With novel properties at nanoscale (e.g. surface reactivity, unique mechanic, catalyze and optical properties) engineered nanoparticles have been used widely in various sectors such as electronics, construction, health, energy, and agriculture. Despite the desired properties of NPs as commercial products, the environmental risks associated with NPs are largely unknown. Metal based NPs, in particular, have drawn considerable environmental concerns due to their increased toxicity with decreased particle size (e.g. Ag NPs, TiO₂ NPs, and CuO NPs).

Over the past decade, metal based NPs production is growing exponentially due to their enhanced physico-chemical properties and biological activities compared to their bulk parent materials. With sunlight blocking ability, ZnO NPs and TiO₂ NPs have been utilized extensively in sunscreens, cosmetics, and surface coating. TiO₂ NPs also have been broadly applied in the manufacturing of paints, plastics and papers. Iron based NPs, including iron oxides, iron hydroxides, and iron oxide-hydroxides NPs, are showing a great potential in biotechnology due to their superparamagnetic properties, biocompatibility and low-toxicity^[2]. CeO₂ NPs have been used as a combustion catalyst in diesel fuels to increase fuel burning efficiency^[3]. In agricultural section, nanoscale CuO particles have been applied as fungicides due to their high efficiency and broad-spectrum bioactivity^[4]. Metal based NPs also been applied

together with carbon nanotubes as hybrids with new properties arising from interactions between the two entities. Due to the desired properties, studies of synthesis method and new application of metal oxides based NPs are continually expanding. As a result, high volume of metal based NPs production and their wide spread in the environment can be anticipated.

Agriculture land can be one of the major receiving ends of the discharged metal based NPs. To assess the impacts of metal based NPs on agriculture ecosystem, it is essential to understand their transport and transformation in agriculture environment. Agriculture soil is often characterized with abundance of dissolved soil organic matter which may have significant impact on the fate and transport of metal based NPs. Plants as key component in agriculture practice also shown complexed and dynamic interactions with metal based NPs. Several reviews have been presented focusing on stability and aggregation of NPs in environment^[5]; NPs transport in environment media ^[6,7]; NPs interaction with plants; ^[8] bioavailability, toxicity, and fate of NPs in ecosystems. ^[9–11] However, most investigations on the environmental impact of metal based NPs consider agricultural soil environment and plant system separately and seldom emphasize them as integrated system, which is critical for agriculture ecosystem analysis. This review presents an overview of current study, discusses and future perspectives on metal based NPs stability, transformation, transport, and interaction with plants in agriculture plant and soil system.

2. Direct and indirect metal based NPs inputs

Metal based NPs can enter the agriculture system through both direct and indirect pathways.

One of the major sources of indirect metal based NPs input is sewage sludge land application. After NPs containing products application, NPs are easily released from the products matrix then enter swage system. For example, TiO₂ NPs can release to environment from building's painting [12]; NPs can be released from fabric during laundry or from plastic container during the usage [13]; TiO₂ and ZnO nanoparticles can be released from sunscreens into outdoor swimming pools [14,15]. In wastewater treatment system, metal based NPs tend to be retained and accumulated in sewage sludge, rather than the treated waste water effluent [16]. As a result, various metal based NPs have been detected in the bio solid of waste water treatment plant. Since sewage sludge often had been used in agriculture land as soil conditioner or plant fertilizer, it can be one of the important sources of metal based NPs in the arable land. [17,18]

Direct input of NPs into soil is mainly through applications of Nano formulated agriculture chemicals including Nano fertilizer and Nano pesticides. Nanostructured fertilizers such as Fe, Mn, Zn, Cu, Mo NPs can promote plant-growth and agronomic yields at a small dose, leading to significant economic and environmental benefits [19,20]. For example, ZnO NPs or Fe₂O₃ NPs applied to peanut seeds, resulting in greater seed germination, increased stem and root growth while other form of Zn or Fe used for comparison had limited impact [21,22]. Study conducted by Hanif et al. [23] indicated when 100 mg kg⁻¹ TiO₂ NPs soil was applied the concentration of phytoavailable P in soil increased up to 56% after 72 h incubation at room temperature (25°C) in Petri dishes. After culturing *L. sativa* plants onto soil applied with 100 mg kg⁻¹ TiO₂ NPs for 14 days, shoot and root lengths were increased up to 49% and 62% respectively, as compared to the control treatment.

Pesticides or fungicides also been developed into Nano size for better plant protection, since Nano formulation can generally increase bioavailability through increasing the solubility of active intergradient or decrease the harmful effect on the non-target organisms [24]. Nano structured metal used for pesticides or fungicides NPs mainly include, Silica, Titanium, and Copper [24]. Silica NPs (15–30 nm) shown better efficient for insects control compare to with bulk silica [25]. Nano formulated TiO₂ used alone or with other active intergradient over all have better efficient to reduce bacterial spot disease than standard treatment [26]. Copper based NPs can effectively suppress the bacteria growth on pomegranate at concentrations of 0.2 mg L⁻¹ much lower than copper oxychloride application concentration (2500–3000 mg L⁻¹) [27].

Despite increasing concern about NPs in the environment and subsequent ecosystem effects, little information available about the quantity of NPs entered agriculture soil system thorough direct or indirect input. Research of the fate, transport, bioavailability and potential environmental risks of metal based NPs are still in early stage.

3. Behavior of metal based NPs in agriculture soil

The environmental behavior of discharged Metal based NPs plays an important role in determining their mobility, reactivity, toxicity and potential risks in agriculture system. Metal based NPs may undergo aggregation then precipitated onto soil matrix, or stabilization through dispersion in soil solution, or physical or chemical reactions with other environmental components and changing their properties. In agriculture system, the environmental behavior of metal based NPs controlled by their properties and the characteristics of both soil and soil pore water. NPs possess unique physical and chemical properties due to size-dependent 'quantum effects'[28]. In addition, Metal based NPs often manufactured with certain features to enhance their effectiveness, such as chemical composition, unique morphology, surface coating, and surface functionality. These features can be controlling factors for their environmental behavior. Besides, consisted of solid, solution and gas phases, soil matrix presents a complexed system for understanding of the environmental behavior of metal based NPs. Due to these complexity of the system, analysis and predict the environmental behavior of metal based NPs still remain challenging.

3.1. Aggregation and dispersion

Metal based NPs in environment tend to aggregate into larger cluster thus lost their size related nanoscale properties [5]. In soil matrix, NPs aggregation can be quickly fixed into soil solids and largely lost their reactivity. [5] NPs with little aggregation can typically travel long distance; thus have high impact on surrounding environment. Therefore aggregation process governs metal based NPs mobility, reactivity and risks in the agriculture system. Many properties of NPs influence aggregation process, such as size, chemical composition and surface charge[5]. Besides, NPs in the environment may undergo series physical or chemical interaction with different environmental components, thus the environmental condition (e.g. solution pH, ionic strength, natural organic matter) where the NPs released also play important role for NPs aggregation[7].

Colloid science principles have been applied to interpret environmental behavior of metal based NPs in recent studies, since the size of NPs (less than 100nm) is within the range of colloids (less than 1000nm).

However NPs challenge traditional colloids science due to their decreased particle size, unique chemical composition, non-spherical shapes, surface coating, and surface functionality. [5] Decreasing metal based particle size to Nano range can alter particle surface and near-surface atomic structure making NPs more reactive than colloids[29]. Kinetic stability study of hematite NPs conducted by He et al. [30] shown at the same conditions smaller hematite nanoparticles (12nm) are more susceptible to aggregation than larger particles (65nm) due to the change of structure and surface energy characteristics, which demonstrated colloid theory cannot be used to fully explain the aggregation behavior of NPs.

Surface characterizations of metal based NPs control their surface charge and potential interactions with environmental components which play critical roles in determining NPs aggregation. For uncoated NPs, surface element, element speciation and crystal structure are important for NPs stability. Without surface coating, metal based NPs usually have surface charge due to the presents of oxygen atoms or hydroxyl groups that can release or uptake protons. Electrostatic double layer (EDL) may form around these charged surface with both charged surface layer and a diffused layer containing ions attracted from soil solution. The zeta potential of metal based NPs typically show positive at low pH and negative at high pH because of protonation and deprotonation process. Due to the repulsive forces between particles, particles with a high zeta potential (positive or negative) have lower aggregation tendencies compared with particles with a low zeta potential given the same solution chemistry. [5,31] However when pH approach to zero point charge where overall surface charge close to zero, the stability of metal based NPs decreases. Surface coatings (e.g. surfactants) are often used to enhance NPs stability by increasing hydrophobicity or by providing electrostatic, steric, or electro steric repulsive forces between particles. [27,32,33] Organic coatings include different varieties such as organic acid, polysaccharides, surfactants, proteins, and polymers. Surface coating commonly added to NPs surface through surface adsorption. The surfactant attached may desorb or be displaced by natural polymers such as natural organic matter that changes in the stability when the metal NPs are released into the environment[5].

3.2. Interaction with soil dissolved organic matter

Most productive agriculture soils are high in organic matter content. Dissolved organic matter (DOM) is one of the most reactive and mobile soil organic fractions and has a major influence on metal based NPs in soil matrix [34]. The soil DOM is a complex mixture of different organic compounds typically

including humic acid, fulvic acid, hydrophilic acid, fatty acid, carbohydrate acid, amino acid, hydrocarbon [35]. Major sources of DOM originated from plant biomass, litter, humus, root exudes, amendments applied on agriculture soil, etc.

DOM often interacts with metal based NPs through different pathways then alters their environmental behavior. The interaction process involves a complex combination of electrostatic interaction, van der Waals forces, and hydrophobic interaction between DOM and NPs surfaces. The DOM adsorbed on NPs surface can usually decrease NPs aggregation through increased electrostatic stabilization or increased hydrophobicity. For instance, humic acid can significantly improve Fe_xO_y NPs stability by increase their electrostatic and steric stability at different pH range [36,37]. Humic acid derived from Amherst peat soil showed a strong influence on Al_2O_3 NPs steric stability [38]. Ghosh et.al studied the effect of humic acid structure on Al_2O_3 NP's stability shown that the NPs aggregation will be weakened by increased humic acids' aliphaticity and low polarity [38]. Suwannee River fulvic acid was found effective to stabilize a variety of metal based NPs, including Silver based NPs; Gold based NPs; ZnO NPs and TiO_2 NPs [39–42]. In general, the effectiveness of NPs stability enhancement largely depend on the characteristics of the DOM, such as concentration, hydrophobicity, molecular mass, and polarity.

DOM can also promote NPs aggregation through bridging effect or changing the critical characters of NPs aggregation behavior. [41,43] Study of the effect of Suwannee River humic acid on the ZnO NPs aggregation conducted by Omar et.al. indicated when solution pH below pH_{pZC} of ZnO NPs, negative charged humic acid can promote positive charged ZnO NPs aggregation; although, when pH equal or above pH_{pZC} of ZnO NPs, similar concentration of humic acid can decrease ZnO NPs aggregation [41]. Baalousha et.al studied the aggregation of iron oxide NPs and found Suwannee River humic acid can lower iron oxide NPs aggregation pH values from pH 5 to 6 (absence of Suwannee River humic acid) to pH 4 to 5 due to charge neutralization effect [43].

Overall, the effect DOM on the stability of metal based NPs depends on the characteristics of metal based NPs, DOM and environmental matrix. Given the complexity agriculture soil and water system, a better understanding of the interaction of metal based NPs and DOM is needed to improve our predictive capacity in the metal based NPs environmental behavior.

3.3. Heteroaggregation with inorganic colloids

Given the ubiquitous presence of natural clay minerals are in soil matrix, the interaction between colloids and metal based NPs are inevitable. NPs released can

attach to inorganic colloids through collisions then attachment as heteroaggregation. Opposite surface charges and/or high ionic strength favored the formation of primary heteroaggregates with natural clay colloids via the attachment of nanoparticles to natural clay colloids, therefore pH play an important role in controlling heteroaggregation due to the surface charge on NP and soil colloid surface are both pH dependent [44,45]. Study conducted by Smith et al. investigated heteroaggregation between hematite (α -Fe₂O₃) colloids and citrate-capped gold nanoparticles (Cit-AuNPs) [46]. Their result shown in the absence of soil organic matter at pH values where Cit-AuNPs and hematite are oppositely charged, attachment efficiencies are high and Cit-AuNPs are capable of destabilizing hematite following an 'electrostatic patch' mechanism [46]. Praetorius et al. reported similar results with study of TiO₂ NPs (15 nm) interact with SiO₂ colloids, (0.5 μ m). At pH 5 the TiO₂ NPs and the SiO₂ particles are of opposite charge, resulting in α_{hetero} values close to 1; at pH 8, where all particles are negatively charged, α_{hetero} was strongly affected by the solution conditions, with α_{hetero} ranging from <0.001 at low ionic strength to 1 at conditions with high NaCl or CaCl₂ concentrations [44]. However, Praetorius et al.'s study also shown the presence of humic acid stabilized the system against heteroaggregation. The heteroaggregation prevention effect of co-existing humic acid can be explained by the increased energy barrier and the Critical Coagulation Concentration of the binary system (colloid + NPs) [47].

4. Transformation of metal based NPs in agriculture soil

4.1. Dissolution

Dissolution and ion release is common for metal based NPs. Dissolution is a dynamic process largely related to metal based NPs' reactivity and environmental toxicity. Both solubility and dissolution rate are depending on particles' intrinsic properties, as well as the matrix of surrounding media.

It is well known particles with same intrinsic properties in same solution matrix generally smaller particles have higher dissolution rate due to the increased specific surface area. Studies on Ag, ZnO and CuO NPs indicate in general solubility increase as particle size decreases. [48–50] Although size is the primary physicochemical property affecting solubility of NPs, this trend can be altered especially by NPs' surface coating. Sharma et al. [51] studied the solubility of organic-coated Ag nanoparticles indicating organic coating can promote or inhibit Ag NPs dissolution depend on the surface coating and ligands presented in the media. Li et.

al. [52] also reported similar results Ag NPs dissolution rate can be increased by tween surface coating, however the effect on dissolution of citrate coating is limited.

For metal based NPs with same chemical composition, their solubility can differ with different morphology. Surface morphology of metal based NPs (e.g. mesoporosity, hollow/compact) is a determining factor for their specific surface area and their dissolution rate. Study comparing reactivity and dissolution of spheres (7 nm) and rods (7 \times 40 nm) CuO NPs indicated the dissolution rate of spheres CuO NPs (0.49 h⁻¹) was significantly higher than rods CuO NPs (0.050 h⁻¹) [53]. Study conducted by Borm et al. [54] shown smaller radius particles with positive curvature (convex) tend to be energetically unstable therefore can have preferential dissolution and higher equilibrium solubility.

The properties of the soil and water matrix such as solution chemistry (pH, ionic strength) and presence of natural organic matter or colloids also play an important role of metal based NPs dissolution. These properties can affect metal based NP aggregation/heteroaggregation and further affecting the exposed surface area and thus particle dissolution. The effect of natural organic matter on metal based NPs is more complicated since chemical reaction may happened with certain natural organic matter and metal based NPs. Research on Cu based NPs shown in freshwater (pH 6.32), the presence of natural organic matter reduces Cu dissolution rate, possibly through a combination of chelation and by coating particle surfaces [55]. However, Bian et al. [56] studied dissolution of 4 nm ZnO NPs indicated the relative solubility of ZnO NPs increases in the presence of humic acid at high pH range by the ligand promoted dissolution. Study conducted by Miao et al. [48] also shown natural organic compounds either enhance or reduce Zn²⁺ release from ZnO NPs, depending on their chemical composition and concentration. Overall, the chemical reaction with metal based NPs and chemicals in environmental matrix can either reduce the dissolution through steric protection or increase the dissolution through ligand promoted processes. Therefore, dissolution process in environmental relative media can significantly differ from the observed in simplified studies.

4.2. Chemical transformations

Metal based NPs may undergo chemical transformations such reduction or oxidation in agriculture soil (Figure 1). Reduction and oxidation are coupled processes in natural systems and involve the transfer of electrons to and from chemical moieties. [57] Metal based NPs such as silver based NPs, [58,59] gold based NPs [60], and iron based NPs etc., [61] are active for reduction or oxidation reactions. Aerated agriculture soils are predominantly oxidizing environments,

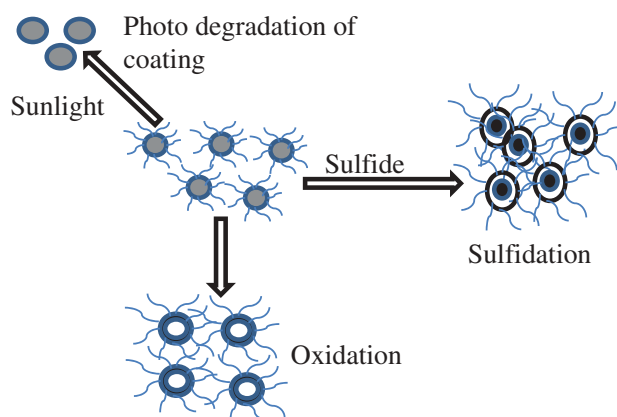


Figure 1. Representative chemical transformations of metal based nanoparticles in agriculture soil.

while saturated subsurface with limited oxygen may result in reduction of metal based NPs. In dynamic redox environments such as paddy rice soil metal based NPs may undergo different stages of redox process. [62]

Sunlight-induced redox reactions may prove to be very important chemical transformation processes affecting metal based NPs, oxidation state, generation of reactive oxygen species, and persistence. [57,63] Under sunlight irradiation, Ag nanoparticles coated with gum arabic and polyvinylpyrrolidone both shown aggregation and sedimentation due to strong sun light induced oscillating dipole–dipole interaction [63]. Certain metal based NPs such as TiO₂ NPs or ZnO NPs are designed to be sensitive to sunlight, potentially producing reactive oxygen species when exposed to sunlight [64]. Some metal based NPs may change their redox state and their potential toxicities under natural sunlight [65].

Sulfidation is also important chemical transformation process of metal based NPs, affecting NP chemical composition [66,67], ion release [67,68], and toxicity [66]. Metal based NPs made from Class B soft metal cations (e.g. Ag, Zn, and Cu) are likely to sulfidize once released. Recent study indicated the ZnO NPs sulfidation can reach to 100% conversion can be obtained in 5 days given sufficient addition of sulfide though a dissolution and reprecipitation mechanism; the sulfidation can lead to NP aggregation and a decrease of surface charge [67]. CuO NPs can also be sulfidized by inorganic sulfide to several copper sulfide (Cu_xS_y) species with the extent of sulfidation depends on the sulfide to CuO molar concentration ratio used [69]. Sulfidation can increase the soluble fraction of Cu species. This high solubility is a result of oxidative dissolution of Cu_xS_y, formation of relatively more soluble copper sulfate hydroxides, and the formation of small CuS nanoclusters that pass the 3 kDa filter [69]. These findings suggest that sulfidation of metal based NPs may change their behavior, fate, and toxicity in the environment.

5. Transport of metal based NPs in soil

Understanding the transport behavior of metal based NPs in soil is essential to revealing their potential impact on the agriculture system. The transport of metal based NPs are largely determined by the physical chemical properties of both NPs and environmental matrix.

In porous media, the transport of NPs is controlled by the NPs filtration rate by the porous media, which is often determined by diffusion, as the high diffusivity of nanoparticles leads to a higher incidence of being captured by soil grains [7]. Theoretically the NPs mobility is decrease with increasing particle size [70]. However, the aggregation status of NPs has strong influence on NPs mobility, since aggregation can increase the size of NPs and aggregate straining is common for NPs capture in porous media. The change of particle size by aggregation can actually result from the more complex effects such as change in particle surface charge and particle morphology; therefore aggregate straining is still challenging to precisely describe. In addition, the capture of NPs by the soil matrix is also determined in large part by the interaction between particles and soil grain surface [6]. NPs Properties such as size, surface charge, and surface modification can substantially influence their mobility in porous media. Physical parameters of the media, such as particle size, fluid velocity and grain size can also play important roles in the filtration of NPs.

NPs Surface chemistry is a controlling factor of the NPs mobility in porous media. NPs with hydrophilic surface can be relatively easily dispersed and lead to greater mobility; NPs with hydrophobic surface have the tendency to aggregate and separated from solution phase. NPs with higher negative charges are believed to be more mobile since soil particles are normally negatively charged and the repulsion between the them can reduce capture rate [71]. Positively charged NPs will be readily attracted to the negatively charged soil surface, thus, various surface modification methods have been applied alter NPs surface charge and their motilities in environment matrix. For instance, adding phosphate to positively charged Al₂O₃ NPs can producing a net negative surface charge of Al₂O₃ NPs, therefore enhance the mobility of Al₂O₃ NPs [71,72]. Surface modification can also alter the hydrophobic properties of NPs. Fe NPs with anionic, hydrophilic carbon and poly(acrylic acid) surface modification shown decreased aggregation and increased mobility in sand porous media compare to pristine Fe NPs [73].

Characteristics of the soil matrix such as size and porosity also influence the filtration of NPs. In general, NPs mobility decrease when the soil median grain size decreased[6]. Clay content in Soil can act as anionic support materials to prevent NPs aggregation and

enhance their mobility [73]. The solution flow rate has also been shown to affect the mobility and aggregation status of NPs [74]. Usually, as flow rate is increase, the mobility of NPs increase [74,75].

Solution pH, temperature and ionic strength are all important factors affecting NPs mobility. Solution pH controls surface charges of both NPs and soil grains and thus the electrostatic interactions in system. Increased temperature can increase Brownian motion of NPs and enhances the capture of Brownian particles by the media particles [70]. In environmental matrix, dissolved counter ions in solution will shelter the long-range electrostatic interactions and thus decrease the stability and mobility of NPs. With increasing concentration of dissolved salt, ionic strength is increased and attraction between NPs will outweigh the repulsion to form aggregation. Critical coagulation concentration was used to describe the electrolyte concentrations for complete destabilization of NPs to generate rapid aggregation. Base on Derjaguin-Landau-Verwey-Overbeek theory, increased ionic strength decreases the repulsive forces between NPs or NPs and soil matrix leading to increased aggregation and sorption [30]. For example, French et.al. [76] showed that for TiO₂ NPs suspension holding the pH constant, but increasing the ionic strength from 0.0045 M to 0.0165 M, leads to the formation of micron-sized aggregates within 15 min. In addition, divalent cations typically have better effect to enhance aggregations [76].

6. Interaction of metal based NPs and plants

NPs may have positive effect or negative effect on plants. The NPs up taking abilities varies amongst plants because of the diversity of their physiological and morphological [77]. For instance, different uptake mechanisms can result from different root and vascular morphologies through which NPs reach the inside of plant tissues [77,78].

6.1. Interaction with plant roots

NPs adsorption is considered to be the first step for the NPs plants bioaccumulation [79]. For instance, CuO-NPs can be strongly adsorbed on the plant root surface partially through mechanical adhesion; the adsorbed CuO-NPs cannot be desorbed by competing ions [80]. Larue et al [81]. reported TiO₂-NPs can accumulated in wheat roots then distributed distribute through whole plant tissues without dissolution or crystal phase modification. Zhu et.al conducted study comparing the root accumulation ability of Au NPs in four plant species indicated radish and ryegrass roots generally accumulated higher amounts of the AuNPs (14–900 ng mg⁻¹) than rice and pumpkin roots

(7–59 ng mg⁻¹)[78]. Ag NPs also been observed can be easily adsorbed by rice roots[82].

NPs accumulation rate by plant root can be influence by the properties of NPs and the environmental conditions. The study on Au NPs indicated that positively charged Au NPs are most readily taken up by plant roots compare to positively charged Au NPs. [78] Doolette, et al. [83] studied the plant uptake of Ag from biosolids-amended soil containing Ag₂S-NPs, reported that ammonium thiosulfate and potassium chloride fertilization significantly increased the Ag NPs concentrations of plant roots and shoots. Zhang, et al. [84] reported smaller ceria nanoparticles have higher accumulation rates in cucumber roots. Zhao et.al reported soil organic matter can reduce CeO₂ NPs accumulation by corn plants roots. [85]

One of the mechanisms for increased bioavailability of metal based NPs in rhizosphere is the presence of microbial siderophores and root exudates. It is known that plants and microorganisms produce organic ligands to solubilize minerals from poorly available sources. Microbial siderophores are low molecular weight organic molecules produced by variety of organisms to chelate iron under iron limiting conditions. Recent study indicated siderophores also have high affinity for other metals such as Cu, Zn, and Ag [86]. Therefore, with the chelation between siderophores and metals, promoted dissolution and increased bioavailability of metal based NPs can be expected. In addition, plant roots often release exudates to enhance nutrients uptake from insoluble sources [87]. Recent study conducted by Huang et al. indicated synthetic root exudates can promote Cu NPs dissolution rate and increase the bioavailability of free Cu ion in the soil systems. [88] For different plants organic matter composition in rhizosphere, therefore their effects on metal based NPs are different. Judy et al. [89] studied bioavailability of Gold NPs to plants indicating the differences in root exudates between wheat and tobacco resulted into different aggregation of Gold NPs, affecting their bioavailability to plants.

6.2. Metal based nps translocation

NPs accumulated by plant roots can translocated to plant shoot or other plant tissues including newly developed seeds [90,91]. Peng et al. [92] reported that CuO NPs can be transported from the rice roots to the leaves after exposed to 100 mg L⁻¹ CuO NPs for 14 days. Zhu et al [78]. studied Au NPs can accumulate in rice shoot to statistically significant extents. TiO₂ NPs been reported can be translocated inside cucumber from root to shoots and cucumber tissues [93]. Study of Magnetite (Fe₃O₄) NPs shown Fe₃O₄ NPs can absorb, translocate, and accumulate the particles in the pumpkin plants (*Cucurbita maxima*) tissues [94].

Lee et al. [95]. studied translocation of Cu NPs in mungbean (*Phaseolus radiata*) and wheat (*Triticum aestivum*) and their study indicated that the Cu NPs can accumulated inside plant cells through cell membrane.

Characteristic of both NPs and plants play important role on NPs translocation. For example, study conducted by Zhu et al [78]. indicated Au NPs can accumulate in rice shoots, while Au NPs cannot be accumulated in the shoots of radishes and pumpkins. Additionally, their research also shown positively charged Au NPs are most readily taken up by plant roots, while negatively charged Au NPs are most efficiently translocated into plant shoots (including stems and leaves) from the roots [78]. Hernandez-Viezcas et al [96]. studied CeO and ZnO NPs translocation from soil into soybean showing only CeO NPs can be translocated in nano particle form inside plant tissue and Zn was bio transformed into Zn-citrus. Study on transport of CuO NPs in maize shown CuO NPs can be transported from roots to shoots via xylem and CuO NPs could further translocate from shoots back to roots via phloem. [97] Study of the NPs diameter effect on TiO₂ translocation in wheat suggested that the a threshold diameter, 140 nm, above which NPs are no longer accumulated in wheat roots, as well as a threshold diameter, 36 nm, above which NPs are accumulated in wheat root parenchyma but do not reach the stele and consequently do not translocate to the shoot[81].

6.3. Phytotoxicity of metal based NPs

The toxicity of metal based NPs to plants may involve to three mechanisms. [98,99] First, released toxic ions from NPs may be toxic to exposed plants. [100] For instance, Ag ions released from Ag NPs may affect cellular respiration or transport of ions across cell membranes, with ultimate cell death. [101] Second, NPs interactions with plant or environmental media may produce chemical radicals to generate plant oxidative stress. Third, NPs interact directly with plant as particles, e.g. CuO NPs interaction with membranes. Because some of metal based NPs (e.g. ZnO NPs, CuO NPs) are partially soluble, both soluble and particulate species can be toxic to plants. [92,102]

6.4. Effect of nps on seed germination

Seed germination inhibition is common toxic effect of metal based NPs. Lin and Xing [103] reported seed germination inhibition of zinc NPs on ryegrass and zinc oxide NPs on corn at 2000 mg L⁻¹ possibly due to the toxicity of dissolved zinc cations. El-Temsah and Joner [104] studied the toxic effect of zero-valent iron NPs and Ag NPs differing in average particle size from 1 to 20 nm on ryegrass, barley, and flax seed

germination with exposed to 0–5000 mg L⁻¹ zero-valent iron NPs or 0–100 mg L⁻¹ Ag. Their study shown inhibitory effects were observed in aqueous suspensions at 250 mg L⁻¹ for zero-valent iron NPs. Complete inhibition of germination was observed at 1000–2000 mg L⁻¹ for zero-valent iron NPs. For Ag, Ag NPs inhibited seed germination at lower concentrations, but showed no clear size-dependent effects, and never completely impeded germination. However, positive effect of NPs on seed germination also been observed. Feizi et al. [105] reported TiO₂ NPs at 2 and 10 mg L⁻¹ concentrations can promote wheat seed germination and seedling growth.

6.5. Effect of nps on root elongation

Root growth inhibition typically indicted toxicant existed in surrounding environment. Lin and Xing [103] studied the effect of NPs on root elongation of six higher plant species (radish, rape, ryegrass, lettuce, corn, and cucumber). Suspensions of 2000 mg L⁻¹ Zn NPs or ZnO NPs practically terminated root elongation of the tested plant species. Fifty percent inhibitory concentrations (IC₅₀) of Zn NPs and ZnO NPs were estimated to be near 50 mg L⁻¹ for radish, and about 20 mg L⁻¹ for rape and ryegrass. Yang and Watts [106] investigated the phytotoxicity of Al NPs loaded with and without phenanthrene (Phen) on corn, cucumber, soybean, cabbage, and carrot root elongation. It was found that when loaded with 10.0%, 100.0%, or 432.4% monomolecular layer (MML) of Phen, the degree of the root elongation inhibition caused by the particles was reduced. Ma et al. [107] studied the phytotoxicity of four rare earth oxide NPs, CeO₂ NPs, La₂O₃ NPs, Gd₂O₃ NPs and Yb₂O₃ NPs on seven higher plant species (radish, rape, tomato, lettuce, wheat, cabbage, and cucumber) by means of root elongation experiments. Their effects on root growth varied greatly between different NPs and plant species. Their result shown a suspension of 2000 mg L⁻¹ CeO₂ NPs had no effect on the root elongation of six plants, except lettuce, however 2000 mg L⁻¹ suspensions of La₂O₃ NPs, Gd₂O₃ NPs and Yb₂O₃ NPs severely inhibited the root elongation of all the seven species. Inhibitory effects of La₂O₃ NPs, Gd₂O₃ NPs, and Yb₂O₃ NPs also differed in the different growth process of plants. For wheat, the inhibition mainly took place during the seed incubation process, while lettuce and rape were inhibited on both seed soaking and incubation process.

7. Conclusion and future study of metal based NPs in agriculture system

With both direct and indirect input into agricultural ecosystem, metal based NPs can enter soil and plant system and remain active. Due to the unique physical

and chemical properties of metal based NPs, to fully understand and predict their environmental behavior remain challenging. The presents of soil organic matter, soil colloid, plants and microorganism further complicate analysis the fate and transport of NPs in soil matrix. The critical factors determine the mobility of metal based NPs includes various core metals of NPs and their speciation, size, surface coating, surface charge, and physical and chemical condition of the environmental medium (e.g. pH, cation condition, and organic acid).

Metal based NPs can be accumulated by plant roots and further translocated to different parts of the plant. Characteristics of metal based NPs, plants and their interactions all play important roles on NPs translocation. Although some metal based NPs are shown positive effect on plant growth, unwanted NPs translocation to edible part of the plants may be harmful to human health [91]. In addition, a group of metal based NPs (e.g. Ag NPs, CuO NPs) also shown phytotoxicity to certain plants indicated by germination and root elongation inhibition. [92,102] The phytotoxicity of NPs are related to toxic ions dissolution from NPs, [100] radical generation through NPs interactions with plant or environmental media, or direct interaction of NPs with plant as particles [92,100,102].

Aggregation as a key behavior of metal based NPs can significantly affect their fate and toxicity in agriculture system. Although well-established colloid science theories can be used to explain part of aggregation behavior of metal based NPs, fully understanding the aggregation of metal based NPs is still challenging due to their novel Nano scale properties (e.g. shape, structure, composition). [5] The presents of organic coating further altered the potential interaction of metal based NPs in the environment matrix. Much work is needed to establish a theoretical understanding of NP aggregation in the agriculture environment.

To understand the interaction of metal based NPs with soil component (natural organic matter or colloids) can be comprehensive due their high reactivity. Recent studies have provided valuable information concerning the interaction of NPs with natural organic matter; however most of these researches are focused on humic acid or fulvic acid. Therefore further research is needed for systematic evaluations of different types of natural organic matter (e.g. low molecular weight organic acids, protein, Polysaccharide). Only few studies are available on interaction of metal based NPs with colloid minerals, new investigations are needed to elucidate the dynamic interaction and interaction mechanisms. In agriculture soil system with both natural organic matter and colloids are presented, systematic determination is necessary for accurate

evaluation of heteroaggregation between NPs and NCs, which are crucially for developing the environmental fate models of metal based NPs.

For toxicity evaluation of metal based NPs, an important challenge is to identify whether the toxicity is due to the metal based NPs or caused by the metal ions released (dissolution), or a combination of both. Dissolution of metal based NPs can lead to delivery of highly toxic ions such as Zn^{2+} or Ag^+ [48,100]. As a result, in environmental matrix with discharged metal based NPs, dissolution of NPs in media will produce a complex suspension with both metal based NPs and free/complexed ions released from the NPs. Comprehensive models with full evaluations of all potential toxicants are needed to predict NPs dissolution process rather than simple correlations with one of physicochemical properties of NPs [108].

In consider of the complexity of agriculture soil and plant system, to characterize and predict environmental behavior of metal based NPs is still challenging. Fate and transport of metal based NPs are proven to be highly sensitive to surrounding environment, such as solution pH, ionic strength, redox state, organic matter presented. Besides, metal based NPs will likely undergo different physical, chemical or biological transformations simultaneously (e.g. oxidation and aggregation). Most lab experiment is too simplified to represent agricultural environments. Therefore, research of metal based NPs in environmentally relevant concentrations and conditions is in urgent need for the future study.

Metal based NPs may have both positive and negative effect on plant. As toxicity occurs at all physiological to biochemical and molecular levels, so beneficial effect also displays in accelerating growth, photosynthetic yield, fruit yields and pest control [90]. However, the mechanism for NPs phytotoxicity and the NPs translocation pathways inside plants are still largely unknown. The interaction of metal based NPs with soil, plant root and soil microbial in root rhizosphere should also be emphasized in future studies to truly reflective the effect of metal based NPs in natural environmental conditions. Therefore, field-based life studies to better understand the effect of metal based NPs in agriculture system is in urgent need.

Nanotechnology has been considered as key component of sustainable development, however the promise of nanotechnology can only be achieved if the exposure and toxicity can be fully evaluated and properly managed. Understanding the fate, transport and toxicity is critical for environmental risks assessment of metal based NPs. More information on the interaction of NPs with soil, plant and soil microbial in the agriculture system is need to better analysis and predict ecotoxicity of metal based NPs.

Acknowledgments

This research was supported by USDA Evans-Allen Research Program.

Disclosure statement

No potential conflict of interest was reported by the author.

Funding

This work was supported by the USDA National Institute of Food and Agriculture, Evans-Allen project 1016348.

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