Review

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Engineered Nanoparticles (ENPs) in Aquatic Environments and Soil-Plant Ecosystems: Transformation, Toxicity, and Environmental Challenge

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Abstract: The ever-increasing use of engineered nanoparticles (ENPs) in industries, medicine, and consumer products has resulted in their uncontrolled release into aquatic environments and soil-plant systems. Upon release, ENPs may transform and release toxic by-products, raising concerns about their environmental behavior and potential risks. However, accurately measuring ENP concentrations in these ecosystems remains a significant challenge. Recent studies have highlighted the toxic effects of ENPs on various organisms, but assessing the risk in aquatic and soil-plant systems remains a critical issue in nanoecotoxicology. ENPs interact with environmental materials, including organic matter, soil, sludge, and other pollutants, forming complex assemblies that may alter their toxicity and environmental fate. This study examines the interactions of ENPs in aquatic and soil-plant environments, focusing on their transformation, toxicity, and ecological impact. The goal is to identify knowledge gaps and outline directions for future consideration for a better understanding of the environmental risks of ENPs. Additionally, the research addresses the challenges of evaluating nanotoxicity and highlights the need for improved environmental regulations and assessment techniques for engineered nanomaterials.

Keywords: nanoparticle toxicity; engineered nanoparticles; aquatic environment; soil-plant system; risk of nanoparticles

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1. Introduction

Engineered nanoparticles (ENPs) are deliberately manufactured materials characterized by particle sizes ranging from 1 to 100 nanometers in at least one dimension [1]. These particles can exist in various structural forms, including spherical shapes, nanowires, nanotubes, and nanorods [2]. ENPs are categorized into five primary types based on their composition: carbon-based, zero-valent metals, metal oxides, quantum dots, and dendrimers [3]. ENPs exhibit distinct physicochemical properties, such as a high surface area and enhanced optical, magnetic, and electrical behaviors, setting them apart from their bulk material equivalents. Due to these advantages, the past decade has seen a significant rise in their application across diverse industries, including cosmetics, textiles, coatings, and antibacterial products. With over 1,800 ENP-containing products available globally and

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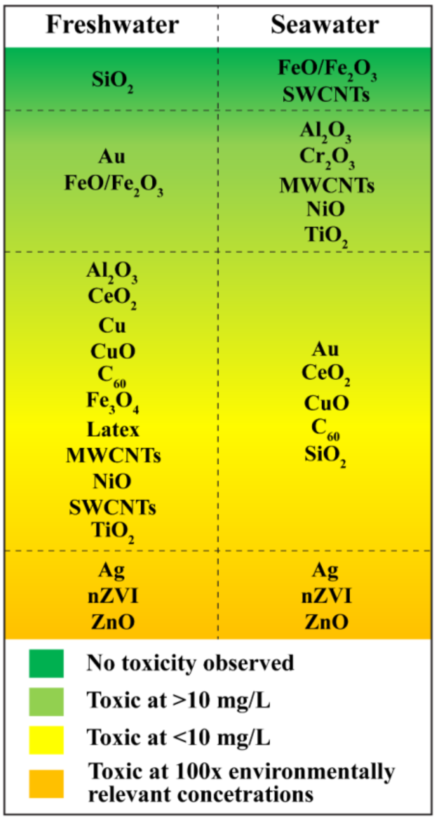
an estimated market value projected to reach $125 billion by 2024 [4], the impact of nanotechnology on human life is profound and growing. Projections indicate that the global population will surpass 9 billion by 2050, creating substantial concerns regarding food security [5]. Nanotechnology can play a significant role in promising solutions to enhance agricultural productivity and ensure food security, safety, and sustainability [6]. For example, ENPs are being used to improve the efficiency of fertilizers, pesticides, herbicides, and plant growth regulators through mechanisms like controlled release [7]. Beyond agriculture, ENPs are integral in modern medicine, electronics, and environmental science, offering solutions that improve production efficiency and sustainability [8,9]. The precise control of size, shape, and synthesis conditions of these nanoparticles has revolutionized traditional sectors, fostering innovation and functionality. [10].

The rapid development of nanotechnology and the increasing production and ever-expanding applications of ENPs in various industries cause the release of ENPs in aquatic environments and soil–plant systems [11,12]. The usages of ENPs cause an intentional or unintentional release into the natural environment. This causes a potential threat to the aquatic environment and soil-plant systems, as well as humans [13] and other organisms [14]. However, ENPs show unique toxicity characteristics in the aquatic environment and soil-plant system compared with conventional inorganic and organic contaminants, including their colloidal and soluble forms [15,16]. Thus, it's a very challenging task to regulate the release of ENP into the aquatic and soil-plant environments [17]. Moreover, there is a lack of established and documented standards to regulate the discharge of ENPs. Now it's critical to develop new approaches for standardizing the characterization and toxicity analysis of ENPs across the aquatic environment and soil-plant system.

In different environmental settings, the rates at which ENPs transform, as well as their toxicity and bioavailability, are affected by how ENPs interact with natural organic matter. Additionally, factors such as water chemistry, the movement of water, and physical and electrical characteristics play a significant role. ENPs undergo various transformations in the environment such as physical, chemical, and biological transformations that modify the behavior, fate, and toxicity of these materials [18]. Understanding these transformation processes is significant in controlling and characterizing the fate and toxicity of ENPs in aquatic and soil-plant systems. Among the numerous transformation processes, the leading reactions are redox reactions, dissolution/sedimentation, adsorption, photochemical and biologically mediated reactions, agglomeration/ deagglomeration, etc. Recent environmental health and safety (EHS) research predominantly focuses on the fate, transport, and toxic effects of pristine or "as manufactured" nanoparticles [19]. However, this does not explicate the harmful effects of ENPs under various environmental exposure conditions. Therefore, it's necessary to fully understand the transformation-related toxic properties of ENPs in numerous environmental conditions. Assessing the potential toxicological effects of ENPs requires an understanding of these effects from acute and chronic exposures. Moreover, having a high surface-to-volume ratio and reactivity makes them highly dynamic in the aquatic environment and soil-plant system. Recent research has found that if ENPs are present in high enough concentrations, they have the potential to harm aquatic organisms [20–24]. The environmental effects of these ENPs have stimulated studies to predict environmental concentrations in air, aquatic environments, and soil-plant systems and to determine threshold concentrations for their ecotoxicological effects on these systems.

ENPs can enter aquatic systems and soil-plant environments either directly, through fertilizers or plant protection products, or indirectly, via the application of land or wastewater treatment products such as sludges, biosolids, or industrial discharges. Once dissolved in the environment, ENPs release potentially toxic components. Additionally, their aggregation with other nanomaterials or with natural mineral and organic colloids can significantly alter their fate and toxicity in the environment. Consequently, assessing the risks to aquatic systems and soil-plant ecosystems presents a critical challenge in nanoecotoxicology. Furthermore, reliably measuring ENPs at environmental concentrations remains difficult. The growing use of ENPs across various applications is expected to lead to increased environmental concentrations in the near future. At this early stage, it has been shown that the predicted environmental concentrations of ENPs are orders of magnitude below those known to have environmental effects on biota. Indeed, more toxicity data should be generated under environmentally relevant conditions for risk assessments for nanomaterials, which will improve the production of accurate assessments that assure environmental safety. Figure 1 presents the results of 61 ecotoxicity studies on ENPs in freshwater and seawater, based on predicted release concentrations, to estimate the level of risk [25]. The estimated release concentrations for ENPs range from the low ng L^{-1} to µg L^{-1}.



Freshwater	Seawater
SiO_2	FeO/Fe_2O_3 SWCNTs
Au FeO/Fe_2O_3	Al_2O_3 Cr_2O_3 MWCNTs NiO TiO_2
Al_2O_3 CeO_2 Cu CuO C_{60} Fe_3O_4 Latex MWCNTs NiO SWCNTs TiO_2	Au CeO_2 CuO C_{60} SiO_2
Ag nZVI ZnO	Ag nZVI ZnO

🟩 No toxicity observed
🟩 Toxic at >10 mg/L
🟨 Toxic at <10 mg/L
🟧 Toxic at 100x environmentally relevant concetrations

Figure 1. Toxicity of ENPs in freshwater and seawater [25].

The soil and water act as natural sinks for the ENPs. The ENPs have the potential to build up in sediments and biosolid-amended agricultural soils and thus enter the food chain through accumulation in plants [26]. The safe use of ENPs in the production of food crops largely depends on understanding the transformation of ENPs in both the soil and plants [27]. When ENPs are introduced to soils, the transformation that occurs dominates their behavior and therefore their bioavailability. Several factors of soils, such as soil components and properties, especially organic matter (OM), ionic strength, water regime, pH, and texture, influence ENP characteristics. Considering the transformation of AgNPs in soil and sediment within freshwater mesocosms, it was found that AgNPs primarily transformed into Ag_2S. The observed transformation rates were 52% in soil and 55% in subaquatic sediment [28]. However, until today, limited information is available about the characteristics of ENPs in natural soils, which made it difficult to extrapolate and understand the comportment of ENPs under realistic field scenarios. Another potential pathway for the translocation of ENPs into the food web is through plants. In recent years, the biological uptake and accumulation of ENPs by plants have drawn great attention from researchers. The ENPs travel through different food webs and interact with different environments. ENPs interact with plants either through aboveground surfaces or belowground organs, such as roots and tubers, and are subsequently absorbed into the plants [29]. However, ENPs have both positive and negative effects on plants. ENPs cause harmful effects on biota by causing the formation of reactive oxygen species (ROS), an ion release that affects the biological structures as shown in Figure 2 [30,31].

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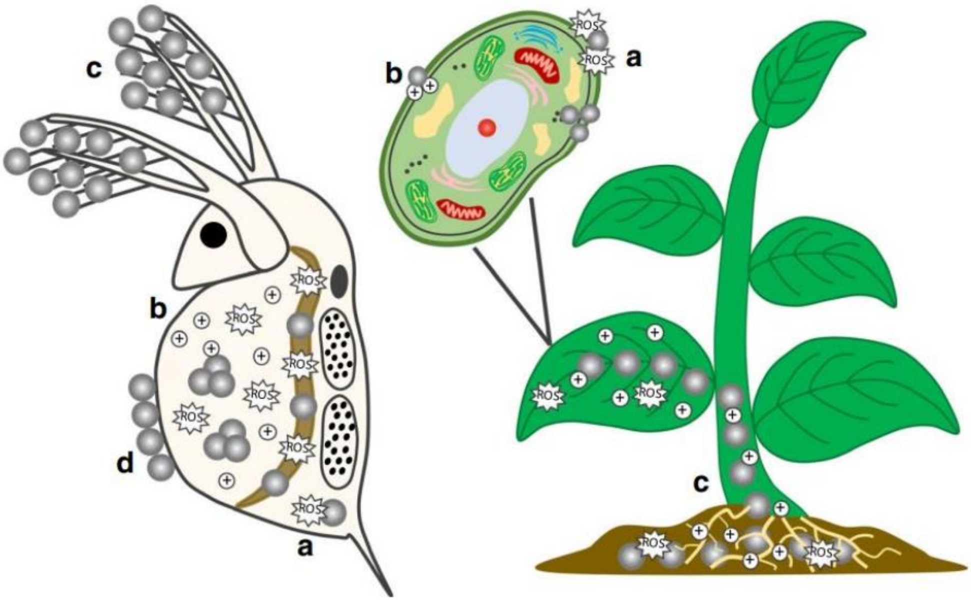

Figure 2. Ecotoxicity of ENPs in aquatic regimes, showing the mechanisms as a) formation of ROS, b) ion release, c) internalization, and d) biological surface coating [30,31].

The objective of this study is to summarize the fate and all possible toxic forms of ENPs in the aquatic environment and soil-plant system. Finally, based on current knowledge, some important recommendations are made based on our research results, and the technical challenges associated with the nanotoxicity evaluation. We identify the key knowledge gaps and research questions that need to be addressed in future nanomaterial environmental studies and the safe use of ENPs. Overall, the future use of nanomaterials should fully consider the health, safety, and environmental impacts of these nanomaterials.

2. ENPs in Aquatic Environment

2.1. ENP Interactions with Aquatic Organisms

The interactions of ENPs with aquatic organisms are not only complex but dynamic too. The amount and form of ENPs interacting with aquatic organisms are influenced by several physicochemical processes, as illustrated here. The fate, behavior, and transportation of ENPs in aquatic environments are controlled by their physical factors, such as size, shape, etc., and chemical factors, such as surface charge potential, surface coating, crystal structure, and composition. ENPs undergo several changes in aquatic systems due to biotic and abiotic components, which, therefore, regulate ENPs' bio-accessibility, bioavailability, uptake, and toxicity potential while interacting with aquatic biota [32]. Therefore, as soon as released into aquatic environments, aquatic biota interacts with transformed ENPs rather than pure ENPs [33]. The metal-based ENPs go through several transformations in water media. However, dissolution potential is one of the key determinants of the environmental fate of metal-based ENPs. A chemical characteristic of ENPs is the releasing of dissolved ions or metallic forms, which is often improved by reducing the nanoscale size and thus increasing their potential reactivity [34]. Hence, metal-based ENPs interact with aquatic biota according to the following forms: (i) particulates; (ii) dissolved metals; and (iii) new chemical matters created through interacting with abiotic and biotic factors. So, it's needed to focus on the bio-accessible portions of metal-based ENPs due to their related implications for toxicity and uptake. In an aqueous solution, metal-based ENPs frequently agglomerate, where gravity forces can overcome buoyancy, producing deposition of particles and, as a result, dropping exposure concentration. Nevertheless, the reverse outcome of deagglomeration is often overlooked as the evolution of ENPs is multi-dimensional and dynamic. Besides, the reduction of metal actions (e.g., Ag^+) is one of the chemical processes that can create secondary particles, which are smaller, in suspension, thus initiating newer bio-accessible size and shape states [35]. For identifying exposure, bio-accessibility, size, and endurance in aqueous systems, changes in the size and shape of ENPs are vital. The interaction of agglomeration, deagglomeration, deposition, and suspension of ENPs has effects on both free-floating and rooted plants of the aquatic environment, causing temporal and spatial distinctions in exposure scenarios. Aquatic systems may get purified from such contaminants by the settling of ENPs on sediments, but this argument ignores the reality that aquatic systems are multi-dimensional. For example, ENPs can de-agglomerate or dissolve and still interplay with pelagic biota during re-suspension. In the transformation of ENPs, the properties of aquatic systems, such as ionic strength, pH, total organic matter, and inorganic constituents, are important. These physicochemical properties may change surface properties and bio-accessible size or control the rate of dissolution. In general, such transformations have an impact on the bio-accessible condition of ENPs to aquatic biota. The rate of dissolution of ENPs is dependent on pH, suggesting that changing pH states will also affect the different bio-accessibilities of metal-based ENPs to plants in aquatic environments [36].

Free metal activity, soluble metallic species, etc. are largely involved in the toxicity of metals in aquatic environments [37]. Indeed, the analysis of metal speciation is related to the identification of metal chemical forms, which include free metal ions, organo-metallic compounds, and both organic and inorganic complexes. For example, organic matter and electrolytes govern the stability of ENPs by altering characteristics like charge potential and the coating of the ENP’s surface. In the case of ENPs interacting with aquatic higher plants; the bio-accessible size of ENPs can be increased by dissolved organic carbon (DOC). Deposition, adsorption, and internalization are the processes through which ENPs, whether in dissolved or particulate form, interact with the aquatic environment’s higher plants. At present, the interaction of ENPs with organic substances, such as fulvic and humic acids (HA), is generating significant interest, with the intention of better understanding how these might affect the stability of ENPs in water media and their capacity to attach and work as a major transporter of all other pollutants.

The above information pointed out that a complex interaction of ENPs and exposure to aquatic characteristics underlies the bioavailability and bio-accessibility of metal-based ENPs to aquatic higher plants. Therefore, while investigating the behavior of ENPs in aquatic environments, it is required to consider ENP characteristics and aqueous properties in an integrated manner, rather than treating those separately. Eventually, the complex interaction of the spatially and temporally dynamic processes helps determine the bioavailability of ENPs in aquatic systems. Components affecting the bio-accessibility of ENPs are important because, in turn, those components also determine the bioaccumulation, bioavailability, and toxicity of ENPs to aquatic higher plants.

2.2. Behavior and Fate of ENPs in the Aquatic Environment

The behavior of natural nanoparticles and colloidal matter in aquatic environments and soils has been studied for a long time. ENPs will thus become components of these colloids and their subsequent behaviors upon entering aquatic systems. Transportation of ENPs depends on both interactions with other colloidal components and the physicochemical nature of the aqueous medium. In recent times, several studies have been initiated to determine the role of physicochemical factors in the formation of aggregates relating to aquatic media as well as the size of ENP aggregates. ENP aggregate formation has constantly been found to be dependent on concentration in the medium (0.1–100 mM), the concentration of dissolved organic carbon, fulvic acid, HA, the pH of the aquatic medium, etc. These factors have key implications for the exhibition of aquatic organisms, as sedimentation and aggregation of ENPs decrease the possibility of transportation inside the water column. This indicates minimal transportation of ENPs in cation-rich estuarine and marine environments, and hence benthic and sediment-dwelling species tend to be more exposed than pelagic species [38]. Changes in these situations, nevertheless, may help the stabilization of ENPs, providing them with the major potential for uptake and transport within aquatic systems. Standard models have yet to be developed that can predict this behavior. For determining the behavior of ENPs in aquatic environments, the physicochemical characteristics are also vital elements. The zeta charge potential on the ENPs surface has been found to affect aggregation behavior. When the values are closer to zero charges (i.e., 0 mV), aggregation increases [39]. The existence of coatings and functional groups on the ENP's surfaces also influences the nature of the interactions among ENPs and with other elements of the water medium and consequently plays a role in determining the stability of ENPs. It has been found that the colloidal substance from environmental waters is coated by an organic material layer, and as surface charges of ENPs and interactions between nanoparticles are influenced by adsorbed layers, this has crucial implications for determining the processes by which colloids bind pollutants and trace elements. Adsorption of humic acid (HA) onto zinc oxide (ZnO), titanium oxide (TiO_2), or aluminum oxide (Al_2O_3) has been observed to decrease the zeta potential of these particles. This suggests that HA-coated nano-oxides are more easily dispersed, suspended, and stable in suspension compared to uncoated ones, owing to enhanced electrostatic repulsion [40]. In conclusion, the behavior, fate, and toxicity of ENPs vary with the type of aquatic environment, with significant differences observed in freshwater at higher dilutions compared to seawater.

2.3. Toxicological Effects of ENPs in Aquatic Environment

Improving our knowledge of the ENP's eco-toxicology requires better knowledge of the behavior and fate of ENPs in aquatic systems and their interactions with other particles in aquatic environments. Eventually, this will permit a better evaluation of the characteristics of the ENPs. However, most of the studies conducted on nano-toxicology have been focused on inhalation issues in terrestrial vertebrates, with considerably less concentration on exposure to various organisms residing in other environments. Recently, studies have expanded in discovering the effects of ENPs on aquatic organisms, exploring potential paths of uptake, transmission, fate, and effects, including affected uptake and effect because of the ENP's characteristics as well as the exposure medium surrounding them. In this section, an in-depth analysis of the findings for the effects of exposure to ENPs on vital organisms from aquatic environments such as microbes, algae, invertebrates, and vertebrates will be provided. The toxicity of ENPs in aquatic systems is exaggerated by some factors that can be broken down into three different groups: (i) functional behavior of ENPs; (ii) physicochemical characteristics of ENPs; and (iii) interaction with other pollutants present in the same medium [41]. The production of reactive oxygen species (ROS) and the dissolution of ENPs into metal ions are some examples of the functional behavior in aquatic media. For instance, some ENPs, such as copper-based nanoparticles, surface silver on silver nanoparticles, dissolve readily in water, releasing Cu^{2+}, Ag^{2+}, and reactive oxygen species (ROS) like R_2O_2 radicals. It has been found in many previous studies that metal ions present greater toxicity than NPs. In contrast, one of the vital parameters for analyzing the toxicity of ENPs in the aquatic system is the concentration of ENPs. Low concentrations, ranging from 5 to 50 $\mu g\ L^{-1}$, cause oxidative stress, chromosomal alterations, and physiological changes. On the other hand, a higher concentration of about 1 $mg\ L^{-1}$ was found as a direct cause of death [42]. Furthermore, the toxicity of ENPs in aquatic environments is quite particle-specific and depends on the process of entering the cells of the specific organism. The mechanism of entering the cell of the organism initiates with the sticking of ENPs to the membrane pores of the cell, followed by a complete entrance of ENPs inside the cell by a process called endocytosis or through the transportation of ions. The intervention with the process of transportation of ions or the ROS produced during the entrance of ENPs has negative effects, ranging from cell membrane damage to damage of nucleic acid as well as organelle functions. All the parameters that have a dominant effect on the toxicity of ENPs are summarized in Table 1.

Table 1. The impact of various parameters on ENP toxicity in freshwater and seawater environments.

Parameters	Impacts of toxicity	Summary of the study	Reference
Size of ENPs	The strength of toxicity is inversely related to ENPs' size.	Al_2O_3 NP was found to show low toxicity to bacteria in contrast with the same Al_2O_3 NPs of a size of less than 50 nm.	[43]

Crystal structure	Cytotoxicity and genotoxicity are associated with the ENPs' crystal structure.	The toxicity of Anatase nTiO$_2$ due to oxidative stress was found greater than that of rutile nTiO$_2$.	[44]
Surface charge	Surface charge controls the toxicity of NPs by affecting the agglomeration rate.	The silver NPs toxicity was discovered to be dependent on surface charge.	[42]
Morphology	Surface charge controls the toxicity of NPs by affecting the agglomeration rate.	Plate-shaped silver NPs have higher toxicity effects on fish gills and zebrafish embryos in contrast with spheres or wire-shaped NPs.	[45]
Surface coating	The ENP's toxicity effects increase or decrease according to the chemistry of their coatings of ENPs.	PVP or citrate-coated silver NPs were more toxic than PEG-coated silver NPs.	[46]
Co-pollutant	Inadequate information is found regarding the interaction of nanoparticles with other pollutants in the aquatic media.	Exposure of the blue mussel to both TiO$_2$ and benzo (a) pyrene resulted in greater chromosomal damage while inducing lower results in individual exposure.	[47]
Exposure duration and concentration	Both the exposure duration and concentration influence the toxicity of ENPs in the aquatic system.	It is found that the toxicity effects on *Lymnaea luteola*, an aquatic snail, of exposure to nZnO have a dependency on the exposure duration and concentration.	[48]

2.3.1. Toxic Effects of ENPs on Microbes and Algae

Bacterial populations are responsible for a great proportion of the main production or carbon flux within an aquatic system. Therefore, they play a crucial role in the regulation of major processes within the systems, and if these populations or their natural activities get disrupted, there will be an impact on other organisms that share the same environments. There are some confirmations to support the conclusion that many carbon-based NPs display antibacterial activity. Fullerene (C60) suspensions in aqua have been proven to have negative effects on Bacillus subtilis when their concentrations are between 0.1 to 1 mg, *E. coli* is at 140 µM, and this antibacterial effect has been attributed to the production of ROS [2]. In addition, carbon nanotubes have also exhibited antimicrobial activity with damage to the membrane because of direct contact with nanotubes having a single wall [49]. Moreover, it has been proven that the strain of bacteria also has an impact on the sensitivity to carbon nanotubes. When E. Coli is exposed to purified as well as unpurified carbon nanotubes with multiple walls at 100 mg L^{-1}, the survival probability reduces to 50%, but for the same case, there isn't any change in the survival of *Cupriavidus metallidurans*. It has been well established that many metal oxide NPs, such as ZnO, TiO$_2$, CeO$_2$, and Al$_2$O$_3$, have antibacterial properties. It has also been suggested that the toxicity of such ENPs to bacteria in aquatic environments is dependent on size, shape, chemical composition, surface charge, ability to produce ROS, and photo-catalytic properties [50]. In a significant amount of research, it has been found that silver NPs have antibacterial properties, and the use of silver NPs in consumer products and industrial applications has been increasing. Just like the metal oxide NPs, the antibacterial nature of silver NPs has been interrelated with the production of ROS and with the existence of Silver (Ag$^+$) ions on the surface of the particles. However, not all sorts of bacteria are equally susceptive, and based on the strain of bacteria, nitrifying bacteria are particularly sensitive. Although exact mechanisms of toxicity have not completely been explicated for the maximum number of ENPs, probable mechanisms, illustrated in Figure 3, consist of membrane disruption or membrane potential disruption, protein oxidation, genotoxicity, energy transduction interruption, ROS formation, and discharge of hazardous constituents [51].

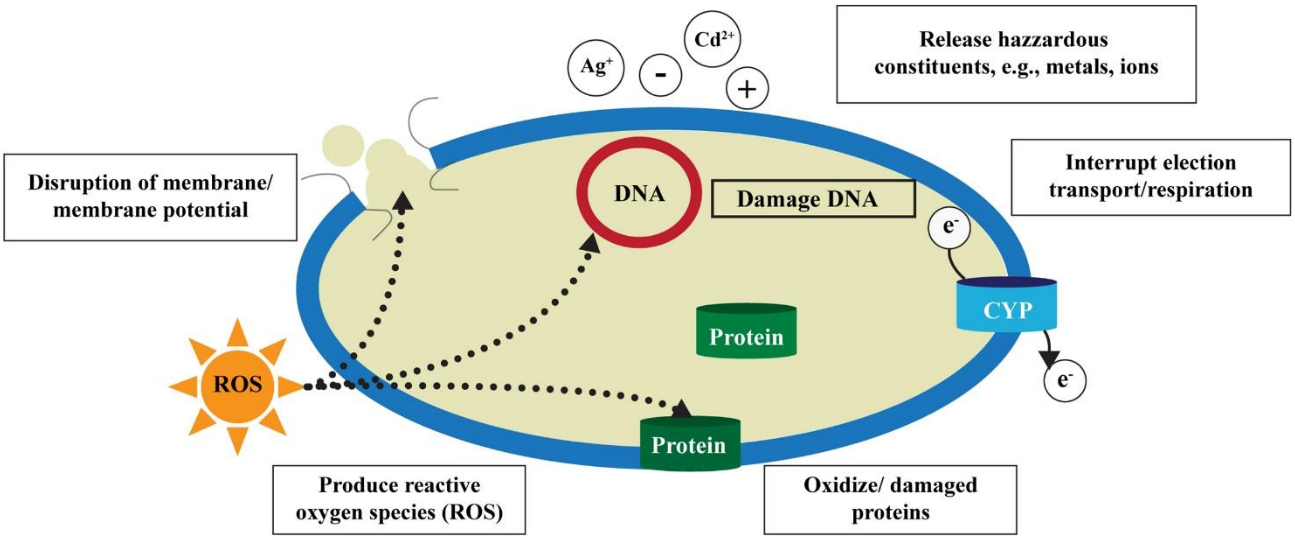

Figure 3. Mechanisms of toxicity of ENPs to bacteria [51].

In contrast with this finding, a study investigating the antibacterial effects of silver NPs in the sediments of estuarine bodies found no proof of any changes in bacterial diversity due to exposure. Like bacterial populations, algal populations play a significant role as primary producers in the water environment. Most of the studies on algal populations have concentrated on demonstrating a dose-response relationship to toxicity. TiO_2 NPs, at concentrations of about 1~5 mg L^{-1}, are toxic to some algae, such as *Pseudokirchneriella subcapitata*, but for *Desmodesmus subspicatus*, the concentration must be around 44 mg L^{-1} [49]. In different studies, at comparable concentrations, no sign of algal toxicity has been reported for TiO_2 exposure. These studies collectively illustrate the difference in insusceptibility of algal populations to TiO_2 exposure as well as suggesting potential differences in exposure regimes. In addition to that, TiO_2 NPs, according to their types, may strongly influence the level of toxicity for any algae. The studies conducted on *Chlamydomonas reinhardtii* and *Pseudokirchneriella subcapitata*, suggest that the dissolved ions originated from various metal NP types, but not from the ENPs themselves and are the root cause of toxicity [49]. However, Navarro et al. [50] proved that all the toxicity in the exposure of *Chlamydomonas reinhardtii* to silver NPs could not be ascribed to Ag^+. Collectively, this research on exposures of microbes and algae to ENPs establishes that many types of ENPs possess the potential to adversely affect and, in the case of microbes, interrupt population growth. Most importantly, the effects discussed so far could have serious implications for all the higher organisms existing in the same aquatic environments.

2.3.2. Toxic Effects of ENPs on Aquatic Vertebrates

Several experimental studies on the toxic effects of ENPs on aquatic vertebrates were completed on a laboratory level in various types of fishes. The very first study was conducted on young largemouth bass in a colloid containing a particular type of ENP. It was observed that lipid peroxidation occurred in the largemouth bass brain [42]. Moreover, two other kinds of fish, i.e., Japanese Medaka and Fathead Minnow were studied by exposing them to a particular ENP for about 72 hours. A decrease in the 70-kDa peroxisomal membrane protein (PMP70) only happened in the case of Fathead Minnow. A succeeding study on the fully grown Fathead Minnow (*Pimephales promelas*) preserved for about 6-18 hours with fullerene, prepared by tetrahydrofuran (THF), in a suspension of THF, exhibited a hundred percent mortality. On the contrary, zero mortality was recorded when the THF suspension was replaced by water, however, lipid peroxidation was detected. Therefore, it was clear that the method of solution preparation considerably influences toxic effects.

Another study [52], focusing on Rainbow Trout found a concentration-dependent effect of ENP exposure, significantly impacting the liver and gills, with increases of up to 18% and 28%, respectively, in total glutathione levels. In some cases, pathologies in the brain, liver, and gills were observed, leading to the death of the specimens. Zebrafish embryos are often preferred for toxicity studies due to their small size and rapid development. A study conducted by Souza et al. [53] on the organs of the fish *Cyprinus carpio*, has shown that exposure of a fish to ENPs for a long period causes necrosis and cellular damage. Additionally, in the zebrafish (*Danio rerio*), the damage to the liver and gills, because of the stress of oxidative, was also observed, which is the result of exposing *Danio rerio* to ENPs for the long term. Yet, fish have comparatively stronger immune systems and hence, they are not as much at risk as the other organisms in aquatic environments.

In a nutshell, ENP effects evaluations on microbes, algae, aquatic invertebrates, or aquatic vertebrates contrast extensively, even for one type of ENP. Even though some proof of adverse effects is available, the lack of dependability in those observations can't be entirely denied. Such shortcomings may come from the dissimilarities in the resources used in the laboratories where these studies are being conducted. Commonly there remains a shortage of comprehensive data on characterization to make a reliable comparative analysis of the exposure situations and all over, effects found to take place at concentrations more than anything is most likely to take place in aquatic environments.

2.3.3. Toxic Effects of ENPs on Aquatic Invertebrates

Exposure of aquatic invertebrates, to carbon-based NPs, has related to numerous detrimental effects. Those detrimental effects have not only been associated with the chemical properties of the NPs but also with the method used for preparing the NPs. For instance, it has been found that fullerenes cause a significant rate of mortality in bare Daphnia magna, whether it is being prepared by the exposure medium of sonication or through filtering in subsequently evaporable THF. Fullerenes, filtered in THF, were found to be more toxic in comparison with fullerenes prepared by sonication, causing 100% mortality at 0.8 ppm in aquatic environments. On the other hand, the sonicated fullerenes, at 9 ppm which is the maximum tested dose, caused a lower rate of mortality in the same environments. Suspensions of fullerene have also been discovered to create a hindrance in molting as well as a decreased amount of progeny at concentrations of about 2.5 and 5 ppm, respectively, after a three-week exposure. Just like carbon-based NPs, metal oxide-based NPs show similar characteristics. The toxicity that results from the exposure of Daphnids to TiO_2 NPs changes primarily because of two factors; the physicochemical features of the NPs themselves and the method of preparation for the TiO_2 NPs exposure. In a study, sonicated TiO_2 NPs at 500 ppm were found to cause nine percent mortality in *Daphnia magna* while TiO_2 NPs, filtered in THF, at 10 ppm caused complete mortality [42]. The collective effects of combinations of metallic pollutants with ENPs and the environmentally significant aquatic species are presented in Figure 4.

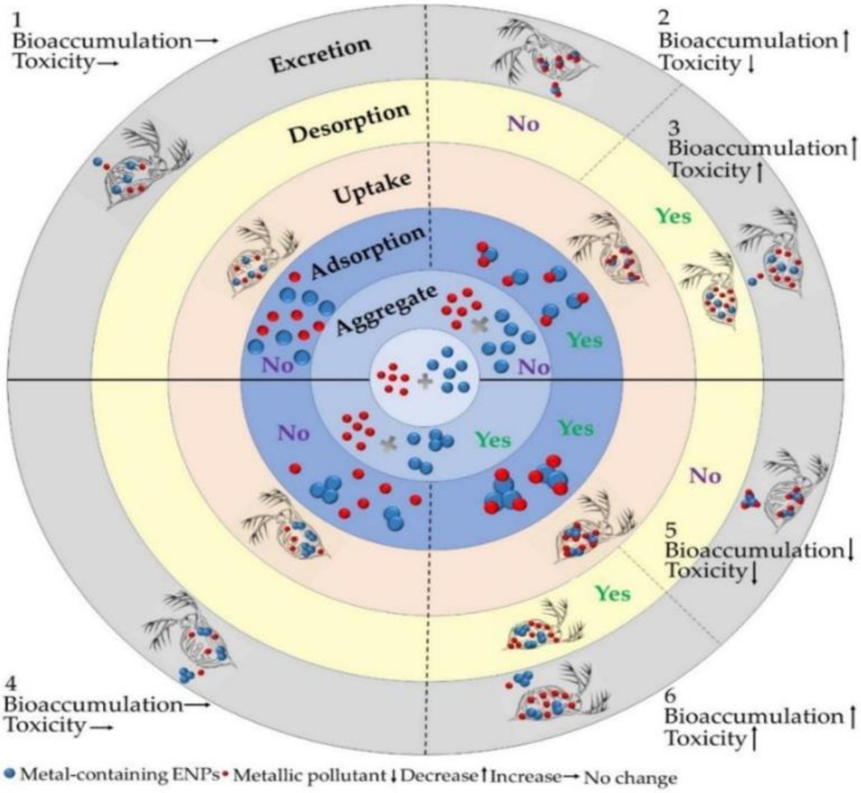

Figure 4. Conceptual demonstration of various situations regarding collective effects of combinations of metallic pollutants with ENPs and to environmentally significant aquatic species *Daphnia magna* [49].

Some other studies have shown an inconsiderable amount of effect on the exposure of *Daphnia magna* to TiO_2 NPs. For example, exposure of *Daphnia magna* to 30 nm TiO_2 NPs at 2 ppm didn't cause any change in the set of behaviors and heart rates [54]. Similarly, exposure of *Daphnia magna* to either 7 nm or 20 nm TiO_2 NPs at 1 mg mL^{-1} didn't cause any effects on mortality or reproduction. In addition, it has also been found in the same research that contacts with both 15 nm and 30 nm cerium oxide NPs were found to cause breaking DNA strands in *Daphnia magna*. Similar studies operated on *Daphnia magna* by implementing the same exposure concentrations, however, found zero effect on breeding, aging, or mortality in *Chironomus riparius*, an aquatic midge. Very few studies have been done focusing on the probable effects of many other ENP types in invertebrates habituating in aquatic environments; nevertheless, for *Ceriodaphnia dubia*, exposure to quantum dots found zero mortality up to 0.11 ppm [2].

3. ENPs in Soil-Plant System

3.1. Interactions of ENPs with Soil-Plant Systems

A considerable amount of ENPs is being released into the environment through industrial waste, consumer items, research labs, and regulatory bodies due to the rapid advancements in nanotechnology. In soils, there are primarily two kinds of NPs. The first kind is the natural nanoparticles (NNP) which are soil colloids comprised of inorganic colloids (silicate clay minerals, Al, or Fe oxides/hydroxides) and organic colloids (humic organic matter including black carbon and large biopolymers such as polysaccharides). The second kind of NPs has been ENPs or manufactured nanoparticles (MNPs) by humans for agricultural, medical, industrial, and other uses. These nanoparticles end up in soil and plant systems. Therefore, it is crucial to perform research on how nanoparticles change and interact with soil organic and inorganic colloids, microbial biofilms, and their transfer from soil to plants to understand the soil-plant continuum. The five main types of ENPs found in the environment include carbon-based nanomaterials, zero-valent metals, metal oxides, quantum dots, and nano polymers [42]. In terrestrial ecosystems, plants serve as the primary producers. They have evolved in environments with high concentrations of naturally occurring nanomaterials, such as those close to active volcanoes [55]. The agriculture sector is more at risk of exposure to ENP than to naturally produced NPs. It has been revealed that the effects of metal-based, carbon-based, and quantum dots (QDs) ENPs on plants vary. These include food quality, production, physiological and biochemical features, accumulation, effects of growth, and more [56]. For determining the fate of ENPs in the soil-plant systems and their potential toxicity, a thorough understanding of the interactions between ENPs and soil-plant systems is of paramount importance. Precipitation–dissolution, adsorption-desorption, and complexation are the most significant processes controlling the bioavailability and translocation of ENPs from soil to plant [3].

Plants are a significant part of the ecological system and closely interact with surrounding environments. The extensive release of ENPs into the environment results in the migration of the ENPs to different parts of the plant system. Plants execute a crucial role in the transport and fate of the ENPs through uptake and bioaccumulation. Figure 5 shows the fate of ENPs in soil-plant systems [57]. Consequently, a substantial amount of physical and chemical toxicity has been observed in different plant parts and the gradual increase in the concentration of the ENPs in soil and sediment elevates the level of nanotoxicity at a faster pace. Additionally, much concern has been associated with the transfer of ENPs to the other organisms and animals of the ecosystem, even to humans as different parts of the plant are consumed regularly. In this context, a considerable amount of research has been done to locate phytotoxicity and nanotoxicity on different plant species such as soybean, wheat, barley, tobacco, maize, etc. [54,58,59]. Several further studies are ongoing for better evaluation of ENP toxicity as ENPs are being used extensively by the modern world.

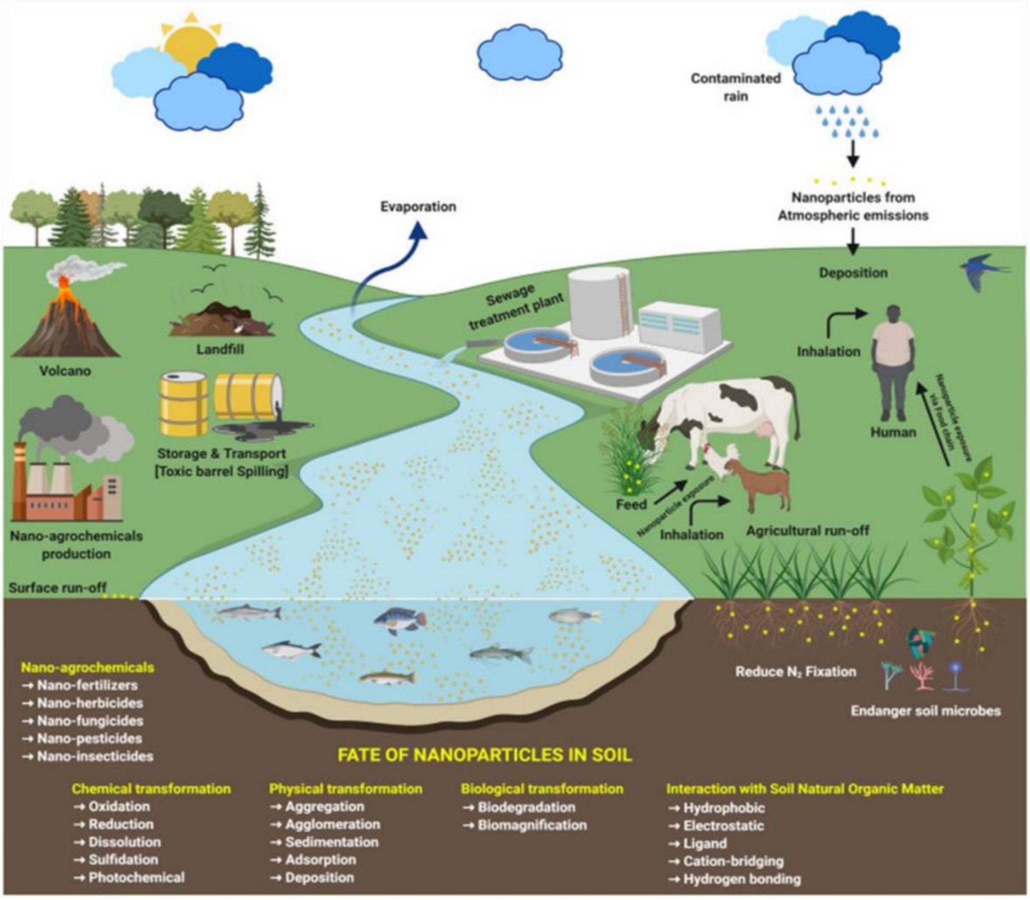

Figure 5. Illustration of the fate of ENPs in Soil-Plant Systems [57].

There is an additional serious threat regarding ENP's exposure to the plant system as ENPs can cross the cellular barriers easily due to having extremely small size [60]. The ENPs can transfer to the plant system mainly through roots, stomata, and leaves. The ability of each nanoparticle to infiltrate within plant cells is decided by the size of pores in cell walls which ranges from 5 to 20 nm. Despite several advancements in ENP characterization, the investigation of the process of accumulation, translocation, and generation of phytotoxic response by ENPs in plant species is still poorly correlated. While some of the ENPs have been found to have phytotoxic effects, others show growth-promoting effects, even reports showing the formation of nanoparticles inside the live plants.

Once ENPs are entered into the soil-plant system, they may go through a series of biotransformation, which eventually regulates the bioavailability, and produce toxicity and oxidation stress of ENPs. ENPs are absorbed by plants and thus possess a possible threat to our health through transmission in the mainstream food chain [61,62]. As far as soil and agro-system are concerned, extensive applications of nano pesticides, nano fertilizers, hydroponic solutions, and seed treatment are likely to disclose new pathways for discharging ENPs into the cultivable soils. For instance, it is hypothesized that about 95% of copper (Cu) released in the environment would ultimately end up in the aquatic or soil sediments up to 500 $\mu g\ kg^{-1}$ in concentration [63]. ENPs start to undergo a series of transformations just once they are released into the soil and agro-environment to facilitate the accumulation of ENPs into the environment. However, the rate of transformations differs depending on the aggregative state of ENPs. Properties of soil or constituents, such as organic substances, pH, water content, etc. can intervene in the dissolution activities of metal-based ENPs, being a possible source of free ions [64].

The transformation of NPs in soil largely controls the bioavailability of NPs. The dissolved NPs exhibited more bioavailability as well as an environmental risk. The environmental threat of ENPs mostly depends on two major factors namely the bioavailability of NPs and their chemical characteristics in the soil-plant systems [65]. Nevertheless, fast, and precise evaluation of the bioavailability of ENPs in soil remains a critical matter that needs to be resolved. The ENPs are prevalent in soil and interact with the plants as shown in Figure 6 [66]. Accumulating in plants, ENPs come into the mainstream food chain through uptake and thus decide their fate in the terrestrial environment [67]. Inside soil-plant ecosystems, the deliberately applied water-borne NPs also interact with plant tissues [68]. Firstly, the plant roots encounter the NPs released from soil or wastewater relents containing soil used for crop nutrition. In this condition, the impact of NPs on plants and edible crops grown for an extended duration in soil ecosystems adulterated with NPs should be evaluated. For example, copper oxide (CuO) ENPs can be firmly adsorbed on the surface of the plant root, partly through mechanical adhesion. In these circumstances, the already absorbed CuO could not be reversed throughout the contest for ions [69].

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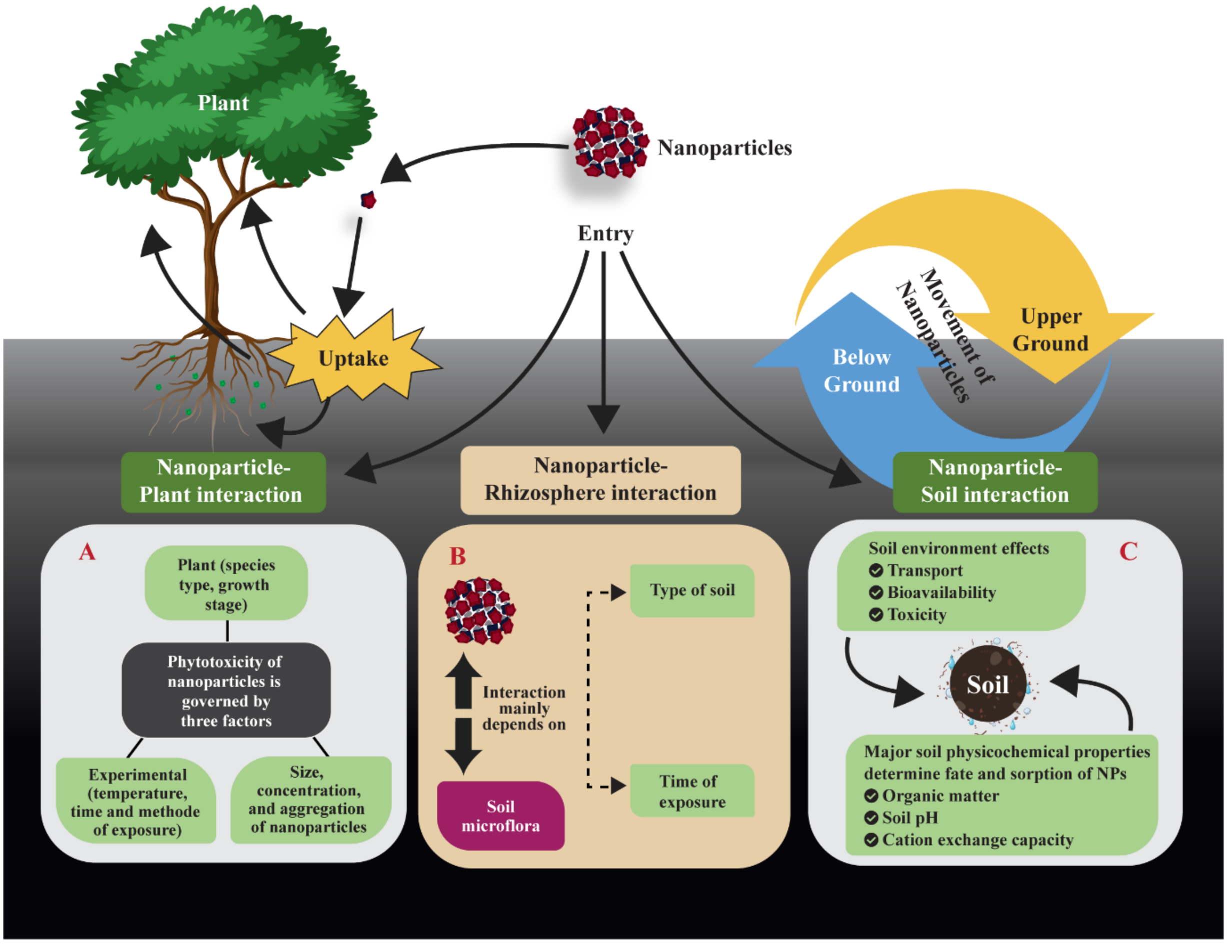

Figure 6. Interactions of ENPs with three elements of soils- (i) soil itself, (ii) soil microflora, & (iii) plants. NPs and Plant interaction (panel A) showed the three factors by which phytotoxicity of NPs is governed which are: (i) plant: species type and growth stage (ii) experimental: temperature, time, and method of exposure, and finally (iii) physicochemical characteristics of NPs, i.e., size, concentration, aggregation, and chemical composition of NPs; NPs and soil microflora interaction (panel B) illustrated that the interaction mainly depends on soil type and exposure time. NPs and soil interaction (panel C) physicochemical characteristics of soil control the bioavailability and transportation of NPs in soil and the consequent impact of toxicity on plants [66].

Several researchers assessed some ENPs and concluded that the accumulation of ENPs in plants happened through adsorption in plant roots subsequently distributed via plant tissues with the help of some adjustments, for example, the crystal phase dissolution, the bioaccumulation, and the biotransformation [70]. These evaluations recommend that both the shoot tissues and roots of plants are the ENPs receiving hosts. The accumulation rate of ENPs by the plant's root can also be influenced by the environmental conditions and the properties of ENPs as well. The latest study suggested that the siderophores exhibit an immense affinity to other metal-based ENPs such as Zn, Cu, and Ag [71]. As a result, augmentation, and dissolution of ENPs can be advanced by the chelation between siderophores and metals. Moreover, the roots of the plant often discharge exudates to enhance nutrient uptake from insoluble sources. In a particular study, it has been suggested that the exudates of the synthetic root can advance the Cu NP's rate of dissolution and enhance the bioavailability of free-ion Cu^{2+} in the soil [72].

3.2. Toxicological Effects of ENPs in Soil-Plant

ENPs can be classified into highly soluble (Ag, Cu/CuO, FeO, QDs, and Zn/ZnO), poorly soluble (CeO_2, TiO_2), and insoluble (CB, CNTs, graphene, and fullerenes) materials. By dissolution chemical transformation process, the ENPs release the water-soluble ions or molecules. The properties of ENPs influence the dissolution process as these regulate the available surface area for reactivity. Various types of contaminants, such as potentially toxic elements (PTEs), radioactive elements, polychlorinated compounds, and pesticides found in sediments, soil, or suspended as solids in water, bind to the surface of ENP through chemical bonding, van der Waals interaction (physical sorption), and ion-exchange reaction (chemical adsorption). A recent study by Sun et al. [73] shows that the sorption of the antibiotics (levofloxacin and ciprofloxacin) on graphene oxide (GO) increased their mobility and transport through porous media, potentially increasing their risks to ecological receptors and the potential to contaminate groundwater [73]. The transport of gold ENPs is facilitated and acts as a carrier in porous media by the pluronic acid-modified single-wall carbon nanotubes (PA-SWCNTs). ENPs can carry different pollutants and enter into the organism as a particle-contaminant complex. As a result, the complex pollutants are released inside the organism, increasing the bioavailability and toxicity of the contaminants due to the ENPs' "Trojan horse effect" [74]. Prolonged existence, poor biodegradability, and enormous increment in the deposition of ENPs into the environments created additional survival stress on edible crops and plants. The dominance of NPs in terrestrial environment and reciprocity with plants cause toxicity as shown in Figure 7.

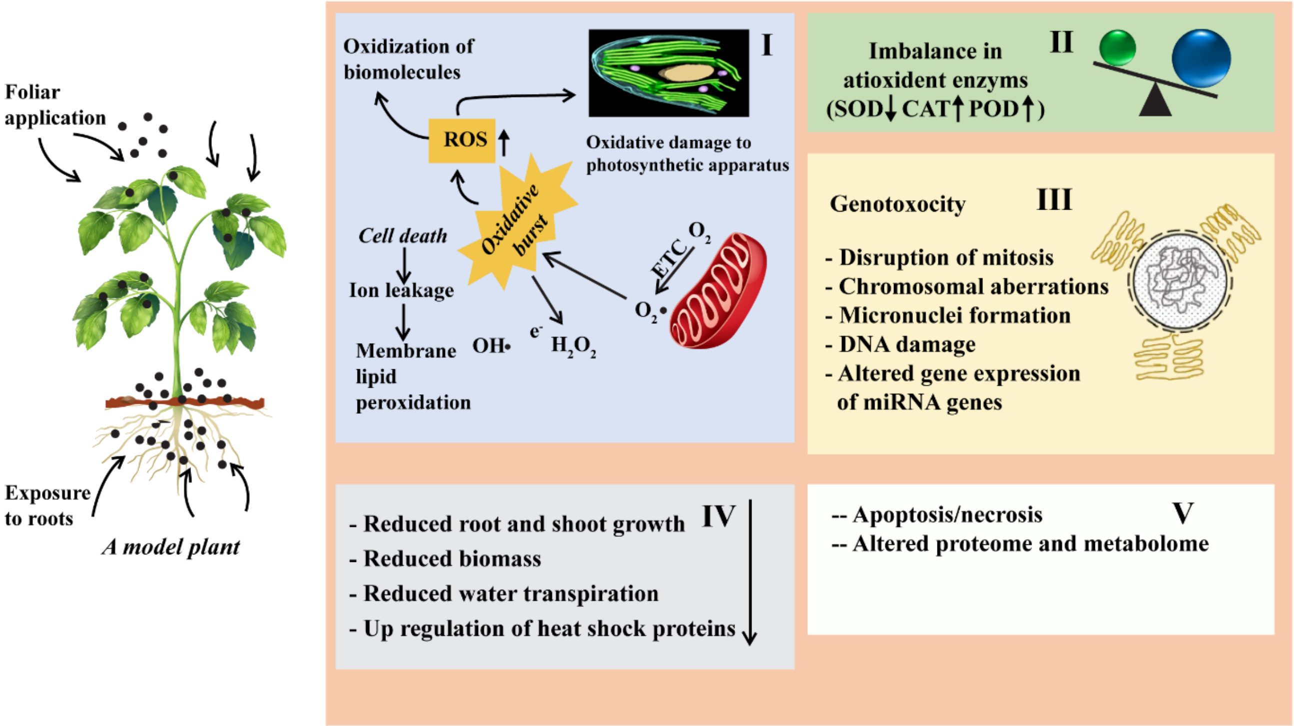

Figure 7. Toxic effects of ENPs on the plant through ROS generation, peroxidation of the lipid membrane, and damage of mitochondria and chloroplasts (Panel-I). Oxidative stress creates an imbalance in enzymes (Panel-II); interaction of NPs with plant cells causes genotoxicity through disruption of the usual cell cycle, generation of micronuclei, anomalies of chromosomal, etc. (Panel-III). Disturbing effects of NPs on plants contain biomass reduction and water transpiration etc. (Panel-IV); interaction of NPs with cells of plant results in necrosis, apoptosis, and change in metabolome and proteome (Panel-V), which eventually lead to the death of plant cell. [66].

Disregarding the pathways, bioaccumulation, transportation, and toxic effects of NPs on plants mostly depend on several factors. For plant genotypes, physiological activities, and growth stages are the deciding factors whereas size, shape, chemical composition, surface functionalization, exposure time, stability, etc. are the factors for NPs. Microbiological composition and physicochemical characteristics of soils also play a crucial role [75]. Another study by Strekalovskaya et al. [76] explains that the environment-friendly ZnO nanoparticles (NPs) have antimicrobial

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properties that can impact soil microbiota and key processes like nitrogen fixation and plant growth. While they positively influence plants and soil microorganisms at low concentrations, higher levels can lead to toxic effects. The toxicity of ENPs (Table 2) on various physiological processes and growth stages of several plants is evaluated and discussed in brief in the subsequent sections.

Table 2. Toxic responses of nanoparticles to agriculturally important plants.

ENPs	Size and dose rate	Test Crop(s)	Results	Reference
Ag	10 nm and 0.001-10000 mg L^{-1}	*Raphanus sativus*, *Allium cepa*	The growth of plant roots was inhibited.	[77]
CuO	20-100 nm and 34.4 g m^2	*Brassica oleracea* var. *viridis*, *Brassica oleracea* var. *sabella* & *Lactuca sativa*	Large amounts of CuO accumulated on the surface of lettuce leaves and subsequently kale and collard green.	[78]
ZnO	<100 nm and 20-900 mg kg^{-1} soil	*Triticum aestivum*, *Pisum sativum*, *Zea mays*, *Lactuca sativa*, *Raphanus sativus*, *Beta vulgaris*, *Solanum lycopersicum*, and *Crocus sativus*	Toxic effects of ZnO NPs depend on plant species; ZnO NPs reduced the availability of Zine while interacting with calcareous soil and as a result toxicity to accumulation of biomass by wheat, beet, and cucumber, whereas maize, pea, and wheat showed resistance in acidic type soil.	[79]
TiO_2	25 nm and 250–1000 mg L^{-1}	*Crocus sativus*, *Brassica oleracea* var. *capitata*, *Avena sativa*	Growth of roots of edible crops such as corn, oat, cabbage, lettuce, etc. was inhibited and germination of cucumber and soybean was reduced.	[80]
Al_2O_3	13 nm and 50 mgm L^{-1}	*Triticum aestivum*	H_2O_2 content, lipid peroxidation, and superoxide dismutase activity were increased; the production of anthocyanin and photosynthetic pigment was reduced.	[81]

3.3. Toxic Effects of ENPs on Plants Growth

The accumulation of ENPs in plants usually changes physiological development by reducing photosynthesis and the rate of transpiration, disturbing the cellular integrity, and affecting growth rate and plant performance. In a few cases, reductions in the quantum yield of photosynthesis and rate of transpiration are also observed [70]. Several studies [82–85] suggested that the ENPs might affect crops by decreasing the germination rate, reducing shoot and root length, changing photosynthesis, producing antioxidants, and oxidative stress, and interrupting the balance of the nutrient content of edible crops and yield quality. It has been observed that ENPs enter the cells, either by accumulating in chloroplasts and vacuoles or confiscating in cell walls that remain in their novel form or as ions. Still, it could vary due to differing physicochemical factors [69]. In the case of plants, the uptake capabilities of ENPs differ since they have major diversification based on physiological and morphological factors. For instance, variable mechanisms of uptake could be caused by the diverse root as well as vascular morphologies through which ENPs enter the plant tissue. The ENP accumulation inside the plant tissues may also harmfully modify lipids, proteins, and nucleic acids by producing hydroxyl radicals.

4. Future Outlook to Address the Impacts of ENPs

In future to address the impacts of ENPS on the aquatic environment and plant-soil systems, we have outlined the following action items which can be considered.

- **Reuse and recycle:** Promoting the reuse and recycling of ENPs is vital for reducing resource wastage and environmental contamination. Unlike bulk materials, nano waste recycling is still a relatively new concept, with limited implementation in industrial and municipal waste management systems, where disposal often involves landfills or incineration. Developing efficient recovery techniques from industrial, agricultural, and wastewater sources, alongside designing ENPs for easier reuse, can advance sustainable practices. Establishing innovative recycling processes and integrating best practices into waste management systems can help recover ENPs for reuse in the same or diverse applications, promoting a circular and environmentally responsible approach to their management. Additionally, designing ENPs for easier recovery and reuse should be a priority for researchers and manufacturers. Several methods for reuse, recycling, and disposal have been described by Pandey et al. [86]. Those methods can be considered.
- **Development of disposal management strategies**: Effective waste management strategies for ENPs are essential to reduce their environmental and health impacts. Nano wastes, originating from industrial, residential, and medical sources, contribute to pollution and bioavailability concerns. Current waste management systems face challenges in addressing the rising volume of nano waste. Advanced filtration, adsorption, and containment technologies, along with specialized disposal methods, can prevent ENP leaching into aquatic environments, soil-plant systems, and water sources. Establishing dedicated facilities for ENP waste treatment while assessing the environmental implications of novel materials will further mitigate risks to ecosystems and human health.
- **Implementation of regulatory policy:** Globally harmonized regulatory policies are essential to ensure the responsible production, application, and disposal of ENPs. Such policies should enforce stricter disposal standards, encourage sustainable practices, and incentivize research into safer alternatives. Equally important are public awareness campaigns and transparent communication about the risks and benefits of ENPs to enable informed decision-making by industries, consumers, and policymakers. Collaborative efforts among governments, industries, researchers, and stakeholders can bridge gaps between policy and practice, while social awareness programs can highlight ENP impacts on ecosystems, fostering safer and more sustainable nanotechnology practices.
- **Understanding toxicity and transmission by further research:** A deeper understanding of the toxicity and environmental transmission of ENPs is essential to address their impact on aquatic environments and soil-plant systems. Although current studies rely heavily on modeling and concentration predictions, more comprehensive research is needed to evaluate the real-world effects of ENPs, particularly in relation to their transformation, aggregation, and degradation. Toxicity mechanisms, especially for nanoparticles like Ag-NPs, remain unclear, highlighting the need for thorough risk assessments before their widespread use. Developing high-precision analytical methods and real-time monitoring systems that integrate nanotechnology and digital tools is crucial to detect and quantify ENPs in environmental matrices. Future research should also prioritize the development of environmentally friendly, biodegradable ENPs through green synthesis methods, ensuring their reduced ecological impact and enhancing their sustainability from production to disposal.
- **Risk assessment for ENP life cycle:** As the deposition and accumulation of metal and metallic oxide ENPs in soils increase over time, their effects on soil properties, such as pH, electrical conductivity, and soil organic matter, become more significant. ENPs can compact soil particles, altering their rigidity and interacting with nutrients, potentially forming complexes that modify nutrient availability. While the benefits of ENPs in agricultural systems are being explored, research into their potential risks, especially their impact on soil health and microbial communities, is still in its early stages. Future studies should not only focus on the advantages

of ENPs in agriculture but also evaluate their long-term effects on soil quality, plant growth, and microbial ecosystems. To better understand these impacts, developing robust risk assessment models that consider the life cycle, bioavailability, and cumulative effects of ENPs is essential. These frameworks should address ENPs' unique properties, transformation behaviors, and their long-term risks to ecosystems.

5. Conclusions

The aquatic environment and soil-plant system are typically exposed to multi-component mixtures of ENP pollutants. Many studies have been conducted about the interaction of ENPs with the environment, and their transformation, fate, and toxicity; however, there are still abundant knowledge gaps and challenges that need to be filled in assessing their impact upon environmental exposure. It is necessary to understand how an ENP will behave in the aquatic environment and soil-plant system over a specific time. The interaction between ENPs and the environment (i.e., air, plants, water, and soil systems) is crucial and ultimately determines their toxicity. The ENPs used in the agriculture sector have a beneficial effect but may harm the agricultural sector due to ENP-based pollutants. It also depends on the interaction of ENPs with the plants. ENPs can be beneficial to aquatic environments and soil-plant systems at a particular concentration; they can affect both negatively at high concentrations. Moreover, ENPs can pass through the plant cell wall and get accumulated in the plants and lastly enter animals and humans through food chains. This can cause serious health effects for animals and humans. Therefore, necessary international rules and regulations for the usage, treatment, and disposal of wastes containing ENPs are essential. Social awareness programs should be developed for the public about ENP's effects on the aquatic environment and soil-plant system as well as human health. A comprehensive understanding of transformed ENP-induced toxicity will provide to design of environment-friendly ENPs and promote sustainable nanotechnology.

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Data Availability Statement: The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request. Any additional materials or resources used in this study are likewise available and may be shared upon request, ensuring compliance with any ethical and confidentiality guidelines.

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Abbreviations

The following abbreviations are used in this manuscript:

Al_2O_3	Aluminum oxide
ENP	Engineered nanoparticles
HA	Humic acids
ROS	Reactive oxygen species
THF	Tetrahydrofuran
TiO_2	Titanium oxide
ZnO	Zinc oxide

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