Chapter 2
Impact of Emerging Metal-Based NPs on Plants and Their Influence on the Phytotoxicity of Other Pollutants

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Abstract Metal-based nanoparticles (NPs) are one of the most manufactured nanomaterials and deserve singular attention given their continuous input to the environment, lack of degradation, and accumulation risk. In agricultural soils, the use of organic amendments and wastewater and the application of nanotechnology are important NP inputs. Metal-based NPs have beneficial applications as fertilizers and increase plant resistance to pathogens and environmental abiotic stressors. Ag-, Zn-, Cu-, Ti-, and Ce-based NPs are the most widely used to improve crop production. NPs can also have negative impacts, including phytotoxicity, lower nutrient content in plants, and soil microorganism toxicity. The potential NP interaction with other soil contaminants, including metals and organic compounds, is a major concern because it can modify the bioconcentration or affect the intrinsic toxicity of both substances with the consequent biological impact on plants. Exposure to NP-contaminant mixtures may induce unexpected toxic effects via several different mechanisms that affect the availability, uptake, and metabolic processes involved in the detoxification and degradation of compounds. However, the mechanisms underlying the effects of the NP-contaminant interaction on joint toxicity are poorly understood. This chapter covers some of the most relevant issues concerning the effects of metal-based NPs on plants.

Keywords Metal-based nanoparticles · Nano-agrochemicals · Co-exposure · Phytotoxicity · Bioaccumulation · Chemical mixtures

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Abbreviations

CAT	Catalase
DDE	Dichlorodiphenyldichloroethylene
GPX	Glutathione peroxidase
OTC	Oxytetracycline
QD	Quantum dot
QNC	Quinclorac
ROS	Reactive oxygen species
SOD	Superoxide dismutase
TC	Tetracycline
ZVI	Zero-valent iron

2.1 Introduction

Nanoparticles (NPs) are materials with the three dimensions below 100 nm and applications in a variety of sectors (e.g., biomedical, chemical, textile, food, agriculture). Their tiny size confers specific characteristics that can intensify their properties. In the natural environment, a small NP size can increase environmental negative impacts compared to the bulk form, but demonstrated beneficial applications as nano-remediators or nano-agrochemicals have been reported (Yang et al., 2019). NPs' morphology is also crucial for showing toxicity in some cases. The coating of NPs' surface and their encapsulation are common practices that can help their stability and change their reactivity and toxicity (Sturikova et al., 2018; Zeng et al., 2019). In the natural environment, NPs are subject to transformation processes like dissolution, aggregation, reduction/oxidation, sulfidation, and adsorption. Aging also drives NPs' properties, including fate and toxicity (Fernández et al., 2021; Romero-Freire et al., 2017; Jośko et al., 2020; García-Gómez et al., 2020).

Overproduction, use, and abuse of NPs have rapidly led to them be released to several environmental compartments, which increases environmental threats to living organisms. The three major sources of terrestrial plant exposure to nanomaterials are air, water, and soil. In soil, the largest amounts accumulate (up to 1.5%, 7%, and 28% of total NPs' production, respectively) (Liu et al., 2020). Atmospheric NPs can be easily deposited on various plant surfaces and infiltrate the plant system via stomatal apertures and across cuticles. The use of wastewater containing aged NPs is another source of NPs to plants. In agricultural soils, the use of amendments (manures, sludges, etc.) and the application of nanotechnology deliberately enable the input of NPs in agricultural environments. In recent decades, the agriculture has faced a wide range of challenges, such as climate change, salinity and drought, soil pollution, and the increasing food demand for a growing population. The use of nanomaterials in modern agriculture helps to gain maximum output from available resources and contributes to mitigate the aforementioned challengers (Rajput et al., 2021). Nonetheless, to promote sustainable progress, it is necessary to assess NPs' toxicity to non-target organisms at the same time as NPs are being investigated and developed.

It is remarkable that NPs at nontoxic concentrations can still be hazardous because of their interaction with other contaminants present in the environment. Previous studies show that NPs can facilitate the intake of metals and organic compounds in plants and other organisms, which can lead to these chemicals' increased toxicity (Deng et al., 2017; Naasz et al., 2018). In some cases, these indirect effects can be more significant than the direct impacts associated with NPs' exposure. Thus acquiring knowledge of the potential effects that result from the interaction of NPs with co-existing organic and inorganic contaminants is critically important for evaluating and regulating the environmental impacts of NPs on plants.

The plant relation with NPs is very complex, and NPs' absorption mechanisms in plants are still poorly understood. Plant systems provide a route for NP uptake, accumulation, and translocation that depends on the physiological properties, functionalization, and the form of exposure of NPs to plants (Agrawal et al., 2022). One of the most important limitations to impact plant uptake of NPs is particle size. Several studies establish 20–50 nm as the size limit for NPs to penetrate and move to plant tissues. In plants, NPs are firstly adsorbed on the root surface, and root exudates and transporter proteins can participate in uptake processes. Tiny NPs can diffuse through epidermal cell wall pores and enter the apoplastic and/or symplastic flow. The apoplast form takes place outside cell membranes through extracellular spaces, cell walls of adjacent cells, and xylem vessels. The symplastic form involves substances and water moving between the cytoplasm of adjacent cells. Larger NPs are first blocked, which results in osmotic pressure and capillary forces that finally help NPs to reach the endodermis by either crossing the cortex cells and diffusing through the apoplastic pathway or merging on symplastic route to penetrate the vascular system (Lv et al., 2019; Deng et al., 2014). The foliar NPs' application implies crossing the cuticle layer, and uptake occurs via two routes: one for polar solutes by polar aqueous pores (hydrophilic pathway) and another for non-polar solutes via diffusion and permeation (lipophilic pathway) (Pérez-de-Luque, 2017; Ali et al., 2021).The cuticle serves as a primary barrier to prevent NPs larger than 5 nm from entering (Molina et al., 2021). This entrance does not prevent root damage because there is evidence for the transport of NPs from the aerial parts to roots (Chichiriccò & Poma, 2015).

Metal-based NPs are one of the most frequently manufactured nanomaterials due to their widespread uses, including environmental applications. Furthermore, given their non-biodegradable nature, significant amounts of these compounds are expected in soil.

This chapter focuses on the impacts that metal-based NPs have on plants. Indirect effects due to NPs are also discussed, such as changes in the plant-soil environment and the influence of co-occurrence with other soil contaminants like organics, metals/metalloids, and nanomaterials.

2.2 Nanoparticles and the Plant's Environment

These new-age materials have the potential to alter biotic and abiotic systems, alterations that are governed mostly by the concentration and physiochemical properties of NPs. Of these, the most dominant are size, shape, and surface charge. Soil properties, mainly pH, organic matter content, cation exchange capacity, texture, moisture content, etc., have the capacity to modify the reactivity, fate, and, ultimately, the toxicity of NPs (Rawat et al., 2018; Gao et al., 2019; García-Gómez & Fernández, 2019). In soil, NPs may undergo several physical-, chemical-, and biological-mediated processes that lower their bioavailable concentration and, hence, their toxicity. In particular, aggregation, retention, adsorption or desorption, dissolution or precipitation, transformation, interaction with other molecules, or incorporation (ingestion-egestion) by organisms are common processes undergone by NPs in natural environments (Amde et al., 2017). Most of these processes depend on soil pH. Under acidic conditions, metallic NPs are transformed into ionic species at high rates, while alkaline environments help the aggregation of NPs. For example, ZnO NPs are differently reactive in acidic (pH 5.4) vs. alkaline (pH 8.3) soils, which results in positive germination and growth responses of nine plants in alkaline soil, but also in negative responses in acidic soil (García-Gómez et al., 2018c). CuO NPs are more toxic to barley at low pH, which is coincident with greater Cu dissolution from NPs (Qiu & Smolders, 2017). Hetero-aggregation induced by the pH of metal-based NPs with soil components enhances their electrostatic/steric stability, but hinders their diffusion and transport in soil (Dimkpa, 2018; Ju-Nam & Lead, 2016). Aggregation also involves a diminished particle surface made available for the release ions, which results in a lower dissolution rate that can attenuate their effects on biological systems.

Regardless of soil physiochemical properties and NP intrinsic characteristics, other factors influence the impact of NPs on plants. Root secretions contain organic molecules of high- and low-molecular weights (polysaccharides, fatty acids, amino acids, metal ions, etc.) that can modify the environment of the rhizosphere, the associated microbiome, and the fate of metal-based NPs (Ahmed et al., 2021). That is, NPs can be deposited on or adhered to the root surface, they can release free metal ions, and they can even be chemically modified as a result of the acids and oxidizing-reducing components of exudates (Gao et al., 2018; Zhang et al., 2017). Low-molecular-weight acid root exudates in rice largely determine the aggregation, sedimentation, and dissolution of CuO NPs (Peng et al., 2019). In cucumber, the binding of Cu NPs to synthetic root exudates significantly reduces both Cu uptake and accumulation (Huang et al., 2017). ZnO NPs applied to soybean plants transform into Zn^{2+} and Zn-citrate due to the lowering soil pH caused by the organic acids secreted by roots. Fe and Cu NPs precipitate as hydroxides (unavailable to plants) owing to exposure to root exudates (Dimkpa et al., 2015; Gao et al., 2018). In turn, the presence of metal-based NPs on the root surface can change the surface chemistry of roots, root secretions, and rhizosphere microbial composition and can, consequently, affect the uptake of nutrients in plants and soil properties. TiO_2 and

Fe_3O_4 NPs rise cysteine and methionine contents and induce alterations in phosphorous speciation in lettuce and wheat root exudates (Zahra et al., 2015; Rafique et al., 2018). Ag NPs apparently induce changes in the root exudates of wheat, cowpea, and mustard (Pallavi et al., 2016) and increased the abundance of diazotrophic bacteria in soil (Shah et al., 2014), while CuO NPs induced plant growth-promoting bacteria in the rhizosphere of red sage (*Salvia miltiorrhiza*) (Wei et al., 2021).

2.3 Positive Effects of Metal-Based NPs on Plants

At appropriate concentrations, metal-based NPs can promote plant growth. They can facilitate nutrient uptake and enhance the efficiency when acting as fertilizers through their slow release (Madzokere et al., 2021; Bindraban et al., 2015) and have the potential to increase plant tolerance to both pathogens and environmental abiotic stressors. Acting efficiently depends on plant species, type and dose of NPs, application method, and growing media (Ananthi et al., 2020). Of the nano-agrochemicals proposed to increase agricultural productivity, metal-/metalloid-based NPs are the commonest ones. Of these, mostly Zn and Cu oxide NPs, followed by Ti and Fe oxide NPs, are used in numerous commercial applications. Hence vast amounts of them will remain as residues (Ruttkay-Nedecky et al., 2017). In crop protection terms, ZnO NPs, Ag NPs, and Cu-based NPs are the most frequently studied ones for their antifungal and antibacterial toxicity (Worrall et al., 2018; Shang et al., 2019; Khan et al., 2019a).

Many studies have evaluated the efficiency of metal-based NPs as fertilizers (Beig et al., 2022; Adisa et al., 2019). Non-nutrient NPs, such as CeO_2, TiO_2, or SiO_2, have positive impacts on plants. By way of example, TiO_2 NPs enhance seed vigor and enzyme activities in maize (Shah et al., 2021) and increase P uptake in soybean (Hussain et al., 2021). SiO_2 NPs positively affect maize seed germination by making larger amounts of nutrients available after altering the pH and conductivity of the growing medium (Suriyaprabha et al., 2012). Despite this, most fertilizer knowledge pays special attention to those that include micronutrients (Zn-, Fe- and Cu-based NPs). Biofortification by means of nanofertilizers with Zn is an effective method for removing zinc deficiency. ZnO NPs act as a micronutrient source, especially in calcareous soils where the available Zn concentration is generally very low, and slow steady zinc release is needed to adapt and match the plant growth stage (Almendros et al., 2022; Du et al., 2019). FeO NPs applied to lettuce at low concentrations increase the germination rate and root length (Delfani et al., 2014), and Fe_2O_3 improves the root growth of peanut plants (Rui et al., 2016). Cu NPs enhance shoot length in lettuce and also coriander germination (Verma & Khanam, 2020), and CuO NPs significantly improve wheat and maize yields (Seleiman et al., 2020). Recent reviews include tables that compile the fertilizer effect of several metal-based NPs by detailing NP concentration, crops, and impacts (Agrawal et al., 2022; Ahmed et al., 2021).

Additionally, new NPs have been proposed to overcome the impact of abiotic stress factors. Abiotic stress is a crucial global issue, and climate conditions and environmental contaminants are the primary causes of crop yield loss worldwide. The effects of metal-based NPs, along with other pollutants, are discussed in a specific section of this chapter. Regarding climate conditions, NPs play a beneficial role in overcoming both salinity and drought stress in plants by inducing the expression of several genes involved in stress response, such as those that enhance their antioxidant defense, trigger the signaling pathway of phytohormones, or alter root hydraulic conductance and water uptake (Zhao et al., 2020; Sarraf et al., 2022). It has been recently stated that several NPs also possess antioxidant "enzyme-like" activities: CeO_2, Fe_3O_4, and Co_3O_4 NPs imitate catalase (CAT); CeO_2, Fe_3O_4, Co_3O_4, MnO_2, CuO, and Au NPs mimic peroxidase; CeO_2 and Pt NPs mimic superoxide dismutase (SOD) activity (Sarraf et al., 2022; Liu et al., 2021). Other authors point out another possible way by which NPs reinforce plants' self-protection against environmental conditions by demonstrating a noticeable rise in the level of some biochemicals like proline or tryptophan. These amino acids play an important role in osmotic adjustment, stomatal regulation, and reactive oxygen species (ROS) scavenging by protecting plants from dehydration (Helaly et al., 2014; Sun et al., 2020; Ramadan et al., 2022). Some examples of NPs that alleviate climatic stress effects on crops are as follows: ZnO NPs improve salt tolerance in tomato (Raghib et al., 2020) and okra (*A. esculentus*) (Alabdallah & Alzahrani, 2020); Ag NPs relieve saline stress in pearl millet (Khan et al., 2020); doped Fe_2O_3 NPs mitigate drought stress in *B. napus* by decreasing the amount of H_2O_2 and the peroxidation of membrane lipids (Palmqvist et al., 2017); a pretreatment of TiO_2, followed by ZnO NPs, improves wheat tolerance to heat stress by enhancing glutathione peroxidase (GPX) and SOD activities, which allows H_2O_2 levels to lower and membrane stabilization to improve (Thakur et al., 2021). A modern review includes a very comprehensive study about the mechanisms involved in the relation between metal-based NPs and abiotic stress in plants (Sarraf et al., 2022).

An emerging research field is the application of metal-based NPs in agriculture to amplify the production of secondary metabolites in plants. Secondary metabolites are small organic molecules, such as alkaloids, terpenoids, coumarins, phenols, etc., which are derivatives of primary metabolism. They are not necessary for both growth and development, but perform special defensive physiological functions like resistance to diseases and insect pests, adaptation to environmental factors, or participation in biochemical processes related to the crop quality and flavor (Rana et al., 2021; Osbourn, 2000). NPs based on Mn, Cu, Zn, Al, Si, Ti, and Ag have been reported to increase the content of these metabolites. For example, 800 mg kg^{-1} of CuO NPs increases p-coumaric acid content in cucumber by 225-fold, while 100 mM of Ag NPs rises the anthocyanin level in *A. thaliana* by 18-fold (Predoi et al., 2020; Zhang et al., 2022). In addition to their protective function for plants, secondary metabolites promoted by NPs have the potential to be used as active ingredients for different purposes in agriculture, medicine, or food sectors (Rana et al., 2021; Predoi et al., 2020).

2.4 Negative Effects of Metal-Based NPs in Plants

The continuous deposition, low biodegradability, and long persistence of metal-based NPs in soils can adversely impact plants and soil organisms, and once these NPs come into contact with plants, they have the potential to alter plant physiology. The evaluation of NP phytotoxicity is a prior key condition for promoting nanotechnology applications and avoiding potential ecological hazards. The negative effects of metal-based NPs on plants are evidenced by the inhibition of the seed germination index (rate and time), alterations to root elongation, root tip morphology, shoot growth, delayed plant development and yield, and lower nutrient uptake, which cause a significant productivity and crop quality losses (Jan et al., 2022). With some exceptions, metal-based NPs are harmful at much higher concentrations than those expected to be found in the environment and those needed for correct plant development (Coman et al., 2019; García-Gómez et al., 2018c). Special attention should be paid to ZnO and CuO NPs because Zn and Cu are essential elements, and the differences between concentrations that act as fertilizers or toxics are small and depend mainly on both soil characteristics and plant species (Obrador et al., 2022; Baskar et al., 2018). Soil pH plays a fundamental role in the phytotoxicity of NPs of metallic origin. In this context, bean and tomato seeds have been grown in two agricultural soils of pH 8.3 and 5.4, in lysimeters, containing ZnO NPs' concentrations ranging from 3 to 225 mg Zn kg^{-1} in a greenhouse experiment for 90 days. After 30 days in acid soil, bean plants died regardless of the Zn level, and tomatoes died at the highest dose. On the contrary in calcareous soil, all the tested concentrations allowed normal crop development (García-Gómez et al., 2017). Tables 2.1 and 2.2 provide some examples of phytotoxicity of non-essential and essential metal-based NPs, respectively. Given the large number of found results, only references published in recent years are cited.

Loss of nutritional value of the edible plant part is a negative issue linked with some metal-based NPs. Exposing tomato plants to several metallic NPs (TiO, Ag, Co, Fe_3O_4, CeO_2, and Ni) leads to a reduction in nutrient elements like Mg, P, and S. Exposure of plants to CeO_2 NPs results in the smaller amount of starch, antioxidants, glutelin, iron, lauric, and valeric acid in rice harvest grains and altered Mo micronutrient and sugar and phenolic contents, along with protein fractionation in fruit of cucumber plants (Ananthi et al., 2020).

The previously mentioned visible signs are macroscopic evidence of other biochemical, physiological, and molecular alterations of plant processes due to the stress caused by NPs being present at a high rate. As mentioned in the above section, low levels of metal NPs can increase plants' protective antioxidant mechanisms to limit ROS generation and, hence, oxidative damage. In contrast at high exposure levels, the reaction of NPs with organelles of cells can lead to excessive ROS generation, and cells are unable to maintain normal physiological redox-regulated functions. Excess ROS damages cellular membrane integrity and induces protein denaturation, deficient enzymatic activity, loss of photosynthetic efficiency, and other genotoxic alterations like damaged DNA structure and chromosomal aberrations (Katarína et al., 2021; Yang et al., 2017; Budhani et al., 2019; Tripathi et al., 2017a).

Table 2.1 Summary of studies on the phytotoxic effects of non-essential metal-based NPs in different exposure media

NP type (size)	Experimental conditions	Plant species	Concentration	Effects	Ref.
Ag NPs					
(10 nm)	Sand, 14 d (7-day-old seedlings)	Wheat	0.5, 1.5, 2.5, 3.5, 5 mg kg^{-1}	Reduced the length of shoots and roots in a dose-dependent manner	Dimkpa et al. (2013)
(20 nm)	Agar (germinated seeds)	Rice	0.3, 60 mg L^{-1}	Reduced the fresh shoot and root weights and root elongation Decreased Chl b and increased carotenoid content	Mirzajani et al. (2013)
(20 nm)	Soil, 120 d (seeds)	Bishop pine	350 and 790 mg kg^{-1}	30 d: reduction of the root length with small effect on aboveground plant biomass at 790 mg kg^{-1} 120 d, all Ag NP levels: reduction of root and shoot biomass and lack of lateral root development	Sweet and Singleton (2015)
(22 nm)	Germination in Ag NPs' solution, 3 d, followed by hydroponics, 14 d	Pea	0.5, 1, 3 mg L^{-1}	0.5 mg L^{-1} did not affect plant parameters. 1 and 3 mg L^{-1} reduced the length and fresh weight of root and reduced the fresh and dry weigh or shoot. Chlorophyll and carotenoids decreased and ROS, MDA contents, and SOD, and APX activities increased	Tripathi et al. (2017b)
(10 nm)	Petri dish, 5 d (seeds)	Wheat	1, 10 mg L^{-1}	Decreased the shoot and root length and fresh biomass 10 mg L^{-1} altered the expression of several proteins mainly involved in primary metabolism and cell defense in plants	Vannini et al. (2014)
(8 nm)	Ag NPs in Hoagland solution, 14 d (seedlings)	Turnip	1, 5.0, 10.0 mg L^{-1}	1 mg L^{-1} did not affect plant parameters. 5 and 10 mg L^{-1} decreased seed germination, growth, biomass, and chlorophyll contents of plant. Induced DNA damage and elevated ROS production	Thiruvengadam et al. (2015)
(10 nm)	Ag NPs' solutions in Petri dish, 14 d (seeds)	Pea	20, 40, 80, 160 mg L^{-1}	Decreased seed germination rate, root fresh weight, and number of secondary roots in a dose-dependent manner. Root dry weight did not change. Shoot length and weight were significantly reduced at the higher doses	Labeeb et al. (2020)

Ce NPs					
(6–48 nm)	Soil (pH 7.8), 84 d (seeds)	Common bean	50, 100, 200 mg kg^{-1}	Reduced fresh weight and increased the mineral contents of the green pods. No effect on the organic nutrient contents Increased stomatal conductance. Decreased antioxidative defense	Ma et al. (2020)
CeO$_2$ NPs					
(10–30 nm)	Foliar application at 45 d and 52 d post sowing (flowering stage), 57 d in greenhouse	Mung bean	250, 500, 1000 mg L^{-1}	250 and 500 mg L^{-1}: increased dry matter and ROS and stimulated antioxidant enzyme activity 1000 mg L^{-1}: delayed plant growth. Strong accumulation of ROS, enlargement of starch granules and swelling of chloroplasts, reduction of photosynthetic pigments, and chlorosis	Kamali-Andani et al. (2022)
(8 nm)	Soil, 30 d (seeds)	Cilantro	125, 250, 500 mg kg^{-1}	No negative effects were observed in germination and growth. All doses hanged the plant's nutritional status (carbohydrate in the shoots) and increased CAT (shoot) and APX (root)	Morales et al. (2013)
(20–200 nm)	Two soils: RS (residential, pH 5.9) and AS (agricultural, pH 6.7), 28 d (7-day-old seedlings)	Soybean Corn Lettuce Zucchini	500, 1000, 2000 mg kg^{-1}	RS, 500 mg kg^{-1}: increased root biomass of soybean 1000 mg kg^{-1}: reduced shoot and root wet biomass in corn 2000 mg kg^{-1}: reduced shoot wet biomass of lettuce and zucchini and root fresh weight of corn AS: Fresh biomass of lettuce shoots increased at 500 mg kg^{-1}. Root wet weight of zucchini increased at 2000 mg kg^{-1}	Servin et al. (2017a)
(8 nm)	Soil, 48 d in greenhouse (18-day-old seedlings)	Soybean	100, 500, 1000 mg kg^{-1}	500, 1000 mg kg^{-1}: leaves showed visible damaged after 29 days of exposure and increased ROS. Leaf chlorophyll concentrations were not affected	Priester et al. (2017)
(8 nm)	Soil, entire life cycle study in field, 210 d (seeds)	Wheat	100, 400 mg kg^{-1}	No effects on final biomass and yield. No effects on Ce concentration in shoots and sugar and starch contents in grains Grain protein increased (all doses). The chlorophyll content decreased, and CAT and SOD activities increased at 400 mg kg^{-1}	Du et al. (2015)

(continued)

Table 2.1 (continued)

NP type (size)	Experimental conditions	Plant species	Concentration	Effects	Ref.
(25 nm)	Soil, 60 d in greenhouse (seeds)	Ragged-robin	20, 200 mg kg^{-1}	Decreased root and stem biomass. There was no affectation of leaf area and leaf dry weight	Lizzi et al. (2021)
(8 nm)	Soil, 40 d entire life cycle study in greenhouse	*Radish*	62.5, 125, 250, 500 mg kg^{-1}	Germination delayed. Antioxidant capacity increased	Corral-Diaz et al. (2014)
TiO_2 NPs					
5 nm	Soil, life cycle study, 145 d (seeds)	Peanut	50, 500 mg kg^{-1}	Grain weight slightly lowered. Resveratrol content (response to stress) of grains increased Additionally, 500 mg kg^{-1} reduced the total amino acid content	Rui et al. (2018)
24 nm	TiO_2 suspensions in Petri dish, until 2 cm root length in controls (seeds)	Cabbage, carrot, corn, cucumber, lettuce, oats, onion, ryegrass, soybean, tomato	250, 500, 1000 mg L^{-1}	TiO_2 NPs decreased germination in cucumber and soybean but increased in cabbage. The average root length was higher in cucumber and ryegrass but shorter in cabbage, corn, lettuce, and oats related to controls	Andersen et al. (2016)
20–30 nm	Soil, two foliar applications (at 40 and 80 d post sowing), 125 d life cycle study of sowed seeds in field	Sunflower	2.6 mg L^{-1}	No negative effects were observed on the number of plants and seed heads per hectare. However, head diameter, weight of dry seed head, dry seed head weight, and grain yield increased, as well as oil content in the treated plants	Kolenčík et al. (2020)
25 nm	Petri dish, 21 d (seeds)	Tobacco	100, 1000, 25,000, 50,000 mg kg^{-1}	All concentrations reduced root length and plant biomass as TiO_2 NPs increased. At the highest dose, germination rates and the number of leaves decreased	Frazier et al. (2014)

Table 2.2 Summary of studies on the phytotoxic effects of essential metal-based NPs in different exposure media

NP type (size)	Experimental conditions	Plant species	Concentration	Effects	Ref.
Cu NPs					
(15–30 nm)	Soil, life cycle study. Cu NPs were added to soil after seedling emergence	Wheat	25 mg L^{-1}	The spike length decreased, but the number and the weight of grains improved. The SOD activity and sugar content increased	Yasmeen et al. (2017)
(100 nm)	Soil, 60 d (seeds)	Oregano	50, 100, 200 mg kg^{-1}	50 mg kg^{-1}: Increased root and shoot Cu content. Reduced shoot biomass. Not affected shoot length, MDA, or chlorophyll. Increased water content. Modified root and shoot Ca, Fe, Mg, and Mn All Cu NPs' treatments decreased starch, total sugar, and sugar in leaves	Du et al. (2018)
(100–1000 nm)	Soil, 35 d (seeds)	Cilantro	20, 80 mg kg^{-1}	No effect on germination. Shoot length was reduced at 80 mg kg^{-1}. Micro and macro elements in shoot and roots were differently affected: Mn and Ca increased at 20 mg kg^{-1}, but B, Zn, Mg, P, and S reduced at both doses	Zuverza-Mena et al. (2015)
CuO					
(10–100 nm)	Soil, 35 d (seeds)	Cilantro	20, 80 mg CuO kg^{-1}	Both concentrations decreased seed germination. In shoots, both doses reduced Mn, P, and S content but B was increased at 80 mg kg^{-1}	Zuverza-Mena et al. (2015)
(30 nm)	Hydroponics, 10 d (4-day-old seedlings)	Transgenic cotton	10, 200, 1000 mg CuO L^{-1}	200, 1000 mg L^{-1}: reduced shoot and root length, number of root hairs, and Mg, Ca, Mn, Mo, B, and P contents in shoot 1000 mg L^{-1} reduced shoot biomass	Nhan et al. (2016)
(30–50 nm)	8-month aged soil, 80 d (seeds)	Spring barley	300, 2000, 10,000 mg CuO kg^{-1}	2000, 10,000 mg kg^{-1}: decreased root length, plant height, stem, spike length, and grain weight	Burachevskaya et al. (2021)

(continued)

Table 2.2 (continued)

NP type (size)	Experimental conditions	Plant species	Concentration	Effects	Ref.
(25 nm) (50 nm) (250 nm)	Soil (outdoor microcosm), life cycle study, 120 d (seeds)	Soybean	50, 100, 200, 500 mg CuO kg^{-1}	The two highest concentrations reduced seed production regardless NP size. CuO NP size and concentration influenced lipid peroxidation and antioxidant biomarkers	Yusefi-Tanha et al. (2020a)
(40 nm)	Soil, life cycle study, 145 d (seeds)	Peanut	50, 500 mg CuO kg^{-1}	Fresh shoot biomass and grain weight decreased at 500 mg kg^{-1}. Both concentrations reduced total amino acid content and increased resveratrol content (response to stress) of grains	Rui et al. (2018)
Fe_2O_3					
(20 nm)	Soil, life cycle study, 145 d (seeds)	Peanut	50, 500 mg Fe_2O_3 kg^{-1}	Grain weight decreased at 500 mg kg^{-1}. Both concentrations reduced total amino acid content of grains	Rui et al. (2018)
Fe_3O_4					
(12 nm)	Universal soil, 21 d (seeds)	Sunflower	50, 500 mg Fe L^{-1}	Germination decreased at 500 mg Fe L^{-1} and wet weight of seedlings at 50 mg Fe L^{-1}	Kornarzyński et al. (2020)
ZnO NPs					
(20–80 nm)	Soil, 21 d (seeds)	Wheat, radish, vetch	1000 mg Zn kg^{-1}	Shoot lengths was reduced in vetch Shoot weight was reduced in wheat, radish, and vetch	García-Gómez et al. (2015)
(20–80 nm)	Two soils: CS (calcareous soil, pH 8.3), and AS (acidic soil, pH 5.4), 35 d (seeds)	Bean Corn Radish Wheat Cucumber Beet Lettuce Tomato Pea	20, 225, 450, 900 mg Zn kg^{-1}	In CS: ZnO NPs reduced both seed germination of bean at 450 and 900 mg Zn kg^{-1} and shoot growth of wheat, cucumber, and beet at 900 mg Zn kg^{-1}. All doses increased the shoot fresh weight of corn and radish In AS: Decreased seed germination of bean, lettuce, tomato, and beet. Improved germination rate of radish. Declined shoot growth of all plant species at all ZnO NPs' concentrations except pea	García-Gómez et al. (2018c)

(20–80 nm)	Two soils: CS (calcareous soil, pH 8.3), and AS (acidic soil, pH 5.4) in greenhouse, life cycle study, 90 d (seeds)	Bean Tomato	3, 20, 225 mg Zn kg^{-1}	In CS: Increased photosynthetic pigments and soluble protein content In AS: Tomato plants died 1 month after sowing. Chlorophyll and carotenoids decreased in bean. Increased of ROS production at 225 mg Zn kg^{-1} in bean. Soluble protein levels were not affected	García-Gómez et al. (2017)
(10 nm)	Soil, 48 d (18-day-old seedlings)	Soybean	50, 100, 500 mg ZnO kg^{-1}	Leaves resulted damaged after 35 days at 50 and 100 mg Zn kg^{-1}. Leaf total chlorophyll decreased with increasing Zn dose. Genotoxicity was evidenced at 500 mg Zn kg^{-1}	Priester et al. (2017)
(38 nm) (59 nm) (500 nm)	Soil, life cycle study, 120 d, outdoor mesocosm (seeds)	Soybean	40, 80, 160 and 400 mg Zn kg^{-1}	Seed yield increased up to 160 mg kg^{-1} (max for 38 nm size) but decreased at 400 mg Zn kg^{-1} H_2O_2 and MDA content and antioxidant enzyme (SOD, CAT, POX) activities decreased as doses increased up to 160 mg kg^{-1}, but increased at 400 mg Zn kg^{-1} (all sizes except 500 nm, this did no change)	Yusefi-Tanha et al. (2020b)
(<100 nm)	Two soils: CS (calcareous soil, pH 7.8), and AS (acidic soil, pH 4.5), 7 d (seeds)	Wheat	125, 250, 500 mg Zn kg^{-1}	In CS: no effects on root and shoot length In AS: dramatic decrease in root growth, whereas shoot growth was little affected	Watson et al. (2015)
(54 nm)	Soil, 90 d	Tomato	300, 600, 1000 mg ZnO kg^{-1}	In the root, ZnO NP significantly reduced the antioxidant enzyme activities (APX, SOD) and increased H_2O_2 and ROS content. CAT activity was enhanced In leaves, SOD activity increased in all doses and APX at 1000 mg kg^{-1}. CAT activity and total chlorophyll content were reduced In fruits: reduction of phenols, flavonoids, beta carotene, and lycopene	Akanbi-Gada et al. (2019)

(continued)

Table 2.2 (continued)

NP type (size)	Experimental conditions	Plant species	Concentration	Effects	Ref.
Size no detailed	Sand (watering with ZnO NPs' suspensions), 14 d (21-day-old seedlings)	Tomato	200, 400, 800 mg ZnO L^{-1}	400 and 800 mg L^{-1}: significantly inhibited tomato root and shoot dry biomass 800 mg L^{-1}: reduced Chl a and b content but increased carotenoids. The SOD, CAT, and APX activities increased in a concentration-dependent manner	Wang et al. (2018b)
(58 nm)	1-year aged soils: CS (calcareous soil, pH 8.3), and AS (acidic soil, pH 5.4), 90 d, life cycle study (seeds)	Pea Beet root	20, 225 mg Zn kg^{-1}	In CS: no effects on beet. In pea, stem weights were seriously affected at 225 mg Zn kg^{-1} In AS: Beet plants died 1 month after sowing at 225 mg Zn kg^{-1}, and pea plants showed a decreased in stem, leaf, and fruit weights	Obrador et al. (2022)
(58 nm)	1-year aged soils: CS (calcareous soil, pH 8.3), and AS (acidic soil, pH 5.4), life cycle study, 90 d (seeds)	Pea Beet root	20, 225 mg Zn kg^{-1}	In CS: decreased ROS levels and enzymatic activities in leaves. In pea (60 d), soluble protein levels decreased and in beet (90 d) increased In AS: Beet plants died at 225 mg Zn kg^{-1} after 30 d. In pea, the generation of ROS was increased, as well as MDA, GPOD, and APX levels. These effects were not observed on beet	García-Gómez et al. (2018b)

The presence of metal-based NPs in soil may indirectly affect plant growth. The soil environment is a complex system in which each component (soil, soil biota, plants) is interconnected with one another. Some metal-based NPs can increase the abundance of beneficial microbes for soil health and plant development, but even at fertilizer doses, other NPs adversely affect soil microbiota. These are microbes, mainly bacteria and fungi, with key functions, such as plant growth promoters (rhizobacteria), producers of bioactive molecules, or those involved in cellulose/lignin degradation processes (Ameen et al., 2021).

NPs may also impair the soil microbiome involved in biogeochemical processes, mainly the degradation of organic compounds and the recycling of nutrients, including N, P, S, and C, which can ultimately affect plant development (García-Gómez et al., 2018a). Recent reviews include detailed data about the effects of several metal-based NPs on soil and beneficial plant-associated microorganisms (Ameen et al., 2021; Kalwani et al., 2022). For example, Ag NPs affect the symbiotic relation between fava bean (*V. faba*) with *R. leguminosarum* or *G. aggregatum* or a combination of both cultures. Moreover, Ag NPs significantly stunted nitrogenase activity, nodulation, mycorrhizal colonization, and glomalin content (Abd-Alla et al., 2016). Similarly, TiO_2 NPs disrupt the Rhizobium–legume (garden pea) symbiosis system. TiO_2 NPs induce morphological changes in pea roots, such as delayed nodulation development, which hence lead to the onset of nitrogen fixation and damage to the cell surface of *Rhizobium leguminosarum* (Fan et al., 2014).

NPs can indirectly impact the plant growth and development due to the combined action with other contaminants present in the exposure media. This issue is of major concern and is dealt with separately in the next section.

2.5 Nanoparticle Interactions with Co-existing Contaminants

The co-existence of NPs and other contaminants in the environment may result in unexpected toxic effects and changes in the accumulation of both NPs and convectional contaminants in plants. The majority of the works published in the literature deal with the influence of NPs on the toxicity/accumulation of these contaminants. The impact of other contaminants on NPs toxicity is examined to a lesser extent, although these studies are increasing in number. The third group of studies focuses on the joint toxicity of both pollutants (NPs and conventional contaminants) by taking into account the mutual interaction of chemicals in the biological effects of the mixture. Joint toxicity can be similar (additive), stronger (synergistic), or weaker (antagonistic) than that expected from the toxicity of individual components. The application of mathematical models, based on a two-factorial analysis of variance (ANOVA), an isobologram analysis, and toxic unit indices, allows the type of interaction to be determined (Cedergreen, 2014; Uwizeyimana et al., 2017). The application of these models to evaluate the joint toxicity of NP-chemical mixtures to plants is still scarce, although some exceptions exist (Ma et al., 2017).

The combined action of NPs and contaminants depends on several factors, such as the intrinsic properties of NPs and chemicals, crop species, experimental conditions (hydroponic or natural soil media), and exposure mode (direct to soil, foliar, seed treatment, etc.). Most studies have investigated the joint toxicity and bioaccumulation of metal-based NPs and co-contaminants on plants under hydroponic conditions, although the tests conducted with natural soil provide the most reliable data. These tests generally measure traditional endpoints, such as germination, growth, and development, as well as biomarkers of oxidative stress. Gene and protein expression measurements (Pagano et al., 2017), DNA alterations (Zhu et al., 2019), and metabolic profile changes (Lian et al., 2020) have been investigated to a lesser extent, even though they may help to reveal the mechanisms of interaction between contaminants. These assessments with chemical mixtures are generally made at much higher concentrations than realistic environmental concentrations to observe significant toxicity. They are also carried out with pristine nanomaterials despite NPs in the environment being subject to transformation processes (aging), which can affect the interactions of NPs with co-existing contaminants and, hence, their accumulation and toxicity (Jośko et al., 2021a; Servin et al., 2017b). However, studies with environmentally transformed NPs are very scarce.

2.6 Mechanisms Underlying the Influence of NP-Contaminant Interaction on the Joint Toxicity

The mechanisms that underlie changes in toxicity due to co-exposure are complex, scarcely investigated, and poorly understood, especially those conducted in soil. They involve several processes that can individually or simultaneously occur. Combined exposure can alter both availability and degradation in exposure media, modify uptake and internalization in plant cells, and modulate the metabolic processes related to the mechanisms of action, detoxification, and excretion of components from mixtures (Naasz et al., 2018; Deng et al., 2017). Figure 2.1 summarizes the relevant mechanisms.

Many studies attribute co-exposure effects on the toxicity and accumulation of NPs and contaminants to changes in the availability of chemicals for organisms (Khan et al., 2019b; Zhang & Zhang, 2020; Adrees et al., 2020). NPs are characterized by high reactivity, a large specific surface area, and strong adsorption capacity. If contaminants are adsorbed to NPs or held in precipitating NP aggregates, the availability and bioaccumulation of these co-existing contaminants are likely to reduce (Bao et al., 2019; Ma et al., 2017). Co-contaminants can modify surface properties and/or transform the functional groups that coat NPs, which lead to changes in their electronegativity and promote the formation of homo- and hetero-aggregates of NPs (Xiao et al., 2021). Both aggregation and adsorption processes can reduce bioavailability and slow down the dissolution of metal-based NPs and, therefore, the release of metal ions (Xiao et al., 2022) with consequent effects on plant toxicity. Indirectly co-present heavy metals can also induce excretion of root exudates, which affects NP aggregation (Sharifan et al., 2020). In soil, complex interactions (adsorption, competition) occur among NPs, co-contaminants, soil

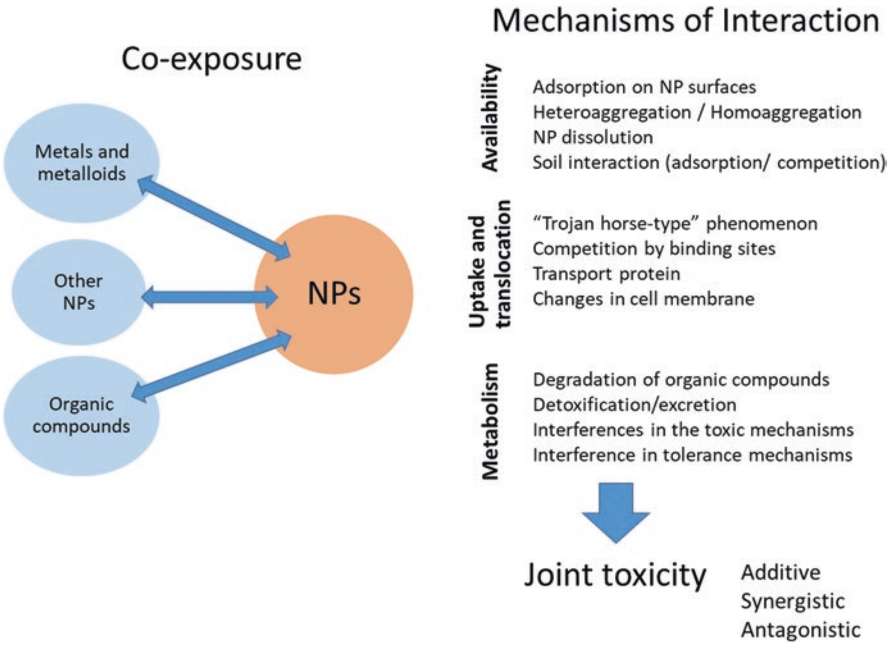

Fig. 2.1 Potential mechanisms responsible for the interaction between NPs and other co-contaminants in plants

particles, and organic matter. The NPs and metals released from them can compete with other metals and contaminants for sorption sites, which might alter the availability of NPs and chemicals for plants under co-contamination conditions (Zhang et al., 2019; Naasz et al., 2018). NPs can also affect the formation of soil aggregates and can, thus, indirectly change heavy metal distribution in soils and their availability (Zhang & Zhang, 2020). In turn, NPs can be modified by edaphic and soil biotic factors.

The second mechanism of interaction focuses on the processes related to the uptake and translocation of metals (Skiba et al., 2020; Sharifan et al., 2020) and organic contaminants (Bao et al., 2019; De La Torre-Roche et al., 2013) in plants as a result of co-exposure. The uptake of xenobiotics by plants can be affected because the contaminants in the mixture can (i) compete for the same transporters and binding sites on the cell membrane; (ii) modify hydrophobicity or damage the cell membrane's physical integrity; and (iii) alter the performance of membrane transport proteins, as well as the metabolic processes involved in the uptake and sequestration of substances in cellular compartments. In addition, the adhesion of NPs to the root surface can act as a physical barrier, which can hinder the uptake of other substances by plants. Organic compounds can change the electronegativity or affect the coating groups on the NP surface, which affects the nano-interaction with organism/cell surfaces.

Adsorption of metals and organic compounds on NP surfaces can display dual behavior with contradictory consequences. NPs can act as carriers of chemicals, which facilitate the entry of substances in cells (the Trojan horse-type phenomenon) (Naasz et al., 2018). Once inside organisms, the subsequent release of adsorbed contaminants can enhance the phytotoxic effects of these substances. Conversely, sorption of compounds to NPs can prevent chemicals from accumulating in plants if NPs reduce the availability of contaminants, as indicated above, or the NP-compound complex is negligibly internalized by plants. A third scenario can occur, in which NPs facilitate the uptake of compounds, but sorption is irreversible, and compounds remain attached to NPs inside organisms. In these cases, the toxicity of NP-contaminant combinations can be expected to diminish.

Finally, the impact of combined exposure can result from alterations to the metabolic processes involved in toxicity and detoxification mechanisms or those related to tolerance to contaminant stress (e.g., antioxidant enzymes involved in oxidative stress tolerance) (Jośko et al., 2021a; Kamali-Andani et al., 2022; Rizwan et al., 2019a, b). NPs can increase the toxicity of organic compounds by either facilitating transformation to compounds being more toxic than parents or hindering the interior degradation rate of these organic compounds and their excretion, which can imply a higher compound concentration in organisms (Deng et al., 2017).

2.7 Effects of Combined Exposure to NPs and Co-existing Contaminants on Their Accumulation and Toxicity to Plants

In plants, the interaction of NPs with pre-existing contaminants leads to changes in their biological effects (bioaccumulation and/or toxicity). Most studies have observed reduced chemical accumulation in plants in the presence of NPs (Hussain et al., 2019; Rizwan et al., 2019a, b). However in some exceptions, NPs promote the accumulation of metal ions (Xiao et al., 2022; Venkatachalam et al., 2017) and organic compounds (Bao et al., 2019). Changes observed in the bioaccumulation of contaminants do not always correlate with changes in toxicity in plants. Negative biological effects generally decrease with declining bioaccumulation (Ma et al., 2017; Ji et al., 2017; Hussain et al., 2019). In some cases, enhanced chemical accumulation in the presence of NPs does not lead to greater toxicity compared to individual treatments (Venkatachalam et al., 2017; Zhang et al., 2019). Some studies report changes in toxicity upon mixture exposure, but no changes in accumulation (Haisel et al., 2019).

2.7.1 The Interaction Between NPs and Metal/Metalloid

The phytotoxic effects of co-exposure to NP-contaminant mixtures on plants are tested mainly with metals as co-contaminants where the combination with Cd predominates (Table 2.3). Cd is one of the major pollutants in soils, and it is

Table 2.3 Summary of studies on the effects of NP interaction with metal/metalloid on their accumulation and toxicity to plants in different exposure media

NP type	Co-contaminant	Experimental conditions	Plant species	Concentration	Joint effect	Ref.
Ag	Sb(III)/(V)	Aqueous suspension, 6 d (16-day-old seedling)	Soybean	1 mg Ag L^{-1} 100 mg Sb(III) L^{-1} 100 mg Sb(V) L^{-1}	Synergistic toxicity (growth and stress oxidative) Ag NPs increased and decreased Sb(III) in roots and leaves, respectively, and increased Sb(V) (stem and leaves) Sb(V) increased Ag in plant	Cao et al. (2020)
CeO_2 ZnO	As(III) As(V)	Aqueous suspension, 6 d (42-day-old seedling)	Rice	100 mg Ce L^{-1} 100 mg Zn L^{-1} 1 mg As(III) L^{-1} 1 mg As(V) L^{-1}	ZnO NPs decreased As(III) in roots and shoots and As(V) in roots CeO_2 NPs did not affect As in roots and shoots As(III) and As(V) increased Ce in shoots As did not affect plant uptake of Zn	Wang et al. (2018c)
CuO	Fe(II)	Aqueous solution, 3 d (30-day-old seedling)	Rice	100 mg Cu L^{-1} 3 mM Fe	Fe reduced Cu in roots and shoots	Yuan et al. (2021)
Fe_2O_3	Cd	Soil and foliar exposure in plants grown in Cd-contaminated soil, 125 d (seed sowing)	Wheat	Soil exposure: 5, 10, 15, 20 mg Fe kg^{-1} Foliar exposure: 5, 10, 15, 20 mg Fe L^{-1} 7.38 mg Cd kg^{-1}	Fe_2O_3 NPs enhanced the plant growth, photosynthesis, and grain yield and decreased Cd (grains, shoots, and roots)	Hussain et al. (2019)
Fe_2O_3	Cd	Cd-contaminated soil, under normal and water-limited conditions, 120 d (seed sowing)	Wheat	25, 50, 100 mg Fe kg^{-1} 7.67 mg Cd kg^{-1}	Fe NPs increased the plant growth and photosynthesis and reduced oxidative stress and decreased Cd in wheat grains	Adrees et al. (2020)

(continued)

Table 2.3 (continued)

NP type	Co-contaminant	Experimental conditions	Plant species	Concentration	Joint effect	Ref.
Fe_2O_3 ZnO	Cd	Cd-contaminated soil, 124 d (sowing of 24-hour seed primed)	Wheat	5, 10, 15, 20 mg Fe L^{-1} 25, 50, 75, 100 mg Zn L^{-1} 7.38 mg Cd kg^{-1}	Fe_2O_3 and ZnO NPs increased the plant growth, grain yield, and photosynthesis in Cd stressed plants and decreased the Cd accumulation	Rizwan et al. (2019a)
Si	As(V)	Irrigation of plants grown in peat moss and perlite, 150 d (seedling)	Tomato	250, 1000 mg Si L^{-1} 0.2, 0.4. 0.8, 1.6, 3.2 mg As L^{-1}	Si NPs decreased tomato yield at the highest doses of As and Si Si NPs decreased As translocation at leaves, at all tested concentrations	Gonzalez-Moscoso et al. (2022)
Si	Cd	Soil and foliar exposure in plants grown in Cd-contaminated soil, 124 d (seed sowing)	Wheat	Soil exposure: 300, 600, 900, 1200 mg Si kg^{-1} Foliar exposure: 300, 600, 900, 1200 mg Si L^{-1} 7.38 mg Cd kg^{-1}	Si NPs (soil and foliar exposure) increased the plant growth and photosynthetic pigments and reduced oxidative stress in Cd stressed plants and reduced Cd in shoots, roots, and grains	Ali et al. (2019)
TiO_2	Cd	Kimura solution, 10 d (10-day-old seedling)	Rice	10, 100, 1000 mg Ti L^{-1} 10, 20 mg Cd L^{-1}	TiO_2 NPs decreased Cd toxicity (net photosynthetic rate and chlorophyll content) and Cd in roots and leaves Co-exposure decreased Ti in roots	Ji et al. (2017)
TiO_2	Cd	Root and foliar exposure of plants grown in Hoagland suspension, 14 d (14-day-old seedling)	Corn	100, 250 Ti mg L^{-1} 50 Cd mM	Root co-exposure caused synergistic effects (growth and chlorophyll content) and increased Ti in root and shoot TiO_2 NPs increased and reduced Cd uptake at 100 and 250 mg Ti L^{-1}, respectively Foliar application of TiO_2 (100 mg Ti L^{-1}) decreased Cd toxicity and the Cd accumulation in shoots	Lian et al. (2020)

TiO_2	Cu	Hoagland suspension, 6 d (5-day-old seedling)	Soybean	10 mg Ti L^{-1} 1, 2, 5, 20 mg Cu L^{-1}	TiO_2 NPs enhanced Cu toxicity (growth of root and shoot) and accumulation and inhibited the translocation of Cu, at 1 and 2 mg Cu L^{-1} TiO_2 NPs did not affect Cu toxicity and accumulation at 5 and 20 mg L^{-1}	Xiao et al. (2021)
ZnO	Cu Fe Mn	Hoagland suspension, 12 d (7-day-old seedling)	Pea	100 mg Zn L^{-1} 0.05 mg Cu L^{-1} 0.4 mg Mn L^{-1} 10.28 mg Fe L^{-1}	ZnO NPs increased Cu, decreased Mn, and changed Fe concentration (root and shoot)	Skiba et al. (2020)
ZnO	Cd Pb	Hoagland suspension, 15 d (seedlings)	White leadtree	25 mg Zn L^{-1} 50 mg Cd L^{-1} 100 mg Pb L^{-1}	ZnO NPs decreased Cd toxicity (growth and oxidative stress) and increased the Cd and Pb accumulation	Venkatachalam et al. (2017)
ZnO	Cd	Liquid RH medium, 11 d (35-day-old seedling)	True fox sedge	10, 50 µM Zn 10 µM Cd	ZnO NPs increased Cd toxicity (photosynthetic pigments) and did not affect the Cd accumulation	Haisel et al. (2019)
ZnO	Cd	Soil and foliar exposure in plants grown in Cd-contaminated soil, 125 d (seed sowing)	Wheat	Soil exposure: 25, 50, 75, 100 mg Zn kg^{-1} Foliar exposure: 25, 50, 75, 100 mg Zn L^{-1} 7.38 mg Cd kg^{-1}	ZnO NPs enhanced the plant growth, photosynthesis, and grain yield and decreased the Cd accumulation	Hussain et al. (2018)
ZnO	Cd	Foliar exposure of plants grown in Cd-contaminated soil, 75 d (seed sowing)	Corn	50, 75, 100 mg Zn L^{-1} 7.86 mg Cd kg^{-1}	ZnO NPs improved the plant growth, chlorophyll content, and gas exchange and reduced Cd in roots and shoots	Rizwan et al. (2019b)

(continued)

Table 2.3 (continued)

NP type	Co-contaminant	Experimental conditions	Plant species	Concentration	Joint effect	Ref.
ZnO	Cd	Cd-contaminated soil, under normal and water-limited conditions, 125 d (seed sowing)	Wheat	25, 50, 100 mg Zn kg^{-1} 7.67 mg Cd kg^{-1}	ZnO NPs increased the plant growth, grain yield, and chlorophyll levels, decreased oxidative stress, and reduced Cd in shoots and roots	Khan et al. (2019a, b)
ZnO	Cd	Soil, 60 d (30-day-old seedling)	American pokeweed	500 mg Zn kg^{-1} 10, 100 mg Cd kg^{-1}	Synergistic inhibition of the plant growth and increase of stress oxidative ZnO NPs increased the Cd accumulation	Xiao et al. (2022)
ZnO	Cd	Soil, 120 d (8-cm seedling)	Rice	50, 100, 500 mg Zn kg^{-1} 1.0, 2.5, 5.0 mg Cd kg^{-1}	ZnO NPs (500 mg kg^{-1}) decreased Cd toxicity (shoot and total biomass) and increased Cd in root, shoot, and grain	Zhang et al. (2019)
ZnO	Cd	Soil, 63 d (48-hour germinated seeds)	Sweet sorghum	50, 250, 500 mg Zn kg^{-1} 5 mg Cd kg^{-1}	Co-exposure (ZnO NPs 250 and 500 mg kg^{-1}) showed synergistic effects on the plant growth Co-exposure (ZnO NPs 50 mg kg^{-1}) showed antagonistic effects on the plant growth ZnO NPs significantly decreased Cd in shoot and root The effect of Cd in the Zn accumulation depended on the Zn rate	Wang et al. (2018a)

well-known that it affects the biochemical and physiological plant functions and can accumulate in edible tissues. Many authors have reported data collected from experiments performed in hydroponic media with conflicting results. For example, TiO_2 NPs alleviate Cd toxicity (net photosynthetic rate and chlorophyll content) and decrease Cd uptake in roots and leaves of rice (*Oryza sativa* L.) (Ji et al., 2017). In turn, the presence of Cd significantly decreases Ti accumulation in rice roots. Similarly, Venkatachalam et al. (2017) report that phycomolecule-coated ZnO NPs (25 mg L^{-1}) enhance seedling growth, reverse the oxidative stress symptoms induced by Cd and Pb, and induce desirable genomic alterations in *Leucaena leucocephala*. However, unlike the previous paper, NPs increase Cd and Pb accumulation in plant tissues. An opposite trend is indicated in a hydroponic study with *Carex vulpina* (Haisel et al., 2019), where ZnO NPs at low concentrations (10 or 50 μM of Zn) significantly aggravate the negative effect of Cd, which is reflected mostly in changes in the content of photosynthetic pigments. Exposure mode and contaminant levels are key factors in plant response to co-exposure to NPs and metals according to Lian et al. (2020), who studied the combined effect of TiO_2 NPs and Cd on metal accumulation and toxicity to hydroponic maize (*Zea mays* L.). Root applications of TiO_2 NPs and Cd synergistically inhibit plant growth and development, while the foliar spray of TiO_2 NPs can partially protect plants from Cd stress. Similarly at low Cu concentrations (1 and 2 mg Cu L^{-1}), TiO_2 NPs enhance the toxicity and accumulation of Cu in soybean, whereas the effects caused by the co-presence of TiO_2 NPs disappear at 5 and 20 mg Cu L^{-1} (Xiao et al., 2021). Cu adsorption in TiO_2 NPs increases with a rising Cu concentration, with the subsequent reduction in the zeta-potential, aggregation, and sedimentation of TiO_2 NPs. This fact can lead to a lower Cu and Ti concentration in hydroponic media, and, consequently, Cu toxicity can be alleviated.

The contaminant type also plays an important role in joint bioaccumulation. A hydroponic study with five forms of ZnO NPs (100 mg L^{-1}) reports that NPs alter Cu, Mn, and Fe uptake and translocation in pea (*Pisum sativum* L.) plants, but effects are element-specific (Skiba et al., 2020). Similar behavior has been observed with two non-essential metals (Pb and Cd), where the influence of ZnO NPs on the accumulation of these metals in the edible tissue of three leafy green species is impacted by the co-contaminant nature (Sharifan et al., 2020). Additionally, metal-based NPs with oxidizing or reducing properties can regulate the oxidation states of some metals and, hence, their uptake and toxicity to plants (Cao et al., 2020). Combined exposure to CeO_2 NPs or ZnO NPs and inorganic As species differently affects As(III)/As(V) accumulation and speciation in rice (*Oryza sativa* L.) (Wang et al., 2018c).

The joint toxicity and bioaccumulation of NPs and metals have been also studied in plants growing in soil. A fair number of studies conducted with Cd-contaminated soils indicate that ZnO NPs and Fe_3O_4 NPs applied by different routes (soil exposure, foliar spray, seed priming) mitigate Cd phytotoxicity to wheat (*Triticum aestivum*) (Hussain et al., 2018, 2019; Rizwan et al., 2019a, b). Decreased toxicity has been generally associated with reduced Cd accumulation in plants, which might be due to a drop in available Cd in soil. These outcomes are similar to those obtained in two experiments performed under water-limited conditions (Khan et al., 2019b; Adrees et al., 2020). Si NPs applied directly to soil or as foliar spray also promote yield and reduce Cd accumulation in wheat (Ali et al., 2019). Si NPs reduce Cd accumulation in plants by lowering Cd available concentrations in soil. With foliar applications, diminished Cd accumulation may be due to other causes, such as dilution effects because of increased growth or compartmentation into vacuoles, which restrict metal translocation to grain.

In contrast, co-exposure to ZnO NPs and Cd amplifies toxicity (root cell damage and increased oxidative stress) to *Phytolacca americana* L. (Xiao et al., 2022). In this study, Cd^{2+} promotes the release of Zn ions from ZnO NPs due to the interaction of Cd on NP surfaces, which can explain the increased toxicity of the mixture. In addition, ZnO NPs considerably increase Cd accumulation.

Interestingly, both synergistic and antagonistic effects of the ZnO NPs and Cd mixture appear in sweet sorghum (*Sorghum bicolor*) grown in soil depending on the contaminant concentration (Wang et al., 2018a). The mixture shows synergism at the two highest doses (250 and 500 mg Zn kg^{-1}) of ZnO NPs. ZnO NPs are non-phytotoxic at the lowest dose (50 mg Zn kg^{-1}) and show antagonistic interactions with Cd in plant growth. All the ZnO NPs' doses significantly lower the Cd concentrations in sorghum shoots and roots, whereas the effect of Cd on Zn accumulation depends on the Zn rate. In addition to the application rate, the plant growth stage is an important factor for the biological effects that result from co-exposure. In a soil-rice system (Zhang et al., 2019), the main impact of NPs on Cd toxicity and bioaccumulation appears in the tillering stage, where ZnO NPs ameliorate toxic Cd effects (plant height). However, this effect diminishes over time and disappears in the fruiting stage.

2.7.2 The Interaction Between Different NPs

Only a few studies have investigated the impact of NP mixtures on plants, even though a variety of NPs may co-exist in the natural environment (Table 2.4). Two experiments in soilless culture media have assessed the effects of binary mixtures of metal-based NPs on plants with different results. In a germination assay with five different NPs (ZnO, CuO, TiO_2, Cr_2O_3, and Fe_2O_3) and four plant species (cress, flax, wheat, and cucumber), Jośko et al. (2017) have found that co-exposure at 100 mg L^{-1} exerts significantly less toxicity (root growth inhibition) compared to single exposure and regardless of its components. In another study, binary combinations of five NPs have shown increased or decreased metal content and toxicity to zucchini (*Cucurbita pepo* L.) grown in vermiculite for 21 days depending on NP combinations (Pagano et al., 2017). Both experiments suggest that the differences in toxicity observed between simple and combined treatments, and between different binary NP mixtures, can be explained by distinct solubility and the ratio of the particulate/ionic forms that derive from NPs, as well as greater particle aggregation under combined stress conditions.

Table 2.4 Summary of studies on the effects of the interaction between different NPs' types on their accumulation and toxicity to plants in different exposure media

NP type	Co-contaminant	Experimental conditions	Plant species	Concentration	Joint effect	Ref.
CeO_2 CuO La_2O_3 ZnO CdS QDs	Binary mix	Aqueous solution, vermiculite, 21 d (7-day-old seedling)	Zucchini	NPs 500 mg L^{-1} CdS QDs 100 mg L^{-1}	Synergistic and antagonistic effects on toxicity (growth, photosynthetic pigments, and gene expression) and accumulation depending on binary NP combinations	Pagano et al. (2017)
CeO_2 Se	Binary mix	Foliar application in plants grown in soil, 59 d (seed sowing)	Mung bean	250, 500, 1000 mg Ce L^{-1} 25, 50, 75 mg Se L^{-1}	Se NPs (25 and 50 mg L^{-1}) ameliorated the stress (dry matter, photosynthetic pigments, and antioxidants) of CeO_2 NPs	Kamali-Andani et al. (2022)
CuO Cr_2O_3 Fe_2O_3 TiO_2 ZnO	Binary mix	Aqueous solutions, 3 d (seeds)	Cress Flax Wheat Cucumber	10, 100, 1000 mg L^{-1}	Antagonistic toxicity (root growth) at 100 mg L^{-1} No differences at 10 and 1000 mg L^{-1}	Jośko et al. (2017)
CuO ZnO	Binary mix	LUFA soil, 7 and 30 d (4-day-old seedling)	Barley	300 mg Cu kg^{-1} 300 mg Zn kg^{-1}	Co-exposure caused synergistic and antagonistic effects on toxicity (antioxidative enzyme activity and relative gene expression) depending on plant part and exposure time and increased Cu and Zn in leaves at 30 d	Jośko et al. (2021a)
CuO ZnO	Binary mix	LUFA soil, 7 and 30 d (4-day-old seedling)	Barley	300 mg Cu kg^{-1} 300 mg Zn kg^{-1}	Co-exposure caused changes in mineral composition in leaves and downregulated genes related with metal influx to cells	Jośko et al. (2021b)

Two soil experiments have confirmed the influence of dose and exposure time on the toxicity magnitude of NP mixtures. Kamali-Andani et al. (2022) have observed that Se NPs modify the stress caused by CeO_2 NPs on mung bean (*Vigna radiata*) plants grown under greenhouse conditions, but this effect depends on the foliar application rates of both NPs. The low concentrations of Se NPs (25 and 50 mg Se L^{-1}) improve photosynthesis by increasing antioxidant activity and proline content, which lowers the levels of ROS and lipid peroxidation caused by CeO_2 NPs. Other noteworthy studies indicate that the effects of co-exposure to CuO and ZnO NPs on toxicity and metal accumulation on soil-grown barley (*Hordeum vulgare* L.) vary with exposure time (7 and 30 days), although a general tendency is not easy to identify (Jośko et al., 2021a, b). Their findings reveal that co-exposure results in the downregulation of the genes related to the metal influx to cells. Interestingly, the binary mixtures of CuO and ZnO NPs have antagonistic effects on Zn and Cu availability in soil, whereas mixtures of their metal salts show synergism. Soil-extractable Zn and Cu concentrations weakly correlate with Cu and Zn contents in barley.

2.7.3 The Interaction Between NPs and Organic Compounds

Both decreases and increases in toxicity and contaminant accumulation in plants due to interactions between metallic NPs and organic compounds have been reported (Table 2.5). For example, in an interesting study, Ma et al. (2017) have investigated the joint effects of TiO_2 NPs and tetracycline (TC) on rice (*Oryza sativa* L.) grown in hydroponic media for 10 days. Three mathematical models are applied to toxicity (plant growth, changes in oxidative stress enzymes, and macro-/micronutrient contents) data to establish the type of toxic interaction, i.e., synergistic, additive, or antagonistic, to result from co-exposure. The analyses indicate that TiO_2 NPs and TC antagonistically interact, showing overall phytotoxicity alleviation compared to that expected of the toxicity of individual treatments. Decreased phytotoxicity is accompanied by low TC levels in plants. This is probably due to the sorption of the antibiotic into TiO_2 NPs, which can decrease its availability for rice seedlings. However, Ti levels in rice shoots and roots rise in the combined treatment, which is attributed to the alteration of surface charges of TiO_2 NPs caused by TC. In contrast, hydroponically exposed wheat (*Triticum aestivum* L.) to phenanthrene and ZnO (NPs and bulk) mixtures shows greater toxicity compared to individual treatments (Zhu et al., 2019). This effect is more evident in DNA damage in wheat root cells, especially for ZnO NPs. In another study, the plant response to the combined exposure to NPs and an organic contaminant strongly depends on the concentration of both xenobiotics (Zhang et al., 2020). At low concentrations (50 and 250 mg L^{-1}), zero-valent iron (ZVI) NPs alleviate the toxicity (root length) of quinclorac herbicide (QNC) to *Oryza sativa* L. However, this effect disappears at the high ZVI NPs' concentration (750 mg L^{-1}), which is possibly due to the toxicity of ZVI NPs itself at this concentration. QNC content in both shoots and roots lowers compared to the tissues exposed to QNC alone, probably because ZVI NPs remove QNC from culture solution.

Table 2.5 Summary of studies on the effects of NP interaction with organic compounds on their accumulation and toxicity to plants in different exposure media

NP type	Co-contaminant	Experimental conditions	Plant species	Concentration	Joint effect	Ref.
Ag	Dichlorodiphenyldichloroethylene (DDE)	Hoagland solution, 19 d (5–7-day-old seedling)	Soybean Zucchini	500, 2000 mg Ag L^{-1} 100 µg DDE L^{-1}	Ag NPs decreased DDE in soybean Ag NP (500 mg L^{-1}) decreased DDE in zucchini	De La Torre-Roche et al. (2013)
Cu	Kinetin	Soil, 55 d (seeds)	Bean	50, 100 mg Cu kg^{-1} 10, 100 µM kinetin	Kinetin decreased Cu in roots and increased Cu in leaves	Apodaca et al. (2017)
nZVI	Quinclorac (QNC)	Aqueous solution, 7 d (14-day-old seedling)	Rice	50, 250, 750 mg Fe L^{-1} 5, 10 mg QNC L^{-1}	nZVI (50 and 250 mg Fe L^{-1}) alleviated toxicity (root length) of QNC and reduced QNC in shoots and roots	Zhang et al. (2020)
γ Fe_2O_3	Oxytetracycline (OTC)	Rice nutrient solution, 10 d (16-day-old seedling)	Rice	25 mg Fe L^{-1} 25, 100 mg OTC L^{-1}	Fe_2O_3 NPs increased OTC in root and on root surface and reduced OTC in shoot at 25 mg OTC L^{-1} OTC increased Fe on root surface and in shoot and did not affect Fe in root	Bao et al. (2019)
TiO_2	Tetracycline (TC)	Hoagland solution, 10 d (18-day-old seedling)	Rice	500, 1000, 2000 mg Ti L^{-1} 5, 10, 20 mg TC L^{-1}	Antagonistic effects on phytotoxicity (plant biomass, oxidative stress, and macro-/micronutrient contents) Co-exposure diminished the TC accumulation and increased the Ti accumulation	Ma et al. (2017)
ZnO	Phenanthrene	Hoagland solution, 15 d (6-day-old seedling)	Wheat	250, 500, 1000 mg Zn L^{-1} 1 mg phenanthrene L^{-1}	Co-exposure increased toxicity (plant growth) Phenanthrene increased the DNA damage of wheat root cells caused by ZnO NPs ZnO NPs reduced the phenanthrene accumulation in roots and leaves	Zhu et al. (2019)

Experiments conducted simultaneously with other size particles and metal-based salt are particularly interesting because they allow the role of NP-specific properties in the interaction to be evaluated. Several works have evidenced that NPs' co-exposure with metals or organic compounds can elicit different biological responses in plants to those caused by the other chemical forms. For example, De La Torre-Roche et al. (2013) have demonstrated that the effects caused by Ag NPs on the accumulation and translocation of dichlorodiphenyldichloroethylene (DDE) in soybean (*Glycine max* L.) and zucchini (*Cucurbita pepo* L.) grown in vermiculite differ from those caused by bulk or ionic Ag.

Similarly, the influence of oxytetracycline (OTC) on Fe accumulation in rice tissue (*Oryza sativa* L.) differs for plants exposed to ionic Fe or Fe_2O_3 NPs (Bao et al., 2019). OTC promotes Fe accumulation on root surfaces and shoots in Fe_2O_3 NPs treatments, which is the exact opposite result of Fe-EDTA treatments. The presence of ZnO (NPs and bulk) reduces phenanthrene accumulation in wheat (roots and leaves), but this effect is stronger for NPs than for bulk counterparts. This is probably due a stronger sorption capacity of NPs than bulk material (Zhu et al., 2019). Interestingly, ZnO (NPs and bulk) increases the detrimental effects of Cd on hydroponic *Carex vulpina* L. plants, whereas Zn salt protects plants against Cd-induced toxicity (Haisel et al., 2019). Although these results are not conclusive, they indicate some possible underlying mechanisms related to the NP properties inherent to their size that affect the interaction of NPs with conventional co-contaminants. This fact emphasizes the need to consider the combined action of NPs with other contaminants present in media to assess and regulate the environmental impacts of NP applications.

2.8 Conclusions

Metal-based NPs have many positive effects on plants which encourage their use to improve crop production and sustainable agriculture, although they also have detrimental effects. Among others, they may produce physicochemical soil alterations, modify the rhizosphere environment, and have toxic effects on plants and soil biota, particularly on beneficial microbial populations. Notwithstanding, the demonstrated fertilizing effects of metal-based NPs on crops, and the increased resistance ability of plants exposed to climatic stressor factors and pathogens, make nanotechnology a promising tool that is currently underused. Controversial results have been found in the published literature, which show positive or negative effects of NPs depending on many factors related not only to NPs' properties and plant species, but also to culture media and exposure conditions. The potential effects of NPs on plants due to the interaction with other contaminants have been less studied. The results confirm the active interactions between NPs and co-existing contaminants, which can be synergistic or antagonistic depending on the intrinsic properties of NPs and co-contaminants, plant species, and, more importantly, the application rate. Other factors like exposure mode, plant growth stage, and exposure time also influence joint toxicity. From a risk perspective, the occurrence of synergistic interactions is the biggest concern.

One of the most evident difficulties that limits the use of NPs in agriculture is to compare the results between the studies performed under different experimental conditions that determine outcomes. Therefore, a more systematic approach with standardized protocols that defines the many involved parameters as much as possible is necessary. In addition, a gap has been detected in knowledge of the real joint effects of NP-chemical mixtures. Further studies are needed to acquire more knowledge about the mechanisms of NP interactions with co-existing contaminants, including a comparative study with bulk particles and their ionic counterparts. The possible applications and uses of nanotechnologies in agriculture require the joint effects of NPs and co-contaminants being taken into account to establish regulatory guidelines.

Future research into metal-based NPs will address the precise release of nutrients adapted to soil features and crop needs. NPs will regulate the uptake of beneficial and harmful chemicals by plants. Simultaneously, NPs will allow plants to enforce their defenses against external stress agents and to improve their potential in stimulating plants to produce natural active molecules. Ultimately in the near future, NPs will enable us to accomplish sustainable agriculture by reducing inputs and chemical residues in crops.FundingThis chapter was supported by the Community of Madrid, project AGRISOST-S2018/BAA-4330.

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