

Soil properties influence the response of terrestrial plants to metallic nanoparticles exposure

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Abstract

Metal-based nanoparticles such as Ag, ZnO, CuO, TiO₂, and others possess unique properties that lend them to a wide array of uses. This means that during manufacture, use, or upon disuse, these nanoparticles can become constituents of the soil. Upon interaction with soil, nanoparticles affect soil processes, and in turn are affected by soil properties. The soil factors affecting nanoparticles can be classified into chemical (e.g., pH, organic matter, and ionic strength) and biological (e.g., plant root exudates, microbes, and microbial activities). Some well-known fates of nanoparticles in soil include aggregation of individual nanoparticles (homoaggregation) or of nanoparticles with other soil constituents (heteroaggregation); dissolution to ionic species and, potentially, sorption of the ions onto organic matter or precipitation with chloride; acquisition of surface coating; change in surface charge; and change in shape. These modifications alter nanoparticles reactivity, which diminishes or enhances their bioactivity in plant systems. Thus, the degree to which nanoparticles influence plants depends to a large extent on the complexity of soil property.

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Introduction

Due to their unique properties, metal-based nanoparticles (NPs) (e.g., Ag, ZnO, CuO, Fe₂O₃/Fe₃O₄, TiO₂, CeO₂, SiO₂) are increasingly incorporated into various applications to enhance quality and functioning [1]. Such extensive use of NPs implies they can become constituents of the soil either by deliberate use (e.g., nanofertilizers and nanopesticides) or inadvertently as contaminants [2,3]. In soil, NPs interact with

rhizosphere processes influencing plants, which affects plants in subtle or extreme ways. The exact degree and nature of such effects are dependent on factors like soil structure and chemistry, exposure dose and duration, the biological species encountered, and the intrinsic properties of the NP [2,4–6].

There is a lack of harmonization of experimental designs in the bio-nano-science literature. NP sources and properties, exposure matrices, durations, doses, toxicological endpoints of interest, and biological species vary widely, making results from these studies less relevant to real environmental scenarios [7]. Yet, a myriad of studies have suggested that NPs are more phytotoxic than their micro-scale or ionic counterparts [e.g., [8,9]]. However, this assumption has increasingly been demonstrated to be an overstatement, given that the preponderance of these studies have been conducted using non-soil media; often involved high NP doses designed to evoke toxic responses; are characterized by short exposure durations that assess acute, rather than acute-chronic, responses; and that lack the presence of microbes that contribute in shaping NP effects. Even, in many cases, plant response to metal exposure is not size-specific, as non-nano (ionic or micro-scale) materials have been shown to evoke no more, or less, strong responses than nano-scale products in plants or soil microbes [2,10–13].

No doubt, the outcome of NP exposure in agricultural soils is interactive; hence, although NPs in soil influence plants, they are also influenced by the soil and plant. However, the relationships between soil properties and their influence on the biological impacts of NPs have yet to be fully understood [4]. The transformation of NPs in soil leads to different fates: aggregation, dissolution, or stabilization. In turn, transformation remodels (escalates or attenuates) the outcomes of plant exposure to NPs [14–21]. Given the general lack of unified endpoints in the literature and the number of studies with contradictory findings on the toxicity of NPs, it is hard to not argue that NPs are not always phytotoxic [2,5]. Rather, soil or environmental properties, perhaps to a greater degree than particle size, appear to direct the eventual effects of NPs on plants. A lot has been discussed on the effects of NPs on plant growth and productivity [e.g., [2,5,22]]. In comparison, reviews on the effects of soil on NPs that influence plant responses are relatively limited. This review, therefore, focuses on the effects of soil on metallic NPs, to better understand

the influence of soil properties in transforming and modulating the impacts of NPs on plants.

Soil properties influencing plant response to nanoparticles exposure

pH

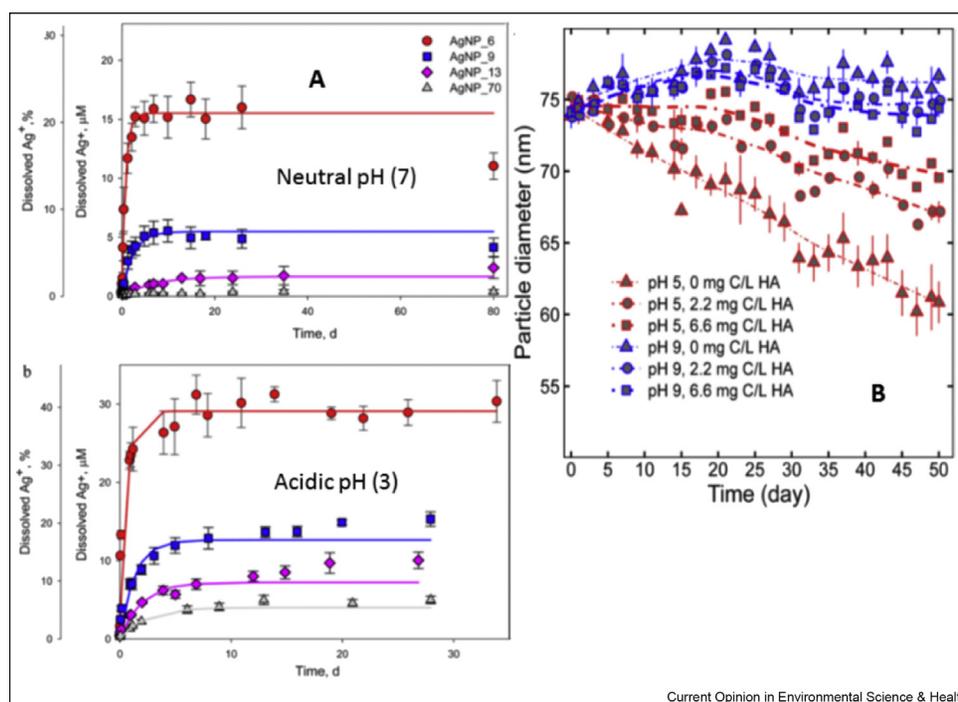
Soil pH is one of most critical properties regulating NP behavior. Under acidic conditions NPs are transformed into ionic species at high rates, while alkalinity promotes aggregation of NPs [23–25]. Figure 1A shows the dissolution of Ag NPs of 4 different sizes at 2 different pHs, as a function of time. In contrast to dissolution, Figure 1B shows the effect of pH on the particle size of Ag NPs as a function of time, where particle size decreased at pH 5, but increased at pH 9 (compare data without addition of humic acid; HA). When NP dissolution is stimulated, the pool of reactive ions increases; the NPs serve as reservoirs for continued release of ions. However, upon dissolution, so-called NP-specific effects are attenuated, as the dissolved ions are complexed by soil chemicals, and assume similar fate as ionic species originating from non-NP sources [26]. Likewise, when NPs aggregate under alkaline pH, they lose their nano-specific properties, and the rate of subsequent dissolution into ions reduces. Furthermore, the reactivity of NPs depends strongly on their surface charge, which itself is a function of pH. With titanium oxide (TiO₂), for instance, highly negatively-charged NPs typically occurring at alkaline pHs are more stable (i.e., maintain

their pristine nano size) than NPs at neutral pH. At acidic pH, surface charge is highly positively-charged, and particle size is smaller. Thus, with TiO NPs, as likely with other metal oxide NPs, there is a pH window (about 5.5–7.5) where aggregation is predominant [27]. This also suggest that NPs can return to a prior state with a pH change, such as occurs during aggregation and disaggregation of NPs. Nevertheless, aggregation induced by pH reduces NP retention and transport in the soil and, accordingly, results in the attenuation of their effects upon biological systems. As indicated in studies involving wheat and different NPs, soil pH affects NPs differently [28,29]. Both CuO and ZnO NPs were differently reactive in acidic (pH 4.5–5.4) vs. alkaline (pH 7.8–8.8) soils, resulting in positive growth responses in alkaline soil with both NPs, but negative responses in acidic soil (Figure 2) [28,29]. Similarly, CuO NPs were more toxic to barley at low pH, coincident with more Cu dissolution from the NPs [30]. In summary, available data clearly demonstrate the profound effect that soil pH has on NPs and the outcome of their interaction with plants, and indicate the need for soil-specific assessment of each NP, especially given the large swathes of global agricultural lands with soils that are distinctly acidic or alkaline.

Ionic strength

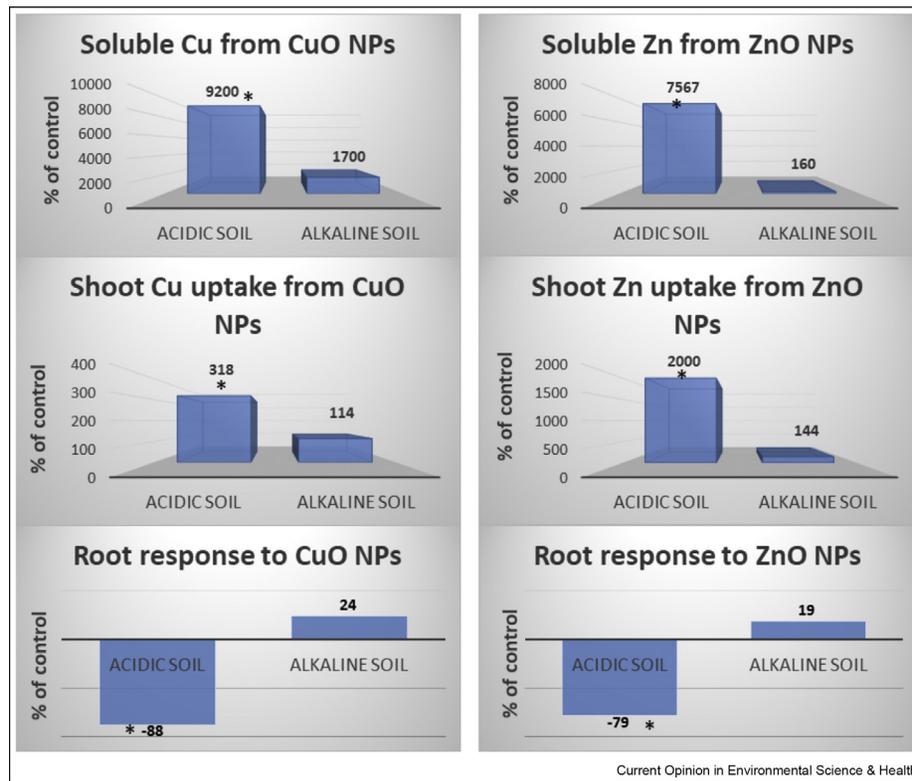
Ionic strength - the presence and amount of salts - affects NP behavior and subsequent plant responses. Most pristine NPs aggregate to a greater degree at high

Figure 1



Effect of pH on the dissolution (A) and aggregation (B) of Ag nanoparticles. Images courtesy Peretyazhko et al. [24], and Zhou et al. [25]; with permission.

Figure 2



Effects of soil pH on the dissolution of CuO or ZnO nanoparticles, shoot uptake of dissolved Cu or Zn, and root response of wheat to CuO or ZnO nanoparticles exposure. Data used for Figure adapted from Watson et al. [28], and Anderson et al. [29]; with permission. Bars with and without asterisks are significantly different, separately for each NP and measured parameter.

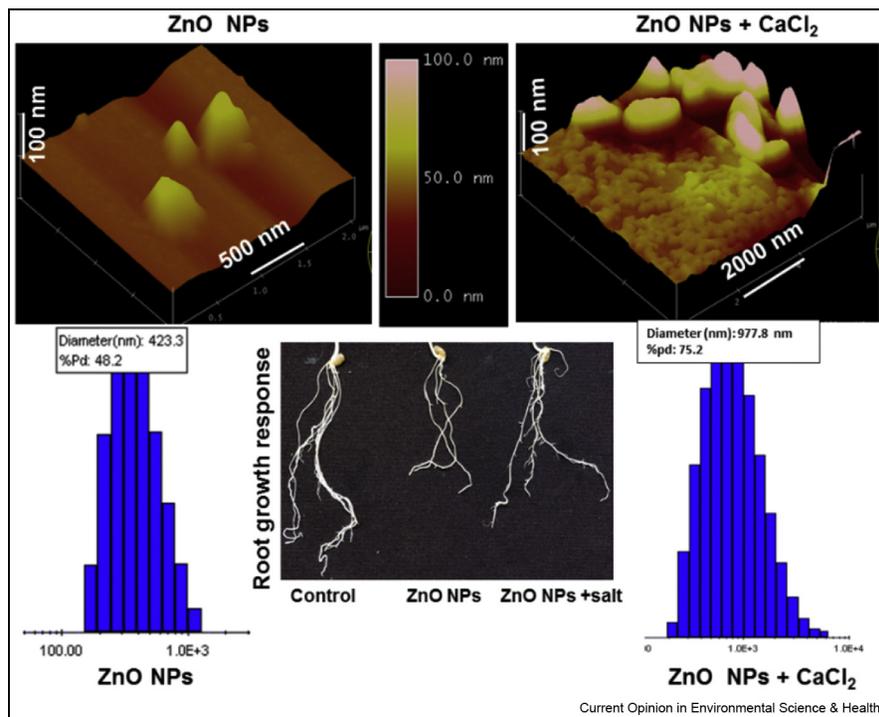
than at low ionic strength [31]. Figure 3 demonstrates the effects of high ionic strength (50 mM CaCl₂) on the aggregation potential of ZnO NPs, which was less at low (5 mM) CaCl₂ concentration (see Ref. [32]). As demonstrated using both microscopy and dynamic light scattering, the particle sizes increased in the presence Ca-salt [32]. While ZnO NPs (500 ppm) induced lateral root proliferation in wheat, which is a stress adaptation marker related to hormonal regulation, the presence of the salt, even at a low concentration, reduced the formation of lateral roots, although ZnO NP-induced inhibition in root elongation was not significantly reduced by the salt. Notably, Ca-salt reduced shoot loading of Zn in the plant. Similarly, KCl and NaCl at low ionic strength (5 mM) each counteracted the inhibition of root and shoot elongation, or lateral root proliferation, caused by CuO or ZnO NPs, while decreasing Cu uptake [32]. Mechanistically, Na, K or Ca at high levels could reduce plant uptake of Cu or Zn ions dissolved from NPs by competitively out-binding them at the root surface. Salts could also alter the composition of wheat root exudates, thus, regulating Cu or Zn chelation, solubility and bioavailability [33,34]. Related to this is the finding of Larue et al. [4], in which soil having a high cation exchange capacity (i.e., soil with high K, Ca, Na, Mg) showed reduced leaching of TiO₂ NPs, inhibited Ti

uptake by wheat, and did not inhibit plant biomass production. One additional point to stress is that salts can influence NP transformation differently. For instance, CaCl₂ at 5 mM increased ZnO NP dissolution, but decreased CuO NP dissolution [32]. Clearly, salt type and concentrations have different implications in the degree to which plants thrive and accumulate metals from metal oxide NPs, and consequently on their productivity and the food chain. This could be more significant in calcareous soils with high Ca contents that could affect different NPs differently.

Organic matter

Soil organic matter (OM) may include such compounds as organic acids, chitosan, dextran, and starch, among others. Although the influence of OM on NPs revolves mainly around surface modification, the outcome on NP behavior, and thus, on plants, can be complex and dynamic, dependent on the charge modification on NP surface [35]. Certain organic compounds, when they coat NP surface, cause them to aggregate, while others induce disaggregation. As shown in Figure 1B above, dependent on pH, humic acid (HA) modified the aggregate size of Ag NPs, whereby particle size increased with increasing HA concentration under acidic condition, whereas aggregate size reduced or was

Figure 3



Atomic force microscopy (upper panel) and dynamic light scattering (lower panel) of zinc oxide nanoparticles without and with calcium chloride at 50 mM. The as-manufactured nominal size of the nanoparticles is 50 nm. However, aggregation (to 423 nm) of the particles is observed in water (left panel) which significantly increases in the presence of the salt to 978 nm (right panel). Middle insert shows the effect of ZnO NPs, without and with CaCl₂, on plant root elongation. Figure is partially modified from reference 32, with permission.

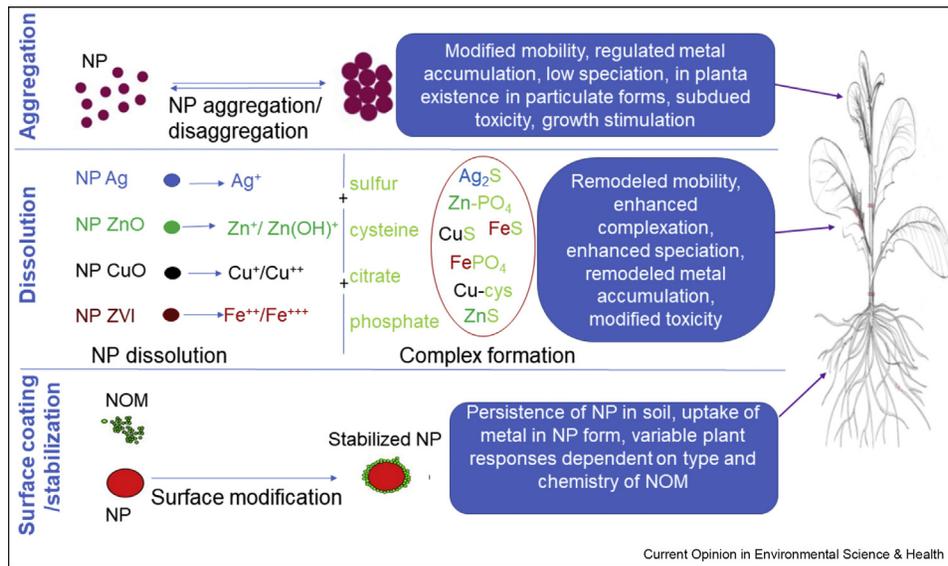
unaffected by HA under alkaline condition. Similarly, coating with HA also caused disaggregation of Ag NPs at alkaline pH, stabilizing them [36]. Starch has been demonstrated to stabilize zero-valent Fe NPs, presumably by acting as a dispersant that keeps the particles apart [37]. Collectively, OM-induced reduction or maintenance of pristine particle size likely results from their ability to lessen particle–particle interaction that cause homoaggregation, or particle interaction with soil factors that cause heteroaggregation. Sulfur and nitrogen-rich HA and fulvic acid are thought to be highly effective in stabilizing Ag NPs, due to their richness in metal affinity sites [38]. In contrast to HA, oxalic acid resulted in aggregation of TiO₂ NPs, increasing aggregate particle size from around 100 nm to about 1000 nm [39]. However, stabilization of NPs due to coating by HA could result in the reduction of the particle surface available for oxidative dissolution into ions. Thus, for NPs whose bioactivity is dependent on dissolution, this would lower their effects upon biological systems, which could explain the attenuation by HA of the toxicity of Ag NPs to the plant-associated soil microbe, *Pseudomonas fluorescens* [40]. Alternatively, HA could cause Ag ions dissolving from Ag NPs to precipitate, especially in the presence of chloride ions, or themselves rebind onto the Ag NPs, lowering free Ag ion concentration [41,42]. Ultimately, the long-term effect of HA on Ag NPs is

dependent on soil HA concentration, as HA plays a role in the mobility of the NP, as well as in the reconversion of Ag oxidative products to elemental Ag [43]. Moreno et al.'s review [35] catalogued the effects of NP coating by different organic compounds on crop growth response. Coating with citric acid generally resulted in positive responses with Fe₃O₄ NPs; no, or negative, responses with CeO₂ NPs; and negative responses with Ag and Au NPs. Similarly, chitosan coating of CuO NPs yielded positive responses, while coating of CeO₂ with alginic acid increased Ce uptake, with potentially negative implications in terms of Ce trophic transfer. A more recent study [4] reported a clay soil rich in OM to reduce mobile Ti concentration from TiO₂ NPs in the leachate. Furthermore, the Ti interacting with plant root remained mostly in anatase form, suggesting stabilization by OM, resulting in reduced Ti accumulation and lack of toxicity in the clay soil.

Phosphate

Under the intensive P fertilization common in advanced cropping systems, the presence of applied P at elevated levels can significantly influence the fate of NPs. Phosphate forms complexes with Fe, Zn and Cu to reduce their bioavailability. Specifically for Zn, upon dissolution from ZnO NPs, Zn ions may precipitate with PO₄, resulting in the formation of insoluble Zn-PO₄

Figure 4



Schematic representation of key nanoparticle-soil-plant processes governing nanoparticle fate in soil and effects on plants. Upon exposure in soil, NPs undergo one or more of three major fates, namely: (i) Aggregation that causes them to lose their intrinsic nano-scale properties, resulting in a variety of outcomes indicated in the blue box. However, aggregated NPs may also disaggregate, subject to changes in soil properties. Under aggregation, the uptake of the cognate element by plant is reduced and toxicity is subdued. (ii) Dissolution is influenced by soil pH, leading to formation of highly reactive ionic species. Uptake of the ions is stimulated and complex formation with a variety of organic and inorganic molecules occurs both in soil and in planta, creating new species of chemical compounds. Toxicity is enhanced as a result of increased uptake of reactive ions. (iii) Stabilization of NPs in soil as they encounter natural organic matter (NOM) derived from chemical or biological (plant or microbial exudates) sources. Dependent on surface charge, NOM coating of NPs occurs, which both reduces surface oxidation that permits dissolution and increases the electric double layer that pulls particles apart, lowering the potential for particle-particle aggregation. NOM-coated NPs are stabilized and functionalized, with subsequent plant responses dependent mainly on the surface chemistry and compatibility or otherwise with the plant cell surface.

aggregates. The rate and amount of Zn-PO₄ formation is highly dependent on PO₄ concentration and exposure time, and inversely correlate with ionic dissolution of the NPs [44]. Ultimately, such complex formation potentially reduces P leaching, and potentially also ZnO NP dissolution and plant uptake of both P and Zn [12,13,44,45]. Notably, the speciation of the Zn detected in plant tissues exposed to ZnO NPs has been mainly Zn-PO₄ [15,16]. On a much broader scale, reduced uptake of Zn from ZnO NPs in the presence of added phosphate, combined with rhizosphere or in-planta transformation of ZnO NPs into insoluble and less mobile Zn-PO₄, could have two contrasting environmental health ramifications (i) reduced shoot Zn content which may affect human Zn nutrition with chronic consumption of affected plants; and (ii) less phosphate run-off, and consequently, less eutrophication of water bodies.

Soil biology

Soil biology also influences NP fate and effect in plants. Roots of terrestrial plants co-exist with soil microbes, and plant ecological success in the presence of NPs can be strongly dictated by the nature of plant-microbe interaction [17,18,46]. While much has been reported on the effects of different NPs on plant-associated soil microbes [e.g., [47–53]], the influence of soil microbes

on NP-plant interactions is less accounted for. Accordingly, the routine inclusion of microbial components in NP-plant studies has been advocated for [54]. Bacteria, fungi, and bacterial exudates alike influence NP fate. For instance, the inoculation of bean plant with a root-colonizing bacterium, *Pseudomonas chlororaphis* O6 (*PcO6*) reduced Zn uptake under ZnO NP exposure. This appears to have come, however, with the cost of reducing the bacterial cell density, albeit slightly [55]. In other studies, *PcO6* altered the expression of stress-responsive genes induced by CuO NPs in wheat [19,20]. It is likely that the stimulation of bacterial extracellular polysaccharides (EPS) in *PcO6* by CuO NPs [56], as by Ag NPs in *Escherichia coli* [57], permitted both coating of NP surface and trapping of ions dissolving from the NPs by EPS, thereby limiting wheat exposure to NPs, and reducing Cu uptake and growth inhibition resulting from CuO NP exposure. Also, inoculation of maize plant with arbuscular mycorrhizal (AM) fungi exposed to ZnO NPs increased essential nutrient accumulation and growth, while reducing Zn uptake at toxic concentrations. Notably, in the absence of AM, the ZnO NPs were phytotoxic [58]. These few examples aptly demonstrate the need for acknowledging the presence of soil microbes in the plant rhizosphere and their inclusion in assessments of NP-plant interactions.

Conclusion

A cocktail of soil interactions can remodel metallic NP fate and effects in soil-plant systems, and regardless of whether the soil factor influencing NPs is chemical or biological, metallic NPs undergo fates that are often too difficult to disentangle due to the complex nature of soil. The processes and outcomes of these NP-soil interactions can be captured in the schematic presented in Figure 4. Given the increasing use of NPs in our daily lives and the observed and predicted effects they portend, disentangling the cocktail of soil interactions with NPs that remodel their fate and effects requires holistic study designs involving assessing the roles of all key players (namely NPs, microbes, and plants) under natural rhizosphere systems using soils of varying chemical properties. Moreover, there should be a better harmonization of exposure conditions including media type, dose, duration, and endpoints. That way, the most relevant information regarding the mechanisms and extents of NP influence on plants can be obtained for devising risk mitigation measures, and for using NPs manufactured from metallic mineral nutrients for crop fertilization.

Conflict of interest statement

Nothing declared.

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