**Uptake of metallic nanoparticles containing essential (Cu, Zn and Fe) and non-essential (Ag, Ce and Ti) elements by crops: a meta-analysis**

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**Abstract**

The specific properties of nanoparticles can induce toxic or promoting effects on plant growth. We performed a meta-analysis of 173 studies to evaluate the uptake and accumulation of metallic nanoparticles (MNPs) by crops. Studies on the main cereal/vegetable crops (wheat, tomato, bean, maize, rice and cucumber) and Ag, Zn, Ce, Fe, Cu and Ti containing MNPs were mostly found; 63% of the studies used MNPs with size < 30 nm, and root application accounted for 84% of all studies. Under root exposure, metal concentrations were reduced by up to 2 orders of magnitude from root through shoot to leaf. Moreover, the uptake preference of MNPs or dissolved metals was element-specific and varied among tissues. Plants accumulated generally higher concentrations of the three essential elements (Cu, Zn and Fe) than of the non-essential ones (Ag, Ce and Ti). Also, foliar application was more efficient than root exposure. Metal concentrations in shoots increased with decreasing particle size for non-essential elements, but showed a variable increase for essential elements as size decreased. Besides, the uptake of MNPs increased with more negative zeta potential (especially for Cu and Zn). Overall, the plant essential elements (Cu, Zn and Fe) were preferred taken up as MNPs, while for non-essential elements (Ag and Ce) uptake as dissolved metals was more common. We conclude that for plant nanofertilizers, foliar application of essential elements as small MNPs might be more efficient for crop uptake than the uptake of dissolved metals.

**Keywords**

Engineered nanoparticles, metal uptake preferences, plant tissues, particle size, zeta potential

**Highlights**

Uptake of essential elements was significantly higher than that of non-essential elements.

Metal accumulations increased with smaller particle size and more negative zeta potential.

Non-essential elements (Ag and Ce) are acquired preferably as dissolved metals.

Essential elements (Cu, Zn and Fe) are preferably taken up as nanoparticles.

**Graphical abstract**

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**1. Introduction**

Nanotechnology has been predicted to have great potential in enhancing global agricultural productivity and food security in a sustainable manner (Kah et al., 2018; Lowry et al., 2019; Marchiol et al., 2020). Nanoparticles (NPs) have unique properties, such as a large specific surface area, specific optical and electrical properties, tunable functionalities, and high adsorption capacities (Colvin, 2003; Khan et al., 2019; Marchiol et al., 2020; Rai et al., 2018). Engineered nanoparticles (ENPs) have been used in many applications such as optics, electronics, paints, pigments, coatings, cosmetics and personal care products as well as in products for agriculture such as agrochemicals (fertilizers, pesticides and herbicides), as delivery carriers of bioactive molecules, nano-sensors for pathogen and pesticide detection, and even as agents for soil conservation and remediation (for a review of commercial nano products in various applications, see Figure S1) (Ahmed et al., 2021a; Ghormade et al., 2011; Sharma et al., 2020; Wang et al., 2016b). In addition to these ENPs with high purity and defined shapes (Hochella et al., 2019; Hochella et al., 2015), NPs like clay minerals and metal (hydr)oxides are also formed by natural processes and have proven to be significant carriers of many essential plant elements, such as phosphorus (P), aluminium (Al), and iron (Fe), in both aquatic environments (Gottselig et al., 2017; River & Richardson, 2018) and soils (Hens & Merckx, 2002; Jiang et al., 2015; Li et al., 2021a). Nowadays, due to their ubiquity in the environment, plants have significant contact with both ENPs and naturally formed NPs.

Plants can be exposed to ubiquitous natural NPs, or ENPs that have been applied in agriculture as either pesticides or fertilizers (Ghormade et al., 2011). Several studies have reported that NPs may be taken up by plants, which can result in potential toxic or promoting effects on plant growth (Ahmed et al., 2022; Dietz & Herth, 2011; Huang et al., 2022b; Khan et al., 2019; Liu et al., 2020; Ma et al., 2010; Miralles et al., 2012). From the published data, however, it has become clear that plant exposure to metal or metallic NPs (MNPs, e.g., Ag (silver), TiO2 (Ti, titanium), CuO (Cu, copper), ZnO (Zn, zinc), Fe/Fe2O3/Fe3O4, hydroxyapatite) leads to metal accumulation or the presence of intact MNPs in plant tissues (Avellan et al., 2019; Larue et al., 2012; Li et al., 2021b; Marchiol et al., 2019; Wang et al., 2018; Wang et al., 2012; Zhao et al., 2012). An overall assessment of the accumulation of different MNPs in crops, however, is still lacking and the reported beneficial or harmful impacts on plants due to MNPs’ applications are not consistent (Dodds et al., 2021; Landa, 2021; Liu et al., 2021). This indicates the need for a systematic data analysis of potential factors in plant uptake of MNPs(Avellan, et al., 2019; Larue, et al., 2012; Li, et al., 2021b; Marchiol, et al., 2019; Wang, et al., 2018; Wang, et al., 2012; Zhao, et al., 2012). Moreover, it is unclear whether the plant uptake of MNPs differs for essential and non-essential elements.

The uptake of metals from MNPs can involve either direct internalization of MNPs, or entry of dissolved MNPs, or uptake of both nanoparticulate and ionic metals simultaneously. Although studies have addressed plant uptake of MNPs (Avellan et al., 2019; Lin & Xing, 2008; Ma et al., 2017; Su et al., 2020; Wagener et al., 2019; Zhu et al., 2008), the uptake mechanisms involved are less understood, with only some basic mechanisms having been reported. The MNPs from the air, water and soil can be internalized via both the roots and the leaves (Lv et al., 2019; Su et al., 2019).

In root entry pathway, the uptake of MNPs first pass the mucilage layer and then the cuticle: a layer of waxy lipid polymers which inhibits the passage of particles larger than a few nm (Wang et al., 2016b). The cuticle is underdeveloped in developing root tips allowing MNPs to reach the epidermis directly (Nowack et al., 2006). After reaching the root epidermis MNPs have two pathways to reach the xylem, the apoplastic and symplastic pathways (Liu et al., 2020). In the apoplastic pathway, the Casparian strip acts as another physical barrier, with size exclusion limits (SEL) even smaller than SEL of the cuticle, and prevents large particles from passing through. In the symplastic pathway, there is no need to overcome the Casparian strip barrier but MNPs do have to cross the cell wall (with SEL ≤ 10 nm) and plasmodesmata (with SEL from 1 to 100 nm) (Wang et al., 2016b). Endocytosis is another possible mechanism for MNPs to enter cells, and is believed to be dependent on clathrin on the plasma membrane (Miralles et al., 2012). Once in the xylem vessels, MNPs could be transported upward to shoot and leaf tissues (Ma et al., 2017). For foliar exposure, the uptake mechanism is similar to that found in roots. The leaf surface is also covered with waxy cuticle, and MNPs can be internalized via the symplastic or apoplastic pathway once they penetrate it (Avellan et al., 2021). Apart from crossing the cuticle, an additional pathway for foliar exposure is via the leaf stomata. This pathway has a SEL > 20 nm, and it is therefore theoretically more favorable for larger MNPs to approach the endodermis and then enter the leaf apoplast towards the phloem (Eichert et al., 2008). The MNPs in the leaf phloem vessels can then be transported down to the shoots and roots (Avellan et al., 2019).

As discussed above, particle size may be one of the most important factors in plant uptake of MNPs, regardless of whether plant uptake of MNPs is via endocytosis or through cell wall pores (Carpita et al., 1979; Miralles et al., 2012). The SEL of plant cells allowing MNPs to penetrate is still unclear and depends upon factors such as plant species and growth stages (Hu et al., 2020; Lv et al., 2019). Theoretically, MNPs with a size (especially the hydrodynamic diameter) smaller than the SEL are more able to be internalized by the plant than larger sized particles. However, even if the size of MNPs is less than the SEL, it does not mean that NPs can easily enter the plants, other factors such as surface charge of MNPs can have an effect, e.g., the negatively charged root surface attracts positive charged MNPs but repels negatively charged ones (Lv et al., 2019; Onelli et al., 2008). Another potential factor controlling metal uptake is which part of the plant is exposed to MNPs, i.e., root or leaf. Wang et al. (2016b) recently summarized a list of possible internalization sites for MNPs, spanning a SEL range from < 1 nm to hundreds of nanometers for different physiological and chemical barriers in root and leaf tissues. The uptake of MNPs can also be affected by other plant related factors, such as plant transpiration rates (Zhang et al., 2019b), and root exudation patterns (Shang et al., 2019). Meanwhile, microbial activities could affect the uptake of MNPs by plants. For example, bean roots colonized by *Pseudomonas chlororaphis* O6 (a beneficial root-associated bacterium) showed reduced uptake of Zn when exposed to toxic levels of ZnO NPs (Dimkpa et al., 2015). The formation of mutualistic symbioses between arbuscular mycorrhizal fungi and maize plants also reduced the accumulation of Zn after application of ZnO NPs to the roots (Wang et al., 2016a).

MNPs can undergo physical (aggregation, agglomeration, and deposition), chemical (dissolution, sulfidation, and redox reactions), and biological alterations within the soil-plant system (Ahmed et al., 2021a; Guasch et al., 2017). These transformation processes are affected by many intrinsic and environmental factors. For example, the dissolution of Ag NPs can be influenced by the method of synthesis, particle size, surface coating, zeta potential (ζ), concentration, pH, temperature, light, dissolved organic matter (DOM), dissolved O2, root exudates, accompanying ions, and ionic strength (Azimzada et al., 2017; Kittler et al., 2010; Pradas del Real et al., 2016; Su et al., 2020; Zhang et al., 2011). Before or upon exposure to plants, MNPs can be transformed by the above processes. This can result in changes to the properties of the MNPs, such as increasing size (e.g., enhanced aggregation of TiO2 NPs with DOM in the environment (Zehlike et al., 2019)), or surface modification (e.g., Ag NPs in the surface of spheric Ag NPs be sulfidated to Ag2S NPs (Wang et al., 2018)).

We are not aware of any study that has fully explored the uptake of MNPs by different crops as a function of element, size, and exposure pathway. Moreover, there is a lack of systematic knowledge of the differences between the uptake of essential and non-essential elements by plants and the preferences for nanoparticulate and dissolved forms of elements by crops remains unclear. Here, we performed a meta-analysis to examine the metal accumulations within plant tissues after MNPs applications for crops in agroecosystems. Our main focus was to explore: 1) accumulation behaviors of essential and non-essential elements in various plant tissues, 2) the factors that affect metal accumulation in various plant tissues, and 3) the degree to which metal accumulation from MNPs in plants is affected by the method of exposure, also compared to the pure application of the metals in dissolved forms.

**2. Materials and methods**

2.1. Data collection

We constructed our database in multiple steps as recommended by Moher et al. (2009). First, we searched for articles at the Web of Science Core Collection Database on 25 Feb 2021 with “plant and nanoparticles” as title; the publication year was left un-restricted. Since we focused on studies of the uptake of MNPs in crop plants, the resulting records were screened according to the certain criteria (See detailed methods in Supplementary Information). Ultimately, 173 publications were assembled in the database (Excel S1).

Based on the data available in the collected literature, we focused on the six elements (three essential elements for plants: Cu, Zn and Fe; and three non-essential elements: Ag, Ce (Cerium) and Ti) that appeared most abundantly in MNPs-crop studies. Essential and non-essential element groups were sorted according to decreasing solubility of corresponding MNPs. More details in extracting data and grouping factors were described in Supplementary Information.

2.2. Statistical analysis

All statistical analyses were performed in R 4.0.5 (R Core Team, 2021). The standardized mean difference (SMD) estimator of the magnitude of effect was calculated using the following equation:

(1)

where *SMD* is the magnitude of effect of metal accumulations in plants; *mt* and *mc* are the mean concentrations of the treatment group and the control group in each experiment, respectively. More details in calculating the magnitude of effect and comparisons between treatments were shown in Supplementary Information. The package “ggplot2” was used for plotting figures.

**3. Results**

3.1. Dominance of specific MNPs in plant uptake studies

Collecting information for crop plant uptake of MNPs showed that there were 35 types of MNPs included, and that most studies focused on Ag- (Ag and Ag2S), Zn- (Zn and ZnO), CeO2, Fe- (Fe, Fe2O3, Fe3O4 and FePO4), Cu- (Cu and CuO) and TiO2-based MNPs (Figure 1,andExcel S1). Some precious metal (Au and Pt) NPs, and plant essential elements containing NPs such as apatite and MgO were moderately studied. Other MNPs, such as Mn, PbS, Pd, Cu/Se, and CuFe2O4 were less studied, contributing only one study each to our database. In contrast, NPs consisting of Ag, CeO2, ZnO, CuO and TiO2 were the top five MNPs in all studies found, with each type having been included in > 15 studies.

Data collection revealed that most MNPs studied had a size range between 10 and 30 nm. The size of MNPs used in this study indicated the primary TEM/SEM size, except for additional notes. The majority (63%) of all studied MNPs were smaller than 30 nm, while 19% studies were performed with MNPs < 10 nm (subfigure in Figure 1). More than 30 different crops have been studied (with no discrimination between varieties), with wheat (31), tomato (24), bean (21), maize (20), rice (19) and cucumber (17) being the most abundant (Figure S2). About 58% of all studies were conducted in hydroponics while not with soil medium, particularly when the trial plants were cucumber and rice. The vast majority of all studies (84%) examined root exposure to MNPs rather than exposure of leaves or stems. MNPs concentrations that plants were exposed to ranged from 1 to 1000 ppm (Figure S3).

3.2. Uptake of metal elements by crops

To evaluate the uptake of MNPs by crops, we concentrated on MNPs that had been frequently studied, categorized these as elements that are either not essential elements (Ag, Ce, and Ti) to plants or are additionally essential for plants (Cu, Zn and Fe), and then recorded their accumulation in various plant tissues (Figure 2). For all studies, we observed that median metal concentrations in tissues decreased by as many as two orders of magnitude from the root through the shoot to the leaf (Figure 2). Note, the Figure 2 has an exponential scale for y-axis. For instance, the ratios of median Ag concentrations of root to shoot and root to leaf were 41:1 and 152:1, respectively. For Ce, concentrations in roots exceeded those of the shoots by 2 orders of magnitude; relative differences for the other elements were one magnitude lower (Figure 2). The only exception was Zn, where the median Zn concentrations among root, shoot and leaf were relatively similar. The statistical tests confirmed that the metal concentrations in root were significantly higher than those of shoot and leaf following root exposure (Figure S4-1), while foliar exposure led to significantly higher metal concentrations in leaf than shoot and root (for Ce and Zn, Figure S4-2). The one exception to this is Ti, where there was less data and the distribution was more skewed. The ratios of median concentration in shoot for each metal with foliar exposure to that under root exposure ranged from -31 to 232% (data not shown). Moreover, plant essential metals like Zn and Fe were mainly accumulated in higher concentrations (especially in shoot and leaf) than observed for non-essential metals like Ag and Ce, when comparing data from similar exposure concentration ranges (mainly applied at 1-100 or 100-1000 ppm as shown in Excel S2;Figure S4-3 and S4-4). Intriguingly, comparable levels of Cu and Ti were accumulated in plant tissues (Figure 2).

As some MNPs can be dissolved prior to metal uptake, we also evaluated the differences between metal concentrations in plants after exposure to both MNPs and dissolved metal salts. The differences in element uptake among these treatments were displayed in Figure 3.We subtracted the metal concentrations from tissues receiving MNPs treatments from the concentrations in tissues exposed to dissolved metal salts. In this figure, a negative value in Figure 3 indicated the preferred uptake of dissolved metals, while a positive one suggested a preferred uptake of MNPs. The results showed that in each plant tissue, the preferred uptake of a given metal form was generally element-specific. Generally, non-essential elements (Ag and Ce) containing MNPs are more prone to be taken up as dissolved forms especially in root and leaf, while essential elements (Cu and Zn) were more internalized as nano forms in root and shoot, and Fe as nano forms in root and leaf. It should be noted that there were no data points in Figure 3 for Ti as TiO2 NPs essentially do not dissolve. Specifically, in root, Ag was primarily accumulated from dissolved metal salts, while Zn and Fe were primarily acquired as MNPs. Variations were large and the uptake differences were not significantly differed from zero, likely indicating that both uptake mechanisms are possible, especially for Zn. The pattern slightly changed in the shoots, which were more prone to take up Ag and Zn as MNPs, while Fe in dissolved metal salts. No apparent uptake preferences on MNPs or dissolved metal salts were found for Ce and Cu in the shoots. Differences in the preferred form of metal uptake was most pronounced in the leaves, which exhibited a preferred uptake of dissolved forms of Ag, Ce and Cu, but of MNPs for Zn and Fe (Figure 3). In addition, we subtracted the metal concentrations in plant tissues under MNPs treatments from the metal concentrations of dissolved metal treatments based on soil and hydroponic conditions separately, there were more evident uptake preferences of non-essential metals under hydroponics than soil culture (Figure S5). The overall uptake preferences (based on data of both soil and hydroponic cultures) on dissolved Ag and nano Fe for root, dissolved Fe for shoot, dissolved Ag and Ce and nano Fe for leaf, are similar to that in hydroponic growth medium, while uptake preferences were obscure in both root and shoot under soil culture, except for Cu which showed slightly preferred uptake of nano forms.

3.3. Magnitude of effects

To evaluate potential factors affecting the plant uptake of MNPs, we related the element accumulations in root, shoot and leaf to the properties of the MNPs (particle size, zeta potential, surface coating, and MNPs type) and growth conditions (applied concentration, crop plant, growth medium, exposure-period, and method of exposure) (Figure 4-1 and 4-2, andFigure S6-1 to S6-4). The magnitude of effects relative to controls without metal additions as MNPs or dissolved metal salts were calculated as SMD. The results showed that the overall SMD for the accumulations of Ag declined in the order of root (5.5) > shoot (2.1) > leaf (1.7) (Figure 4-1), all indicating increased plant uptake of Ag after exposure to Ag-based NPs. In roots, the SMD and its 95% confidence intervals (CIs) were always above zero, demonstrating that all factors under consideration facilitated the accumulation of Ag in the roots. In contrast, there were SMD values in shoot with their 95% CIs overlapping with zero, which indicated insignificant positive or negative effects on plant uptake of MNPs affected by factors such as the particle-size range of “30 ~ 60 nm”, surface coating with “citrate” and “PEG + Tween 20”, growth media other than soil and hydroponics (“other media”), exposure period between “1 week ~ 1 month” or a modification in Ag speciation (e.g., Ag2S NPs rather than Ag NPs) (Figure 4-1). It can be concluded that plants all tended to accumulate Ag from exposure to MNPs, while varying the MNPs properties showed little if any effect on Ag accumulation in plant tissues. Only a modification of Ag NPs to Ag2S NPs seems to hinder Ag uptake, as deduced from the lower SMD (-0.03, CIs (-0.75, 0.68)) of Ag2S NPs (Figure 4-1).

The results for Ce and Ti are displayed in the Figure S6-1 and S6-2. Similar to Ag, the Ce and Ti based MNPs exhibited the same overall decrease in SMD from roots through shoots to leaves. Cereals seem to accumulate Ce more than some other crops. In general, much like Ag, varying the properties of Ce or Ti MNPs hardly affected the degree of both Ce and Ti accruals in root and shoot (Figure S6-1 and S6-2). There were more insignificant effects on Ce accumulation in leaf than that in root and shoot, while for Ti accumulation in leaf, all factors showed insignificant effects. Exceptions included where large particle size, “60 ~ 100 nm”, for Ce based MNPs resulted in a significant decrease in Ce concentration in leaf and where intermediate zeta potentials between 0 and 20 mV seemed to hinder Ti uptake by root of barley (Figure S6-2). It is worth noting that the magnitude of effect in shoot decreased with increasing particle size for MNPs containing non-essential elements (Ag, Ce and Ti), and shoots accumulated metals with smaller MNPs. In contrast, MNPs with elements essential for plants (Cu, Zn and Fe) showed an initial decline followed by an escalating trend of shoot SMD with increasing MNP size.

The metal uptake of MNPs containing Cu also mostly showed positive effects by most of the factors (Figure 4-2). In general, the SMD values for Cu-based MNPs increased with higher applied concentrations in all three plant tissues. Similar trends were also found for Zn- and Fe-based MNPs (Figure S6-3 and S6-4), with the exception that in shoot there was reduced enrichment with increasing concentration of Fe-based MNPs. We also found that the SMD for all three essential elements Cu, Zn and Fe increased in roots and shoots as the zeta potential became more negative, i.e., when the absolute value of the negative surface charge of MNPs increased. In contrast to the non-essential elements especially Ce and Ti, mainly factors showed significant positive effects on leaf SMD for essential elements Cu and Zn. It also appeared that Zn was more easily taken up than Fe from MNPs with all factors promoting leaf accumulation of Zn. The accumulation of Fe in leaf, however, declined for specific factors such as in “muskmelon” plant, a soil growth medium, and exposure periods exceeding one month. Zero valent Fe generally exhibited larger SMD values than other Fe MNPs, such as Fe2O3, Fe3O4 and FePO4 (Figure S6-4). Plants grown in hydroponics, usually showed larger metal enrichment (more positive SMD) than soil cultures.

To compare the accumulation of different metals by each crop, we concentrated on the top five crops (three cereals and two vegetables) studied in soil cultures and calculated the SMD (Figure S7-1 to S7-5). The SMD for non-essential elements in shoot was less than that detected in root, which was observed with Ag and Ti in wheat (Figure S7-3), and Ce in tomato (Figure S7-4). For essential elements, the variations of SMD were generally minor. Since metal concentrations after both root and foliar application of MNPs were used in Figure S7-1 to S7-5, we assessed differences of metal accumulations in each crop primarily based on metal concentrations in shoot. This could minimize the influences of unrinsed root or leaf surface adhered MNPs to the results. Maize took up significantly higher concentrations of both essential (Zn and Fe) and non-essential (Ag and Ce) elements from the MNPs treatments than no metal addition (positive SMD), and tomato and cucumber also accumulated significantly more MNPs-derived Cu and Zn than the control. Wheat had positive SMD for essential elements (Zn and Fe), but negative SMD for non-essential elements (Ag and Ti), while rice exhibited uptake preference of Cu relative to Zn. (Figure S7-1 to 7-5).

**4. Discussion**

4.1. Main MNPs in plant uptake studies

It is well accepted that plants acquire nutrients as dissolved or ionic elements. Over the last two decades, however, there has been increasing evidence that plants can also take up NPs (Khodakovskaya et al., 2009; Lin & Xing, 2008; Onelli et al., 2008), even if it remains challenging to distinguish between the internalization of elements in intact NPs and from those dissolved NPs (Avellan et al., 2019; Ma et al., 2017; Su et al., 2020). Our meta-analysis studied metal accumulation in commonly studied crops (wheat, tomato, bean, maize, rice and cucumber) that usually have high economic yields and/or involve large harvesting areas worldwide (Excel S3). It should be noted that only studies where the concentrations of applied MNPs were recorded in units of mg kg-1 or mg L-1 were included in this study. Ag-, Zn-, Ce-, Fe-, Cu-, and Ti-based MNPs (Figure 1) were the most commonly studied for their specific MNPs properties and their potential applications in precision and sustainable agriculture (Kah et al., 2018; Raliya et al., 2018). Ag NPs have received intense research due to their broad spectrum of antimicrobial properties (Nair et al., 2010). However, the high cost of Ag has limited its use in agriculture compared to its other applications such as textiles, cosmetics and food packaging (Huang et al., 2022a). Cu based MNPs, such as Cu0, CuO, and especially Cu(OH)2), are promising nanopesticides (Adisa et al., 2019), which can be effective even at concentrations lower than traditional soluble Cu salts (Borgatta et al., 2018; Zhao et al., 2016). Apart from acting as nanopesticides, some MNPs are commonly applied as nanofertilizers. Seed coatings with Cu and Zn based MNPs generally increased seed germination by efficiently providing essential micronutrients (Gilbertson et al., 2020; Sturikova et al., 2018). Nanoparticulate Fe-based (Fe0, Fe2O3 and Fe3O4) fertilizers could alleviate impaired plant photosynthesis and respiration induced by Fe deficiency (Li et al., 2020; Yuan et al., 2018). ZnO NPs helped to improve grain Zn content thus promoting crop growth in Zn deficient soils (Yusefi-Tanha et al., 2020) at lower dosages than dissolved Zn salts sprayings (Elhaj Baddar & Unrine, 2021). Even TiO2 NPs have been suggested as a nanofertilizer to improve CO2 assimilation and photosynthesis due to enhanced activity of a key photosynthetic enzyme ribulose-1,5-bisphosphate carboxylase/oxygenase (Gao et al., 2008; Raliya et al., 2018), although Ti is not an essential element for plants. Hence, the elements most studied are also those most commonly in use; even though the use of commercial agricultural products containing MNPs is still in its infancy (Figure S1).

4.2. Plant uptake and translocation of MNPs

The entry tissues of MNPs generally accumulated higher metal concentrations than other plant organs: i.e., when roots were exposed to MNPs first, the metal concentrations in roots were 1-2 orders of magnitude higher than those in shoots and leaves, whereas foliar exposure to MNPs, such as of Ce and Zn based MNPs, led to elevated metal accumulations in the leaves (Figure 2 and Figure S4-1 and S4-2). Examination of the magnitude of effects confirmed that root exposure resulted in higher root SMD than foliar exposure, while leaf SMD by foliar exposure exceeded that when the exposure occurred in the root. Exceptions to this pattern were observed with Ag accumulation in leaf and Zn accumulation in root (Figure 4-1 and 4-2 and Figure S6-1 to S6-4). The overall result was in line with studies on the uptake of CeO2 NPs by hydroponic cucumber (Ma et al., 2015), the exposure of rice to CuO NPs in soil (Peng et al., 2017), and outdoor lysimeter experiments where wheat and canola had been exposed to sewage sludge containing Ag NPs (Schlich et al., 2017). Some of these differences can be induced by methodological challenges. In principle, MNPs could adhere to root surfaces or the outer epidermis and risk not be rinsed out efficiently by deionized water (Zhang et al., 2012). However, there are reported methods which could rinse root adhered MNPs efficiently. For example, rinsing with CaCl2 solution reduced > 92% of iron that had accumulated on or in cucumber roots (from zero valent iron NPs) in comparison to the unwashed control (Dwivedi et al., 2018). The Na4EDTA elution combined with 45 Hz and 300 W ultrasonication for 30 min method removed root adsorbed CuO NPs completely (Almendros et al., 2022; Zhou et al., 2011). The authors also suggested that it was root surface coordinated or mechanically adhered CuO NPs which were hard to be rinsed, rather than electrostatically attracted ones as the positive or negative zeta potentials didn’t affect the desorption of CuO NPs (Zhou et al., 2011). Even if MNPs adsorbed onto the mucilage layer or waxy cuticle of the root surface could be washed out to some degree; however, this is no longer possible once the MNPs have crossed the root surface and entered into epidermis (Geisler-Lee et al., 2013; Lv et al., 2019). Physical barriers with SEL of a few nm would prevent root cells from internalizing of larger MNPs, which in turn can promote the aggregation of MNPs and thus concentrate the metal contents on the root (Wang et al., 2016b).

The foliar application of MNPs seems to be more efficient than root exposure. In our study, foliar applications always resulted in higher shoot SMD values than for root applications, suggesting that metal accumulations in shoot were more efficient when applying MNPs on the leaf (Figure 4-1 and 4-2 and Figure S6-1 to S6-4). This trend was also suggested by other studies. In case of CeO2 NPs, leaf spraying of 100 mg L-1 CeO2 NPs led to 13, 163 and 915 mg Ce kg-1 in root, shoot and leaf of spinach grown in soil, respectively (Zhang et al., 2019a); while root exposure to 1.0 g kg-1 soil CeO2 NPs accumulated 210.7 and 0.1 mg Ce kg-1 in soybean root and shoot (Priester et al., 2012). The latter has much larger differences of Ce concentrations between root and shoot than the former, which indicates low shoot uptake of CeO2 NPs via root exposure. Note, MNPs applied to the leaf can adhere to and be retained by the leaf in a similar manner as occurs in root (Keller et al., 2018). The SEL of leaf stomata has been estimated to exceed 20 nm (Eichert et al., 2008), which is larger than that of the cell wall. This enables much larger MNPs to enter the plant via the stomata into the leaf apoplast (He et al., 2022). Once trapped in the concave structure of stomata, it also becomes difficult to wash the MNPs out, which increases the possibility of internalization (Zhu et al., 2021). Effective uptake via leaf exposure with subsequent internalization and translocation was especially supported by the data for Zn and Fe, which revealed fairly high concentrations in shoot and root tissues after foliar exposure to MNPs (Figure S4-2).

The higher concentrations of MNPs-derived metals in entry tissues compared to those in other tissues (Figure 2) demonstrated that plant translocated a proportion the metals via the vascular system (Su et al., 2020). Plant tissues (except for entry tissues) accumulated significantly higher essential metals (Cu, Zn and Fe) from MNPs than non-essential metals (Ag, Ce, and Ti) (Figure S4-3 and S4-4). Generally, crops do not favor the uptake and accumulation of non-essential or toxic elements, with plants using common mechanisms such as transporter discrimination between non-essential and essential elements; hence, there is usually a restrained translocation of non-essential elements to upward tissues (Khan et al., 2014). An efficient translocation to the aboveground tissues of soybean was reported for Zn from ZnO NPs, while CeO2 NPs enriched only roots (Priester et al., 2012). Foliar application of ZnO NPs to tomato leaves accumulated more Zn than shoots and roots, whereas applying TiO2 NPs in the same manner led to higher Ti concentrations in roots rather than in shoots and leaves (Raliya et al., 2015).

4.3. Factors of the uptake of MNPs by crops

4.3.1. Particle size

Particle size has been generally assumed to be important in governing plant uptake of MNPs (Huang et al., 2022a; Liu et al., 2020; Lv et al., 2019). Our collected data indicated that only 19% of all studies used MNPs < 10 nm (Figure 1), which are more prone to be taken up by roots directly as the SEL of cell wall pores is ≤ 10 nm (Carpita et al., 1979; Miralles et al., 2012). However, it is challenging to link the primary size (TEM/SEM size) of applied MNPs to the SEL of plant barriers, because the MNPs’ hydrodynamic sizes are normally larger than their TEM/SEM size (Table S1) (Gao et al., 2021; Ma et al., 2012; Zhang et al., 2019a). Moreover, the hydrodynamic sizes of MNPs are influenced by factors such as ionic strength, dissolved organic carbon and root exudates (Su et al., 2020; Yang et al., 2019). Accordingly, uptake of elements from MNPs ≥ 10 nm can still occur if they partially dissolve, which can take place following the release of root exudates (Peng et al., 2015). Huang et al. (2017) reported that malic and citric acids could be more efficient in dissolving nano Cu than oxalic and succinic acids. Crops with different compositions of root exudates may, therefore, differ in their uptake of MNPs. Moreover, the effects of soybean root exudates were reported to vary depending on the MNPs concerned, i.e., aggregation of nano Cu(OH)2, but dissolution of nano CeO2 (Cervantes-Aviles et al., 2021). Further research is needed to expand our knowledge of the effect of root exudates on plant uptake of MNPs, as well as transformations of MNPs at the root-soil interface. Both are critical if the uptake of MNPs by root is to be understood.

Our analysis confirmed a systematic increase in shoot SMD with decreasing particle size diameter for all six elements. The one exception was shoot SMD of Fe in the size range of 30 ~ 60 nm (Figure S6-4). Since both root and leaf were the main entry tissues for MNPs, the metal accumulations in these tissues can partially be attributed to MNPs that adhere to the surface and are difficult to remove by surface washing of the tissue as discussed above. Metal concentrations in shoot should mainly be due to the transport of MNPs within the plant via vascular system. Cell wall pores, which were not permeable for particles > 20 nm, exhibited a size-exclusion effect for MNPs that contained Fe (Kulikova et al., 2017). Smaller particles can overcome the SEL of entry tissues and exhibit facilitated transport of MNPs to other tissue parts (Larue et al., 2012). Another contributor to size dependent internalization and transport of metals in the plant is that MNPs of smaller particle size have a larger surface to volume ratio and, as a result, can be more easily dissolved (Schwabe et al., 2015).

4.3.2. Zeta potential

In addition to size, it is likely that the zeta potential affects the internalization and transport of MNPs (Avellan et al., 2019; Liu et al., 2019; Zhu et al., 2012). Root and leaf have negatively charged surfaces (Lv et al., 2019), meaning that MNPs with zeta potentials < 0 mV will be electrostatically repelled. This interaction will reduce the adhesion of MNPs, but can also facilitate their transport (Avellan et al., 2019). Interestingly, NPs with absolute values of zeta potential higher than 20 or 30 mV are more prone to be internalized by plants (Hu et al., 2020), while electrostatic forces with zeta potentials between -30 to +30 mV could be negligible (Zhou et al., 2011). Our results confirmed enhanced metal accumulations in shoot (higher SMD) for Zn and Cu and for the other metals in roots when the zeta potential became more negative, i.e., from -20 mV < ζ < 0 mV to ζ < -20 mV (Figure 4-2 and Figure S6-3). Note, the retention of MNPs by electrostatic forces between MNPs and root surface can be much weaker than the mechanical retention (Zhou, et al., 2011). Therefore, negatively charged MNPs could be adhered onto root surface and thus might be internalized into root cells rather than be repelled by root surface. Once inside root cells, MNPs could move into xylem or phloem saps. A more negative zeta potential would prevent MNPs from being adhered to negatively charged xylem or phloem surface and facilitate the transport of MNPs (Su et al., 2019). On the other hand, a more negative zeta potential (i.e., ζ < -20 mV) would resist formation of large aggregates of MNPs, which favors the transport of MNPs inside plants.

4.3.3. Other factors

Other factors assessed in this meta-analysis that can affect plant uptake of MNPs are surface coatings, the type of MNPs, the concentration of applied MNPs, the crop species, the growth medium and period, as well as the type of exposure (Huang et al., 2022a; Miralles et al., 2012). There are even more potential factors that can affect plant uptake of MNPs, such as microbial activities or community, or MNPs’ dissolution, but available information was scarce for quantitative data evaluation. The dissolution of Ag NPs can be negligible within hours or few days, and TiO2 NPs do not dissolve (Hedberg et al., 2019). However, large amounts of our collected studies were conducted for more than one week (Figure 4-1 and 4-2, and Figure S6-1 to S6-4). Hence, the contribution of dissolved MNPs to plant metal uptake could be considerable, such as of CuO and ZnO NPs that have relatively high solubilities (Table S1). Moreover, the MNPs inside plant roots may undergo dissolution due to oxidation by like reactive oxygen species (Huang et al., 2022a), and then the released metal could be transported to other plant tissues, while CeO2 NPs may not dissolve once entered into roots (Wojcieszek et al., 2019). Thus, dissolution of MNPs adds uncertainties in evaluating the plant uptake of MNPs. Many factors such as size, shape, DOM, chloride, pH, and crystallinity could play a role in the dissolution of MNPs (see Hedberg et al. (2019) and references therein), which were not the main focus of this study and will not be discussed here.

In our analysis, a PVP coating on Ag NPs enhanced the accumulation of Ag in shoot compared with a citrate coating, while Ag NPs coated with citrate exhibited higher SMD of root than those coated with PVP. This could be because PVP coated Ag NPs have stronger steric repulsion than citrate coated Ag NPs, which resists aggregation and therefore facilitates translocation (Su et al., 2020). CeO2 NPs had a positive surface charge when coated with chitosan, but were negatively charged after coating with polyacrylic acid. While the application of CeO2 NPs with different surface charges had varying effects upon uptake of Ce in both cucumber root and shoot (Liu et al., 2019), the coating material itself may have had minimal effects on uptake of Ce in leaf if the zeta potential was not affected (Schwabe et al., 2015). However, as plant leaf surfaces are covered with cuticular waxes and / or trichomes (as in wheat), coating with surfactants could still promote the delivery of MNPs to leaf surfaces after foliar exposure (Huang & Keller, 2021). Therefore, different surface coatings would not decrease the uptake of MNPs as all coating materials showed positive to significantly positive SMD for all tissues (Figure 4-1, and Figure S6-1).

Increasing the dose of MNPs could also contribute to elevated accumulation of metals in the plants. Our analysis showed larger SMD for higher dosages, particularly for Cu and Zn (Figure 4-2 and Figure S6-3), which was in line with other studies (Rizwan et al., 2019; Rui et al., 2018). Note, an accumulation threshold could be reached if the transport vascular systems or porous membrane structures are blocked due to aggregates of MNPs resulting from too high dosages (Su et al., 2020). Moreover, excess dosage of MNPs could induce toxic effects on plant growth, for example, 500 mg L-1 Fe2O3 NPs inhibited root growth of hydroponic rice which may due to accumulation of reactive oxygen species (Li et al., 2021b).

The uptake of MNPs was crop species dependent but also interacted with other factor such as phosphate, for instance, Zhang et al. (2019b) reported that phosphate has more efficient effects on the translocation of CeO2 NPs derived Ce in monocots (maize and wheat) than dicots (cabbage and soybean). The authors also suggested that root exudate components and plant xylems could mainly contribute to the different uptake performances between crop species. When exposed to equivalent concentrations of Ag NPs, there was a larger accumulation of Ag in wheat than in cowpea (Wang et al., 2015). In our study, the wheat roots were more prone to accumulate Ag from MNPs than shoot, while there were comparable effects for Ag between these two tissues of maize (Figure S7-1, 7-2 and 7-3). As discussed above, plants can inhibit the upward transport of non-essential metals (Khan et al., 2014), this was confirmed by the low accumulation of Ag by wheat shoot (Figure S7-3). However, for some crops, this phenomenon does not seems to occur. The relatively high uptake of Ag by maize shoot and that of Ti by tomato shoot (Figure S7-1 and S7-4), suggested that some types of both mono- and di-cot crops could accumulate MNPs-derived non-essential metals, but some type of crops could not do this (such as wheat). A rough conclusion would be that crop species may be important in affects plant accumulation of MNPs. With only limited data, this conclusion could be over-interpreted.

When evaluating the data in Figure 4-1, it appears that the various factors also interact. The largest magnitude of effects was paired with the largest effect variations for certain surface coatings and crop species in root and leaf but not in shoot, i.e., not for the translocation in the plant. This could allow optimization of the efficacy of MNPs (such as nanopesticides) at tissue surfaces if no further translocation is desired. Due to the presence of these interactions, no specific ranking can be made among the different factors. All factors seem to affect the efficiency of MNPs internalization and transport, and create different and likely also synergistic options to manipulate the MNPs uptake by plants.

4.4. Uptake preferences upon exposure to MNPs and dissolved metals by plants

Many publications on plant uptake of MNPs cannot distinguish metal uptake by direct internalization of MNPs from that of metal ions that can be released from MNPs (Cocozza et al., 2019; Dimkpa et al., 2013; Zhang et al., 2015). However, such a differentiation can be assessed using an exposure to dissolved metals as control. The analyses of available data indicated that there are element specific uptake preferences among various tissues (Figure 3). For elements which are essential for plant growth, i.e., for Cu, Zn and Fe, the preferred uptake of both nanoparticulate and dissolved forms was observed, with a slight bias towards particulate forms (Figure 3). This is presumably due to the specific needs of the plants to internalize these elements and reflecting the specific applications of the MNPs as nano-pesticide or nano-fertilizer. Lin & Xing (2008b) reported that the uptake of ZnO NPs was preferred over elevated concentration of Zn salts in ryegrass roots. Hydroponic exposure to zero valent iron NPs by cucumber roots resulted in significantly higher Fe accumulation than exposure with Fe-EDTA (Dwivedi et al., 2018). In the case of Cu, exposure to nano forms elicited higher metal uptake of soil grown cucumber roots than exposure to dissolved metals (Ahmed et al., 2021b).

The growth medium and the applied concentration of MNPs also play an important role in uptake preferences of MNPs. In soil matrices, there were no obvious root and shoot uptake preferences of non-essential metals (Ag and Ce), while the preferences of dissolved ions became apparent in hydroponics (Figure S5). Both MNPs and dissolved metals being applied into soils could be partially absorbed to soil particles and their availabilities are decreased (Dwivedi et al., 2018). Hence, hydroponic application appears be more efficient than soil culture. While root surface may be blocked under high application rates of MNPs with low solubility, there could be preferred uptake of dissolved metals. However, this may not be true under deficient application dosages with less blockage of root cell wall pores. As reported by Ahmed et al. (2022), there was a preferred uptake of nano Al2O3 NPs by maize shoot at medium application concentrations but higher uptake of dissolved Al3+ salts at elevated dosage under hydroponics.

The uptake of non-essential metals Ag and Ce showed a clearer preference to dissolved forms than essential elements (Cu, Zn and Fe) (Figure 3). The roots exhibited a slight preference for ionic Ag and strong preference for Ce, which was not apparent in the shoots. Saleeb et al. (2019) pointed out that uptake preferences of Ag NPs or of Ag ions are plant-specific. In particular, *Arabidopsis* and poplar have been found to facilitate faster uptake of ionic Ag than of Ag NPs in hydroponics (Wang et al., 2013), while no respective significant differences were observed for soil fescue root uptake of AgNO3 compared to Ag NPs (Layet et al., 2019). In contrast, Ag NPs contributed to higher Ag accumulation in hydroponic rice root than that did AgNO3 (Yang et al., 2019), while modifying the Ag NPs to Ag2S NPs resulted in lower accumulations (del Real et al., 2017). Moreover, it is also possible that dissolved Ag+ can be reduced to nano Ag0 (Guo et al., 2019), or, vice versa, nanoparticulate Ag can release Ag+ with help of root exudates (Stegemeier et al., 2015). With this variability, a final definitive evaluation of preferred uptake of specific Ag forms is difficult. The preference for ionic forms of Ce in root may be due to reduced bioavailability of CeO2 NPs when applied to soils and their subsequent interactions with soil organic matter and mineral particles (Ma et al., 2020). When grown in hydroponics, plant roots acquired more Ce from CeO2 NPs than from Ce salts (Zhang et al., 2015). As both forms of Ce can be taken up by plants, differences in the solubility between nano CeO2 and Ce salts might not be a limiting factor for uptake (Barrios et al., 2016).

Figure 3 also reveals that uptake preferences of different metals in dissolved or nanoparticulate forms varied among plant tissues. Compared with roots, plant shoots did not exhibit any preference for the uptake of non-essential metals in dissolved or nanoparticulate form, while essential elements exhibited some bias towards nanoparticulate Zn and dissolved Fe. Layet et al. (2019) also reported that there were insignificant differences in the uptake of Ag between Ag NPs and AgNO3 in plant shoot at environmentally equivalent concentrations. However, when treated with high concentrations, wheat shoots accumulated more Ag from Ag NPs than from exposure to AgNO3 (del Real et al., 2017). Similarly, Yang et al. (2020) reported that there might be higher translocation of nano Ag into rice shoot than AgNO3, as shown in the variations of the Box-Whisker plot (Figure 3). After being grown in soil for more than 200 days, tomato shoots accumulated low but similar Ce contents from nano CeO2 and Ce salt treatments (Barrios et al., 2016).

The clearest uptake preferences were found in leaves which preferred to take up Ag, Ce and Cu in ionic forms but Zn and Fe in nanoparticulate form. In part, these data indicate a concentration effect. The accumulation of Ag after hydroponic exposure in poplar leaves was higher after the addition of Ag salts than when Ag NPs were added at low concentration (0.1 mg L-1). This difference vanished when the exposure concentrations rose to 1 mg Ag L-1 (Wang et al., 2013). The leaves of fescue accumulated similar amounts of Ag from ionic and nanoparticulate Ag at low soil exposure concentrations (0.0015 and 0.15 mg kg-1) (Layet et al., 2019). For Ce, the effects were opposite: a slightly higher concentration of Ce in tomato leaf was observed when treated with CeO2 NPs than with the application of low concentrations of ionic Ce (62.5 and 125 ppm) (Barrios et al., 2016). In wheat, the uptake of Ce in leaf from ionic forms exceeded that from nanoparticulate forms at a similar concentration (100 ppm), and the effects were more pronounced than for pumpkin and sunflower (Schwabe et al., 2015). Clearly, the uptake preferences depend on exposure concentration, crop-species, and element. Although not yet investigated, factors such as growth duration, particle size, and zeta potential are also likely to affect uptake preferences.

**5. Conclusion**

The uptake of Ag-, Zn-, Ce-, Fe-, Cu- and Ti-based MNPs by wheat, maize, rice, tomato, bean and cucumber were most frequently reported in the literature. 63% of all collected studies with MNPs’ size < 30 nm, and root application of MNPs accounted for 84% of all studies. Our meta-analysis showed that metal concentrations generally decreased by as many as 2 orders of magnitude from root through shoot to leaf under root exposure to MNPs, and foliar exposure showed more efficient metal accumulations in plant shoot than root application of MNPs. The presence of the metals in shoot indicates internal vascular transport of metals or even MNPs. As expected, the plant uptake of MNPs was higher for essential (Cu, Zn and Fe) than non-essential elements (Ag, Ce, and Ti). Metal accumulations in shoot decreased with increasing MNPs size for non-essential elements. There is a decline followed by rising trend of shoot accumulation of essential elements with increasing size of MNPs. The metal accumulation of essential elements in both root and shoot was enhanced as the zeta potential became more negative, except for Cu in leaf. Both element specific and tissues variable uptake preferences of MNPs were reported. Non-essential elements (Ag and Ce) were acquired preferably as dissolved ions particularly under hydroponics, whereas uptake as nanoparticulate forms occurred more frequently for the essential elements (Cu, Zn and Fe), although true tracing studies in this context are rare. There is no clear trend of accumulation of MNPs-derived essential or non-essential metals by cereal or vegetable crops. Nevertheless, precise determination of the dissolution of MNPs upon exposing to plants or after internalization is still a critical challenge for future research. Advanced techniques are needed to pinpoint and trace the fate of MNPs inside the plant and determine the metal form in which it is translocated within and between tissues. It is worth noting that natural NPs like iron oxides and organo-mineral associations are ubiquitous and important carriers for both essential and non-essential elements, i.e., considering plant uptake of those NPs should likely warrant further attention.

**Supporting Information**

Supplementary methods, Table S1, Fig S1-S7, Excel S1-S3, Word S1.

**Acknowledgments**

YJ highly appreciates the Chinese Scholarship Council (CSC201808320415) for supporting his research in Germany. RB, EK and WA acknowledge the funding contribution from POF IV: 2021-2026, grant 2173 Towards a Sustainable Bioeconomy – Resources, Utilization, Engineering and Agroecosystems, as well as of FOR 2179. The authors acknowledge work of the scientists whose data been used in this meta-analysis, and especially those sharing original data upon request.

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Figure 1. The most frequently studied types of metallic nanoparticles (MNPs). The subfigure at the top right is the distribution of size ranges (nm) of MNPs. Data was collected for this meta-analysis on 25 Feb of 2021, more recent publications are not included.

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Figure 2. The metal concentrations (mg kg-1 dry weight) (exponential-scaled y-axis) in different plant tissues after exposure to metallic nanoparticles (MNPs). In order from left to right in each column, it shows metal concentration in root, shoot and leaf tissue. There are four types of plant exposure to MNPs: root exposure (brown rounded dot), foliar exposure (green triangle), seed and foliar application (blue square), and stem injection (yellow upside-down triangle). The left three columns are Ag, Ce and Ti which are non-essential elements for plants and the right three are Cu, Zn and Fe which are plant essential elements. Significant differences between the individual exposure pathways, elements, and tissue concentrations are disentangled in the respective Figures S4-1 to S4-4.

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Figure 3. Metal concentration differences (mg kg-1 dry weight) in various plant tissues treated with either metallic nanoparticles (MNPs) or dissolved metal salts. No data for Ti as TiO2 NPs do not “dissolve”. The three big columns from left to right indicate metal concentration differences in root, shoot and leaf, respectively. Note that the scales of y-axis for three tissues are different. The brown round dot represents root exposure and the green triangle represent foliar exposure. Within each column, the left three metals (Ag, Ce, Ti) and the right three (Cu, Zn, Fe) are plant non-essential and essential elements, respectively. When mainly data points above the zero line (red dashed horizontal line), there is preferred uptake of MNPs by plant tissues; otherwise, the preference is for dissolved metals. Within each column, lower case letters indicate significant concentration differences between the six elements. P < 0.05.

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Figure 4-1 and 4-2. The magnitude of effects (standardized mean difference, SMD) of Ag and Cu concentrations in root, shoot and leaf (from left to right), respectively. The factors were grouped into several groups: particle size (nm), zeta potential (mV), surface coating (for Ag only), application concentration (ppm), crop plant, growth medium, exposure period, MNPs type and exposure way. The error bars represent 95 % confidence intervals. There is insignificant effect if the error bar crosses the vertical red dashed line (SMD = 0). The number beside each error bar indicates number of observations. When there is a significant positive (error bar to the right side of red line) or negative effect (error bar to the left side of red line) the observation number is found to be the right of the bar, while the observation number is found to the left of the bar for insignificant effects. Acronyms used for surface coating are: PVP (polyvinylpyrrolidone), PEG + Tween 20 (polyethylene glycol-thiol and polyoxyethylene (20) Sorbitan mono-Laurat), GA (gum Arabic), and “Bare” indicates no surface coating.