



Interaction of Nanomaterials with Plants: What Do We Need for Real Applications in Agriculture?

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OPEN ACCESS

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Specialty section:

This article was submitted to
Green and Environmental Chemistry,
a section of the journal
Frontiers in Environmental Science

Received: 09 February 2017

Accepted: 24 March 2017

Published: 10 April 2017

Citation:

Pérez-de-Luque A (2017) Interaction
of Nanomaterials with Plants: What Do
We Need for Real Applications in
Agriculture? *Front. Environ. Sci.* 5:12.
doi: 10.3389/fenvs.2017.00012

The number of published researching works related with applications of nanomaterials in agriculture is increasing every year. Most of such works focus on the synthesis of nanodevices, their characteristics as nanocarriers for controlled release of active substances, and their interaction (either positive or negative) with plants or microorganisms under controlled conditions. Important knowledge has been gained about the uptake and distribution of nanomaterials in plants, although there are still gaps regarding internalization inside plant cells. Nanoparticle traits and plant species greatly affect the interaction, and nanodevices can enter and move through different pathways (apoplast vs. symplast), what influences their effectiveness and their final fate. Depending on the effect we are expecting for a nanocarrier, the application method might be critical. However, in order to get that research used in the field, some problems must be addressed. First, the cost for escalating the production of nanodevices must be affordable with the current production cost of agricultural goods. Second, we need to be sure that a technology is safe before spreading it into the environment. Third, consumers will distrust a technology unfamiliar for them in the same way that happened with transgenic crops. We need to broaden our horizons and start looking for real practical approaches, filling the main gaps that hamper our jump from laboratory research into field applications.

Keywords: nanoparticles, smart delivery systems, nanocarriers, nanoagriculture, crop production

IT'S PLENTY OF ROOM OUT THERE

It is possible that Richard Feynman was not aware of the catalytic events he was starting with his lecture “There’s plenty of room at the bottom” back in 1959 (Feynman, 1960). More than fifty years later, nanotechnology is starting to affect our lives and will shape the nearby future of many disciplines such as material sciences, electronic, medicine or pharmacology. But what about agriculture? Will this tiny revolution help to solve the problems that agriculture is facing, such as increasing production and reducing negative environmental impacts within a climate change scenario (Baulcombe et al., 2009)? That is something we want to believe in, but science is about facts and we need to work hard in order to prove it.

Agriculture can benefit through the development of more efficient and less contaminant agrochemicals (nanoformulations), devices that help to detect biotic or abiotic stresses before they can affect production (nanosensors), or new techniques for genetic manipulation allowing higher efficiency during plant breeding programs (Pérez-de-Luque and Hermosín, 2013; Fraceto et al., 2016). Because the topic is really broad, in this article we will focus on applications for the synthesis

of a new generation of agrochemicals, either for plant protection or fertilization, using nanocarriers for controlled release and smart delivery systems. The idea is quite simple: nanodevices can help to deliver the agrochemicals in the right place at the right time and to reduce the action of external agents leading to losses by degradation, leaching, run-off, volatilization, etc. The expected effect should be a reduction in the amount of active chemicals incorporated into the plants and soils leading to a reduced negative impact on the environment.

However, a lot of research and knowledge is needed to accomplish those goals. Not only for the development and synthesis of nanocarriers and nanomaterials, but also for studying the interactions of such nanodevices with the plants and the environment. Indeed, it is necessary to study how plants absorb and uptake nanoparticles, how they move inside the plant, and how they interact with the plant cell.

Plant Absorption and Uptake of Nanoparticles

The plant uptake of nanoparticles is affected by several factors related to the nature of the nanoparticle itself, but also with the plant physiology and the interaction of the nanomaterials with the environment (**Figure 1**).

It is clear that nanoparticle traits will greatly influence its behavior, and hence if the plant will be able to absorb it. Size seems to be one of the main restrictions for penetration into plant tissues, and there are some reports about the maximum dimensions that plants allow for nanoparticles to move and accumulate inside the cells, usually with 40–50 nm as a size exclusion limit (González-Melendi et al., 2008; Corredor et al., 2009; Sabo-Attwood et al., 2012; Taylor et al., 2014). Additionally, the type of nanoparticle and its chemical composition is another factor influencing the uptake (Ma et al., 2010; Rico et al., 2011), whereas morphology has also been demonstrated as determinant in some cases (Raliya et al., 2016). Functionalization and coating of the nanomaterial surface can greatly change and alter the properties for its absorption and accumulation by the plant (Judy et al., 2012).

Plant species can differ in their physiology, and such differences result in variations regarding uptake of nanoparticles, as reported for example by Cifuentes et al. (2010), Larue et al. (2012), and Zhu et al. (2012). These works showed how crops species belonging to different botanical families, and exposed to either magnetic carbon-coated, titanium dioxide or gold nanoparticles respectively, presented diverse absorption and accumulation patterns inside the plants. But the ways of application are also crucial in order to determine how effectively a plant will internalize the nanomaterials: roots are specialized in absorption of nutrients and water, whereas leaves are developed for gas exchange and present a cuticle which hampers penetration of substances (Schwab et al., 2015).

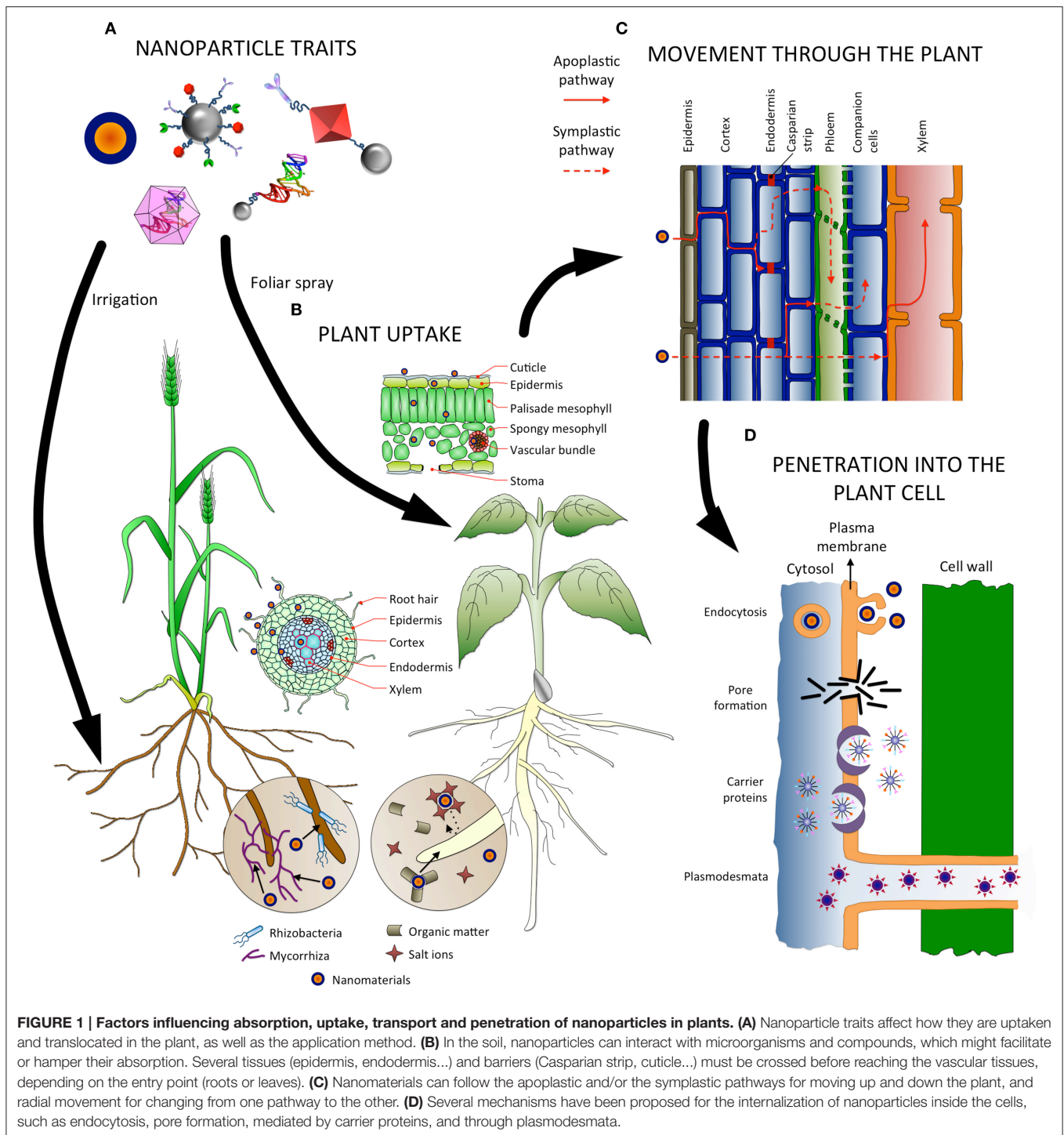
But nanoparticles interact with other components of the environment, and it can affect their properties and their traits for being assimilated by plants (**Figure 1**). For example, humic acids and other organic matter present in the soil can lead to an improved stability and hence a better bioavailability of

nanomaterials, whereas salt ions might induce precipitation and trigger a contrary effect (Navarro et al., 2008). Even more, the presence of other organisms, such as bacteria and fungi, influences the plant uptake of nanoparticles, mainly if those microorganisms establish symbiosis with plants as in the case of mycorrhizal fungi (Feng et al., 2013; Wang et al., 2016).

Movement of Nanoparticles inside Plants

Once the nanoparticles penetrate into the plant, there are two ways for them to move through tissues: the apoplast and the symplast (**Figure 1**). Apoplastic transport takes place outside the plasma membrane through the extracellular spaces, cell walls of adjacent cells and xylem vessels (Sattelmacher, 2001), whereas symplastic transport involves movement of water and substances between the cytoplasm of adjacent cells through specialized structures called plasmodesmata (Roberts and Oparka, 2003) and sieve plates. The apoplastic pathway is important for radial movement within plant tissues, and allows nanomaterials to reach the root central cylinder and the vascular tissues, for further movement upwards the aerial part (González-Melendi et al., 2008; Larue et al., 2012; Zhao et al., 2012; Sun et al., 2014). Once inside the central cylinder, nanoparticles can move toward the aerial part through the xylem, following the transpiration stream (Cifuentes et al., 2010; Larue et al., 2012; Wang et al., 2012; Sun et al., 2014). Nevertheless, reaching the xylem through the root implies crossing a barrier to the apoplastic pathway, the Casparian strip, which must be done following a symplastic way (Robards and Robb, 1972) via endodermal cells. Indeed, some nanomaterials can be stopped and accumulated at the Casparian strip (Larue et al., 2012; Sun et al., 2014; Lv et al., 2015). Another important symplastic transport is possible too, using the sieve tube elements in the phloem, and allowing distribution toward non-photosynthetic tissues and organs (Wang et al., 2012; Raliya et al., 2016). In the case of foliar applications, nanomaterials must cross the barrier the cuticle presents, following the lipophilic or the hydrophilic pathway (Schönherr, 2002). The lipophilic one involves diffusion through cuticular waxes, whereas the hydrophilic pathway is accomplished through polar aqueous pores presented in the cuticle and/or stomata (Eichert and Goldbach, 2008; Eichert et al., 2008). Because the diameter of cuticular pores has been estimated around 2 nm (Eichert and Goldbach, 2008), the stomatal pathway appears as the most likely route for nanoparticle penetration, with a size exclusion limit above 10 nm (Eichert et al., 2008).

The way nanomaterials move inside plants is really important, because it can give indications about what parts of the plant they can reach, and where they might end and accumulate. For example, if a kind of nanoparticles are transported mainly through the xylem and not the phloem, they will likely move mainly from root to shoot and leaves, and not downwards, so they should be applied to the roots in order to get a good distribution in the plant. On the contrary, if the nanoparticles show a good translocation through the phloem, application should be done via foliar spraying. In addition, nanomaterials moving along the phloem will likely accumulate in plant organs acting as sink, such as fruits and grains, so that is another important consideration when trying to avoid further human or



animal ingestion of nanomaterials. However, translocation is not necessarily restricted to a specific cell type, and lateral movement of nanomaterials between xylem and phloem is possible (Pate, 1975).

The characteristics and nature of the nanomaterials, in addition to the plant species, will greatly influence translocation and accumulation in plant tissues. For example, for the same kind

of nanoparticle, differences in translocation and accumulation in different plant species have been observed (Cifuentes et al., 2010; Zhu et al., 2012), whereas slight differences in similar nanoparticles lead to different results within the same plant (Zhu et al., 2012). Cifuentes et al. (2010) reported higher accumulation of carbon-coated iron nanoparticles in the roots of pea compared with sunflower and wheat, and faster translocation to the aerial

parts in pea and wheat compared with sunflower and tomato. On the other hand, Zhu et al. (2012) found that radish and ryegrass roots accumulated higher amounts of gold nanoparticles than rice and pumpkin, and that positively charged gold nanoparticles were taken up faster by the roots than negatively charged one, whereas these last ones were more efficiently translocated to the aerial parts. This phenomenon was explained by the negative charge present in the plant cell walls, favoring accumulation of positively charged nanoparticles in the tissues, and hampering its movement through the plant.

But, where do the nanomaterials go after being translocated to other parts? Typically, nanoparticles will accumulate in certain tissues and organs, in the same way it happens with animals (Varna et al., 2012). As commented above, plant organs acting as strong sinks for sap and nutrients are likely to accumulate nanomaterials traveling through the vascular system, mainly fruits (Servin et al., 2013), grains (Lin et al., 2009), flowers, and young leaves (Cifuentes et al., 2010; Koo et al., 2015). That is something to be used in our advantage when deciding the role of the nanomaterial we want to test. Do we need to deliver a plant hormone during flower development? Or an inhibitor for undesirable substances in the fruit? Perhaps a herbicide against a parasitic plant (Pérez-de-Luque and Rubiales, 2009)? It is also crucial to know the final fate of the nanomaterials if we do not want them to persist for human or animal consumption after the treatment. Some nanoparticles could be transformed or degraded by the plant after some time (Wang et al., 2012; Zhang et al., 2012; Lv et al., 2015), or simply being stored in tissues that will not be used after harvesting. In this last case, could they be recovered and recycled for further use (Liu et al., 2017)?

Interaction of Nanomaterials with Plant Cells

In order to enter the symplastic pathway, nanomaterials must be internalized by the plant cell and cross the plasma membrane (Figure 1). There are several ways for nanoparticles to achieve this, although such mechanisms are better studied in animal cells and less known in plants (Rico et al., 2011; Schwab et al., 2015):

- Endocytosis: The nanoparticles are incorporated into the cell by invagination of the plasma membrane, originating a vesicle that can travel to different compartments of the cell (Etxeberria et al., 2006).
- Pore formation: Some nanomaterials can disrupt the plasma membrane, inducing the formation of pores for crossing into the cell (Wong et al., 2016) and reaching directly the cytosol without being encapsulated in any organelle (Serag et al., 2011).
- Carrier proteins: Nanoparticles can bind to surrounding proteins, including cell membrane proteins that could act as carriers for internalization and uptake inside the cell (Nel et al., 2009). Specifically, aquaporins have been suggested as transporters for nanomaterials inside the cell (Rico et al., 2011), but their tiny pore size, ranging between 2.8 and 3.4 Å (Wu and Beitz, 2007), makes them unlikely as channels for nanoparticle penetration (Schwab et al., 2015), unless such pore size could be modified and increased.

- Plasmodesmata: Another way for nanomaterials entering a cell is through plasmodesmata, specialized structures for transport between cells (Roberts and Oparka, 2003). Of course, it involves that the nanomaterials should be already in the symplast, but this mechanism is really important in plants for translocation through the phloem (Zhai et al., 2014).
- Ion channels: They have been proposed as probable pathways for nanoparticles entry into the cell (Rico et al., 2011; Schwab et al., 2015). However, the size of such channels is around 1 nm, which makes very unlikely for nanoparticles to effectively cross them without important modifications.

How nanoparticles are internalized in the cells is another key question, because it will again influence the practical application of the nanomaterials. If we want to deliver chemicals inside specific cell organelles, then endocytosis appears as the most suitable way. On the contrary, for delivery in the cytosol, pore formation should be the most direct way for it. Additionally, we could be interested in nanomaterials that do not penetrate inside the plant cell but in other organisms, such as bacteria or fungi, in order to treat crop systemic diseases and infections (Rispaill et al., 2014).

BUT THE ROOM IS TOO BIG

During the last years, the number of works dealing with the interaction between nanomaterials and plants has strongly increased. We are starting to get some views on how it works, but getting the whole picture is extremely complicated. Because Agricultural Science takes knowledge previously tested and performed in Medicine and Pharmacology, there are some problems when we try to implement such knowledge.

Firstly, Medicine focuses on one species, humans (or two or three if we consider animals for preliminary test and trials), whereas agriculture deals with more than 7,000 cultivated plant species (Khoshbakht and Hammer, 2008). This situation really complicates the research, because as stated previously, plant physiology affects the interaction with nanoparticles, so results observed in a crop are not necessarily valid for another one.

Secondly, the cost for escalating the production of nanomaterials can hamper their application in the fields. There are many good results with nanoparticles that appear promising as nanocarriers in plants. However, some studies are performed with a few plants/organisms *in vitro* or growth chamber because the cost (both, in time and money) for producing large amounts of the nanomaterial for greenhouse or field tests is not affordable. In the case of medical applications, a (relatively) high production cost can be accepted, but for agricultural production that is not possible and nanomaterials should be produced in great amounts and for a very low price. Promising works in this direction are those dealing with natural polymers such as chitosan (Grillo et al., 2014; Maruyama et al., 2016) and alginate (Silva et al., 2010), and lipids (Pérez-de-Luque et al., 2012; Campos et al., 2015a; de Oliveira et al., 2015). This kind of polymers are easily synthesized and produced from natural existing compounds like chitin from crustaceans' exoskeleton (for chitosan) and from brown algae (for alginate)

(for a review, see Campos et al., 2015b), and they can be obtained in high amounts with a low cost.

Thirdly, this technology involves releasing nanomaterials into the field and inside the crops, so the first alarm bells: are these nanodevices safe for the environment and human/animal consumption? Despite nanotoxicological studies are being developed and carried out in different ways, even involving the food chain (Koo et al., 2015), the best way to avoid toxic effects is using materials that we already know are innocuous. Using certain metal/oxide nanoparticles or nanotubes for edible crop treatments does not seem a good idea. Perhaps under certain circumstances (for example, ornamental plants) would be possible to use some slightly hazardous nanomaterials in a controlled environment, but common sense and caution should be applied here. Again, compounds allowing synthesis of carriers in the nanoscale, innocuous for living organisms and with biodegrading traits are very good candidates. As pointed out previously, chitosan and alginate are ideal materials for this task, being already used in the food industry due to their lack of toxicity, biodegradability and edibility (Zohri et al., 2010; Azevedo et al., 2014).

Finally, consumers tend to distrust a technology unfamiliar for them, so it is necessary to explain them what nanotechnology is and what it involves. We do not want to repeat the story of the genetically modified organisms again, and learn from that (Kah, 2015). As researchers, we have a responsibility for communicating this knowledge, so outreach and popular science activities are tools we have at our disposal for that goal.

In conclusion, nanotechnology has a good potential for applications in agriculture, but there is still a long way down to reach the field. It is impossible to know all the details about how a nanodevice will work in a particular crop, but we need to start with real field and *in planta* tests, solving some of the problems stated above (mainly escalating the production and avoiding hazardous and toxic materials). If we stay behind the frontier of basic research only, the risk of agricultural nanotechnology

becoming hype increases, hindering any further attempts for applications and research. A first step in that direction should be testing nanocarriers already available on crops under controlled conditions, i.e., greenhouse and/or growth chamber. Lipidic, alginate or chitosan nanoparticles should be ready for mass scale production in order to get the necessary amounts for such experiments. Comparisons of treatments between the commercial products and the nanoformulated ones are a must, in order to check if the conventional dose of the active compounds can be effectively reduced. That would involve inoculation with common pathogens affecting the crops in the case of pesticide testing, and measurements of the effectiveness controlling diseases compared with conventional treatments. For fertilizers, development of the crop, physiological parameters and yield measurements are necessary. If the performance of the nanoformulated compounds is better than the conventional ones, then a next step further is needed: the field experiments. The field testing is critical and the last step before we can be sure a nanoformulation will work. All the experiments developed previously in laboratory, growth chamber and greenhouse are performed under controlled conditions, and despite they can show promising results, it does not grant complete success in the field. Tests under field conditions should be similar to those performed in greenhouse or growth chamber, but using the procedures and techniques needed for the crop we are testing. They should involve all the steps of the crop cycle, from sowing/planting to harvest, including conventional treatments for comparison, and others than should be commonly applied, in order to check in they will interfere with the nanoformulated products and vice versa. After that, if the results are positive, we can say the nanoformulation works and is ready.

AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and approved it for publication.

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Conflict of Interest Statement: The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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