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Delivery, Uptake, Fate, and Transport of Engineered Nanoparticles in Plants: A Critical Review and Data Analysis

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Abstract:
The increasing demand for food coupled to various environmental pressures, is increasing the importance of sustainable agricultural practices. Based on results published across a wide range of disciplines, it is becoming evident that nanotechnology can play a crucial role in increasing the sustainability of agriculture, particularly in the area of fertilizer delivery, gene modification, and pest control. In this paper, we review critical plant morphological and physiological indices (pore size in xylem and phloem, xylem/phloem sap composition, xylem/phloem sap flow rate and flow conducting area) for nanoparticle (NP) transport, and examine the efficacy of various delivery methods for NPs (foliar application, root application, and feeding/injecting directly into plant tissue) with an emphasis on NP transport efficiency throughout the entire plant. While only few studies have explored the feeding/injection of NPs, these application pathways are the most efficient in terms of transport, indicating their practical potential (e.g., for agrochemical delivery). In contrast, when applied via soil drenching or foliar spraying, the majority of the applied NPs are not taken up by the plants. However, those NPs that do penetrate the plant exhibit efficient transport from leaf to root, and vice versa. Of these two application methods, foliar application appears to be more effective in both NP delivery and transport than soil drenching. To further explain the data reported in the literature and to study the transport processes of NPs throughout the plant, we applied the Derjaguin-Landau-Verwey-Overbeek model to study the interactions of NPs with the surfaces of the plant vascular system (xylem and phloem), by which these NPs are transported throughout the plant structure. We found that the interaction energy between negatively charged NPs and plant tissue is positive, indicating that these NPs can effectively transport. We discuss future research needs regarding NP transport, which will enable effective utilization of NPs for different agricultural applications.

Environmental Significance:

This review provides a comprehensive look at the challenges and opportunities associated with the application of nanomaterials in agriculture, with particular emphasis on the fate, transport, and transformations of nanomaterials. Specifically, we identify critical plant and nanomaterial properties that control the effectiveness of nanomaterial applications in agriculture, and which environmental conditions impact their use.

1. Introduction.

Based on the definition promulgated by the National Nanotechnology Initiative, nanotechnology is the manipulation of matter with at least one dimension sized between 1 to 100 nm[1]. Based on their composition, nanomaterials can be classified into four main categories: pure carbon nanostructures (e.g., fullerenes, graphene, and carbon nanotubes), inorganic nanomaterials (e.g., metal, metal oxide, zeolite, ceramic), organic nanomaterials (e.g., dendrimers, liposomes), and organic-inorganic hybrids (e.g., metal-organic frameworks, covalent organic frameworks) [2,3]. The large surface area, tunable pore size and structure, as well as their tailored functionality make nanomaterials promising for a wide range of applications, including catalysis, gas/energy harvesting and storage, electronics, environmental pollutant removal, antimicrobial functions, drug delivery, "smart" sensor design, and food production[4–9]. In this review, we focus on the emerging field of nanotechnology applications in agriculture, with an emphasis on the fate and transport of nanomaterials in plants.

Agriculture is critical to the sustainable development of human society. By 2050, the world population will reach 9 billion, and global crop demand will increase by 110 % compared to 2005 levels[10]. New approaches to agriculture, including improvement of agricultural yields and resistance to pests and disease, are critical to achieving global food security. Several approaches to increasing crop yields have been identified. The first approach involves increasing the utilization efficiency of fertilizer[11]. Fertilizer is crucial to healthy crop growth and high crop yields. In fact, the wide application of synthetic fertilizer is responsible for the green revolution that occurred in the 1950s, which triggered a dramatic increase in agricultural production worldwide.[12] However, over the last few decades, nutrient utilization efficiency has declined significantly. For instance, the nitrogen (N) use efficiency for cereal production declined from 75% in 1960 to 30% in 1995[13]. Presently, only 30-50% of N and 45% of phosphorus (P) that are applied to crops are efficiently absorbed by plants[14]. However, a recent study on nanoparticle-based fertilizers (nano-fertilizers; both macro-nutrients and micro-nutrients) has shown promise in terms of nutrient utilization efficiency and crop production, indicating that nanotechnology could play an important role in sustainable agriculture[15].

The second approach to increasing crop yields involves increasing crop resilience to disease (caused by fungi, bacteria, and viruses), pests, and weeds.[16] Based on previous

studies, disease, pests, and weeds are responsible for 10-25%, 15-30%, and 15-35% of total crop losses, respectively[17]. To shield crops from these risks, a wide range of chemical agents (i.e., fungicides, bactericides, pesticides, and herbicides) are heavily utilized. In 2012, pesticide sales in Europe, Asia, North America, Latin America and the Middle East/Africa approached $43 billion[17,18]. However, it has become clear that the widespread use of these chemical agents may have a negative impact on the environment and human health[19]. Thus, safer approaches to ensure plant health are necessary. Nanomaterials, such as silver and copper nanoparticles (NPs), have demonstrated strong antimicrobial properties[20–24], suggesting that NPs could potentially play an important role in managing crop health and preventing plant diseases, if they are applied effectively and safely.

The third approach is to genetically modify agricultural crops, which can introduce new beneficial characteristics to plants[25]. In 2012, over 170 million hectares of land in 28 countries were used to grow genetically modified crops (primarily corn, soybean, rapeseed, and cotton), and it is expected that the global adoption of genetically modified crops will continue to increase in the coming decades[26]. This increasing demand is being met by the use of nanotechnology, which is being extensively applied in the genetic modification of plant DNA[27]. The use of nanotechnology in gene modification enables easy operation, high efficiency (1,000 times less DNA is needed compared to conventional DNA modification techniques), versatility (NPs are capable of simultaneously introducing proteins, nucleotides, and chemicals), target-specific delivery, and on-site release[28–30]. A recent paper reported that chitosan-complexed single-walled carbon nanotubes successfully delivered plasmid DNA to chloroplasts of mature *Eruca sativa* (arugula), *Nasturtium officinale* (watercress), *Nicotiana tabacum* (tobacco) and *Spinacia oleracea* (spinach) plants[31]. Thus, the role of nanotechnology in crop genetic modification is expected to grow, particularly in light of the exciting opportunities that gene modification may play with the increased use of the CRISPR gene editing tools.

Based on current market trends and recent research, it is likely that nanotechnology will play an increasingly important role in agriculture[32]. This is particularly true since the environmental impacts of nanomaterials have so far been determined to be quite limited[33]. However, one of the most critical questions is how to effectively deliver NPs to target plant tissues; and once introduced, how do NP properties impact the transport of these materials inside the plants? In this review, we consider the key micro-morphological and physiological indices of plants that relate to the fate and transport of NPs in plants (pore size in membrane-like structures involved in cell-to-cell movement), xylem/phloem sap composition, and xylem/phloem sap flow rate), summarize experimental parameters and the main findings on NP penetration and translocation for three NP delivery methods, and propose a simplified model that simulates NPs' behavior in a plant's conductive (transport) system. In addition, we identify current gaps in knowledge and future research needs.

2. Plant structure and its impact on NP penetration and transport

Plants are complex living structures with multiple specialized tissues with varying functions and composition. For instance, the structure and function of leaf tissue is very different from that of the roots. Similarly, the upward transport system (i.e., the xylem) differs markedly from the downward transport system (i.e., the phloem) in both structure and function. In the following sections, we discuss how these tissues impact the penetration and transport of NPs into and through the entire plant.

2.1 The surfaces: leaves and roots

In general, plant-NP interactions take place in three steps: i) NP deposition on a plant surface (e.g., on a leaf, root, or stem), ii) NP penetration through the cuticle and epidermis, and iii) transport and transformation within the plant. Attempts to describe the latter two stages must carefully consider the morphological and physiological features of the appropriate plant tissues (e.g., leaf and root surfaces, vascular systems), and these differ among vascular plant lineages. Our review excludes the gymnosperms and other non-flowering plants and is confined to the flowering plant lineages[34] that harbor the vast majority of crops: magnoliids (e.g., avocado), monocots (e.g., rice, wheat, corn) and eudicots (e.g., most fruit, vegetables and nuts). These crops account for a large portion of the human diet, as well as livestock diet[35], we focus primarily on the morphology and physiology common to monocots and eudicots (magnoliids resemble eudicots in their morphological and physiological features), but without attempting to contrast between them unless of major relevance. However, readers are encouraged to refer to other sources for a detailed description of plant micro-morphology and physiology[36–38].

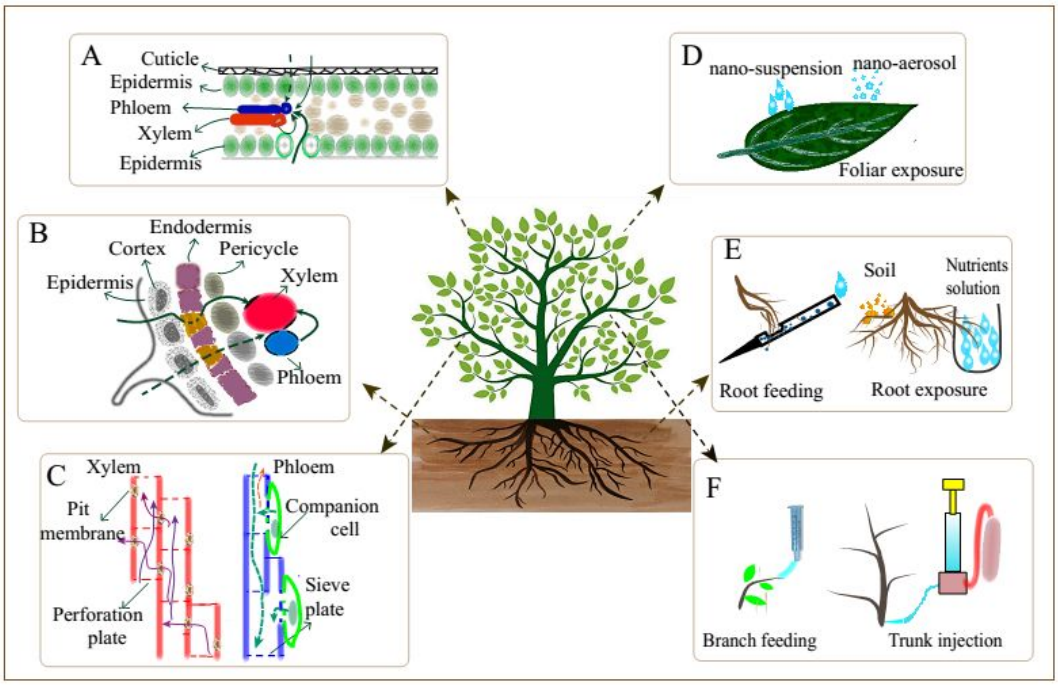


Figure 1. Schematic diagrams of the cross/longitudinal section of (A) a leaf, (B) a root, and (C) xylem and phloem in stem/trunk; schematic diagrams of (D) foliar application, (E) root

feeding and soil drenching, as well as (F) branch feeding and trunk injection. (⟶, apoplastic pathway; ⇢, symplastic pathway, in A, B, and C)

While all leaves have similar features (an epidermis with stomata, mesophyll and vascular tissue) (Figure 1A), the arrangement of these various components in each plant is modulated by environmental factors such as water availability, light intensity, temperature, ecological niches and stressors, and herbivores[39]. The epidermis can be one or more cell layers thick, covered by either a thick (upper surface) or a thin (lower surface) cuticle. This waxy hydrophobic cuticle has very small pores (<5.0 nm) [40], which prevent the uptake of all but the smallest nanomaterials[41]. In addition to these nanopores, plant leaves have larger pores, known as stomata (which can occupy up to 5% of the total leaf surface area) that are used to regulate water and gas exchange with the environment; these stomata have sizes that run in the 10's of microns (e.g., 5 × 13 μm on spinach leaves[42], 5 × 7 μm on watermelon[43] and tomato[44] leaves, 21 × 13 μm on cucumber leaves[45], 16 × 6 μm on lettuce leaves [46]), and are large enough to allow NP penetration when open, although their response (open/closed) largely depends on CO_2 concentrations, moisture, temperature, and light intensity[36,47,48]. Importantly, the location and quantity of stomata is plant-dependent. Most plant species only have stomata on the abaxial (lower) side of their leaves, while a few have stomata on both sides[47,49,50]. When present on both sides (i.e., abaxial and adaxial (upper)), eudicots tend to have more stomata on the abaxial leaf surface (about 1.4 times that of the adaxial surface[46,47,51]), while monocots have similar numbers of stomata on both sides[50]. While the rest of the epidermis will likely impede the penetration of NPs, stomatal openings may facilitate NP entry into plant leaves. Furthermore, the structure of the mesophyll (the inner tissue of a leaf), which can be either compact or loose, leading to small (as in xerophytes) or large intercellular spaces (as in some mesophytes and most hydrophytes), can impact the short-distance transport of NPs after penetrating the epidermis and before entering the vascular system in the leaf.

Plant roots are another organ that can allow NP uptake. It is worth noting that monocots have fibrous root systems, while eudicots have a long-lived primary root[36]. The higher root surface area (per fresh or dry weight) potentially makes monocots more sensitive to NP exposure. As illustrated in Figure 1B, the outer layer of a typical primary root is the epidermis, inside of which is the cortex (which includes the outer cortex and inner cortex). The cortex is located between the epidermis and the endodermis, onto which the pericycle is bound. The vascular system is located in the middle of the root. Among these structures, the cortex changes substantially in response to the availability of water in the culture media[52], which can lead to varying degrees of resistance to NP penetration. In well-drained soils, the entire cortex is compact (called "solid cortex"), while in periodically waterlogged soil or nutrient solution, the middle part of the cortex has large intercellular spaces (called the lacunate cortex)[36,53]. Thus, the degree of soil water saturation can result in varying degrees of obstruction that can impact apoplastic transport of NPs through the cortex. The endodermis is also important to NP penetration and transport. There are two types of cells in the

endodermis: passage cells (with thin walls) and "waterproof" endodermal cells (with thickened walls). The passage cells are usually opposite the xylem, serving as a pathway for water and dissolved solutes from the root hairs to the xylem. However, endodermal cells contain Casparian strips, which prevent the apoplastic flow of water to the inside of the root structure. Thus, it is likely that passage cells are the only avenue available for NPs to penetrate the endodermis in intact roots. However, the emergence sites of new secondary roots, as well as damaged roots, may also be effective NP entry points.

Due to the different morphological characteristics of leaves and roots, the main barriers to NP entry will differ. For example, NPs entering the roots may have to pass through the endodermis. However, the Casparian strip only allows a symplastic pathway through passage cells, which may restrict the transport of NPs. On the other hand, once NPs pass through the cuticle and the epidermis (or simply through stomata) of leaves, they have relatively easy access to the downward vascular system (i.e., the phloem)[43,54]. Mucilage and exudates excreted by the root can trap NPs, which also prevents them from entering the root tissue.[41] The epicuticular waxes on the surface of leaves impose high water/nano-suspension repellency, leading to short residence times for NPs on leaf surfaces, which can affect their uptake[55].

2.2 The conductive system: phloem and xylem

Plants contain a complex conductive system that carries water from the roots to the leaves, known as the xylem, and a parallel system that carries sugar (produced during photosynthesis) from the leaves to the rest of the plant, known as the phloem (Figure 1C). The xylem and phloem are essential for long-distance transport of NPs in plants[56]. The xylem has two types of conductive cells: tracheids and vessel elements. Both cell types are connected to their neighbors via pits, which are small openings lined by a porous pit membrane. In addition to pits on their lateral walls, vessel elements are connected to each other end-to-end by perforation plates. Whereas the pit membrane can act as a barrier to solute movement, perforation plates allow their relatively unimpeded transit. The relative abundance of each type of conductive cell in the axial direction varies between different plants[57]. The phloem mainly consists of sieve cells, which are connected via porous sieve plates (Figure 1C)[58]. These porous structures can prevent the transport of NPs through the conductive systems by acting as sieves[43,59–64]. For the majority of plants, the average sieve plate pores range between 200 nm to 1.5 μm (Table 1)[65], which should allow the passage of most NPs, unless they are in aggregated form. Though porous, pit membranes of the conductive cells of the xylem are designed to restrict the passage of air bubbles and pathogens. Their pore diameters are in the range of 43-340 nm (Table 1)[66,67], and have the potential of restricting the transport of NPs. This may explain why NPs accumulated in some tracheids/vessel elements after plants were exposed to NPs, as their transport was restricted by the pit membranes[51,68]. In addition, the differences in radii of xylem vessels in different parts of the same plant (such as the root tip, mature root zone, stem, petiole, petiolule, midrib, and vein) might affect the transport of NPs from root to leaf[69,70].

Table 1. Pore size distribution of pit membrane and sieve plates in different plants[65–67]

In the xylem and phloem, NPs can move along with bulk water/sap. There are two important physiological factors that can impact the transport of NPs, namely sap composition and sap flow rate. Several studies have explored the sap composition of different plants[71–77]. Sap composition is expected to affect the aggregation, sedimentation and dissolution of NPs, but studies investigating the impact of sap on the fate of NPs are rare[33]. Tables 2, S1 and S2 reveal that, 1) appreciable concentrations of K, Ca, Mg, Na, Cl, P, N, S, sugars, amino acids, organic acids, and proteins are present in the phloem, although their concentrations vary widely; and 2) the xylem contains inorganic ions, but no sugars or organic acids, and the phloem has higher concentrations of these inorganic species. In addition, sap composition depends on the growth stage[71,75], and location of xylem or phloem within the plant (e.g., leaf, stem, trunk, or root) due to differences in water flow and nutrient (both inorganic and organic matters) transport[75,78–80]. For example, in 24 wild plant species with C_3-type photosynthesis, the average concentration of minerals and organic acids in leaves were 116 mg/g and 82.5 mg/g, respectively, while those in roots were 166 mg/g and 30.5 mg/g, respectively[78]. It is unknown how sap components (e.g., sugars or proteins) interact with the surface of NPs. It is known that organic molecules can interact with the surface of NPs to form organic "coronas", which can change the hydrodynamic size of the NPs, as well as modify NP surface properties[81,82], although this has not been investigated in plants.

Table 2. Xylem and phloem sap composition[70,80]

The bulk flow of sap is responsible for the transport of NPs throughout plants, with the sap flow rate determining the transport velocity of NPs. Sap flow occurs in the xylem (flow in tracheid/vessel, as well as pit membranes), phloem, and cell wall interstices[70]. Resistance to flow mainly results from the small size of the flow channels, while the driving force comes from a hydrostatic pressure gradient. It is worth noting that the approximate turgor pressure drop between the source and the sink along the sieve tube results in a positive hydrostatic pressure in the phloem[65], and the tension created by vapor flow in substomatal cavities causes the negative hydrostatic pressures in the xylem[83,84]. The average sap velocity in the phloem[85] and xylem[70] can be expressed as follows:

$$\nu_{Ph} = -\beta \frac{r^2}{8\mu_{Ph}} \frac{\partial P_{turgor}}{\partial z} \quad (1)$$

$$\nu_{Xy} = 8r^2 \mu_{Xy} \frac{\partial P_{tension}}{\partial z} \quad (2)$$

where ν is the velocity, μ is the viscosity, r is the radius of phloem or xylem, and $\frac{\partial P}{\partial z}$ is the gradient of hydrostatic pressure. Because the amount of NPs found in plants is very low (refer to Tables 5 and 6), it is reasonable to assume that NP concentrations in the xylem or phloem

are likely to be much lower than 2% (v/v) under most conditions. Thus, NPs are not expected to dramatically impact fluid velocity[86,87]. Based on this assumption, Eqs. 1 and 2 can be used to express the approximate transport velocity of NPs in the phloem and xylem, respectively. Apart from the advection caused by sap flow, NPs in sap can also experience Brownian diffusion. In terms of Brownian diffusion, when the Péclet number (*Pe*) is >>1, its influence on NP transport can be neglected[86]. Otherwise, Brownian diffusion has to be considered.

Sap flow rates can be experimentally measured. According to the literature,[88,89] flow rate can be quantitively estimated through dyes or radioisotopes as tracers, or with magnetic resonance imaging. In Table 3, we have collected the values of phloem and xylem flow rates under different conditions, while in Table 4 we collected the average cross sectional areas of xylem vessels and phloem sieve tubes in different plants[89–94]. The sap velocity of the phloem ranges between 0.07 to 0.58 mm/s, while the sap velocity of xylem is an order of magnitude higher, varying between 0.47 to 4.8 mm/s[89,90]. In other words, even at the lowest velocity (0.07 mm/s), NPs can transport up to 6 m in 24 h, suggesting that once NPs reach the conductive system of a plant they can travel rather fast (unless impeded by sieve plates or pit membranes). The sap velocity in the phloem remains quite constant throughout the day, while the xylem sap velocity is greater during the day time than at night; also, xylem sap velocity reduces to zero when stomata are closed (e.g., during hot days) (Table 3). Additionally, at different growth stages, plants exhibit changing sap velocities (Table 3). For instance, the xylem sap velocity in a 6-day and a 3-week old castor bean was 0.47 mm/s and 3.7 mm/s, respectively. In contrast, the phloem sap velocity in the younger plant was 0.58 mm/s but it was 0.25 mm/s in the older plant[89,90]. Changes in sap velocity can impact the deposition and mobility of NPs in vascular tissue, in ways that are similar to their behavior in porous media[95]. The sap conducting area can also influence the transport efficiency (*TE,* defined in section 3.1) of NPs, where plants with larger sap conducting areas are expected to facilitate more effective transport. In Table 4[89], the xylem sap conducting area in 3-week old poplar, tobacco, castor bean and tomato declined by approximately 30% at night compared to day time values. However, the phloem sap conducting area was slightly higher at night than during the day. Thus, it is likely that the *TE* of NPs will be impacted by the time of day.

Table 3. Sap flow velocity in different plants[89–94]

Table 4. Sap conducting area (mm^2) adapted from the study carried out by Windt et al.[89]

While there are some data regarding sap flow rates in a limited number of plants (see Table 3), it is possible that these rates vary significantly in others. In addition, it is possible that NP exposure could impact sap flow rates, which can impact their transport. Therefore, measuring sap flow rates in different plants under various conditions is necessary to properly predict NP transport in plants. In addition, based on the sap velocity values (Table 3), we quantitatively evaluated the impact of Brownian diffusion on NP transport by calculating the *Pe* number[88] (detailed description on *Pe* calculation can be found in *Supporting Information*). The

diffusion coefficient (D) and typical Pe number calculated for NPs of different sizes in the phloem and the xylem are shown in Figures S1 and S2. The Pe values for NPs in the xylem are at least two orders of magnitude greater than 1, suggesting that diffusion has limited impact on NP transport in the xylem[87]. Similarly, in most cases (NPs with $r > 4$ nm), the Pe number for NPs in the phloem is also much greater than 1. However, when $r < 4$ nm, the Pe number declines from 100 to 20 (Figure S2), and a decrease in sap density and sap flow rate can result in a rapid drop of Pe to 1 and even < 1 (data not shown), in which case, the diffusion of NPs has to be taken into consideration when thinking about NP transport.

3. NP uptake and transport in plants

Given the complexity of sap composition, it is necessary to understand the influence of pH, ionic strength, inorganic ions (e.g., Cl^-, SO_4^{2-} and NO_3^-), and high concentrations of organic matter on the fate, transport, and transformation of NPs in plants[96–98]. For the understanding of the fate of NPs in plants, lessons can be gleaned from other complex matrices (such as natural waters, soil, sediments, etc.) in which the behavior of NPs has been widely studied. Previous work on NP fate in the environment report that[99–107]:

1. High ionic strength can lead to fast aggregation of NPs,[108–110] while organic macromolecules (such as humic acid, fulvic acid, citric acid, and extracellular polymeric substances)[111–113] can enhance NP stability and reduce sedimentation and/or deposition. These phenomena could be partly explained by the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) or the modified DLVO theory[33,114,115].
2. Specific ion species or organic macromolecules can accelerate or inhibit NP dissolution [116]. For instance, at a low Cl/Ag molar ratio, Ag NP dissolution is inhibited, while a high Cl/Ag molar ratio stimulates Ag NP dissolution[117]; the presence of humic or fulvic acids tends to inhibit the dissolution of Ag NPs[118], while extracellular polymeric substances promote the dissolution of Cu NPs[106].
3. Certain inorganic chemical species can result in the transformation of NPs. For instance, the presence of phosphate, nitrate, or sulfide leads to the formation of $FePO_4$[119], Fe_3O_4[120] or FeS[121–123] on nFe^0, respectively.
4. Surface modification with synthetic organic matter (e.g., poly(methacrylic acid)-poly(styrene sulfonate)-poly (methyl methacrylate)[124], olefin-maleic acidcopolymer[125], sodium carboxymethyl cellulose[126], poly(acrylic acid) and polyvinylpyrrolidone[127]) enhances the transport of NPs in porous media, by minimizing NP aggregation and deposition.

While extensive studies on the fate and transport of NPs in plants have not been conducted, it is reasonable to expect NPs to respond to the various constituents in plant sap in a similar manner to that recorded in other complex systems. For example, it is likely that the high ionic strength (and abundant divalent cations) would lead to NP aggregation in the sap, unless the NPs were sterically stabilized[128,129]. This stabilization could occur by design

(e.g., by synthesizing polymer-coated NPs) or through NPs being coated by naturally occurring polymers in the sap, although this has not been explored in plants[113,130]. In addition to aggregation, NP deposition on plant cell walls would also be expected unless the NPs were sterically stabilized[107,131].

3.1 NP uptake

While several papers have reviewed the barriers to NP uptake and transport in plants[41,132–134], there is still a shortage of studies that systematically evaluate NP transport given different NP delivery methods. In this section, we classify studies by the method used to introduce NPs to the plant: 1) foliar application (Figure 1D), 2) root application (mainly soil drenching) (Figure 1E), and 3) trunk feeding/injection (Figure 1F). Further, we identify the key factors influencing NP uptake and transport in plants.

Foliar application, root application and trunk feeding/injection are the three most common delivery methods used to introduce NPs to plants. While foliar and root application are relatively easy to implement, plant barrier tissue (that is, leaf and root epidermis) and the local environment (e.g., rain falling on a leaf, the rhizosphere around a root) retard NP uptake, leaving the majority of the applied NPs on the outside of the plant[41,42]. This implies that foliar and root application could be effectively employed for nano-pesticide or nano-fertilizer delivery (where the entry of NPs into plant is not desired). In foliar applications, while spraying a NP suspension (with careful application) can deliver 60-70% NPs onto the surface of leaves, exposing plants via a NP aerosol is estimated to deliver only 3.3-5.0% of NPs onto the surface of leaves[43]. If no interference occurs (e.g., rain, wind), NPs will begin to penetrate through the cuticle/epidermis (and even stomata), but in the meantime, they will aggregate on the surface of a leaf (e.g., 24-37 nm CuO NPs aggregated to 230-400 nm aggregates on lettuce leaf after 2 h)[135]. Larue et al. (2014)[136] reported that 80% of NPs delivered on leaves were detected in the first 200 nm beneath the leaf cuticle after a 7-day exposure. A similar study showed that after 18 days post exposure, less than 30% of NPs deposited on leaves entered the cucumber leaf tissue, with the majority of these NPs trapped in the epidermis[45]. Moreover, NPs on leaves can be easily washed away by water (removed 73% of CeO_2 NPs on cucumber leaves)[45], 10 mM $CaCl_2$ solution (removed 81% of CeO_2 NPs on cucumber leaves)[45] or 10 mM acetic acid (removed 37% of Ag NPs on lettuce leaf surface)[46]. In addition, the elevated hydrophobicity of many leaves makes rinsing off NPs relatively easy[135], indicating the potential loss of NPs in practical applications during irrigation and rainy seasons. However, making NP surfaces more hydrophobic (e.g., by functionalizing with hydrophobic polymers) makes them more “sticky”, which reduces their tendency to wash off the surface[137]. In addition, hydrophobic NPs exhibit superior penetration through the leaf’s waxy cuticle[138], although it is unclear how these hydrophobic particles move throughout the plant’s tissues.

The abundant stomata on leaves have the potential of allowing rapid and efficient NP uptake[41,139]. One study of stomatal uptake of polystyrene NPs (43 nm) in an aqueous suspension by *Allium porrum* leaves reported that following four sequential NP

applications/drying cycles, NP uptake via the stomata varied from <1% to 20%, with the percent uptake varying between various leaves, and even parts of the leaf; the highest stomatal uptake (20%) was reported on apical leaves[140]. In 2010, Uzu et al.[59] reported that submicron atmospheric Pb-containing particles were continuously taken up by the stomata (mostly on lower surface) of lettuce leaves within 43 days (a linear increase of leaf Pb content was found during this exposure period). Moreover, while no Pb-containing particles were identified on epidermal cells (implying no penetration through epidermis), the base of the central vein contained more particles than any other area on the leaf. Similarly, 2.8 ± 1.2 nm TiO_2 NPs mostly accumulated in some of the stomata (seldom in epidermal cells) on an *Arabidopsis* leaf after 24 hours exposure[139]. Although it is difficult to differentiate the contribution of epidermal penetration and stomatal uptake to total NP uptake in foliar exposure, it is important to take stomatal aperture size and stomata density into consideration. Schreck et al.[141] found that after 6 weeks following foliar exposure to submicron Pb-containing atmospheric dust, the shoot content of Pb in ryegrass (with average stomatal aperture size of 2-4 μm and stomatal density of 75/mm^2)[142,143] was about 700.1 ± 27.5 mg/kg dry tissue with 14% of Pb in its elemental state[141], and over 49% of Pb combining with organic acids or cell walls[144], while the shoot content of Pb in lettuce (with average stomatal aperture size of 8.5-10.6 μm and stomatal density of 280 #/mm^2) was 171.5 mg/kg dry tissue with 81% of Pb in its elemental, state and 19% of Pb combined with organic acids or cell walls. These findings indicate that the stomatal uptake pathway may be responsible for up to 98 mg Pb/kg dry shoot tissue in ryegrass and 138.51 mg Pb/kg dry shoot tissue in lettuce. Thus, it is very likely that the stomata serve as a more efficient pathway for NP uptake, with high stomata density leading to higher uptake of NPs. Because of variations in the density of stomata, the location of these stomata, and the environmental variables that govern the opening of these pores, more research is warranted on this promising NP uptake pathway.

In root application, it has been reported that little to no NP uptake was observed, with the NPs remaining in the culturing media or attached to the root surface[30,145–148]. For example, following an 84-day exposure to 1800 mg and 3600 mg of CeO_2 NPs in 4.5 kg soil, corn plants absorbed 1.075 mg (0.06% of total NPs) and 3.828 mg (0.11%) of CeO_2 NPs, respectively[149]. In another study, it was reported that the number of NPs transported to leaves of poplar plants after 6 days of exposure to a root application accounted for 0.05%, 0.10%, and 0.03% of total Au NPs used, with diameters of 15 nm, 25 nm, and 50 nm, respectively[150]. Thus, it is likely that root applications cannot efficiently deliver NPs into plants. However, if the goal is to deliver specific ions (sourced from a dissolving NP), then root applications may be a reasonable delivery method.

Feeding/injecting NPs directly into plants is an emerging delivery method; however, it is a more complicated process that is more suitable for larger, woody crops (e.g., vines, trees)[151–154]. Importantly, delivery efficiency using these methods is near 100%, as the entire volume of a NP suspension is forced into the plant. Thus, the choice of delivery method is dependent on the desired application (e.g., an antimicrobial NP targeting a systemic virus would need to

penetrate the plant and distribute throughout the plant tissues), as well as the economic value of the crop and the cost of the NP itself.

Once NPs enter the plant through a specific organ (e.g., leaf, stem, root), they can be transported to other parts of the plant via the vascular system[33,134,155]. For instance, foliar application (where 10 to 1000 ppm suspensions of NPs are directly sprayed onto leaves) of metallic NPs can result in an increase in the corresponding metal content in the root and stem (ranging from 10 to 70 mg/kg dry weight) due to NP transport within the plant[43–45,156,157]. Similar results were reported for root-exposure studies[30,158]. While it is widely accepted that the upward movement of NPs mainly occurs through the xylem and the downward movement occurs through the phloem[45,51,148,159–161], the degree of transport varies with other factors such as plant species, NP delivery methods, and exposure time. These factors can affect transport of NPs even when the administered NPs have similar composition and morphology and are delivered using the same method. For instance, an 84-day exposure to 800 mg ZnO NPs (24 ± 3 nm) per kilogram soil increased the Zn content in leaves of corn to 183 ± 31.7 mg/kg dry tissue[149], while a 12-day exposure to 1000 mg ZnO NPs (20 ± 5 nm) per liter NP suspension only increased Zn content in ryegrass to 1.36 mg/kg dry tissue[162]. An important caveat is that the average metal content of tissues is not a perfect representation of NP transport, since the plant dry weight differs among different plants and plant parts[163]. To evaluate the transport of NPs in a plant, we defined the *TE* for each application method as the ratio between the mass of the NPs in parts of the plant other than the application area and the total mass of NPs added to the plant (Equations 3-4):

$$TE_{foliar} = {(w_{root} \times C_{root} + w_{stem} \times C_{stem})}\Big/{(w_{leaf} \times C_{leaf} + w_{stem} \times C_{stem} + w_{root} \times C_{root})} \quad (3)$$

$$TE_{root} = {(w_{leaf} \times C_{leaf} + w_{stem} \times C_{stem})}\Big/{(w_{leaf} \times C_{leaf} + w_{stem} \times C_{stem} + w_{root} \times C_{root})} \quad (4)$$

where, $w_{leaf,\ stem,root}$ is the weight (either dry or wet) of a leaf, stem or root (kg), and $C_{leaf,stem,root}$ (background subtracted) is the mass concentration of NPs (m/m) in leaf, stem, or root (i.e., mg/kg). Eq. 3 is used for foliar application, while Eq. 4 is for root application. When calculating the *TE* from previously published reports, we assume that the data doesn't include the NPs on the leaf/root surface (i.e., NPs that did not penetrate the plant's epidermis), but rather only the mass of NPs that penetrated the plant. Through comparing the *TE* derived from different studies, we can identify the crucial factors impacting the transport of NPs, such as particle size, surface charge of NPs, plant species and cultivation conditions. In addition, due to a lack of data regarding feeding/injection applications, we did not include it in the *TE* definition or discussion.

3.2.1. NP transport following foliar application

Foliar application (Figure 1D), which has been used to fertilize crops since 1843[40], has been extensively tested as a NP delivery approach for sustainable agriculture. Foliar applications of nano-fertilizer (including macro-nutrients such as P, Ca, Mg, and Fe, and micronutrients such as Mn, Zn, Cu, Mo)[15], functional NPs (such as photocatalytic TiO_2 NPs[164,165]), and antibacterial NPs (e.g., copper oxide[166] and graphene oxide[167]) have all been described in the literature. These NPs were used to facilitate better nutrient uptake, enhance the plant's photosynthetic properties[168,169], and used as antimicrobial agents to combat diseases.

Three NP formulations have been explored in foliar delivery: nano-aerosols, nano-powders and nano-suspensions. Nano-aerosol and nano-suspension spraying onto watermelon leaves successfully introduced gold NPs (20-70 nm) into the plant tissues[170]. The gold NPs were transported throughout the plant (to both stem and roots) 48 h after exposure. Although the *TE* varied (30-70%) among gold NPs with different shapes in both application methods, the small size (at least in one dimension) leads to high *TE*[170]. Moreover, we note some clear differences between the two NP formulations in terms of their uptake and transport in different studies. The direct spraying of aerosolized Fe_2O_3, MgO, ZnO and TiO_2 NPs on leaves under open-air conditions effectively delivered these NPs into watermelon plants, with an estimated *TE* of 89.1%, 55.8%, 47.4%, and 38.8%, respectively, 3 days after a 4 h exposure. In the meantime, the corresponding *TE* of these NPs were 76.7%, 7.7%, 33.09% and 20.49%, respectively, on plants exposed to a nano-suspension spray[43]. Similar to nano-aerosols, nano-powder application also resulted in better NP transport performance in plants compared to nano-suspension. Hong et al. (2014) reported that by simply exposing plants to airborne nano-powders for 15 or 45 minutes in a sealed chamber, 21.4% (17.2% in stem and 4.2% in root) and 19.9% (16.0% in stem and 3.9% in root) of CeO_2 NPs were transported after 72 h in a cucumber plant. In contrast, less than 3% of a CeO_2 NP suspension sprayed onto the leaves of these plants was transported after 18 days of exposure[45]. It is likely that NPs delivered via nano-aerosol and nano-powders can make use of stomata as an entry pathway, and thus have relatively easy access to the plant's vascular system, which facilitates transport. In addition, hydrophobic NPs can better penetrate the waxy cuticle surface[138,171], but it is unclear if they effectively penetrate beyond this layer.

Aside from NP formulations, another important NP-related factor that affects *TE* is the concentration of NPs. It was estimated that at a concentration of 10, 100, and 1000 ppm Fe_2O_3 NPs (nano-suspension), the corresponding *TE* was 76.7%, 45.0%, 30.3%, respectively, in watermelon plants 3 days after exposure, while the total amount of NPs entering the plants under these three conditions remained similar (2.71 mg, 2.87 mg, and 2.64 mg, respectively) [43]. Similarly, increasing Fe_2O_3 nano-aerosol concentrations from 1×10^6 to 5×10^6 NPs/cm^3, the *TE* declined from 76.2% to 35.2%[43]. However, another study from the same group with the same nano-aerosol exposure method reported that increasing TiO_2 NPs concentration from about 5×10^5 NPs/cm^3 to 1×10^6 NPs/cm^3 resulted in a slight increase of *TE* from 54.8% to

61.1%[44]. It is also likely that at low levels of nano-suspension exposure, the *TE* can show a slight increase. For instance, the *TE* of CeO_2 NPs in cucumber plants after 18 days increased from 0.37% to 1.4% when the concentration of the sprayed nano-suspension increased from 40 ppm to 160 ppm[45]. It is possible that higher concentrations can lead to aggregation and deposition of NPs on the leaf surface, in the epidermis, and inside intercellular spaces, and the vascular system, which can limit their uptake and transport. However, we do note a big difference of *TE* from different studies[43–45], and the reason for this difference requires further investigation.

While the ratio of NPs entering the plant to the total NPs applied has been overlooked in previous studies, it is expected that this ratio is small (e.g., 3.3-5.0%[43]), and most foliar-applied NPs remain on the leaf surface. It is currently unclear what drives the uptake of NPs through plant stomata, and why certain plants/NP formulations demonstrate better uptake and transport. Considering the relatively high cost of many NPs, identifying the factors controlling NP uptake from leaves remains an important topic of research, which will likely influence the widespread adoption of this delivery method. It is important to note that the NPs that were taken up by plants via the foliar application route were effectively transported to multiple plant tissues. The potentially high *TE*, along with the ease of application, make the foliar application an attractive delivery route, as long as effective uptake can be guaranteed.

3.2.2. NP transport following root application

Root application (also known as soil drenching) involves the soaking of intact roots (and soil) in a nano-suspension that may contain other constituents, such as nutrients (Figure 1E). Intuitively, this is the most simple and attractive NP delivery method, as irrigation is routinely applied to crops, and is often combined with fertilizer delivery (i.e., fertigation). As a result, root application is the most widely evaluated NP delivery method[149,172–178]. Although mucilage, exudates and the Casparian strip stop the majority of applied NPs from entering the xylem within the experimental timespan[41], NP transport is still observed. For instance, 0.05%, 0.1% and 0.03% of gold NPs with a size of 15 nm, 25 nm, and 50 nm, respectively, were found in the leaves of poplar trees after 6 days of root exposure[150]. Based on this study, and several others, the uptake of NPs through plants roots is size-dependent. Lin et al. found that while natural organic matter coated carbon nanotubes with a hydrodynamic diameter (HD) of 240 nm exhibited virtually no uptake, fullerene C_{70} (bound with natural organic matter) with a HD of 1.2 nm did penetrate roots, and subsequently transported to the stem, leaf, and seeds of a rice plant, with a *TE* 80% and 100% after 2 weeks and 6 months, respectively[176]. While both 7 nm (with a surface potential of -15 mV)[179] and 25 nm (with a surface potential of 34.3 mV in DI water)[161] spherical CeO_2 (in 200-2000 mg/L nano-suspension) resulted in 20-60 mg Ce per kg of leaf or stem in cucumber after 21-day exposure (resulting in a *TE* of 0.3%[179] and 3.0%[161]), no uptake was observed in tomato plants exposed to 50 nm CeO_2 NPs for 5 months (20 mg/L applied twice a week via soil drenching)[180]. Similarly, 61 nm SnO_2 NPs were not able to penetrate tomato roots[180].

However, 67×8 nm rod-shaped CeO_2 NPs, with a surface potential of -22.8 mV (800 mg/kg soil) were taken up by corn plant roots, and were transported throughout the plant, with an average leaf concentration of 1 mg/kg and a *TE* of 8±2% after 84 days of exposure[149]. Zhang et al.[181] also reported that 7 nm CeO_2 NPs led to a significantly higher NP content in cucumber shoots than that of 25 nm NPs after 14 days exposure with concentrations of 2, 20, and 200 mg/L, indicating small size leads to efficient NP transport. These findings imply that the shape and dimensions of NPs impact their uptake by plant roots and their transport to shoots. NPs with at least with one dimension less than 50 nm exhibit better uptake, and based on the literature (summarized in Table 5), NPs below 28 nm exhibit greater transport from the roots. In addition, similar to what was observed during foliar application, at low NP dosages (≤400 mg/L), the *TE* can reach 85%, although some of the reported results may be skewed by the background concentrations of these compounds. At higher NP dosages (≥1000 mg/L), *TE* is typically well below 5% (Table 5). Uptake at high NP concentrations may be limited by homoaggregation between the particles and heteroaggregation between the NPs and soil particles and/or root surfaces[182]. Thus, the concentration of NPs used during soil drenching has a strong influence on *TE*[150].

Aside from the size and concentration of NPs, surface charge and surface coatings are important factors to consider during NP uptake and transport in plants[183]. Zhu et al.[148] comprehensively investigated the impact of surface charge (derived from coated organics) on NPs' adsorption on root surfaces, internalization in roots, and transport from roots to shoots. As demonstrated in Table 6 (adapted from Zhu's study[148]), while positive charge resulted in much higher NP adsorption on root surfaces and NP content in roots than negatively charged NPs, the internalization rate and *TE* of positively charged NPs were much lower than those of negatively charged NPs. A recent study also demonstrated that positively charged CeO_2 NPs were more prone to adsorb on root surfaces, while negatively charged NPs showed greater transport capability inside tomato plants (the average *TE* of NPs with +13 mV, -3 mV, and -15 mV were 0.1%, 0.2%, and 1.1% respectively, after a 14-day exposure)[183]. It is likely that the negative charge assists in both apoplastic and symplastic penetration (from the root surface to the vascular system) and transport (from root to shoot). Thus, tuning the NP surface charge via coating with different organics might help control the transport performance of NPs in plants. Notably, in both studies, a nutrient solution was used as the culturing medium, which excluded the impact of soil on NP availability[148,183]. However, due to the negative charge on most soil particles, the total mass of positively charged NPs reaching the root surface might decrease, which may limit the availability of NPs. Since the flowrate of water in the xylem is quite high (which promotes NP transport)[70], the limiting factor for NP transport from roots is the penetration of NPs into the roots. Furthermore, NP transformation has been reported within plants, but our understanding of this process is currently limited[54,161]. For example, the impact of organic corona formation has not been investigated in plants.

Table 5. Experimental conditions, NP content in different tissues and calculated *TE* of NPs in plants from studies utilizing root application

Table 6. NP uptake and transport (from root surface to the inner part of root, and from root to shoot) in 5-day old ryegrass, radish, and pumpkin seedlings, and 9-day old rice seedlings after a 5-day exposure[148]

Since the majority of NPs introduced via soil drenching do not penetrate through the root epidermis, it is unlikely that this delivery method will be widely adopted for the delivery of high-cost NPs that need to reach other parts of the plant to be effective. However, root application is likely an effective method for introducing nano-sized fertilizer formulations that require delivery to the root environment, as well as nano-sized anti-microbial agents designed to combat pathogenic soil bacteria and fungi[184,185].

3.2.3. NP transport following injection/feeding

Only a few studies have investigated the direct injection and/or feeding (i.e., petiole feeding) of NPs into plants (Figure 1F)[186]. However, it is well-known that injecting and feeding are effective methods of introducing foreign materials into plants[187,188]. Injecting and feeding rely on purposely damaging the outer layer of the plant tissues (e.g., leaf cuticle, tree bark, etc.), and using either gravity, hydrostatic pressure, or diffusion to force compounds into the plant's tissue. Carbon nanofibers (20–25 μm long with a 1-μm base diameter tapering to a <100 nm tip) were developed to deliver biomolecules to *Populus* (cottonwood) through their leaves [189]. In the study, the nanofibers were used to perforate the leaf cuticle, and a solution containing the biomolecules was applied onto the leaf surface. Petiole-feeding, as shown in Figure 1F, involves the trimming of the end of small branches (petioles) and attaching a flexible hose to deliver a solution (or NP suspension) to the wound, typically under gravity (much like an IV bag). Lin et al.[186] reported that petiole-feeding introduced biological compounds (such as mobile RNA molecules, peptides, oligosaccharides and proteins) into dicotyledonous plants within 1-3 h of feeding. A similar petiole feeding method was used to introduce a bioferrofluid (carbon-coated iron NPs in 30 g/L gelatin with 0.45% w/v sodium chloride and 0.21 g/L calcium) into pumpkin plants, and the authors employed a magnetic field to direct the transport of the NPs throughout the plant[190].

Trunk injection (using a hydraulically-actuated injector), which is an effective way to deliver compounds into trees (e.g., citrus[191], apple[153,154], avocados[192], and ash tree[151]), was tested as a delivery method for the systemic introduction of oxytetracycline hydrochloride (OTC; used for controlling bacterial growth). The authors found that OTC was uniformly distributed throughout the tree canopy two days post-injection[191]. Root-feeding facilitated via a special feeding stake (Figure 1E), previously used for liquid nutrient delivery[193,194], may also prove effective for NP delivery. Using the feeding/injection delivery route, large amounts of compounds can be introduced into plant tissues. However, since injection/feeding methods need relatively robust plant structures (e.g., a thick trunk or sturdy branches), they are more suitable for perennial crops, such as trees and vines. In addition, due to the high

particle count and ionic strength around the injecting point, NPs could aggregate to a certain extent, which might impact transport. Given the relatively high cost of nano-formulations, their application in perennial crops may make more economic sense than in annual crops, except in very high-value crops, such as berries.

To date, most studies have focused on how the properties of NPs affect transport, while the influence of the internal structure/environment of plants on NP transport is largely unknown. There is evidence suggesting that the internal environment of plants influences the fate and transport of NPs in plant tissues. For instance, NP aggregates (formed from NPs stabilized with organic coatings) were found inside the vascular structure in the roots and shoots of *Arabidopsis thaliana*[147,195], corn[97], and ryegrass[93]. Based on classical colloidal transport theory, NP transport in plants may be influenced by: 1) the pore size of the pit membrane/sieve plate/cell wall (i.e., size exclusion); 2) the chemical composition of the sap, which can impact NP colloidal stability, aggregation, sedimentation, and dissolution/transformation; and, 3) the sap flow rate and cross-sectional area of the vessels, which determine hydrodynamic conditions. Plant species and growth conditions affect all of the above three parameters, so they play an important role in the transport of NPs: different plants have different sap flow rates, sap composition, and pore sizes in their membrane-like structures[63,67,196,197]. Similarly, cultivation conditions, including soil chemistry, nutrients, temperature, CO_2 concentration, light intensity, and humidity, can all impact sap composition[79,198], transpiration rates and sap flow rates[70]. Therefore, we list all the related experimental parameters in Tables 5 and 7 for a better comparison of NP transport in the different studies.

4. Modeling NP transport in plants using classical colloidal transport theory

As demonstrated in section 3, the surface charge, surface coating, and the primary particle size of NPs play an important role in the transport of NPs in plants. However, the underlying mechanisms have not been fully explored. Using the calculated diffusion coefficient for NPs (Eq. S3, in *Supporting Information*), one can estimate the time for NPs to reach the surface of the xylem vessel element or phloem sieve elements from the middle of the cell cylinder (this is assumed to be the longest time). As shown in Figure S3, even with the small diffusion rates (particle diameter of 100 nm; sap viscosity, 3.0×10^{-3} Pa·s) and large size of xylem and phloem cell (15 μm), it takes less than 1.5 minutes for NPs to reach the vessel wall. Therefore, the interactions between NPs and the surface of the plant vascular system are important to consider, as "sticky" conditions within vessel walls can lead to NP deposition on these walls, which would restrict transport. Here, we adopted the classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory to investigate these interactions based on the following assumptions: infinite flat xylem/phloem surface (compared to the size of NPs), uniform and constant surface charge of both NPs and vessels, and no change in xylem/phloem sap composition[199].

4.1 The interaction energy between spherical NPs and xylem/phloem surfaces

The Classical DLVO model includes Lifshitz-van der Waals (U_{123}^{LW}, attractive energy, Eq. 5) and electrostatic (U_{123}^{EL}, repulsive energy, Eq. 6) interactions between the NPs and the plant vessel surfaces (Eq. 7)[95].

$$U_{123}^{LW} = -\left(\frac{Ar}{6h}\right)\left(1 + \frac{14h}{\lambda}\right)^{-1} \quad (5)$$

$$U_{123}^{EL} = \pi\varepsilon_r\varepsilon_0 r\left(2\zeta_1\zeta_2 \ln\left(\frac{1+e^{-\kappa h}}{1-e^{-\kappa h}}\right) + \left(\zeta_1{}^2 + \zeta_2{}^2 + \right)\ln\left(1-e^{-2\kappa h}\right)\right) \quad (6)$$

$$U^{DLVO} = U_{123}^{LW} + U_{123}^{EL} \quad (7)$$

where A is Hamaker constant (typically set as 10^{-20} J for NPs)[114,200], λ is the characteristic wavelength of the dielectric (typically taken as 100 nm), ε_r is the dielectric constant, ranging between 20 to 40 for xylem/phloem sap (pure water is around 80)[201], ε_0 is the vacuum permittivity (8.8541817×10^{-12} F/m)[202], r is the radius of spherical NPs (nm), h is the separation distance between the NP and the lumen surface (nm), ζ_1 and ζ_2 are the surface charge of a NP and xylem/phloem (mV), respectively, and κ is the Debye-Huckel parameter, which can be calculated via Eq. 8[95],

$$\kappa = \sqrt{\frac{e^2\sum n_i z_i^2}{\varepsilon_r\varepsilon_0 kT}} \quad (8)$$

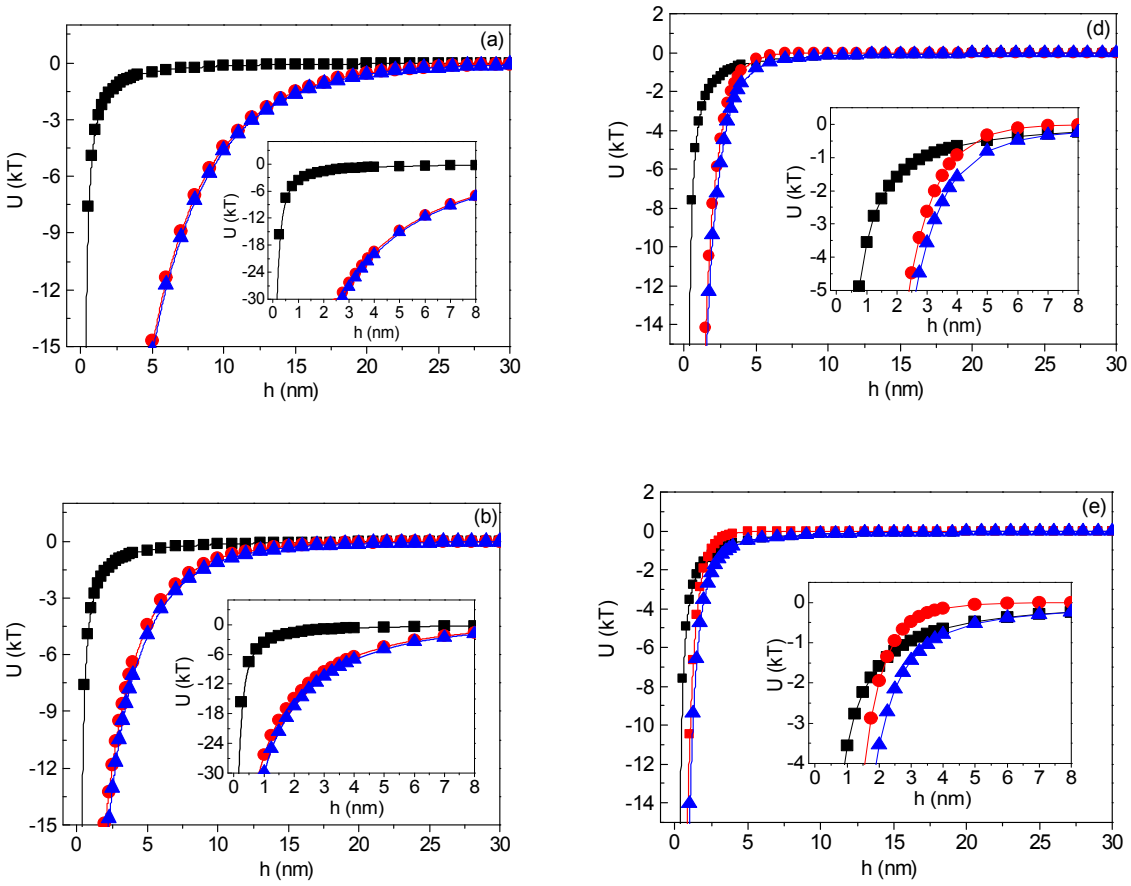
Where e is the electron charge, n_i is the number concentration of ion i, and z_i is the valence of ion i.

This DLVO model leaves out the Born repulsion and acid-base interactions. We calculated the Born repulsion and found that it was several orders of magnitude lower than Lifshitz-van der Waals forces, and so we neglected this aspect from the model. Although acid-base interaction can impact NP deposition and transport[203–205], we were not able to incorporate it into the model due to lack of information on the surface characteristics of vessel and sieve elements. However, we were able to make reasonable assumptions regarding the surface potential of xylem/phloem vessels based on previous studies: in general, the surface of plant cell membranes is negatively charged (as the surface potential of the main components, cellulose fibers and lignin, are -15 mV and -45 mV, respectively), and this charge can be enhanced on the xylem surface[206,207]. Based on previous studies, the surface potentials of xylem vessels were -89.9 mV in the root of *Trifolium repens* L. (clover), and -89.9 mV and -107 mV in the roots of *Lolium perenne* L (ryegrass)[208,209], while the surface potential of phloem elements in *Salix exigua* Nutt. was as high as -155 mV[210]. Thus, for DLVO models, the surface potential of xylem and phloem was set as -90 mV and -150 mV, respectively. At an ionic strength of 0.1 and 0.001 M NaCl, the Debye length ($1/\kappa$) is 1 nm and 10 nm, respectively[211]. Therefore, based on the xylem and phloem sap composition (articulated in Table 2) and Eq. 8, the Debye length for the phloem and xylem was determined to be 1.0 and 5.0 nm, respectively.

Initially, we investigated the influence of NP surface potential on NP- xylem/phloem interactions. As expected, near-neutral (+5 mV) or positive (+35 mV) potentials resulted in attractive interactions between NPs and xylem/phloem surfaces (thus limiting NP transport in vascular system); negative surface potential (-35 mV) on NPs lead to an energy barrier (repulsive force) (Figure 2). This implies that positively charged NPs will likely deposit on cell walls while negatively charged NPs will likely experience better transport throughout the plant, as they have a reduced tendency to stick to vessel walls. Favorable transport of negatively-charged NPs was indicated by high *TE*, compared to the *TE* of positively charged NPs (Table 6). Also, these findings are in line with most experimental results reported in the literature and summarized in Table 7. For instance, polyacrylic acid-ethylene glycol (PEG) modified quantum dots (QDs) (-26.3 mV) transported at a rate of 0.9/0.5 mm/min in the vascular system of young/old leaves, respectively, in 4-week old *Arabidopsis* (rockcress). The PEG-modified QDs NPs did not aggregate in the vascular system. In contrast, polyethylenimine (25.7 mV) and poly (maleic anhydride-alt-1-octadecene)-polyethylene glycol (-6.5 mV) coated QDs traveled much slower, homoaggregated in the vascular system, and only transported a short distance[195]. Similarly, negatively (mercaptosuccinic acid) charged QDs traveled 10 mm (in the stem segments of onion, ryegrass and chrysanthemum) while positively charged (glycine, cysteine or amine modified) QDs traveled less than 3 mm in the vessels after 74 h[147]. It was also reported that glycine and arginine modification (which impart negative potentials) enabled 15 nm ZnS/CdS QDs to travel from the root to shoot in *Poa annua* after 24 h, while the positively charged chitosan-modified QDs did not. Although negative potentials substantially reduce the adsorption of NPs on root surfaces (compared to that of positively charged NPs) [212], they don't necessarily cause the decline in shoot content of NP resulting from the enhanced transport from root to shoot (in some studies, NP content in shoots was even improved). For instance, a negative charge on Au NPs reduced adsorption 30-60 fold, compared to that of positively charged NPs on root surfaces of ryegrass, radish, pumpkin, and rice, whereas the NP content in shoots still saw a significant increase[148]. Spielman-Sun et al.[213] also reported that while NP content in roots treated with negatively charged CeO_2 NPs was one-fifth of that of positively charged NPs, its shoot content was twice the positively charged NPs' shoot content. A similar phenomenon was observed in another study[111], where a gum Arabic coating (negative charge) reduced the adsorption of CeO_2 NPs on pumpkin roots by a factor of 7 (from 96.7 g/Kg dry root to 13.2 g/kg dry root), but the shoot content only decreased by a factor of 5 (from 17.8 mg/kg dry shoot to 3.7 mg/kg dry shoot), compared to that of bare CeO_2 NPs. In addition to the studies mentioned here, several other studies also reported that a negative charge is favorable for NP transport[30,152,158,214].

As seen in Figure 2, the high ionic strength in phloem sap compresses the electrical double layer, substantially reducing the range of interactions compared to that in the xylem. In the meantime, the abundant organic materials in the phloem may adsorb onto NP surfaces, and this adsorption can generate steric barriers and hydration forces, both of which alleviate homoaggregation of NPs and the heteroaggregation between NPs and phloem surfaces[95,115].

In addition, the adsorption of organic materials can modify the surface potential of NPs, which changes the electrostatic interactions between neighboring NPs and the phloem surface. However, the ability of organic materials to stabilize the NPs depends on water chemistry (solutes composition) and the characteristics of the NPs and the organic materials themselves[32]. Thus, it is important to consider the impact of surface coating of NPs on the interaction between NPs and phloem element surfaces. Given the wide variety of organic materials in plants and the variation among different plants[72,75,76,215], efforts are needed to fully understand the impact of plants' organic materials on fate and transport of NPs in phloem.



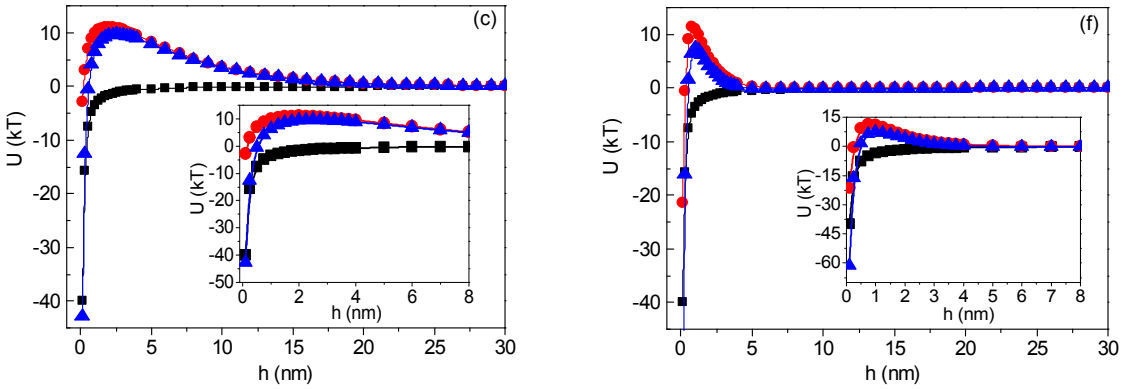


Figure 2. DLVO interaction energy between a 10 nm model NP and xylem (ζ_2 = -90 mV) and phloem (ζ_2 = -150 mV) surface. (a), (b) and (c) in xylem: ζ_1 of NP = +35, +5 and -35 mV; (d), (e) and (f) in phloem: ζ_1 of NP = +35, +5 and -35 mV; ■, U^{LW}, ●, U^{EL}; ▲, U^{DLVO}; insets: DLVO interaction energy within a separation distance smaller than 8 nm.

NP size also has an impact on the interaction between NPs and the surface of the xylem/phloem. We further calculated the DLVO interaction energy between xylem and phloem surfaces and negatively charged NPs with different sizes, as detailed in Table 8. In general, as the NP size decreases, both the secondary minima and repulsive barrier decrease substantially, indicating that small NPs might be favorable for transport in plants.

The presence of a secondary minima in the interaction energy calculations indicates the potential for NP adsorption on vessel walls (Figure 2). To determine whether the adsorption of negatively charged NPs (with different sizes) is reversible or irreversible, we used a CeO_2 NP (ζ_1, -35 mV; ρ =7.22×10^3 kg/m^3) as a model (as this NP is often reported in the literature[149,161,174,180,214,216,217]), and compared the secondary minima to the kinetic energy of NPs in the xylem and phloem. The dimensionless kinetic energy (U^k) can be expressed as[114]:

$$U^k = \frac{mv^2}{2kT} \quad (9)$$

where m and υ are the mass (kg) and velocity (m/s) of the NP, respectively. We obtained the (most likely) minimum and maximum value of kinetic energy for NPs during transport in phloem and xylem. The comparison between the secondary energy minima and kinetic energy is presented in Figure 3. In the phloem, the secondary minima are much greater than the kinetic energy of NPs, confirming that NP deposition on the phloem surface can be caused by the shallow secondary minima (although there is a strong repulsive force between the NP and the phloem surface at h = 1 nm). While the repulsive force prevents the permanent attachment of NPs on the phloem surface, this adsorption can still retard the transport of NPs in the phloem to some degree[218]. In the xylem, when r < 50 nm, the secondary minima are also greater than the kinetic energy of NPs, and the secondary minima might cause weak adsorption on a surface. When 50 < r < 100 nm, the magnitude of the secondary minima is close to the kinetic energy of the NPs, implying that the adsorption is

unstable, where a slight increase in kinetic energy (e.g., homoaggregation of NPs, increase of sap velocity) or decrease in the secondary minima (e.g., surface charge increase derived from pH or ionic strength change) can remobilize these adsorbed NPs. When r > 100 nm, the adsorption of NPs caused by secondary minima becomes less likely since the kinetic energy exceeds the depth of the secondary minima. However, the kinetic energy is still much smaller than the repulsive barrier, which prevents the permanent adsorption of NPs on the xylem surface.

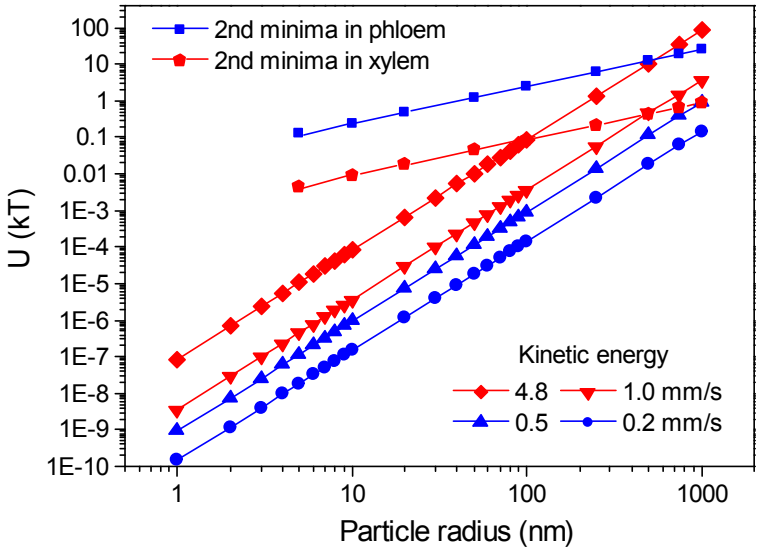


Figure 3. Kinetic energy and secondary minima of CeO_2 NPs in xylem and phloem with different sizes under different flow velocities (Hamaker constant $A=10^{-20}$, λ=100 nm, ε_0 =8.8541817×10^{-12} F/m, ε_r= 35, ξ_1 = -35 mV, ξ_2 = -50 mV, κ=1.0 (phloem)/0.2 (xylem))

However, it should be acknowledged that there are some limitations to the DLVO model: the existence of abundant organics in sap could modify the surface of NPs, which might result in the failure of the model as steric repulsion or acid-base interactions between NPs and phloem/xylem surfaces (which are not incorporated in the model) become significant.[95] Furthermore, the model assumes that NPs are spherical and carry a central charge, and thus, change in NP shape (or charge distribution) will also reduce the accuracy of the results;[219] in addition, the high salt levels in sap might significantly compress the electric double layer, and thus leads to the failure of the model.[110]

5. Future research needs

Research on the application of NPs in sustainable agriculture, though still in the nascent phase, can be classified into two different categories: one group focuses on the performance (e.g., NP-based antimicrobial agents) of NPs in plants[15,220–223] while the other focuses on the distribution of NPs in plants[148,152,161,224,225]. While the former group often does not pay

enough attention to the transport of NPs, the latter typically does not relate NP transport to plant physiology. There is a lack of investigations that comprehensively examine the uptake and behavior (dissolution, aggregation, transport) of NPs with different sizes, surface modifications, and elemental composition in plants, while considering plant physiology. Based on this, there is a need to intensify research in the following areas:

a) Understanding of plant morphological and physiological characteristics before and after NP application. For example, the pore size of porous membranes in plants, sap flow rates in xylem and phloem, connections between xylem and phloem, and sap composition. Moreover, it is of great importance to realize that these factors differ from plant to plant, and between different parts of the same plant (e.g., root tips are different than stems, which are different from nodal regions and old/young leaves), which can impact the transport of NPs.
b) Identification of the key factors that determine the penetration of NPs into plants and their behavior in plants. It is important to understand how to further direct NPs to their intended final destination, where they are expected to play a specific role. After penetrating through the epidermis, NPs have to cross the cell wall and/or membrane to reach the xylem and the phloem through passive/active transport or endocytosis. While it's clear that size determines the diffusion of NPs through porous structures, our understanding of active transport and endocytosis is still poor. First, different NPs have specific affinities to nutrients, such as Si, P and Ca[226], and these NP/nutrient hybrids can be thought of as nutrient bombs for plants growth. It is possible that transporters for these nutrients on cell membranes facilitate the symplastic transport of NPs[227]. Second, endocytosis involves adsorption and internalization, both of which could be impacted by surface charge and/or surface functional group on NPs. However, it's still unclear how these surface characteristics affect adsorption and internalization.
c) Understanding the behavior of NPs in phloem and xylem. In general, sap in plants consists of abundant inorganic and organic substances. Although it is widely accepted that the aggregation, dissolution and transformation of NPs is controlled by water chemistry[33], it remains unclear what are the integrative impacts of the inorganic solutes, high ionic strength, high concentration of organic materials (such as sucrose and amino acids) in sap. The knowledge in this area can contribute to the safer design of NPs for sustainable agricultural practice, such as drug/gene delivery and/or specific part (leaf/root) enhancement.
d) Research on the interactions between xylem and phloem. So far, the transport of NPs has been studied separately in the phloem (downward) and in the xylem (upward). However, plant physiological studies[228,229] have shown that root tips[90], the nodal region[230–232], and the end of leaf veins[233] all have high interconnectedness between phloem and the xylem vessels. Internal circulation between the xylem and phloem at the root tip and endosperm could account for approximately 45% of total flow in the xylem, which means NPs could possibly circulate between the vessels[90]. At the nodal region, where intensive apoplastic

solute exchange between the xylem and the phloem occurs (due to the presence of vascular transfer cells)[230–232,234] extensive NP exchange may occur. In the leaf, the distance between xylem and phloem is a few microns, but there is an appreciable pressure gap between them (-2 MPa in xylem *vs.* +1 MPa in phloem), with part of the water from the xylem directly entering the phloem, with the potential to carry NPs between the two streams[229].

e) Determining potential NP sinks. While NPs can transport throughout the plant, the transport capacity of the phloem and the xylem are different. It remains largely unknown how the downward flow, upward flow and interflow affects the overall fate of NPs. Thus, we need to understand if potential NP sinks (e.g., leaves, roots, fruit) can be controlled. Here, NP composition can play an important role. New plant growth (i.e., young tissue) requires a large amount of particular nutrients, such as potassium and phosphorus[235]. Modifying NP surfaces with essential elements may result in high transport and accumulation of these NPs in young tissue.

f) Careful monitoring and controlling of experimental conditions are critical for NP transport studies and applications. Light intensity, CO_2 concentrations, humidity, temperature, irrigation frequency, nutrient concentrations in culturing media, and even the plant growth stage can all impact both sap flow and sap composition, which further affects the fate and transport of NPs. However, so far, there are limited studies that have investigated the impact of these parameters on NP transport.

6. Conclusion

In summary, NPs have the potential of playing an increasingly important role in sustainable agriculture, although significantly more research is needed to investigate the many pitfalls associated with this technology. In this review, we reported that:

a) For foliar and root applications, the majority of NPs do not enter the plant, while a small fraction of NPs are trapped in the epidermis, and the limited number that do penetrate the plant are sometimes effectively transported throughout the plant, although the form of these NPs is currently unknown (i.e., it is unclear if these NPs are modified by interacting with various plant components). These two methods could be employed for leaf or root enhancement to achieve a particular purpose, such as fertilization and inhibition of bacteria/fungi. Conversely, leaf/petiole/root feeding or trunk injection could potentially deliver a relatively large number of NPs into the plant, which could be beneficial for whole plant activity, such as genetic modification.

b) Foliar application is a more efficient NP delivery method, compared to root application. Also, the *TE* of NPs through foliar application is higher than in root application, suggesting the phloem is a viable conduit for NP transport.

c) Basing on what we've learned from studies about the fate and transport of NPs in environment, besides the size exclusion limit imposed by the plant's membrane structure (pit membrane in the xylem or the sieve plate in phloem), sap composition, sap pH, sap flow velocity, and sap conducting area are important when considering the aggregation,

dissolution, transformation and deposition of NPs in plants.

d) A DLVO model shows that the surface charge of NPs strongly affects their transport. Near-neutral or positively-charged NPs (without steric stabilization) do not transport efficiently (due to deposition on vessel walls), while the transport of negatively-charged NPs is more favorable. Any adsorption of negatively charged NPs on xylem or phloem surfaces is likely reversible, which makes the transport of these NPs more effective.

7. Acknowledgements

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Table 1. Pore size of sieve plates in phloem and pit membranes in xylem [65–67]

Plant	Sieve plate pore diameter (μm)	Plant	Pit membrane pore diameter	
			D_m (nm)	D_e (nm)
Cucurbita maxima	5.08	*Acacia pataczekii*		106 ± 21
Phaseolus vulgaris	1.46	*Acer negundo*	80	148 ± 52
Solanum lycopersicum	1.22	*Acer pseudoplatanus*	189	
Ricinus communis	1.04	*Aesculus hippocastanum*	179	186 ± 37
Phyllostachys nuda	1.22	*Betula ermanii*	78	
Festuca arundinacea	0.6	*Betula nigra*	100	
Beta vulgaris	0.2	*Betula pendula*	234	340 ± 152
Glycine max (petiole)	0.7	*Corylus avellana*	190	
Glycine max (stem)	1.2	*Fraxinus americana*	43	152 ± 8
Glycine max (root)	1	*Ilex aquifolium*	124	
Gossypium barbadense	1	*Populus fremontii*	195	254 ± 141
Sabal palmetto	1.9	*Salix alba*	186	203 ± 29
Yucca flaccida	0.52	*Sambucus nigra*	112	
Robinia pseudoacacia	2.5	*Sophora japonica*	63.3	114 ± 8
Tilia americana	1.2	*Ulmus* americana	59.91	
Ulmus americana	4	*Ulmus procera*	225.2	
Vitis vinifera	1.4	*Vitis vinifera*	39.33	

Note: *Amborella trichopoda* Baill*; Belliolum gracile* A.C.Sm*; Belliolum haplopus* (B.L.Burtt) A.C.Sm*; Bubbia oligocarpa* (Schltr.) B.L. Burtt; *Bubbia semecarpoides* (F.Muell.) B.L.Burt*; Drimys brasiliensis* Miers*; Drimys winteri* J.R.Forst. & G. Forst*; Pseudowintera colorata* (Raoul) Dandy*; Tasmannis lanceolata* Baill*; Tetracentron sinense* Oliv; *Trochodendron aralioides* Siebold & Zucc: 79 ± 54 (D_{max} = 319, D_{min} = 13) nm of pore size on pit membrane. D_m and D_e were estimated by SEM and air-seeding threshold experiments, respectively. Due to the different measurement methods, there are some discrepancies in pore sizes of pit membranes. D_{max} and D_{min}, correspond to the maximum and minimum pore sizes, respectively.

Table 2. Sap composition of xylem and phloem in different plants [70,80]

Solute \ Plant	xylem			phloem		
	Ricinus communis (mM)	*Lupinus albus* (mM)	*Banksia prionotes* (mM)	*Ricinus communis* (mM)	*Lupinus albus* (mM)	*Banksia prionotes* (mM)
sucrose	/	0	0	433 ± 70	652	537 ± 68
potassium	5.21 ± 4.97	9	1.65 ± 0.19	67.1 ± 15.3	67	17.1 ± 2.3
calcium	1.75 ± 1.71	0.4	0.46 ± 0.1	1.21 ± 0.5	1.5	6.1 ± 1.0
magnesium	1.14 ± 1.07	0.7	0.43 ± 0.07	3.71 ± 2.48	3.4	12.2 ± 2.4
sodium	0.65 ± 1.93	/	1.50 ± 0.15	6.96 ± 13.59	/	30.9 ± 3.5
phosphate	0.7 ± 0.72	1.3	0.054 ± 0.01	6.56 ± 3.48	10	0.83 ± 0.16
nitrate	7.16 ± 9.18	0	0.003 ± 0.004	0.59 ± 0.97	/	0.29 ± 0.09
sulfate	0.64 ± 0.93	0.3	0.60 ± 0.24	1.29 ± 1.03	4.3	8.7 ± 1.6
chloride	1.25 ± 1.83	/	2.40 ± 0.9	12 ± 12.8	/	60.1 ± 9.6
malate	0.34 ± 0.69	6	0.61 ± 0.28	8.02 ± 5.23	5	9.8 ± 1.8
succinate	/	3.4	/	/	42	/
total amino acid-N (amino acid nitrogen)	4.9 ± 6.34	7.2	0.42 ± 0.07	67.5 ± 44.6	41	5.8 ± 1.2

Note: /, not provided; standard deviation was provided when it was available.

Table 3. Sap flow rate and volume flow in phloem and xylem[89–94]

	Phloem velocity (mm/s) (volume flow (mm^3/s))		Xylem velocity (mm/s) (volume flow (mm^3/s))	
Plant	Night	Day	Night	Day
poplar (3-week old)	0.24 ± 0.02 (0.87 ± 0.14)	0.34 ± 0.03 (0.91 ± 0.09)	0.60 ± 0.02 (4.7 ± 0.30)	1.70 ± 0.08 (17.50 ± 1.20)
tomato (3-week old)	0.35 ± 0.05 (0.08 ± 0.02)	0.40 ± 0.04 (0.12 ± 0.02)	1.80 ± 0.30 (2.1 ± 0.3)	4.8 ± 0.70 (7.8 ± 0.8)
castor bean (3-week old)	0.25 ± 0.03 (0.23 ± 0.08)	0.25 ± 0.04 (0.23 ± 0.08)	1.2 ± 0.4 (0.8 ± 0.2)	3.7 ± 0.5 (4.0 ± 0.4)
tobacco (3-week old)	0.34 ± 0.06 (0.13 ± 0.06)	0.34 ± 0.06 (0.13 ± 0.06)	0.6 ± 0.1 (0.2 ± 0.04)	1.9 ± 0.4 (1.6 ± 0.2)
castor bean (6-day old)		0.58		0.47
Tomato (seven-leaf stage)				(5.0 ± 2.0)[a]
Ligustrum japonicum Thunb.[b]			(5.56) [c]	(16.7)[c]
Ricinus communis L. (45-55d)	0.27 ± 0.06	0.27 ± 0.06		2.2
Angiosperm tree		0.16		

Note: [a], 0.3 MPa, 9 mm diameter, changing the pressure results in the change of flow rate; [b], 0.67 m tall, stem diameter of 0.01 m and leaf area 0.23 m^2; [c], normalized with leaf surface area (stem diameter 10 mm)

Table 4. Sap conducting area (mm^2) adapted from the study carried out by Windt et al.[89]

	Xylem		Phloem	
Plant	Day	Night	Day	Night
poplar (3-week old)	11	8	2.6	3.8
tomato (3-week old)	1.8	1.5	0.6	0.5
castor bean (3-week old)	1	0.7	0.9	1
tobacco (3-week old)	0.5	0.3	0.7	0.7

Table 5. Experimental conditions, NP content in different tissues and calculated *TE* of NPs in plants from studies utilizing root application

NPs	Size (nm)	Surface potential (mV)	Experiment conditions	Content in different tissue (mg/kg)	*TE*	R
CeO_2	25.2±2.3	34.3±5.1	Third leaf stage cucumber seedlings were treated with NPs suspension by a split-root exposure for 3 days	200/2000 ppm: 200/750 (untreated root), 8000/17000 (treated root), 20/60 (shoot)	2000 ppm, 3.6%; 200 ppm, 2.4%.	161
CuO	20-40	-9.76	Third leaf stage corn seedlings were exposed to 10-100 ppm (nutrient solution) for 15 days	100 ppm exposure: root/shoot, 0.5/0.065.	10/100 ppm, 41.5%/33.1%*;	54
ZnO	20	-2.3±0.6	21-day old ryegrass seedlings were exposed to up to 1000 ppm (nutrient solution) for 12 days	1000 ppm: 40 (root), 0.25-1.36 (shoot); control group with Zn^{2+} treated system, 0.25-19.1 (shoot)	1000 ppm, 2.4%.	162
CeO_2; ZnO	67×8; 24	-22.8±4.5; -15;	Corn plants were exposed to 400/800 mg Ce or Zn/kg soil from germination for 84 days	800 mg/kg, root/stem/leaf: 395.9/2.81/1.09 (CeO_2), 1073/300/183 (ZnO)	CeO_2, 10.4%/6.0%; ZnO, 68.7%/73.1%*	149
CeO_2	7.0	32.9±8.5[a];	13-day old cucumber seedling were exposed to 2000 ppm (nutrient solution) for 21 days	Leaf/stem/root, 35/35/45000. NP transformation was identified.	0.3%	179
CeO_2; Fe_3O_4; SnO_2; Ag; Co; Ni; TiO_2	50-105; 20-30; 61; 1-10; 28; 62; 20-160	/	2-week old tomato seedlings were grown on soil spiked with 20 ppm NP suspension once per week for 13th weeks, then twice until 130 days	No obvious CeO_2 and SnO_2 detected in plant; stem/leaf/root 0.2/1.1/2.6 (Ag), 0.4/1.2/3.7 (Co)	nAg, 88.4%; nCo, 82.3%.	180
TiO_2; ZnO	25+3.5	-22.5±3.4; -29.7±5.8	14-day-old tomato plants exposed to 0-1000 mg/L irrigation for 66 days	Leaf/shoot/root: 30/80/45 (TiO_2), 30/60/45 mg (ZnO).	250 ppm: ZnO, 84.2%*; TiO_2, 85.2%.	44

Note: * these calculated data may not be accurate due to the high background metal content in plants; Size: xx/xx means single particle size/hydrodynamic size (otherwise, it's single particle size); a, surface potential in DI, and surface potential in nutrients solution becomes -15.1 ± 3.5 mV; /, not provided

Table 6. NP uptake and transport performance (from root surface to the inner part of root, and from root to shoot) in the 5-day old ryegrass, radish, and pumpkin seedlings and 9-day old rice seedlings after a 5-day exposure[148]

Plant	Au (+24 ± 5 mV)				Au (-2 ± 1 mV)				Au (-17 ± 6 mV)			
	R_{in} (mg/kg)	R_{in}/R_{tot} (%)	S_{in} (mg/kg)	*TE* (%)	R_{in} (mg/kg)	R_{in}/R_{tot} (%)	S_{in} (mg/kg)	*TE* (%)	R_{in} (mg/kg)	R_{in}/R_{tot} (%)	S_{in} (mg/kg)	*TE* (%)
Rice	40 ± 10	13 ± 3	1.1	2.68	14 ± 2	10 ± 2	2.0	14.89	7 ± 3	42 ± 15	3.0	28.06
Ryegrass	350 ± 100	25 ± 8	2.0	0.49	220 ± 40	22 ± 4	1.6	0.74	14 ± 2	86 ± 10	7.0	35.06
Radish	900 ± 200	25 ± 6	0.5	0.19	670 ± 90	77 ± 10	1.0	0.19	250 ± 50	49 ± 11	0.9	0.39
Pumpkin	51 ± 8	23 ± 4	0.2	0.29	59 ± 5	26 ± 2	0.2	0.49	35 ± 9	43 ± 12	0.1	0.74

Note: R_{in}, S_{in}: Au content inside root and shoot; R_{tot}: Au content on root, including Au inside root and on root surface. R_{in}/R_{tot}, internalization

Table 7. Experimental conditions and transport of NPs with surface modification in plant (both foliar and root application)

NPs	Size & surface	Plant/growth media/exposure time	Uptake and transport pf NP in plants	R
CdSe/ZnS QD	12×6.3 nm; COOH-polymer: -10 ~ -20 mV	3-4 week old *A. thaliana*; QDs in 1/4 strength HS; 7-day exposure;	Most of the QDs adsorbed on the root cell wall. No obvious transport evidence was observed.	236
Au	5/20 nm; PEG: neutral	Barley seedlings; NPs in 1/16-strength HS; 7-day exposure.	NPs (5 ±1.5 nm) did not enter the roots from the external solution. Injected NPs did not move to adjacent cells.	30
ZnS/CdSe QD	<15 nm; Gly-Arg (negative); chitosan-(positive);	30-day old mycorrhizae; soil spiked with QDs in 1/4 strength HS; 24-hour exposure;	ONLY Gly-Arg-QDs appear in tube-shaped vacuoles within hyphae, vascular tissues within roots, and chloroplasts within shoot cells (*Poa annua*).	145
ZnS/CdS QD	5−12 nm; OL-, PEG-COOH-, PEG- NH_2-: −4.3, −21.6, and 17.1 mV	12-month mangrove seedlings; QDs in 1/4-strength HS; 7-day exposure;	OL-QDs were more easily transported to xylem/phloem than located on the epidermal tissues. The retention of QDs on the epidermal tissues was affected by the composition of mangrove root, the endocytosis, and the charge of QD coating.	237
CdSe/ZnS QDs	6.5 nm; Gly-, Cys-, Am-(positive), and MSA-(negative)	12-week old ryegrass and 10-week old onion; QDs in MQW; 48-hour exposure;	Gly-, Cys- and Am-QD travels < 3 mm in vessels while MSA-QD travels 10 mm after 74 h (in stem segments). MSA-QDs aggregated less. No QDs were taken up ryegrass, onion, and *Arabidopsis thaliana*.	147
Cd/Se QD	<5 nm; PAA-EG-, PEI-, and PMAO-PEG-QDs: -26.3, 25.7, -6.5 mV	4 weeks old *Arabidopsis*; QDs in 1/16-strength of HS; 7-day exposure;	PAA-EG QD traveled at 0.9/0.5 mm/min in Y/O leaf; PEI QD traveled at 0.45/0.25 mm/min in Y/O leaf. PEI- and PMAO−PEG-QDs aggregated in plant.	195
Au	1-3 nm; TTMA-, TEGOH-, TEGCOOH-: 24±5, -2±1,	9-day-old rice seedlings; 1.6 mg Au/L (nutrient solution), 5-day exposure	Au content in rice root: TTMA-Au> TEGOH-Au > TEGCOOH-Au, but this order was reversed in shoots.	152

	-17±6 mV;			
Fe_3O_4	10-20 nm; AC-PEG-N-A: -44 mV to -55 mV	9-day old lettuce seedlings, QDs suspension (DI), 24-h exposure	Uptake and transport of NP was size-dependent. >80% NPs were contained in the epidermis of root, and 3%-19% NPs were in the cotyledons (enriched at apex).	158
CeO_2	8±1 nm; Pristine, alginate-, -0.62±2.9, -92.5±0.5 mV	Corn plants, organic enriched or unenriched soil (100, 200, 400, 800 mg NP/kg), 30-day exposure	Both organic in soil and alginate increased NP content in root. Increasing NPs dosage in soil resulted in high NP content in shoot. NPs aggregates were found in vascular tissue.	68
CeO_2	17-100 nm. Pristine, FA-, GA-NPs, -12.3, -22.5, -18.2 mV	21-day old wheat and pumpkin, 100 ppm NPs (HS), 8-day exposure.	Surface modification reduced NP adsorption on root surface. NPs traveled to shoot in pumpkin but not in wheat.	111
CeO_2	3.0±1.0 nm; citrate acid, 40±5 mV	14-day old fescue and tomato, 50 mg CeO_2/kg soil, 8-day exposure.	Clay enhanced the retention of NP and thus reduced Ce uptake, whereas the organic matter in soil and citrate acid on NP surface enhanced Ce uptake.	214

Note: quantum dot (QD); Polyacrylic acid-ethylene glycol (PAA-EG); Polyethylenimine (PEI); Poly (maleic anhydride-alt-1-octadecene)-polyethylene glycol (PMAO-PEG); Glycine and arginine (Gly-Arg); Polyethylene glycol (PEG); Glycine (Gly); Mercaptosuccinic acid (MSA); Cysteine (Cys); Amine (Am); Azide functionalized catechol PEG (AC-PEG-N-A); Gum Arabic (GA); Fulvic acid (FA); HS, Hoagland nutrient solution; MQW, milli-Q water; DI, Deionized water.

Table 8. Secondary minima and repulsive barrier for NPs with different sizes from DLVO interaction energy calculations.

		h (nm)	NP radius (nm)							
			2.5	5	10	20	50	100	250	500
xylem	Repulsive barrier (kT)	2.5	2.4	4.8	9.7	19.3	48.3	96.6	241.4	482.8
	Secondary minima (kT)	43	-0.002	-0.004	-0.009	-0.018	-0.045	-0.089	-0.223	-0.446
phloem	Repulsive barrier (kT)	1	1.9	3.7	7.5	14.9	37.3	74.6	186.6	373.2
	Secondary minima (kT)	7	-0.062	-0.124	-0.247	-0.495	-1.236	-2.473	-6.182	-12.364

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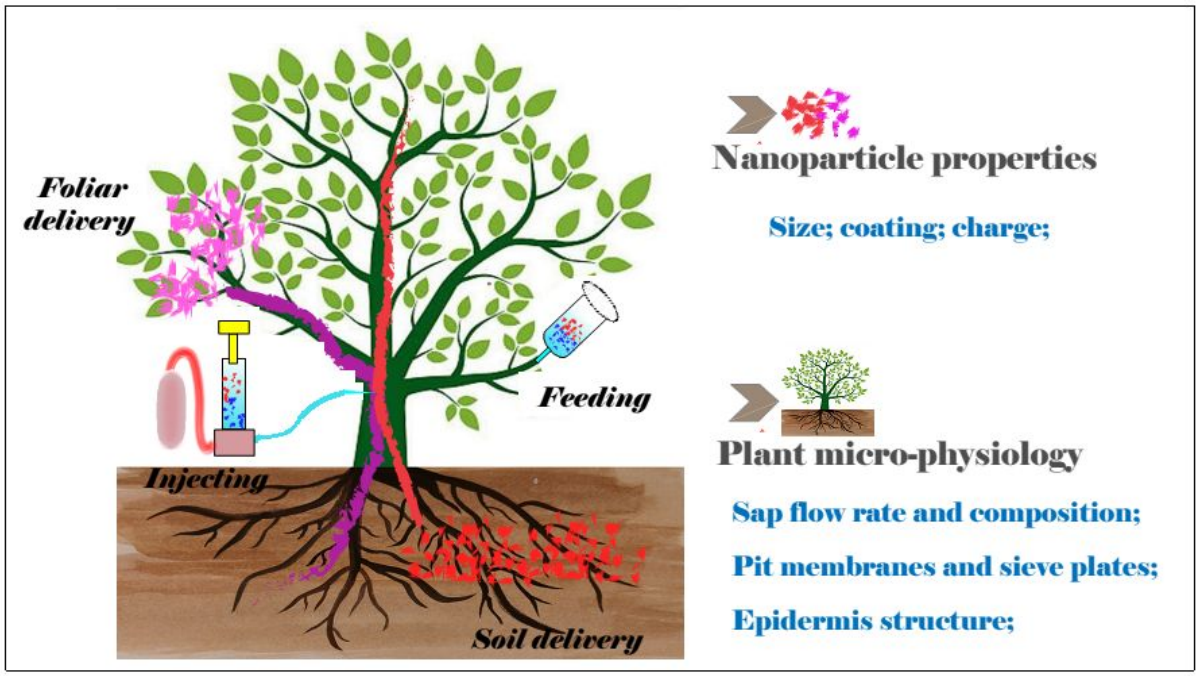
TOC:


Foliar delivery
Feeding
Injecting
Soil delivery
Nanoparticle properties
Size; coating; charge;
Plant micro-physiology
Sap flow rate and composition;
Pit membranes and sieve plates;
Epidermis structure;