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Are nanomaterials leading to more efficient agriculture? Outputs from 2009 to 2022 research metadata analysis†

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Agriculture is responsible for supplying food, feed, fibres, and an increasing fraction of fuel and raw chemicals for industry. Fulfilling such demands sustainably is one of the major challenges of our time. In this metadata analysis, we offer a quantitative overview of how scientists have been addressing the effects of nanomaterials on plants between 2009 and 2022. The analysis showed that cultivated crops (*ca.* 55%) and plant nutrients (54%) are mostly employed in the studies, pointing to the relevance of these aspects to agriculture. Nevertheless, it also revealed that the concentration of elements as nanomaterials is generally more than 2-fold higher than the elemental concentration applied as traditionally formulated fertilisers or those naturally found in soil. Furthermore, the median time span of most studies, *i.e.*, 49 days for plants cultivated in soil, is still quite short compared to annual crop life cycles (90–120 days), and little attention (19% of treatments) has been devoted to soil microorganisms. Also, only a small fraction of experiments (6%) has been carried out under field conditions. Therefore, the data did not allow establishing correlations between effects and experimental parameters, such as concentration range, soil pH, or time of exposure. These observations point to the intricate relationship between our ability to infer conclusions and the experimental design employed. Finally, this comprehensive and up-to-date overview of the effects of nanomaterials on plant systems raises the question of whether nanomaterials will lead to incremental yield gains by replacing current inputs with nanotechnology-based ones, such as the controlled release of fertilizers and pesticides, or will disrupt agriculture by attacking problems so far not practically addressed, such as hacking plant stress and defence mechanisms or modulating metabolism and photosystems.

Environmental significance

The unique properties of materials at the nanoscale has raised expectations for new products and solutions for agriculture, such as enhanced fertilizers, biostimulants, and pesticides. Aiming at gathering and summarizing the collective knowledge so far produced, this metadata review assembled and organized quantitative information focused on the scientific literature of the past decade. The present study represents a source of comprehensive data that can help scientists to clearly grasp what has been done and how much is still to be done.

Agriculture under pressure

Agriculture is currently under a huge strain as the demand for food, feed, fibre, fuel, and biomass-based molecules rises.[1,2] It is expected that agricultural outputs must be increased by 70% in the next few decades,[3] yet shrinking farmlands make it difficult to support the demands on agriculture.[4]

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Meeting higher agricultural yields implies overcoming many challenges, such as promoting nutrient use efficiency, soil protection, drought, salt and high-temperature tolerance, and the management of harm induced by nematodes, arthropods, and pathogenic fungi, bacteria, and viruses as well as parasitic weeds.[5–9]

In this context, how could nanotechnology contribute to developing more sustainable and productive agriculture? Although nanosized particles (NPs) do naturally occur in the environment,[10,11] their many inherent properties, *e.g.*, larger contact surface, size- and shape-dependent solubility, and surface charge alterability,[12,13] are often claimed as beneficial to plant-based systems as they might play crucial roles in plant nutrition, disease management, and crop production.[14] NPs are also credited for driving better protection against biotic and abiotic stresses[15] as well as enhanced photosynthetic efficiency,[16,17] controlled fertiliser release,[18–20] and even the synthesis of doped nanodevices for 'smart' delivery of bioactive compounds and minerals to target tissues.[21,22]

In order to establish the current stage of nanomaterial-based research driven toward plant systems, the present study brings a quantitative overview of previously published studies involving nanomaterials and plants. It includes 1154 peer-reviewed publications found in the Web of Science database between 2009 and 2022. The following keywords and Boolean operators were employed: "nanomaterial OR nanoparticle OR nanotechnology" and "plant OR seed OR agriculture". Papers approaching nanoencapsulation of chemicals, *e.g.*, pesticides and sensors, were not considered, since unbundling the reported effects as either a function of NPs or the loaded chemical is not straightforward (for a comprehensive review of this topic, please read Wang *et al.*[14]). Therefore, this systematic metadata survey aimed at answering nine broad questions:

(1) Which nanomaterials/nanoparticles (NPs) have been tested? (2) Which plant species have been exposed to NPs? (3) What is the size range of the NPs? (4) Did the studies with plants employ any kind of positive control? (5) Where have the experiments been carried out? (6) Which plant parts or organs have been exposed to NPs? (7) How long have plants been exposed to NPs? (8) What was the concentration range of NPs? (9) What were the effects of nanomaterials on soil microorganisms?

Replying to these questions may give a glimpse of how nanomaterial–plant interactions have been addressed. Additionally, it might point out whether the knowledge generated allows us to conclude the real contribution of nanomaterials for optimized and sustainable agriculture.

Due to the variability of experimental strategies and the lack of a standardized procedure employed by the different authors, the survey presented here does not aim at making statistical analyses or extrapolations. We included papers strictly following the keywords and Boolean criteria mentioned above and no intentional bias was exerted in the selection. Further details on the criteria used to select the manuscripts are provided in the ESI.† The raw data for the figures, the strategy for data mining, and the error/uncertainty estimation method are also provided in the ESI.†

Experimental design

Fig. 1 shows that most studies employed NPs as metals (25%) or metal oxides (54%), whereas 11% of the studies explored carbon-based NPs such as fullerenes, graphene, and carbon nanotubes. Among the metal oxides, ZnO, TiO_2, CuO, and CeO_2 account for more than a third of all studied NPs. Moreover, Ag appears in 12% of them, outstanding as the most frequently employed metallic NP.

The analysed articles cluster NPs into four main branches: (1) plant nutrient supply; (2) stimulation of plant metabolism; (3) mechanisms of NP uptake, transport, storage, and metabolism in plants; (4) impacts on and toxicity to plants. The survey identified the leading topic of interest of the scientific community, which is increasing plant productivity through nano-based fertilizers since 54% of the data entries employed plant nutrient NPs or also evaluated NP-driven crop protection.

However, a noteworthy fraction of those studies were either related to toxicity or the evaluation of NP uptake. Although they encompass crucial steps for determining the behaviour of the NPs, one must keep in mind that most of these studies do not relate to the practical application of NPs in cropping systems. In those studies, both NP concentration and experimental conditions explored were usually quite different from practical scenarios, and thus the obtained results might be difficult to transpose to real field applications.

Another approach concerns the use of NPs made of beneficial or non-nutrient materials with stimulatory effects,

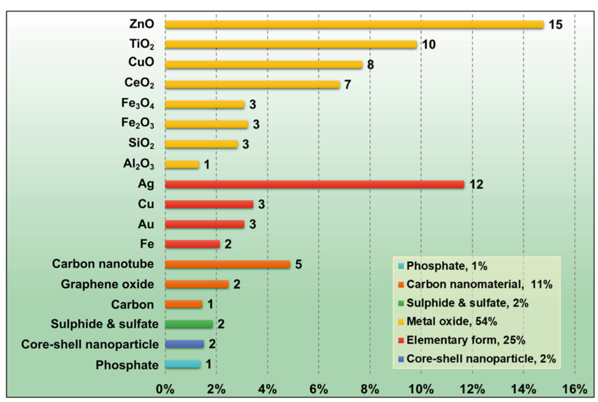

Fig. 1 Most frequently employed NPs (*n* = 1455 NPs) were found in 1154 original research articles published between 2009 and 2022. Each bar colour encompasses an NP group, namely, metal oxides, elemental ones, carbon-based, sulphides and sulphates, core–shells, and phosphate. Particles whose frequency was smaller than 1%, *i.e.*, nano-hydroxides, and mixed oxides, among others, are not shown; thereby the summarisation might not reach 100%. The complete data and references are presented as a worksheet in Table S1 of the ESI† as well as in a data repository.[23] The estimated data uncertainty is *ca.* 4%.

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e.g., enhancing germination, plant development, nutrient translocation, and antioxidant responses.[24–28] ZnO, TiO_2, CeO_2, and Ag NPs are produced in large quantities by industry;[29] hence several studies aimed at evaluating whether these NPs contained in commercial goods will eventually end up in the environment, thereby affecting plants.[30] One can highlight that ZnO and TiO_2 are present in sunscreen products and cosmetics, while Ag presents antimicrobial properties and is used in antimicrobial coatings and many textiles, keyboards, wound dressings, and biomedical devices.[31–37]

Plants are fundamental components of ecosystems, and hence they are widely used as model organisms for toxicity tests.[38] Furthermore, understanding the toxicity mechanisms of NPs is an important point to design safe materials, either through component changes or synthesis routes, leading to NPs with the least environmental side effects. It is worth noting that for a redesign of these systems, an important aspect is that in addition to reducing the toxicity to non-target organisms and relevant environmental compartments, the nanomaterials must still have appropriate properties for their different applications.[39]

Since Ag, Au, TiO_2, CeO_2, and Al_2O_3 are not found in plants in appreciable concentrations, their background signals are very low. This spectral feature faciliates their detection and make them suitable for mechanistic studies of uptake, transport, storage, and metabolism of NPs.

Most studies employed crop species responsible for producing staple food. Fig. 2 reveals that species from Poaceae, Fabaceae, and Solanaceae families encompass *ca.* 55% of all plant species studied. According to the Food and Agriculture Organization of the United Nations, these families address *ca.* 60% of all harvested areas in 2019.[40] In addition, a considerable fraction of the studies raise concerns about the NPs' toxic effects on crop plants and the introduction of NPs in the food chain. Here, one may perceive an opportunity to carry out studies using perennial and arboreal plant species such as those producing coffee, oranges, olives, apples, pears, and vines among others.

Fig. 3 reveals some aspects regarding the experimental design explored by the studies, *e.g.*, particle size, use of positive experimental controls (*i.e.*, the insoluble form of the same NP composition at micrometre range or a soluble compound containing the element of interest), and conditions of plant growth.

Since NP properties are intrinsically related to particle size, this is a piece of crucial information to be considered. Thereby, Fig. 3(a) shows the size range of individual NPs, usually determined by scanning or transmission electron microscopy, and the hydrodynamic diameter of NPs dispersed in liquid media, measured by light scattering techniques. The NP size ranged from a few nanometres up to hundreds of nm, with a mean value of 45 nm and a median size of 28 nm. It is worth mentioning that Auffan *et al.* argue that non-bulk properties arise mainly for diameters below 30 nm,[41] which calls into question the account of a real nano effect for many of these studies.

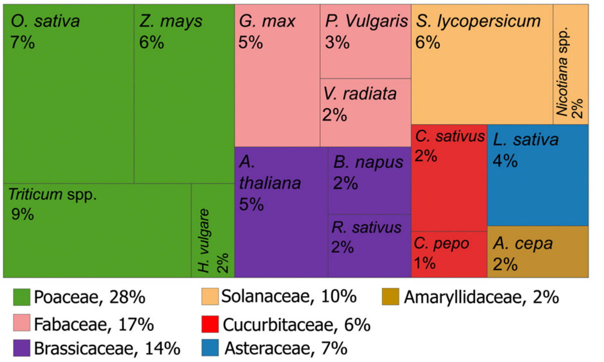

Fig. 2 Frequency of plant species and families found in 1154 original research articles published between 2009 and 2022, summing up an amount of 1374 plants from 253 species and 74 families. Those species and families encompassing frequencies smaller than 1% were not reported. The complete data and references are presented as a worksheet in a data repository.[23] The estimated data uncertainty is *ca.* 4%.

NPs tend to agglomerate depending on physical–chemical interactions, and the primary particle size assessed by electron microscopy does not necessarily reflect the actual size in which they are going to reach plant tissues. The hydrodynamic diameter median size was 174 nm, *ca.* 6-fold larger than the NP primary median size. The attempt at establishing a mathematical relationship between each size analysis did not return a clear correlation.

From an agronomic standpoint, either for nutritional or pest management, the NP size is a key parameter. It is well known that the release of ions can be controlled as a function of particle size since its dissolution rate is inversely proportional to the particle size.[42–44] Ideally, one could develop nanoparticles for which the dissolution rate could be controlled to match plant demand, avoiding losses by volatilization, leaching, runoff, or strong adsorption in soil colloids.

Size also determines whether entire particles will enter plant tissues; several size exclusion limits have been reported, varying from *ca.* 5 nm up to 50 nm.[45–48] However, some studies have demonstrated the uptake and translocation of nanomaterials with diameters greater than the size range stated above,[47,49] which suggests that the uptake of intact particles depends also on NP composition, surface charge,[50] and plant species. The ions released from NPs may be taken up by roots or leaves depending on the dosing method, and then these ions might eventually be precipitated within plants. Additionally, size and chemical reactivity can also be modified through the interaction of these nanomaterials with components of the environment, such as microorganisms and soil organic matter.[51] In this context, dealing with plants is even more challenging because roots can exude protons, organic acids, and siderophores that act as chelating agents[52] as well as several secondary metabolites that might interact with the NPs.[53]

Fig. 3(b) shows that 70.9% of the articles neither employed bulk nor soluble ionic positive controls, whereas 15.1% used

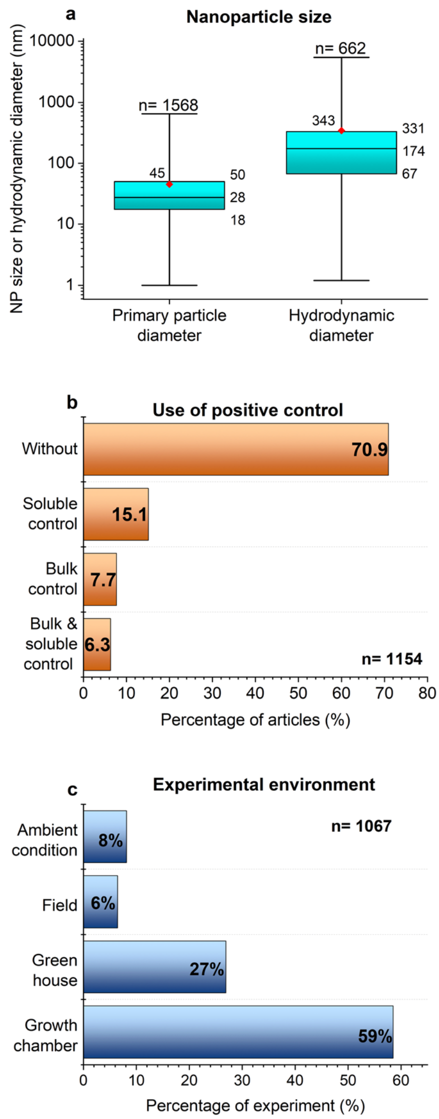

Fig. 3 (a) Boxplots of primary particle diameter and hydrodynamic diameter of NPs. The central line represents the median, whereas the red dots indicate the mean value. The estimated data uncertainty is *ca.* 5%. It is noteworthy that 23% of the consulted articles did not provide any, or supplied incomplete, information about NP primary size, while 63% did not report NP hydrodynamic diameter. (b) Frequency of studies that reported the use of positive control, *i.e.*, either bulk or soluble compounds, in the same experiment as NPs; the estimated data uncertainty is *ca.* 3%. (c) Frequency of the environment in which the experiments were carried out, namely, ambient conditions (without control of light and temperature factors), field, greenhouse, and growth chamber. The estimated data uncertainty is *ca.* 2%. In (a), *n* represents the number of treatments, whereas in (b) *n* indicates the number of papers, and in (c) *n* represents the number of experimental conditions. The complete data and references are presented as a public worksheet available in a data repository.[23]

soluble controls, 7.7% used bulk controls, and only 6.3% considered both soluble ionic and bulk controls. Although establishing soluble controls are not possible for several compounds, such as TiO_2 and carbon-based NPs, one should consider without controls it might be challenging to attribute the observed results to properties arising from the nano dimension of particles. For example, it is known that metallic nanomaterials can be transformed, producing reactive ions able to bind into functional molecules in living organisms.[54] This leads to a myriad of harmful effects, such as destabilization of cell membrane integrity, alteration of cell osmotic balance, deactivation of enzymes, and production of reactive oxygen species (ROS), usually resulting in altered metabolism and cell damage.[54,55] Because of that, providing this kind of control could help interpret the effects of nanomaterials.[54] Nevertheless, several papers aimed at comparing the effects of surface charge, type of coating, or particle size on uptake properties, and in such cases positive controls might not be useful or necessary.

Fig. 3(c) shows the environment in which the experiments were carried out, revealing that 59% of them were performed under growth chamber conditions, whereas *ca.* 27% took place in greenhouses, and only a 6% fraction was conducted under field conditions. Experiments that could not be grouped in these categories were named "ambient condition"; they correspond to 8% of reports. As researchers working on this topic, we acknowledge the difficulties involved in setting up a safe experiment with nanomaterials in the field. On the other hand, to facilitate real-world agricultural applications, this barrier must be overcome by organizing controlled field trials, because those are equivalent to clinical trials in medicine for practical applications.[56]

Growth chambers offer controlled temperature, air moisture, light, and water irrigation, while greenhouses usually grant controlled temperature and irrigation. Most of the experiments carried out either in growth chambers or greenhouse are performed in pots or trays. Nevertheless, it may subject plants to root space confinement and increase the probability of interaction between plant tissues and NPs or their released components, leading to results that would likely differ from those in field trials. A compromise between field and pot can be met by a mesocosm environment, which usually remains within a greenhouse with controlled external parameters but at the same time provides enough space for roots and allows NPs to diffuse across distinct environments. Prominent examples can be found in the studies by the groups of Lowry,[57,58] Wiesner[59,60] and Colman.[61]

Fig. 4(a) shows that 65% of the studies exposed plant root tissues to NPs, whereas only 17% and 14% exposed leaves and seeds, respectively. Within root exposure, 54% of them were carried out using growth solutions or agar-like media, which allow a great level of experimental control, but the results are hardly representative of soil. The preference for root exposure might arise from the fact that roots are the plant's organs designed for water and nutrient absorption, and hence they may unintentionally take up those NPs released into the environment. Nevertheless, although leaves are mainly responsible for transpiration and gas exchange, they can also absorb chemicals, including fertilizers and NPs.[62–64]

If NPs are to be employed as fertilizers, stimulants, or pesticides, their broadcast in the soil makes them more subject to losses. Additionally, the chemical interactions

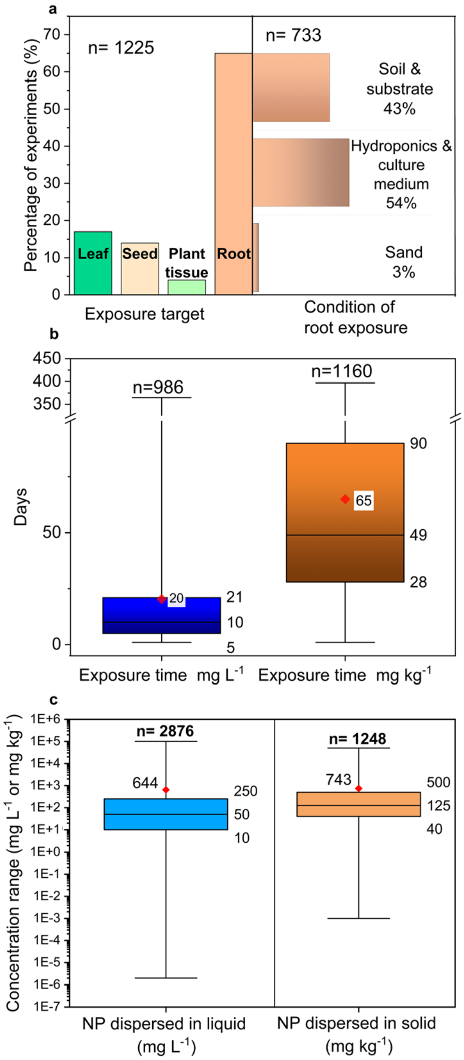

Fig. 4 (a) Plant part or plant organ exposed to NPs and the medium employed in case of root exposure; the estimated data uncertainty is *ca.* 4%. (b) Boxplots presenting the exposure time of plants to NPs dispersed in either liquid solutions or soil. Herein, the estimated data uncertainty is *ca.* 5%. (c) Boxplots of NP concentration range dispersed in either liquid or solid; the estimated data uncertainty is *ca.* 4%. Centrelines represent the median, whereas the dots indicate the mean values in (b) and (c). In (a), *n* represents the number of experiments, in (b), *n* indicates the number of exposure times described by the studies, and in (c), *n* represents the number of treatments reported by the manuscripts. The complete data and references are presented as a worksheet in a data repository.[23]

between NPs and soil colloids, such as clay and organic matter, and the effect of pH can modify the surface properties which will influence the bioavailability and mobility of NPs.[65]

From a practical point of view, the application of NPs in agriculture through seed and foliar treatment would lead to the direct deposition of NPs on plants, increasing the likelihood of assimilation. In this scenario, ZnO NPs applied to seeds enhance germination and increase root and shoot tissue length in maize, rice, and soybean plants.[24,66,67] Hence, the low number of studies evaluating this way of exposure points to an opportunity that can be seized in future studies. For example, coffee plants that received foliar sprays of *ca.* 68 nm ZnO NPs at 10 mg L^{-1} presented 55% higher photosynthetic activity and 90% higher stomatal conductance after 40 days of treatment compared to $ZnSO_4$ and control treatments.[68] Also, foliar application of Cu NPs at 250 mg L^{-1} mitigated salt stress in tomatoes by improving the Na^+/K^+ ratio. In addition, fruits of plants under salinity stress had their content of Cu, vitamin C, glutathione, and phenols significantly increased compared to controls through foliar exposure of Cu NPs.[69]

Fig. 4(b) shows that three-quarters of the studies carried out under hydroponic and soil lasted up to 21 and 90 days, respectively, with a 10 and 49 day median duration, respectively. The most frequently investigated crops shown in Fig. 2 require around three to five months to complete their cycles, *i.e.*, from sowing to harvesting. Here one could point to a gap, and hence an opportunity for long-term studies on the uptake of biotransformation of NPs. Considering the putative potential of nanotechnology to increase agricultural productivity, we should also focus on evaluating the impact of NPs on crop yield. Last but not least, in the middle of a debate on whether the nutrient content of agricultural outputs has been declining compared to the past because of higher yields,[70,71] we should also consider evaluating more frequently the effect of NPs on the quality of vegetal products.[72]

Another parameter that might influence the results is the concentration range of NPs applied, as shown in Fig. 4(c). The median concentration of NPs dispersed in the liquid was 50 mg L^{-1} while the mean concentration was 644 mg L^{-1}. In a general-purpose solution for plant growth, essential macroelements such as potassium, calcium, and phosphorus are found at 235, 160, and 62 mg L^{-1}, respectively. On the other hand, micronutrients such as zinc, copper, and iron are present at 0.13, 0.03, and 1–3 mg L^{-1}, respectively.[73] These concentrations correspond to the number of available nutrients, while the values presented in Fig. 4(c) correspond to those NPs in which most of the elements are not supposed to be dissolved. It is noteworthy that the median concentration range of NPs dispersed in liquid medium exceeds more than 10-fold that of essential micronutrients.

In regular hydroponics, the nutrients are depleted from the solution as they are absorbed by plants. Conversely, in a colloidal NP dispersion, one could expect a more constant concentration level due to equilibrium between solid and aqueous phases. Several studies indicate that the fraction of dissolved ions in ZnO dispersions may vary from *ca.* 4% up to 9%,[44,74] while for CuO these values reach *ca.* 0.1% up to 1.1%,[75,76] and for CeO_2 they range from <0.1% up to 0.9%.[77,78] Nevertheless, the fraction of dissolved ions depends not only on the chemical composition of the NPs but also on the pH and chelating molecules present in the solution.[79]

The range employed in soil was higher than in hydroponics, displaying median and mean NPs of 125 and

743 mg kg^{-1}, respectively. The availability of nutrients depends on soil features, *i.e.*, clay fraction content, pH, organic matter content, and cation exchange capacity. Therefore, the adequate available concentration varies on soil texture; for phosphorus it is slightly above 10 mg kg^{-1}, and higher than 50, 600, 2.5–5, 0.8–3, and 0.5–2 mg kg^{-1} for K, Ca, Fe, Zn, and Cu, respectively.[80]

From an environmental safety standpoint, Reimann *et al.*[81] determined the $HNO_3/HCl/H_2O$ extractable concentration of 53 elements in 2108 samples collected in agricultural and grazing lands of 33 European countries. They found that geochemical threshold values, *i.e.*, concentrations unusually high based on the value of the 98th percentiles of the sampling, for Zn, Ag, Cu, and Ce were 129, 0.19, 78, and 81 mg kg^{-1}, respectively. These elements comprise *ca.* 57% of treatments from the studies published between 2009 and 2019 in which NPs were dispersed into soils, sand or substrate; the median concentration of Zn, Ag, Cu, and Ce in these studies was 200 (n = 264), 31 (n = 99), 100 (n = 106), and 250 (n = 140) mg kg^{-1}, respectively (n corresponds to the number of treatments).

The amount of zinc employed in conventional fertilization depends on the crop and soil features, but it usually remains between a few and up to a dozen kilograms per hectare.[82,83] Liu *et al.*[83] obtained high maize yield by applying Zn at a rate of 11.3 kg ha^{-1} (3.83 mg kg^{-1} of Zn in soil, considering a typical 0.2 m deep soil layer and 1.5 kg dm^{-3} soil density).

To evaluate the potential gains offered by nanotechnology for fertilization, experiments aiming at replacing conventional bulk particulate or soluble fertilizers with nanomaterials should employ realistic field concentrations such as those reported above.

Thus, one should keep in mind that the nanosized properties of particles might have a crucial role in understanding the harmful effects of NPs. As well, the effects of high exposure concentrations should be accounted for. This puzzle could be more assertively solved if the results are backed up by adequate negative and positive experimental controls.

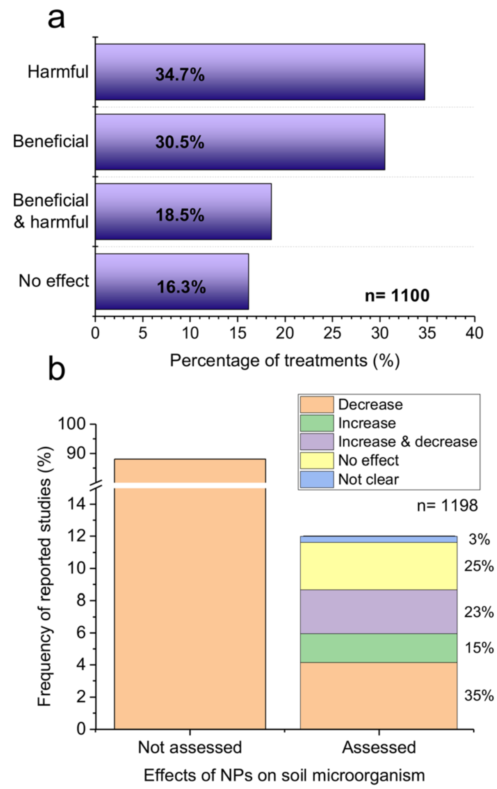

Fig. 5 (a) Frequency of reported effects of NPs on plants whose roots were exposed to the treatments in solid medium, *i.e.*, soil or sand. 'Beneficial & harmful' effect comprises treatments reporting overlapped positive and negative effects, whereas 'no effect' refers to those reporting no changes compared to the negative control group, and 'not applicable' encompasses studies/treatments that did not evaluate plant biological responses as an effect of NP exposure. The estimated data uncertainty is *ca.* 7%. (b) Frequency of treatments that reported effects of NPs on soil microbiota. Double-checking did not return a measurable error. In both figures n refers to the number of treatments reported by the studies. Due to the rounding of the values, the summarisation is 101%. Data were computed from 213 original research articles published between 2009 and 2022. The complete data and references are presented as a worksheet in a data repository.[23]

Effects of nanomaterials on plant and soil microorganisms

Plant morphology and physiology can be impacted by NP exposure as a function of the NP type, size, concentration, and exposure time.[49,84,85] Aiming at making the comparison on equal terms, Fig. 5(a) presents only data extracted from papers in which nanomaterial concentrations were reported on a weight/weight basis and roots were exposed to the treatments through soil/substrate or sand. It encompasses a total of 1100 treatments reported in 213 original articles. The myriad of plant responses evaluated in these studies was classified and grouped as 'harmful', 'beneficial', and 'beneficial and harmful', the latter comprising treatments that concomitantly presented both positive and negative impacts. Studies that did not observe any changes at all were classified as 'no effect', while those that did not evaluate plant morphological and physiological responses were represented as 'not applicable'. Some of the plant responses reported by the authors were changes in plant height, root and shoot tissue length, fruit numbers and weight, crop yield, leaf area, protein, lycopene, beta-carotene, carotenoids, chlorophyll a and b contents, and photosynthetic attributes, whose values higher than that of the control, statistically or suggested by the authors, were considered as beneficial effects. Consequently, their lower values were considered harmful ones. For other features, though, lower values indicate beneficial effects, and higher values, in turn, harmful ones (*e.g.*, fruiting and flowering time). In particular, the increase of antioxidant enzyme activities, such as POD, APX, CAT, and SOD was considered beneficial by some studies and harmful by others. Since these results might reflect either enhanced or improved plant responses to biotic and abiotic stresses, we followed the interpretation given by the authors.

Among the treatments reported in Fig. 5(a), 34.7% resulted in harmful effects, 30.5% pointed out beneficial outcomes, 18.5% presented both harmful and beneficial consequences, 16.3% did not report changes compared to untreated plants, and 15% did not evaluate the effects of NPs on plants.

Notable NP effects on several aspects of agricultural-related research have been reported in recent years. Regarding biofortification, wheat seeds primed with ZnO NPs at 20–1000 mg kg^{-1} boosted the Zn content of the harvested grains. Compared with control, the concentration of Zn in grains was up to 3.3-fold higher and ZnO NPs were more effective than $ZnSO_4$. In addition, at moderate doses (20 mg kg^{-1}) biomass and grain yield were also higher.[25]

In addition, some NP-related photocatalytic properties are claimed to benefit plant light-dependent reactions. In this scenario, root ZnO and foliar Fe-based (Fe and Fe_3O_4) NP exposure have also been reported to significantly increase the net photosynthetic rate of maize and tomato, leading to improved plant growth in both species.[86,87] Zinc oxide, Si, Mn, and TiO_2 NP exposure has also induced higher tolerance either to drought or to salinity stress in mango, cucumber, and wheat plants, which might be related to endogenous NP-driven boosting of plant antioxidant enzymes.[88–90] Wheat plants grown in Cd-contaminated soils negatively affected photosynthesis yield and also caused oxidative stress damage in leaves. However, soil application of Fe NPs at 25–100 mg kg^{-1} not only decreased Cd content in plant tissues but also increased photosynthesis, growth, and yield parameters.[91]

It is worth mentioning that exposing plant roots to NPs might also influence soil microbial communities. Soil microorganisms play pivotal roles in maintaining soil quality since they carry out the decomposition of organic matter, assist plants in water and nutrient uptake,[92] and fix most of the nitrogen used by legumes[93] and a minor part of nitrogen employed by cereals.[94] Hence, microorganisms living in the rhizosphere improve plant development, yield, and disease resistance.[95] In this scenario, any possibility of NP-induced disruption of these ecological services must be a matter of concern.[96]

Despite their importance, Fig. 5(b) shows that the effect of NPs on soil microorganisms was assessed in only 12.9% of the treatments reported in 37 out of the 213 manuscripts assessed. This is a matter of great concern since the soil is expected to be the major sink of the nanomaterials released into the environment.[97] Nevertheless, 25% of the treatments that assessed this parameter declared that the soil microbial community did not change, while 35% reported that either richness or abundance of microorganisms decreased, followed by 15% that increased, and finally 23% reported both increase and decrease in soil microbiota. In this latter case, some papers reported modifications in the structure of the community. According to Simonin and Richaume,[98] inorganic NPs (metal and metal oxide) are usually more detrimental to soil microorganisms than organic ones, *e.g.*, fullerenes and carbon nanotubes.

Several studies associate the diversity and abundance of soil microorganisms with the applied NP concentrations. Albeit another key issue relies on the fact that the plant's developmental stages seem to interfere with microbial diversity in NP-amended soils. Carbon nanotubes at 0.1 and 100 mg kg^{-1} altered soybean rhizosphere prokaryotic community structure more intensely during the reproductive stage than the vegetative one,[99] whereas Ag NPs at 1 mg kg^{-1} showed a transient impact on the structure of the bacterial community during the transition from the seedling to the vegetative stage of wheat, but with a recovery to normal levels 49 days post-treatment.[100]

Several NPs are also known to exhibit antimicrobial effects; their effects on plant pathogens have also been investigated. For example, $Cu_3(PO4)_2{\cdot}3H_2O$ nanosheets and CuO NPs result in suppressed root fungal disease induced by *Fusarium oxysporum* f. sp. *niveum* in watermelon plants.[101] Moreover, soybean plants inoculated with *Fusarium virguliforme* and foliar sprayed with CuO, B, MoO_3, or ZnO NPs presented a significant reduction of root rot severity involved in the sudden plant death syndrome.[102] Although the current work did not explore nano-encapsulated formulations, a recent 500-paper review by Wang *et al.*[14] estimates that the overall efficacy of nanopesticides is *ca.* 32% higher compared to bulk-scale ones.

Moreover, *Medicago truncatula* plants cultivated in soil containing 1450, 100, or 2400 mg kg^{-1} of Zn, Ag, or Ti NPs, respectively, had more significant negative impacts on the microbial abundance in soils more significantly than those with bulk/dissolved treatments.[103] Conversely, Ag_2S NPs were less harmful to tomato mycorrhizal symbiosis and the soil microbial community than Ag^+.[104]

In some cases, soil microorganisms might mitigate nanoparticle toxicity to plants. Mycorrhizal fungi colonization in tomatoes cultivated in Ag NP-spiked soil alleviated nanomaterial-induced phytotoxicity by decreasing Ag accumulation in plant tissues.[105] Similarly, the root colonization rate significantly decreased when exposed to ZnO NPs at and above 800 mg kg^{-1}, but despite that, arbuscular mycorrhizal fungi mitigated the phytotoxic effect by decreasing Zn bioavailability and accumulation in maize.[106]

Plant responses depend on a complex parameter network. The boxplots presented in Fig. 6 correlate the effects observed in plants with the concentration of NPs applied into the soil as a function of NP concentration (a), soil pH (b), and time of exposure (c). Although the highest mean value of the concentration of NPs in the soil comes from treatments that pointed out beneficial effects in plants (*ca.* 1070 mg kg^{-1}), median concentration values of the harmful (400 mg kg^{-1}) and beneficial and harmful (200 mg kg^{-1}) effects are higher than that of the benefits and no effect (both at 100 mg kg^{-1}) (Fig. 6(a)).

As mentioned above, Auffan *et al.*[41] highlight that those non-bulk properties arise mainly for NPs displaying a <30

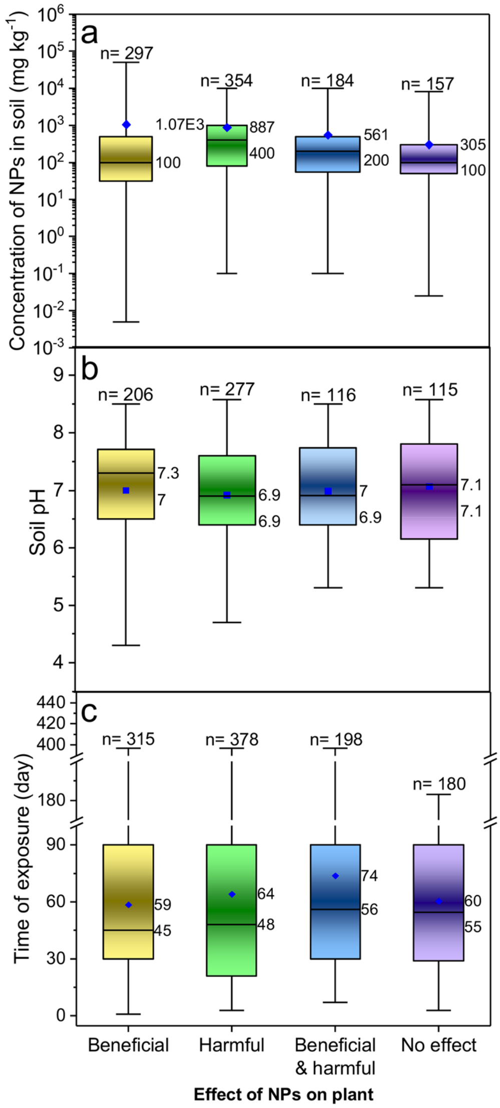

Fig. 6 Boxplots of (a) soil-amended NP concentration (n = 992 treatments from 192 articles), (b) soil pH (n = 714 treatments from 131 articles), and (c) NP exposure time (n = 1071 treatments from 195 articles) as a function of the effects reported. Centrelines point out the median, whereas the blue dots signify the mean values. Due to the high number of variables, the uncertainty values were not recorded. Data were computed from original research articles published between 2009 and 2022. The complete data and references are presented as a public worksheet available in a data repository.[23]

nm diameter. Hence, to verify whether this threshold would lead to effects, the data were split into NPs ≥30 nm and ≤29 nm, then the frequency of treatments resulting in beneficial, harmful, beneficial and harmful, and no effect was counted. Fig. S1 in the ESI† shows that the type of effect cannot be consistently associated with the 30 nm edge. Fig. S2† presents a boxplot showing the size, informed by manufacturer, TEM, and DLS, and the effects, suggesting no correlation between the 30 nm size boundary and effects.

In addition, the frequency effects on botanical families and species were also evaluated. The most frequently employed families were Asteraceae, Brassicaceae, Cucurbitaceae, Fabaceae, Poaceae, and Solanaceae (Fig. S3†), and the species were *Glycine max*, *Triticum aestivum*/*durum*, *Zea mays*, and *Solanum lycopersicum* (Fig. S4†). A higher frequency of the harmful effects was observed in Brassicaceae and Fabaceae families, whereas the beneficial ones were more noticeable in Asteraceae, Cucurbitaceae, Poaceae, and Solanaceae (Fig. S3†). Curiously, a similar trend was observed for *G. max* and *T. aestivum*/*durum*, whereas beneficial and both beneficial and harmful ones were seen for *Z. mays* and *S. lycopersicum* (Fig. S4†).

Furthermore, to reduce the dimensionality of the continuous variables explored as a function of the effects, *i.e.*, concentration, NP size, soil pH and exposure time, a principal component analysis (PCA) was applied to observe their possible relationships with the effects (Fig. S5†). The PCA analysis did not show any clustering of effects and the first two principal components. This information corroborates with Fig. 6 which shows similar amplitudes for the boxplots of concentration.

In other words, harmful effects might be generally associated with higher doses and *vice versa*; however, due to lack of experimental standardization, it does not necessarily configure a cause–effect relationship.

In a range between 50 and 250 mg kg^{-1}, Fe_3O_4 and TiO_2 NPs boosted phosphorus uptake, shoot and root length, and weight of lettuce.[107] At 500 mg kg^{-1}, CeO_2 NPs increased barley height by 34% and shoot biomass by 330% compared with control, but the plants did not form grains.[108]

Besides concentration, soil characteristics play an important role in plant growth. In particular, soil pH is one of the main properties which influence microorganism activity[109] as well as nutrient solubility and availability.[110] The boxplot shown in Fig. 6(b) indicates that the mean and median values of soil pH were almost the same for all the treatments, close to neutral pH values, which suggests that soil pH might not be correlated with the effects caused by the nanomaterials.

Another important parameter that was not assessed in this data review was the effect of soil organic matter. The presence of humic acids and organic matter can alter the bioavailability of the nanomaterials in soils as well as the presence of salts or changes of pH that result in the loss of nanomaterial stability.[46]

Small differences were found in the time of exposure (Fig. 6(c)). The median time of exposure in which nanomaterials caused harmful effects to plants was longer than the time of exposure reported for beneficial effects by a small margin (48 and 45 days, respectively). Beneficial and harmful effects presented a median time of exposure of 56 days, while the treatments that did not affect the plants lasted a median of 60 days.

Altogether, the data presented in Fig. 6 lead us to conclude that positive and/or negative effects as a response to nanomaterial treatment are not solely a consequence of the applied concentration, soil pH, or time of exposure; it seems to be more correlated with the nanomaterial type and plant species.

What to expect for the future?

The properties exhibited by the nanomaterials may contribute to increasing both the yield and the quality of the agricultural outputs. In principle, engineered NPs can be targeted for soil amendments, seed coating, and foliar application, pointing to better nutrient use efficiency or crop protection compared to conventional sources.

In this scenario, the one-decade metadata review herein presented is aimed at understanding the current stage of nanomaterial-based research toward plant systems by quantifying which NPs, and their respective particle sizes and concentrations, have been applied to which plant species. In addition, the experimental conditions, *e.g.*, cultivation environment and NP exposure way and timeframe, as well as the use of control were also considered.

Overall, the big picture presented by the quantified results does reveal an urgent need for improving the description of the experimental procedures. Regarding the experimental settings, a high number of NP assays frequently used in toxicity studies must be supported by positive controls as they otherwise challenge establishing a clear correlation between the results and NP exposure.

Furthermore, the size of NPs employed through multiple measurement techniques that capture both the primary particle size and the agglomerate sizes in the dosing solutions must be included in future studies. The NP suspension medium and the surface chemistry of the NPs should be characterized, and controls with the associated agents but with the nanomaterials should be performed to allow for the determination of the active agents responsible for the effects observed. Last but not least, addressing long-term experiments with NPs utilising perennial plants is of the utmost importance.

One should keep in mind that replacing conventional fertilizers with nanosized ones requires experiments employing compatible NP concentration ranges and long exposure times, as the impacts on plant productivity from a commercial perspective, *e.g.*, quantity and quality of edible parts, do need to be reported in future studies. Additionally, the costs involved in transforming either soluble salts or bulk particles into NPs might constitute a barrier unless the use-efficiency of NPs pays it off. Within this framework, it is also crucial to consider the climate-change-driven menaces to crop production, and in relation to this, explore both biotic and abiotic factors, including soil amendments. Thereby, experiments in large mesocosms and field conditions are a key step that will contribute to fostering and maturing nanotechnology-based solutions for agriculture.

Furthermore, the effects of NPs on soil microorganisms must also be more frequently addressed, and specific tests ensuring that any commercial technology is innocuous to the soil microbiota should be demanded by regulators. Likewise, concentration thresholds for NPs in food and feed should be established, aiming at avoiding possible threats to human and animal health.

The growth rate of agricultural outputs during the 18th century raised so much concern that it led to the statement of the Malthusian catastrophe. However, the observers at that time could not forecast that the development and adoption of disruptive technologies, made possible by science, would promote the manifold gains in productivity during the 20th century. Perhaps, with the contribution of nanotechnology, the next productivity increase leap will come not by replacing current agricultural inputs but by creating new ones. Sensing plant metabolism[111] and quickly modulating it, hacking plant photosystems,[112] and stimulating plant functions are some examples of such technologies that will soon be available.

The use of nanotechnologies is often blamed by the literature and media, even though plants naturally take nutrients in the form of colloids and probably NPs.[113] Nevertheless, the summarized conclusions of the studies herein assessed revealed that 50% have employed NPs that exceed the critical nano size (100 nm) as well as concentrations often unrelated to the appropriate agricultural intentions. Despite these shortcomings, 39% of the studies show beneficial effects or no effects at all, against 30% that show negative ones. These negative effects are not often compared to real stresses experienced by plants in the field, leading to the impression that we still do not have a good knowledge of the properties of NPs under optimized conditions of use.

Altogether, these elements suggest that nanotechnology for agriculture deserves to be further explored. By incorporating the efforts of this very first decade of studies exploring the effects of nanosized materials in plant development, it is now possible to establish enhanced experimental protocols, *i.e.*, including suitable NP characterisation, reasonable NP concentrations, and longer exposure times, that will enable properly addressing the real contribution of nanomaterial-based technologies for more productive and sustainable agriculture.

Data availability statement

The complete data used to the production of all figures have been deposited at Figshare and can be obtained from **https://doi.org/10.6084/m9.figshare.20761264.v1**.

Author contributions

This study was conceived by H. W. P. C., M. H. F. G., L. F. F., R. L., C. S., and S. G. The data collection was carried out by E. S., G. S. M., N. M. D., C. G. C., S. L. Z. R., M. H. F. G., and E. A. Data checking was carried out by H. W. P. C, E. S., G. S. M., N. M. D., C. G. C., S. L. Z. R., E. A., J. L. O., and A. E. S. P. Data discussion and interpretation were performed by H. W. P. C, G. S. M., A. P. L., R. L., S. G, L. F. F, and C. S. The first manuscript draft was written by H. W. P. C., G. S. M, N. M. D., J. L. O., and A. E. S. P. All authors edited the manuscript.

Conflicts of interest

There are no conflicts to declare.

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