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Review

Application of nanoelements in plant nutrition and its impact in ecosystems

América Berenice Morales-Díaz[1], **Hortensia Ortega-Ortíz**[2], **Antonio Juárez-Maldonado**[3], **Gregorio Cadenas-Pliego**[4], **Susana González-Morales**[5] **and Adalberto Benavides-Mendoza**[6]

[1] Research and Advanced Studies Center, Saltillo, Robotics and Advanced Manufacture, Ramos Arizpe, Coahuila 25900 Mexico
[2] Center for Research in Applied Chemistry, Department of Advanced Materials, Saltillo, Coahuila 25294 Mexico
[3] Autonomous Agricultural University Antonio Narro, Department of Botany, Saltillo, Coahuila 25315 Mexico
[4] Center for Research in Applied Chemistry, Department of Polymer Synthesis, Saltillo, Coahuila 25294 Mexico
[5] CONACYT- Autonomous Agricultural University Antonio Narro, Saltillo, Coahuila 25315 Mexico
[6] Autonomous Agricultural University Antonio Narro, Horticulture Department, Saltillo, Coahuila 25315 Mexico

E-mail: abenmen@gmail.com

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Abstract
Agriculture stands to benefit from nanotechnology in areas such as combating pests and pathogens, regulating the growth and quality of crops, and developing intelligent materials and nanosensors. The objective of this paper is to provide an overview of the use of nanomaterials (NMs) and nanoparticles (NPs) in plant nutrition, highlighting their advantages and potential uses, but also reviewing their possible environmental destination and effects on ecosystems and consumers. NPs and NMs have been shown to be an attractive alternative for the manufacture of nanofertilizers (NFs), which are more effective and efficient than traditional fertilizers. Because of their impact on crop nutritional quality and stress tolerance in plants, the application of NFs is increasing. However, there are virtually no studies on the potential environmental impact of NPs and NMs when used in agriculture. These studies are necessary because NPs and NMs can be transferred to ecosystems by various pathways where they can cause toxicity to organisms, affecting the biodiversity and abundance of these ecosystems, and may ultimately even be transferred to consumers.

Keywords: ecotoxicology, sustainability, human health, plant nutrition, plant fertilizers, heavy metals, trace elements
Classification numbers: 1.00 2.10 4.02, 5.00

1. Introduction

Nanoparticles (NPs) and nanomaterials (NMs) are present in ecosystems, resulting from natural processes or the manufacturing processes of different industries and from the treatment and disposal of wastewater and the incorporation of biosolids into the soil. Additional transfers after this primary transfer to the ecological system can occur between the abiotic and biotic components of ecosystems. In terms of natural NPs, it is clear that organisms have adapted to them throughout their evolution; however, the history of manufactured NPs is different in two ways: the first in terms of the amount generated and the second in terms of their chemical identity because many of them are scarce or even non-existent under natural conditions [1]. Agriculture is an economic activity in which nanotechnology applications are emerging [2] and as a result, it represents a new emission source of NPs and NMs into the environment and food.

The safe and sustainable application of nanotechnology in agriculture requires standards for the application of NMs in crop plants as well as the soil and water used for agricultural activity [3]. The agricultural use of nanotechnology materials must be accompanied by a basic knowledge of risk factors, either by direct contact or transfer for the crops and for the persons managing them, as well as the natural ecosystems that the crops interact with, and the animal or human consumers of the foods produced.

The definition of nanoscience is the research and technological development on a scale of 1 to 100 nm using atoms, molecules, or macromolecules [4]. However, the literature indicates that phenomena associated with nanometric scales occur with larger NMs [5] and thus the definition has been expanded to consider structures up to 1000 nm [6].

Nanoscience and nanotechnology are rapidly expanding the range of industrial, medical, food and agricultural applications, becoming an area of rapid development. While exact information is not available, large quantities of synthetic nanotechnology materials are being manufactured. It is estimated that up to 10 000 tons of TiO_2 and up to 1000 tons of CeO_2, FeO_x, AlO_x and ZnO [7] are being manufactured per year, which is expected to increase, resulting in a greater discharge of NPs and NMs to ecosystems [8] from point sources that contaminate soil and water (such as the waste emitted by different industries) or diffuse sources such as those from fuel additives [9] or biosolids [10].

The accelerated advance in the knowledge of nanoscience and nanotechnology synthesis and application is not synchronous with the advance of knowledge about their final location in the environment. Gaining this knowledge is more laborious because the complex interactions between NPs and NMs with different abiotic and biotic components of an ecosystem need to be addressed [11–13]. This is especially true for terrestrial ecosystems, on which much fewer studies have been conducted compared to aquatic ecosystems, because it is relatively easier to conduct controlled studies in aquatic systems than in systems involving soil or solid substrates [1].

The impact of the contribution of NPs and synthetic NMs on human health and on the functioning of complex systems such as soils or ecosystems remains difficult to calculate [14]. Some estimates place the emission of NPs to the environment far below the limit of concern [15], but in fact it is not really known what will happen to all the emissions and how they will interact with each other and with environmental factors and living organisms in the long term [16]. This understanding would require a huge multi-disciplinary effort, with greater involvement of biology and systems ecology-oriented teams in particular [6, 17].

Models with different approaches are available [18] that attempt to serve as a basis to respond to the question of the impact of NPs and NMs in nature. Some authors use a stochastic approach [19], while others opt for a deterministic approach [13, 20], both of which attempt to explain the flow of NPs and NMs in the environment. While the models are suitable approaches to the problem, accurate estimates are difficult to achieve considering the scarce amount of information available on the dynamics and effects of nanomaterials in ecosystems [21–25]. In particular, to provide a more comprehensive view of the impacts of NPs and NMs in nature, an effort derived from different disciplines of chemistry, biology, system theory and mathematics should be considered (figure 1), including at least the following:

- The physico-chemical and biological behavior of NPs and NMs. Modeling is complicated, given the highly variable solubility, specific surface, aggregation state, size, shape, and potential physico-chemical and biological effects resulting from small changes in the morphology of different NPs, in addition to when they interact with the inorganic, organic or biological components of the environment. There is no theoretical framework that predicts, for example, what would occur when the organic coating or the specific surface of a given NP is modified or the changes that may occur when in contact with water, soil, soil microorganisms and root exudates.
- Immediate effects (days to months). These effects are usually observed at a small experimental scale using model organisms and aqueous or porous medium with a given type of NP. These types of data are currently available, but a review of the literature again indicates an enormous diversification in the types of NPs, their application form, the elements used, the cultivation or growth medium, and the organisms and variables that describe their behavior. Although some generalized responses occur for certain organisms, a precise theoretical framework is still not available for modeling and predicting responses during a timeframe from days to months (*i*) for organisms or interacting groups of organisms different from those used for modeling, (*ii*) for the presence of mixtures of synthetic or even natural NPs as well as their combination with other contaminants or (*iii*) for groups of interacting organisms in different environments or soil types.
- Medium and long-term effects (months to years). These effects include the entire abundance of interactions in space and time, the study of which should be conducted not only under laboratory conditions but also in the natural environment. Unsurprisingly, little information is available on this subject, considering the operational and economic challenges associated with these studies. As a result, there are significant knowledge gaps in toxicology and impacts at the genomic level, in community structure,

Figure 1. A multidisciplinary approach for a more comprehensive view of the impact of nanoparticles and nanomaterials on ecosystems and agricultural systems.

and biodiversity and ecosystem functionality, which need to be resolved to verify the long-term impact of nanotechnology on systems that provide environmental services.

- Potential ecological and health impact. This should be weighed against the economic and technological impact, as well as given careful consideration in the corresponding sections of laws and environmental regulations. This issue is the most complicated because many countries lack a legal framework for nanotechnology or NMs and their environmental impacts [26, 27]. At first glance, one might think that if there are regulations on pesticides, hydrocarbons, heavy metals and other contaminants, that should suffice, and that the NMs and NPs would be special cases or simple extensions of the regulations. However, the problem is not so simple because the estimation of risk factors is much more complicated and subject to many uncertainties as a result of the lack of information cited in the previous points.

When chemical elements form NMs, they have properties different from those manifested at the micro- or macro-scopic scale or when they are in ionic form [28]. These emergent properties of NPs and NMs [29] are manifested when the NMs interact with photons [30], molecules, polymers, colloids or living cells [31], constituting a double-edged sword, which on the one hand, can cause toxicity and environmental impacts and on the other hand, permits different applications that together are believed to positively impact agricultural activity. Therefore, such potential applications must be accompanied by a weighting that takes factors beyond the immediate agronomic benefits into account, by carefully verifying the impact on ecosystems and human health [6, 32]. Even normally harmless substances may stop being harmless in the form of NMs [33, 34] because these materials modify the structure of soil microorganism populations [35] with unpredictable long-term consequences and depending on the environmental and temporal context, interactions of a positive nature between cells and NMs may become negative and act as a source of toxicity or metabolic dysfunction [36–38].

NMs can occur in multiple forms [39] but for the purposes of this review, only NPs and NMs reported for some type of application in plant nutrition are considered. The NPs or NMs present in soil, water or plants as a result of pollution, such as TiO_2 NPs, or carbon NMs, for which one may refer to

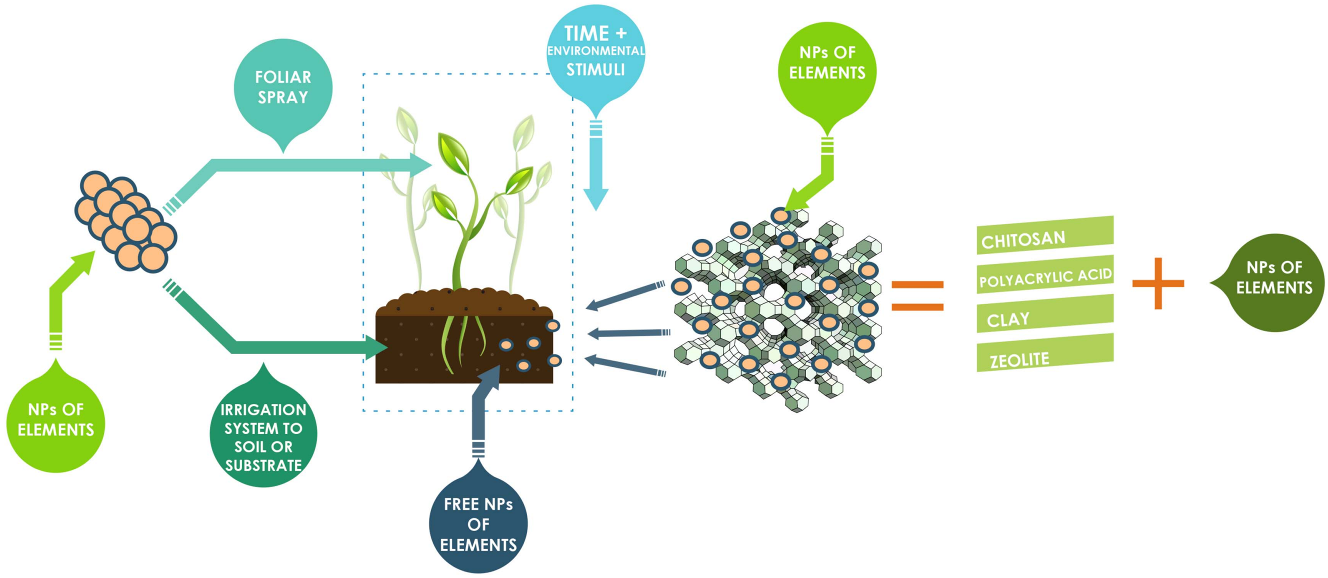

Figure 2. Use of nanofertilizers in crops. On the right side are the recorded nanomaterials containing essential elements under a controlled release as a function of time or environmental stimuli. On the left are the nanoparticles of essential elements that are applied directly to the soil, irrigation water or the surface of plants, fruits or seeds.

Mukherjee *et al* [40], will only be tangentially discussed; further, this review will not delve into the use of NPs for soil remediation [41]. The objective of this paper is to provide an overview concerning the possible use of NMs and NPs as nanofertilizers (NFs), reviewing their possible destination in the environment and potential effects on ecosystems and consumers. The manuscript is divided into the following parts: section 2 is the use of NFs in crop nutrition, the impact of NFs on the nutritional quality and stress tolerance of crops is in sections 3, 4 is the fate of NPs and NMs in ecosystems and section 5 is conclusions.

2. Use of nanofertilizers in crop nutrition

A large number of studies related to the use of NFs in crops have been reported, along with comprehensive lists of plant species tested and the NPs or NMs used. Some of these sources of information are in [42–44].

Mineral nutrients in the form of NFs can contribute to plant nutrition in two ways (figure 2). The first is to use nanostructured elements incorporated in a carrier complex that may or may not be a nanomaterial, as is the case of NPs of essential elements incorporated by absorption or adsorption in a matrix such as chitosan, polyacrylic acid, clay or zeolite [45]. The second is to use the element *per se* in a nanostructured form (in suspension or encapsulated), such as for the NPs of Fe or Zn for application to soil, substrate or by foliar spray [46]. Both types of NF contributions have certain advantages, such as greater solubility and rapid absorption or less leaching, compared with traditional fertilizers. The first method is preferred because it provides greater control over the speed and timing of release of the nutrient element.

The contribution of mineral nutrients in the solid phase (clay + humus and organic matter) from the soil to the soil solution, the complicated changes occurring during these interactions by microbial action in the soil, as well as the absorption of the elements from the soil solution by plants are all complex processes that so far are not well understood [47, 48]. For this reason, fertilizer efficiency is maintained at a low value, especially for nutrients applied in relatively high quantities such as N and P. It is worth mentioning that in many cases, the problem associated with crop mineral nutrition is not the amount of one or more elements present in the soil but rather their availability to plants [49]. Because of this, the encapsulation of fertilizers and other compounds in inorganic NMs has been explored, such as nanotubes of C [50], nanocompounds of clay montmorillonite-urea [45], NPs of SiO_2, nanoporous or mesoporous silica, and natural or synthetic zeolites [44, 51, 52]. Zeolites are not always classified as NMs (their effects do not depend on particle size but rather on the diameter of the internal pores found at a subnanometric range of 0.3 to 1.0 nm); however, they are mentioned in discussions on nanotechnology [53]. Zeolites are materials that are considered safe for soils and improve the conservation and availability of mineral nutrients in the soil [54] that could be associated with NPs to improve crop nutrition and reduce the environmental impact of agricultural activities. The disadvantage of zeolites is that they are not useful in the management of anionic nutrients and need to be complemented with biopolymers and biopolymer complexes, which have the ability to absorb and adsorb anions. It is expected that nanomaterials will generally bring about substantial improvements in increasing the absorption and transport of the fertilizer elements applied, as well as decreasing the amount applied to crops [6, 55].

NPs used as NFs can be absorbed by the root, moving through the apoplastic and symplastic pathways to the xylem, crossing the endodermis and then moving to the rest of the plant through the vascular bundles. This type of transport has been observed for mesoporous silica NPs [56] and SiO_2 NPs [52]. It has been observed that different classes of NPs are transported to the inside of the cells through endocytosis [57, 58] or through pores or channels, as in the case of TiO_2 NPs [59]. ZnO NPs are also absorbed from the root nutrient solution by the root and internally transported by the apoplastic and symplastic pathways; however, these NPs barely move beyond the endodermis [60].

In a substrate or soil, the presence of an element essential for plants in the form of an NF allows better dissolution and faster absorption and assimilation by the plant compared to traditional fertilizers. This has been demonstrated for N, P, K, Ca, Mg, Fe, Mn, Zn, Cu and Mo [44]. It is important that the NFs be released in the correct form and at a rate suitable for plants [6, 55], thus minimizing losses by leaching, gasification or by competition with other organisms [44].

To achieve this, the NMs containing the nutrients should ideally respond to any chemical or physical stimulation that indicates that the plant requires mineral nutrients [55]. Examples of these stimuli would be a specific time period or signals such as rhizosphere acidification or ethylene production by the roots, which occur when there is a deficiency of elements such as P or K. The problem with these internal root signals is that they might be modified by the presence of NPs themselves. As an example, Ag NPs (that can appear as a contaminant in biosolids or as an active ingredient in an agrochemical) interfere with the perception and synthesis of ethylene, additionally modifying other metabolic pathways in *Arabidopsis* [61]. This latter study, carried out under laboratory conditions, is representative of the complex situation that arises in applying NPs: the effects vary according to the morphology and size of Ag NPs, and some of the effects on plants are positive, such as a longer root as a result of the inhibition of ethylene synthesis. However, the authors reported many more changes in antioxidants, in the response of genes to the phytoregulator indoleacetic acid (IAA) and to dessication, etc. From a reductionist approach, it can be agreed that greater root growth is desirable, but in a natural environment, this response should be analyzed in a broader context because on the one hand, it could be a possible indication of stress [62] and on the other, increased root growth derived from blocking the perception and synthesis of ethylene could have a negative effect because it would hinder the normal interaction between plants and soil microorganisms, including mutualists as well as pathogens [63]. In a recent study, it was found that the mobility of TiO_2, CeO_2 and $Cu(OH)_2$ NPs in the soil was limited because these NPs rapidly formed micrometric aggregates with steric hindrance promoted by organic matter. Despite this delay in mobility and reactivity of the NPs, it was found that they changed the soil pH and the release of nutrients from the soil cation exchange matrix [64]. While the conclusion obtained is that NMs apparently do not move far from the point of emission, it would be remiss to ignore the participation of wind, precipitation and organisms as factors that can increase the distance and mobility rate. The point to consider is that it is not known with certainty what the effect of the constant increase in the flow rate of the NPs and NMs would be in the environment because there is not enough information about the complex responses and interactions with soil and sediment components, plants, soil microorganisms and others, including humans.

To reduce the uncontrolled release of NFs in the environment, they are associated with materials such as hydrogels, films or other biopolymers such as chitosan [65, 66], which aggregate the fertilizers in complexes with mineral NPs obtained from the clay in soil or other types of ceramic materials [67] that are used for manufacturing controlled-release blocks, pots, or film for padding. These respond to environmental stimuli (such as temperature or irradiance) by modifying the release of the NFs according to the plants' need, such that more nutrients are available during times of optimal plant growth. This may reduce, for example, nitrogen losses by nitrification associated with low temperature [55].

Another alternative for regulating NF contribution to the environment is by applying a foliar spray, especially for elements with limited bioavailability in the soil such as Fe, Cu and Ni [68]. Emulsions or encapsulated organic NPs can be useful for this purpose [69].

Finally, another way to reduce the release of NPs and NMs in the environment is to match their quantities with the stage of crop growth with the greatest response. An example of when the well-timed application of small amounts of NMs benefits crops is when they are applied to seeds in a pregerminative manner (seed priming) [46, 70]. A higher germination rate was observed in senescent seeds [71] or seeds germinating in unfavorable environments after applying NPs of Au, CuO and TiO_2 [69] and even those associated with carbon nanotubes [72], suggesting that the NPs increase water permeability of the seed coat, similar to what occurs in the cell walls [73] or in cell or organelle membranes when they interact with NPs [74, 75]. The results indicate the applicability of NPs and NMs to the technique of seed priming, for increasing stress tolerance or growth of crops [76, 77], without the potential disadvantages of a negative reaction by plants to nanotechnology materials [52, 78] or their possible trophic transfer [44, 79]. These applications in seed priming (or in tubers, bulbs and tissue culture) may possibly achieve a great positive impact on the growth of plants while at the same time, decrease the toxic effects on the plant, environmental contamination or trophic transfer.

In terms of NF action, in addition to a greater efficiency in the contribution and absorption of the element, it is believed that other processes associated with an increase in gene expression related to stress tolerance occur [80, 81], such as the greater expression of aquaporins, modification in the perception of nitric oxide and an increase in electron transport rates [82, 83]. The responses described depend on the concentration of the element used (which is normally small), being in many cases a hormesis effect [84] that makes it difficult to predict the impacts of NPs and NMs in organisms, given the uncertainty associated with non-linear responses to dosing and that even very small concentrations of NPs and NMs induce changes in the metabolism and gene expression of organisms [85, 86].

Positive effects have been described for NMs as well as carbon nanotubes [83] and NPs of elements classified as non-essential for plant growth. Examples of this were reported for spinach in the presence of TiO_2 NPs, which increased the carboxylation capacity of Rubisco [87] as well as the absorption and assimilation efficiency of N [88]. In general, positive responses to NPs of non-essential elements have been found in carbon NMs [40] and in NMs based on CeO_2 [79], TiO_2 [89], and nano-Si [90]. However, plant response appears to depend on the concentration and possibly the environmental context because not all of the reported responses are positive. For example, in *Arabidopsis*, exposure to NPs of TiO_2 (20 mg l^{-1}), Ag (0.2 mg l^{-1}) and functionalized carbon nanotubes with COOH-groups (25 mg l^{-1}) induced a decrease in the defense response, which was partially reversed with the exogenous application of salicylic acid [91]. Exposure to ZnO NPs (200–300 mg l^{-1}) in the same species reduced the chlorophyll concentration and as a result, the photosynthetic rate, resulting in less biomass [92].

3. Impact of nanofertilizers on the nutritional quality and stress tolerance of crops

The nutritional quality of crops and the stress tolerance of plants may be related. A plant with a proper balance of mineral nutrients, metabolites associated with signaling and response, and antioxidants or osmolytes has a greater capacity for adapting to the environment and whose consumption will increase the well-being and tolerance to negative stimuli in the organism that consumes it.

There are many reports on the application of NPs and NMs in the form of NFs to crop plants. As mentioned previously, the effects of NFs at certain concentrations are generally positive, increasing plant tolerance to abiotic stresses, pathogens and pests, the rate of certain metabolic reactions, the amount of antioxidants, and the quality and/or quantity of the harvest.

Part of the explanation of why the aforementioned effects occur is that NPs and NMs at certain concentrations induce oxidative stress, which is believed to occur from the interactions between the NPs and NMs with proteins, membranes, nucleic acids and different metabolites [80, 93, 94] as well as from the presence of unpaired electrons on the surface of the NPs and NMs [35]. The NPs of transition metals induce oxidative stress in bacteria, fungi, algae and aquatic and terrestrial plants in a dose-dependent manner [95, 96]. In terrestrial plants, if the level of oxidative stress does not exceed the toxic threshold that would lead to cell death, then a defense induction phenomenon is induced that includes the expression of resistance genes [80], the accumulation of proteins and defensive metabolites, and the accumulation of enzymatic and nonenzymatic antioxidants [95, 97]. Increased accumulation of antioxidants in plants has been reported in response to the application of NMs of CeO_2 [79].

An alternative to the defense induction would be the introduction of hybrid materials in plant cells, for example, functional complexes of NMs or NPs (as carriers) and defense metabolites or DNA, mRNA, or miRNA that encode or regulate the synthesis of certain metabolites related to defense, enabling this response to be carried out effectively in the cells of the seed, seedling or plant. Uses for these techniques are broad and refer not only to inducing tolerance or metabolic engineering but also to the manufacture of biosensors, diagnostics and bioelectronics, for example [98]. Preplanting or postharvest is another application where these techniques may have broad potential if the information necessary to synthesize a defense peptide could be applied without having to use traditional genetic selection or transgenic techniques. An example of this are the mesoporous silica NPs that can be used as a transport system of complex chemical compounds and biomolecules [56], including DNA, which makes the application of these NPs an alternative to genetic transformation methods such as ultrasound or gene gun [99].

Based on the information described above, the use of NFs appears to be generally positive in terms of plant composition. The issue again, however, is what happens after the harvest of the crop, as there is little information on the fate of NFs in terms of their transfer to the environment, as well as their successive steps between different trophic levels, to the soil decomposers or pathogenic microorganisms, insects and other herbivores and the end consumers for whom the harvest was intended, which may be domestic animals or humans. Similarly, the effects of NPs and NMs manifested at even sublethal doses must be examined because they may modify gene expression and the metabolism of microorganisms [81]; these responses may not be obvious from the perspective of abundance and microbial diversity in the short term.

For traditional fertilizers where the essential elements are applied incorporated in organic matter in the form of ground minerals such as rock phosphate, dolomite or soluble mineral salts, the presence of elements such as Fe and Zn does not normally pose a health concern for the consumer. However, this topic is not well defined for NFs, as many questions remain about the effect of NPs and NMs applied to plants in this manner, both in the short and long term [100, 101]. One of the first questions would be to ask whether NFs are fully transformed into ionic forms in the plant, after which they are then incorporated into proteins and different metabolites, or whether some part is conserved, such as NPs that could be transferred to consumers. While there is no doubt that the biosynthesis process of NPs in plant cells occurs naturally for some elements, especially transition metals, it is also true that this occurs on a small scale and only when the plant is exposed to excessive availability of the element in question [102].

4. Fate of nanoparticles and nanomaterials in ecosystems

The NFs used for plants could be transferred from crop fields to the soil, water and atmosphere by contaminated leachate, run-off by rain, transport by wind or trophic transfer (by harvested organs or in the agricultural waste incorporated into the soil or used for compost). Use of NFs should be subject to

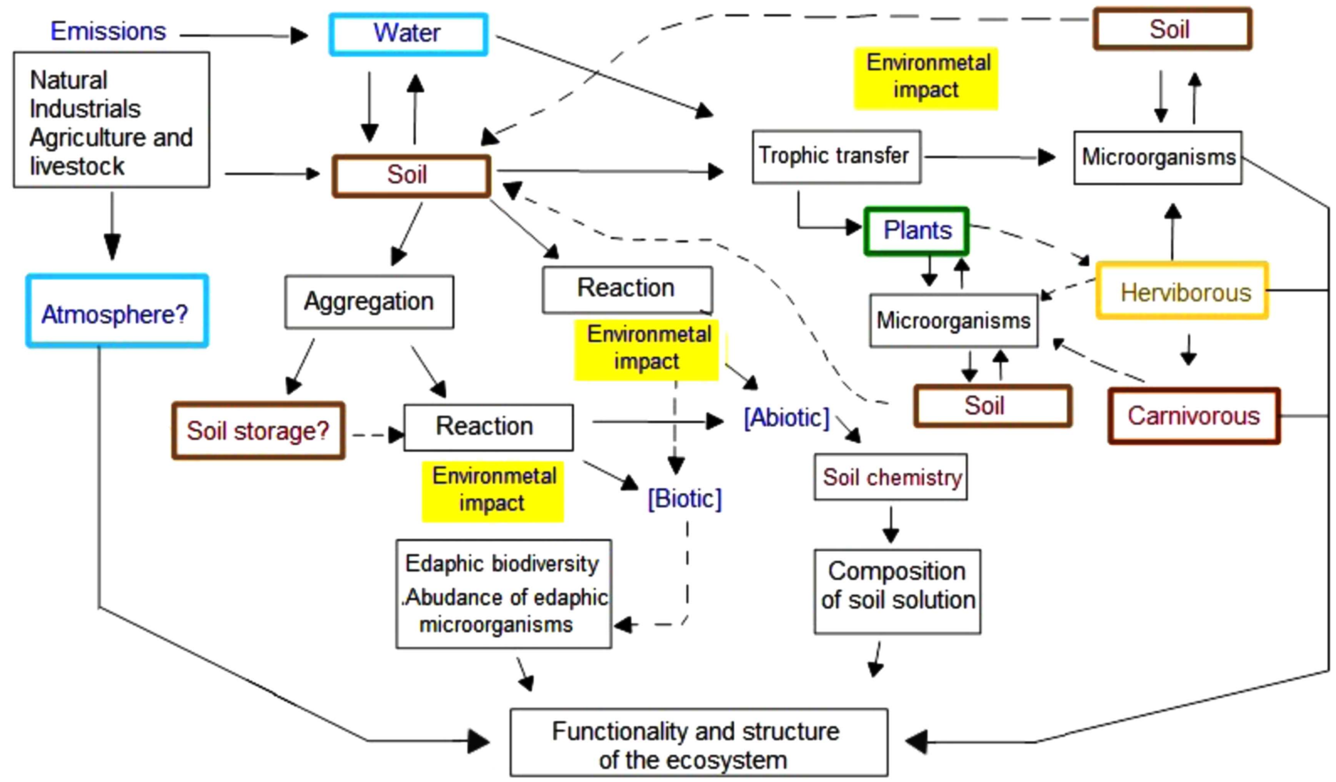

Figure 3. The dynamic flow of nanoparticles and nanomaterials in ecosystems. From the left side are the emissions that flow toward the water, soil and atmosphere; from that point, they are incorporated into the plants and microorganisms present in the soil and water. Transfer to other trophic components of the ecosystem occurs through herbivory, carnivory or decomposition of organism remains by microorganisms present in soils, sediments or water.

careful analysis, considering that their accidental presence in products for domestic animal or human consumption is a poorly documented subject. Various studies on the subject indicate that NPs are absorbed by microorganisms in the soil, the sediment and the roots of plants. They are transported from the roots to other organs of the plant where they accumulate [103]. Transfer to the next trophic level occurs when the microorganisms, plant structures or their waste are consumed by protozoa, arthropods, annelids, mollusks, fish [104], insects [105], and possibly birds and mammals, demonstrating that the negative effects are even manifested in their progeny [106]. This phenomenon has also been demonstrated in marine organisms [96] and confirmed to occur in other plant-herbivore-carnivore food chains [104, 105, 107, 108] (figure 3).

The interaction between plants and NMs is not historically unprecedented, as nanometric structures such as exosomes, lipoproteins, ferritins, magnetosomes and viruses occur naturally in biological organisms [109]. NPs can be generated extrasomatically by natural abiotic and biotic processes such as volcanism and meteoric dust [110], weathering, nucleation and crystallization of minerals, as well as by the action of microorganisms [28, 111] or organic matter in the soil and water [112]. As a result, natural soil can contain NPs of clay, organic matter and Fe oxides [113]; however, it is unlikely that significant concentrations of NPs are present in ecosystems. While it is possible to extract up to 17 $g\,l^{-1}$ of NPs (25–70 nm) formed by natural minerals from soil samples using ultrasound and centrifugation [114], this extraction process is not very realistic. It is, however, well-suited for *top-down* manufacturing of clay NPs that could be associated with mineral nutrients for increasing their availability to plants, which also decreases the leaching rate [45]. Thus far, only catastrophic events such as volcanic eruptions [115] and possibly the impact of massive objects in space [116, 117] can naturally generate large volumes of NMs and NPs in a short amount of time. NPs formed by natural processes usually originate from diffuse sources such as atmospheric precipitation and minerals from soil or water bodies, which results in a relatively constant contribution at very low concentrations.

4.1. Toxicity to plants

Although many studies report positive results when an essential element is present in the form of an NF [44], this does not necessarily imply a positive effect for plants in all situations.

When adverse reactions are reported in plants, these may correspond to slower growth [10], increased oxidative stress [118], chromosomal abnormalities [119], decreased photosynthetic rate [92, 120, 121], disturbances in water transport and the water status of the plant [38, decreases in the concentration of growth hormones such as IAA [52], metabolic disorders or necrosis [60], extensive changes in the transcriptional profile of many genes [80, 91, 122, 123] or increased susceptibility to natural toxins such as As [37]. It is important to note that depending on the experimental situation, the same NPs or NMs may indicate conflicting results: at times toxic, and at other times without apparent changes or even with positive effects [124]. An example of this was described by researchers [125] who applied 20 and 50 mg l^{-1} of NPs biomanufactured from Ag to *Pennisetum glaucum*, which initially improved germination but later had a negative impact on seedling growth. A similar effect was observed in ryegrass, barley and flax upon the application of NPs of Fe and Ag [126].

When determining NP toxicity in plants, it is necessary to consider the fact that their response will vary according to the element or chemical elements that constitute the NPs, their concentration and aggregation state [127], the different metabolic abilities of the plant species, the environmental conditions of their surroundings that normally extensively modify the properties of the NPs [1, 128], and the exposure time [129]. The following are described as important elements for predicting toxicity and transport in natural media such as soil or water [130, 131], surface charge [132], the formation of ions in solution from NMs [133] and the agglomeration or aggregation of NPs. These three variables are modified by the presence of dissolved organic material that causes the formation of organic coatings on the NPs, increasing their solubility such that they act as a surfactant. At the same time, the organic matter interacts with other factors such as irradiance, UV radiation, temperature, the presence of dissolved elements and biotic activity [134, 135], which in turn modify their reactivity with NPs and NMs. This cycle of complex interactions leads to difficulties in modeling the environmental fate of NPs and NMs in the long term [136].

Considering the effect of the different NP coating types is important when estimating their environmental impact because some surface coatings will increase NP bioavailability and toxicity [136, 137]. The pH and presence of complexing agents such as citrate or ascorbate in the water or soil solution (where part of the root exudates form) and bacterial or root exopolysaccharides may significantly modify NP toxicity. This occurs because these factors increase the stability of NPs and decrease their aggregation, which increases the opportunity to contribute potentially toxic ions [138] even from impurities (not expected but present) in supposedly pure NMs [139]. At the same time, other environmental factors such as temperature can change the aggregation speed [140], which is why different interaction scenarios between various abiotic and biotic factors can multiply extensively.

NM toxicity can be direct by absorption or adsorption by the plant or indirect through the release of ions from the decomposition of NMs or by the induction of amplified responses of other environmental toxins. The toxic effect in plants is due per se to NPs from Fe_2O_3, Co_3O_4, Cr_2O_3 and NiO, and CuO toxicity is due to both the NPs and the released ions, compared with only released ions for ZnO [141]. For bacteria, the toxic effects of NPs from CuO, ZnO, NiO and Sb_2O_3 have been reported to be dependent per se on the NPs rather than the ionic form of the elements [142]. In another study that included algae, bacteria, and protozoans, it was found that toxicity from CuO and ZnO (EC_{50} with <1 mg l^{-1}) depended on the released ions, while the NPs of Al_2O_3, SiO_2, WO_3, Sb_2O_3 and MgO were only toxic at concentrations greater than 100 mg l^{-1}. The order of sensitivity shown by the different organisms was algae > bacteria > protozoa [143].

NP and NM toxicity caused to soil microorganisms can occur directly [10] or indirectly by modifications in the radical exudates of plants [144]. This can result in changes in the total populations and/or profile or biodiversity of microbial symbionts [145, 146] This in turn can modify the response capacity or adaptive capacity of the plants [147–149] or other organisms [150] faced with environmental factors or stress. A problem that arises in studies conducted in soils is the lack of information about the interactions between NPs and the organic and inorganic abiotic soil components. Some studies assume that these interactions do not generate a response to NPs in microorganisms and plants [151], but in reality, there is little information on the effect of these interactions. Ideally, long-term experiments using several types of soil should be conducted.

Positive responses of soil bacteria have been reported in some cases, as was the case when 1 or 10 mg kg^{-1} of NPs[7] of FeO were applied to the soil, although the application of NPs of Ag (0.1 to 10 mg kg^{-1}) had a negative effect [152]. The indirect impact on the soil microorganisms may partially explain some mixed positive and negative results on the plants caused by NPs applied to the soil.

Another factor to be considered for determining NP and NM toxicity is that many studies have been conducted under controlled conditions (in Petri dishes and growth chambers), with low irradiance, temperature control, and absence of stress and interactions with different physico-chemical and biotic factors commonly found in situations of extensive agricultural production or under natural conditions. When plants are subjected to less favorable conditions, it is possible that the presence of NPs and NMs (for example TiO_2, CeO_2 and $Cu(OH)_2$) may interact negatively with abiotic factors that cause stress [153]. The toxicity of the NPs and consequently, plant responses to the NPs are modified according to their environmental context, for example, the plant's own concentration of NPs, the dynamic equilibrium resulting from the release and aggregation of ions, irradiance, the presence of other metal ions, pH, the oxidation-reduction potential (ORP), and the amount of organic material in the soil [154–156]. Biotic factors also modify the response to nanomaterials, for example, CuO and ZnO NPs interact with crop root exudates in sand and induce plant toxicity, with toxicity being an inverse function of NP size [157].

The types of NM toxicity reported vary depending on the types of NMs studied, their shape, diameter and reactivity, the experimental design used, the plant species and the stages of the plant life cycle when the materials were applied. In some cases, exposure to NMs does not appear to induce harm [56, 158], but the effect can be different for different plant

[7] 10 mg kg^{-1} is equivalent to 25 kg of NPs FeO per hectare, considering a soil profile of 0–0.2 m and an apparent soil density of 1250 kg m^{-3}.

species in the same experiment [159] because they may differ in their absorptive capacity of the NMs [73] or in their ability to metabolize them. In addition, an experimental model may be used, such as for seed germination and seedling growth, which indicated that toxicity did not occur even at high NP concentrations, similar to those used for nanoremediation process, i.e., higher than 30 000 mg l^{-1} of NPs of Fe [160]. Although the above-mentioned authors found no adverse effects on germination and seedling growth, these concentrations would certainly be toxic to these same plants over a longer time period.

The results of many studies on NP and NM plant toxicity are extremely valuable from the nanoscience point of view because they illustrate the response of different plant organisms to NPs and NMs. However, considering that the behavior of complex systems is modified to include new components, at different temporal and spatial scales [161], the results obtained in laboratories or microcosms cannot be completely extrapolated to conditions of commercial agricultural production systems and their surrounding natural ecosystems. The findings of these studies should be considered carefully before concluding that certain types of NPs or NMs exert an adverse, neutral or beneficial effect at the ecosystem scale.

4.2. Effects on biodiversity and abundance

Considering the phenomenon of NP and NM toxicity in plants from a plant community or ecosystem perspective, many possible interactions as well as emergent properties become immediately apparent that inevitably result from the larger scaled system [161, 162], as well as greater difficulty in predicting outcomes due to their increased complexity [163]. Even in systems with relatively limited biodiversity, such as agroecosystems and deserts, their biodiversity is actually high when the microbial component is considered [164].

Taking this into account, the previously described experiments in the laboratory under controlled conditions, using sterilized crops, Petri dishes or growing chambers with only one to a few plant species, hardly reflect the actual conditions of natural ecosystems. This is because in natural ecosystems, the volume of space, the exposure time and the complex interactions between organisms and the environment [162] or between the NPs and NMs being studied and the natural chemical or biological environment may radically modify their structural and surface properties [165], leading to different responses observed in the laboratory [129] by either amplifying them [166] or perhaps even decreasing them, as found in corn, which exhibited a decrease in NP toxicity of ZnO ([ZnO] $>$ 800 mg kg^{-1}) due to the presence of fungal mycorrhizae [167].

Unless the plant is grown under completely aseptic conditions, both the internal and the external environment will contain a microbial community that, combined with the abiotic environmental factors present, will shape the plant phenotype [168]. Together, these microorganisms (exophytic and endophytic) are called the microbiome, and they modify their relative abundance and biodiversity in response to external conditions [169]. This has a significant effect on crop performance, modifying aspects such as tolerance to stress, pathogens, growth, productivity and the nutritional quality of the harvest [170].

To date, there are no studies on the impact of NPs and NMs on plant biodiversity, but it is known that these materials have a significant effect on soil microorganisms [62, 171, 172], which can indirectly affect the growth and reproduction of plants in the short term and the structure of plant communities in the long term [173]. For this reason, the impact of NPs and NMs on the diversity, composition and abundance of soil microorganisms or the microbiome of plants should be considered. The issue is relevant because very little is known regarding how organisms shape and regulate many of the properties of the soil, groundwater, atmosphere, individuals and plant communities. In addition, there is very little information on the impact of NPs and NMs on microbial populations associated with plants. This is because in general, the experiments reported are those that measured the response variables of plants or microorganisms, as opposed to whole plants and microorganisms [146, 174]. The importance of studying the whole was shown for maize by applying NPs of Ag (100 mg kg^{-1}), which resulted in relatively high plant biomass and few changes in the community of soil fungi. However, there were more significant effects on the bacterial populations, showing a differential change in biodiversity and the metabolism of the bacteria associated with the rhizosphere compared to soil bacteria beyond the volume modified by the roots [172].

The NPs and the NMs released into soil and water can be a determining factor for modifying both biodiversity and the relative abundance of certain species of microorganisms found in the soil [10], the rhizosphere and the interior of plant tissues. When nanotechnology materials were added to the soil during the application of biosolids, it was found that the NPs of ZnO and Cu had no toxicity to soil bacteria, but the NPs of Ag and TiO_2 were toxic, changing both the individual abundance and species structure of the bacterial community [175]. In tomatoes grown in soil to which biosolids of Ag_2S NPs and NPs of Ag with a PVP organic coating and Ag^+ were applied, negative effects were observed on populations of bacteria, fungi and actinomycetes. In addition, decreased colonization of roots by mycorrhizal fungi was observed at concentrations as low as 1 mg kg^{-1} of Ag_2S, with a considerable negative response in plant biomass and the inhibition of the microbial community in response to 100 mg kg^{-1} of all forms of Ag [176]. He *et al* [152] reported that the toxic effect of Ag NPs occurs even at a rate of 0.1 mg per kg of soil.

4.3. Microcosms, mesocosms and models

The key to determining the scope of the results in an experiment is the spatial and temporal magnitude of experiments carried out with NPs and NMs [100]. For example, in a study with a single application of Ag, Ag_2S, CuO and CuS NPs, a significant negative impact was found on the microbial populations in aquatic sediments in the short term, followed by a recovery that over 300 days, resulted in no differences between the control and treated sediments [177]. While an experiment lasting one year should be considered highly relevant, the conclusions of this study, however, should be contrasted against the fact that neither the dumping of NPs by industry nor the appropriate application of NFs to crops constitute specific events because they actually occur as multiple and continuous events over time.

In addition, depending on the volume under experimental control, it could be possible to not draw any conclusions about the impact of NPs and NMs on individuals, populations, communities or ecological processes at a large scale. The most common study is called a microcosm study, which involves an experimentally small controlled volume such as 1 L for a week, obtaining up to 15 m^3 (or its terrestrial equivalent of up to 15 m^2) for several weeks or a couple of months. Mesocosms refer to volumes ranging from 15 m^3 to 1000 m^3 over a period of several months [178]. The conclusions drawn from microcosm studies refer to the effect of NPs and NMs on individuals and possibly populations of microorganisms and small multicellular organisms. Mesocosm studies allow the impact of NPs and NMs on plant populations, their microbial counterparts as well as associated pathogens and pests to be verified. Mesocosm studies [10, 179–181] provide an approach that is better suited to the complexities of the natural situation, but unless they are carried out for several years, they cannot provide conclusions about the effect of NPs and NMs on plant communities and ecosystems.

Considering the difficulty in carrying out in-depth studies on the effects of NMs at the ecosystem level, which may require areas greater than 0.1 km^2 and time periods up to 10 years, the use of a systems biology approach by applying simulation models can be considered.

This would require developing significant experiments that would permit data to be obtained in order to determine different structures, functions and interactions. It would then be possible to develop mathematical models using model identification techniques. The theory of interaction is an area of study that is based on a given list of variables (or nodes) that infers dependencies (or connections) between them using the information contained in the data sets obtained. The goal is to determine existing interactions, such that the models obtained do not include differential equations, and there is no need to estimate parameters such as kinetic constants. The main task of this field of research is to estimate the correlation dependence between the variables contained in the set of experimental data. Most of the methods used to obtain or infer the interactions are closely related to statistics, such as Bayesian statistics, frequency methods and probability [182–184].

Another possible application area for modeling ecological processes impacted by NPs and NMs is the development of dynamic models. From the point of view of identifying the modeling strategy to be used, there are three main problems that can be identified: (i) given a series of dynamic data, such as time series of concentrations and other properties, there is a need to identify the structure of a network that explains or fits the data, for example, that would explain the structure of the kinetic model and its parameters. (ii) given a series of dynamic data and the existence of a dynamic model whose structure can be modified, the objective would be to determine those structural changes and kinetic parameters that fit the data. (iii) given a set of data and a fixed structural kinetic model, the kinetic parameters that fit the data need to be estimated. The development of these models could begin from a collection of data from multiple sources from the literature by applying techniques designed for a wide range of data, called 'reverse engineering', which is quite suitable for the study of complex systems and which will intersect different disciplines such as statistics, artificial intelligence, intelligent learning systems, nonlinear physics, chemical kinetics and biochemistry, optimization, inverse problem theory and control theory [182].

While the fitting of the data is one of the first and main objectives for models, the development of validations crossed with different data sets should be carried out. Different approaches to resolve dynamic models can be based on data that are available in the literature [185, 186].

5. Conclusions

NPs and NMs are an attractive alternative for manufacturing NFs with greater effectiveness and agronomic efficiency compared to traditional sources of fertilizers. In the past 10 years, the number of laboratory or microcosm-scale studies that examine the effect of industrial NPs and NMs in soil, water, plants, microorganisms, and animals has increased significantly. However, because these studies generally use isolated organisms, relatively little is known about the impact and environmental fate of NPs and NMs at the spatial and temporal scales needed to obtain a more comprehensive view of the process in the ecosystem. Therefore, findings from these microcosm and laboratory studies should be considered carefully before concluding that certain types of NPs or NMs do or do not exert an adverse effect on agricultural or ecological systems because there is very little knowledge on the nonlinear effects of NP and NM concentrations or their interaction with other biotic and abiotic components. Very few studies have been conducted at large scales or with the use of mesocosms, and there are no studies available that operate at areas greater than 0.1 km^2 at the time scales necessary to effectively determine the impact on ecosystems, especially the environmental impact resulting from the agricultural use of NPs and NMs. These studies are necessary, however, because the presence of NPs and NMs from nanofertilizers in the environment can be directly toxic to plants and other organisms as well as generate changes in biodiversity or the abundance of organisms, which may impact ecosystem function. Considering the cost of time and resources involved in carrying out experiments with the necessary magnitude, greater effort should be applied toward the development and implementation of models that predict the behavior of ecosystems exposed to these materials under different concentrations, forms of assimilation and even environmental conditions and exposure times.

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