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Recent advances in the applications of nano-agrochemicals for sustainable agricultural development

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Modern agricultural practices have triggered the process of agricultural pollution. This process can cause the degradation of eco-systems, land, and environment owing to the modern-day by-products of agriculture. The substantial use of chemical fertilizers, pesticides, and, contaminated water for irrigation cause further damage to agriculture. The current scenario of the agriculture and food sector has therefore become unsustainable. Nanotechnology has provided innovative and resourceful frontiers to the agriculture sector by contributing practical applications in conventional agricultural ways and practices. There is a large possibility that agri-nanotechnology can have a significant impact on the sustainable agriculture and crop growth. Recent research has shown the potential of nanotechnology in improving the agriculture sector by enhancing the efficiency of agricultural inputs and providing solutions to agricultural problems for improving food productivity and security. The prospective use of nanoscale agrochemicals such as nanofertilizers, nanopesticides, nanosensors, and nanoformulations in agriculture has transformed traditional agro-practices, making them more sustainable and efficient. However, the application of these nano-products in real field situations raises concern about nanomaterial safety, exposure levels, and toxicological repercussions to the environment and human health. The present review gives an insight into recent advancements in nanotechnology-based agrochemicals that have revolutionized the agriculture sector. Further, the implementation barriers related to the nanomaterial use in agriculture, their commercialization potential, and the need for policy regulations to assess possible nano-agricultural risks are also discussed.

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Environmental significance

Modern agricultural practices have started the process of agricultural pollution. This process causes the degradation of eco-systems, land, and environment due to the modern-day by-products of agriculture. To begin with, the earliest source of pollution has been pesticides and fertilizers. Contaminated water used for irrigation is another source of pollution. Further problems are caused by soil erosion and sedimentation. Nanotechnology is presumed to be a vital force in the near future that can contribute to practical applications in conventional agricultural ways and practices. The prospective use of nanoscale agrochemicals such as nanofertilizers, nanopesticides, nanosensors, and nanoformulations in agriculture has transformed traditional agro-practices, making them more sustainable, ingenious, and environmentally efficient. The present review gives an insight into recent advancements in nanotechnology-based agrochemicals that have revolutionized the agriculture sector. The potential applications of nanofertilizers, nanopesticides, nanosensors, and nanoformulations in increasing crop yields, detecting environmental contaminants, and nano-facilitated soil remediation are evaluated with their positive influence on plant growth.

1. Introduction

Agriculture has always been the prime driver in the economy of self-sustaining and developing nations. It provides raw material for food and feed industries, which are responsible for the

survival of a rapidly-growing global population of nearly 7.5 billion.^{1,2} Agriculture can bring a paradigm shift in a country's economy by contributing towards globalization, technology, economic growth, environmental remediation, biodiversity conservation, food security, and safety.³⁻⁵ Currently, the agricultural sector is facing a broad panorama of challenges such as the decline in crop yield, deficiency of soil nutrients, climate change, water unavailability, decrease in soil fertility, deterioration of biotic matter in the soil, crop diseases, lack of awareness towards genetically modified organisms, and insufficient workforce.^{6,7} These challenges, further linked to industrialization and growing human population, necessitate safer agricultural practices in the

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present time. Sustainability in agriculture has always been a fundamental concern owing to its long-term implications on food production and national economics. United Nations has defined the importance of sustainable agriculture to achieve 'Zero Hunger' as one of the 17 sustainable development goals.⁸ The United States Department of Agriculture (USDA) has defined sustainable agriculture for environmental protection, enhancing the soil fertility, and fulfilment of the needs of the present generation without compromising the needs of future generations.^{9,10} Sustainable agricultural practices include the better use of water resources, efficient management of soil nutrients, controlled use of fertilizers and chemicals, management of agro-wastes, pest control strategies, crop disease control, and innovative farming techniques.^{11,12} The assessment of agricultural sustainability is based on national or global concerns such as availability of financial resources for farmers, technological innovations, as well as participation in research & development while employing new technologies.^{13,14}

The application of nanotechnology and nanoscience can significantly enhance the efficiency of agricultural inputs and can offer a significant solution for maintaining the sustainable development of agro-systems and related sectors. Nanotechnology can bring a revolution in the agriculture sector by completely changing the food production and supply systems through improvement in the crop yields while simultaneously preserving the ecological balance, environmental sustainability, and economic stability.^{6,7} Nanomaterials (NMs) are considered to be ideal platforms to lead the agri-nanotechnology revolution. The extremely small size of these materials (less than 100 nm) permits them to cross biological barriers and diffuse into the plant tissue by root or foliar treatment, therefore enabling new efficient routes of delivery of nutrients and pesticides. Moreover, the surface engineering of NMs can be performed to provide desirable properties and functionalities. This will mainly direct them to the appropriate locations within the plant or soil and offer smart release and delivery strategies. Nanotechnology has contributed nano-based formulations such as nanofertilizers, nanopesticides, and nanoemulsions to enhance crop productivity and growth.^{15,16} The most productive applications of nanotechnology in agricultural systems include the growth in productivity by efficient nutrient uptake and delivery, water and soil remediation, genetic engineering of protein-encoding genes, improvement in soil characteristics, and prevention against diseases.^{17,18} Nanofertilizers enhance the fertility of soil through the efficient supply of nutrients, whereas nanoherbicides and nanopesticides can be effectively used for the management of herbs, weeds, and pests.^{18–20} Nanosensors can be used for the detection of moisture level, nutrient concentration, soil water levels, determination of diseases, *etc.*²¹ Currently, there is a focus on nanoparticle (NP)-mediated gene delivery in plants for the development of insect-resistant, disease-resistant, and stress-tolerant crops for increased life.^{22,23} Several NMs such as metal oxide NPs, polymeric NPs, carbon nanotubes, and nanoemulsions with active ingredients have shown positive results in sustainable agriculture and food production.^{24–27} The potential risks that may arise due to NMs in agro-food products can cause damage to human health and

environment. This needs to be taken into account during the safety evaluation of such nano-enhanced products. However, inadequate information about the adverse effects of NMs on human health and environment, toxicological aspects, accumulation of materials in food chains, NM hazard, and exposure can put agriculture at undesirable risk for human health.^{28,29} A general regulatory consensus on the applications of nanoscale materials in the agricultural sector must be made to control and regulate the risks related to the health of agricultural workers and farmers so as to promote safe practices in this sector.³⁰

Several recently reported articles have documented the applications of nanotechnology in agricultural production and the food sector.^{6,31–35} For instance, a review compiled the reports on nano-encapsulates based on silver, titanium dioxide, and silica as the most common inorganic NMs employed in agriculture, food, and feed additives.³⁶ The applications of nano-encapsulates and nano-composites are being investigated in novel foods, food and feed additives, biocides, pesticides, and food contact materials. In the recent years, there has been more focus on the use of organic and polymeric NMs such as chitosan NPs, organic micelles, dendrimers, and liposomes in the agro-food sector. Also, the research on carbonaceous materials such as graphene, CNTs, and carbon dots in the agro-food industry has been tremendously increasing.²⁴ The present review is particularly aimed at providing readers up-to-date information on the latest applications of organic and inorganic NMs for crop improvement and sustainable agriculture. The potential applications of nanofertilizers, nanopesticides, nanosensors, and nanoformulations in increasing the crop yields, detecting the environmental contaminants, and nano-facilitated soil remediation are evaluated with their positive influence on plant growth. It covers several aspects of the application of nanotechnology in agriculture by citing numerous reports from recent scientific literature. The subsequent section has highlighted the challenges of incorporating nanotechnology in the agricultural sector and focuses on the existing regulatory legislation to control NM safety in agriculture. It can be concluded that the NM-enabled technology and products offer an abundance of opportunities as one of the most productive and environmentally friendly alternatives in developing sustainable agriculture.

2. Nanotechnology towards sustainable agriculture

Nanotechnology is knocking on the doors of the agriculture sector through precision farming as it can be employed perceptively to suit the general organization of sustainable agriculture, especially by contributing environment-friendly and resourceful technologies.^{37–39} The recent emergence of nanotechnology in drugs and pharmaceuticals has opened up new opportunities to apply the fundamentals of nanotechnology to the agriculture sector as well.^{40,41} The integration of nanotechnology and various scientific fields have paved the way for the development of novel products, technologies, and more applications in the agricultural sector (Fig. 1). Nanotechnology

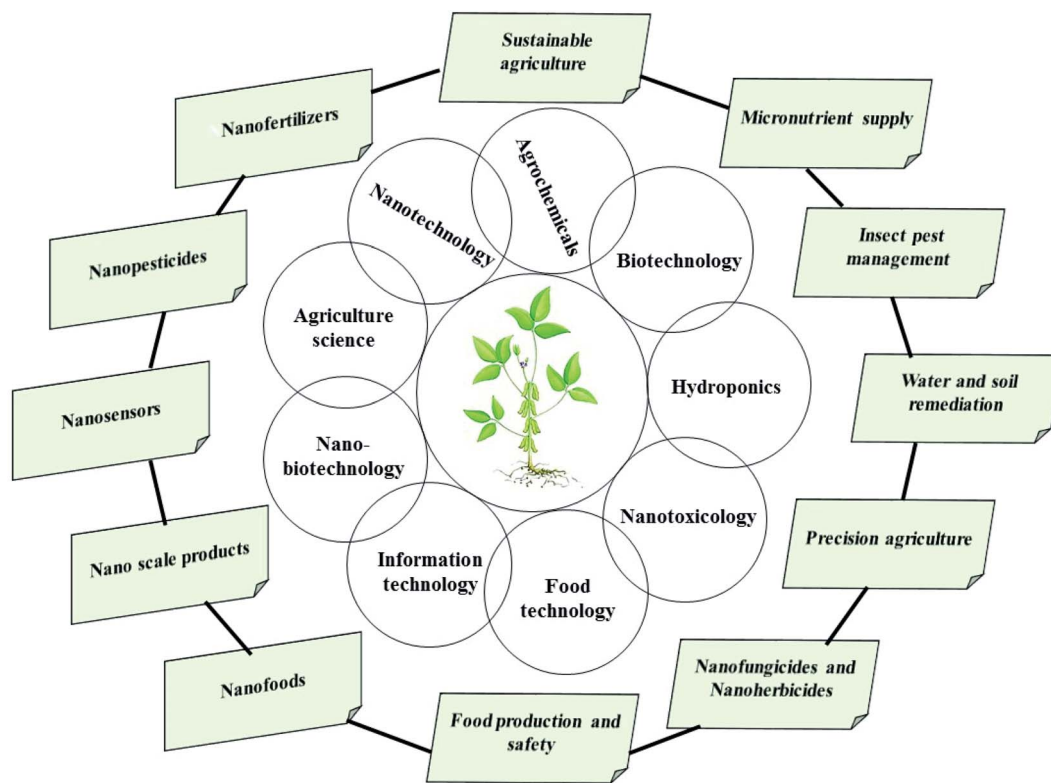


Fig. 1 The potential applications of nanotechnology and various interdisciplinary fields for promoting sustainable agriculture.

has tremendous potential to improve the current agricultural system by the conservation of crop inputs, livestock, animal husbandry, aquaculture, and fisheries. The ultimate goal of agri-nanotechnology aims to maximize crop productivity (yields) using nanoscale products while minimizing the agricultural inputs (e.g., agrochemicals, fertilizers, and herbicides) through continuous monitoring systems.^{42–44} At every stage of agriculture (from seed storage to priming, germination, fertigation, and post-harvest), nanotechnology offers the potential to improve the crop productivity and quality. Nanotechnology plays an important role in increasing the productivity by nutrient control and water quality management for sustainable development in agriculture.⁴⁵ NMs may positively influence the crop yield and soil quality when they enter into the plant surroundings. The release of NM-encapsulated nutrients in the soil biota and organic matter improves the plant morphology and physiology.^{46–48} The remediation of soil and water with NMs will greatly help in maintaining the sustainability by eliminating toxic compounds from the soil, subsequently enhancing its natural quality.⁴⁹ NM-based optical and electrochemical sensors have been used for detecting heavy metals and environmental pollutants in soil media.²¹ The applications of various nano-agrochemicals are represented in Fig. 2.

3. Role of nano-agrochemicals in agriculture

In this section, various nano-agrochemicals, namely, nanofertilizers, nanopesticides, nanosensing materials, and nano-

enhanced products, are discussed, which have been applied in the agricultural sector along with their prospective applications for promoting environmental sustainability (Fig. 3).

3.1 Nanofertilizers: nutrient delivery and uptake

The development of fertilizers is considered to be the most conventional approach to boost plant growth by increasing the nutrient availability and efficient delivery of minerals. Chemical fertilizers provide the plants with essential nutrients for the optimum growth in crop yield and contribute to food security. However, the excessive use of chemical fertilizers has become prevalent in recent times due to decreased soil nutrients, global water scarcity, and reduction in fertile lands.^{50,51} According to the Food and Agriculture Organization (FAO), the total usage of mineral fertilizers in agriculture reached about 110 megatonnes nitrogen (N), 48.5 megatonnes phosphate (P_2O_5), and 38.7 megatonnes potash (K_2O) in the year 2016, which records an increase by 34%, 40%, and 45%, respectively, in the use of these nutrients as compared to the year 2002.⁵² Such extensive use of fertilizers poses a huge risk to environmental sustainability and is known to cause the deterioration of soil quality, ground-water pollution, environmental contamination with heavy metals, greenhouse gas emissions, and risk to human health.^{50,53,54} It becomes essential to develop alternative technologies for fertilizer synthesis to increase agricultural production. The use of nanofertilizers has contributed considerably to sustainable agriculture by increasing the production without causing any damage to the environment.⁵⁵ Nanofertilizers are called 'smart' carriers for the macro/micronutrients that promote the

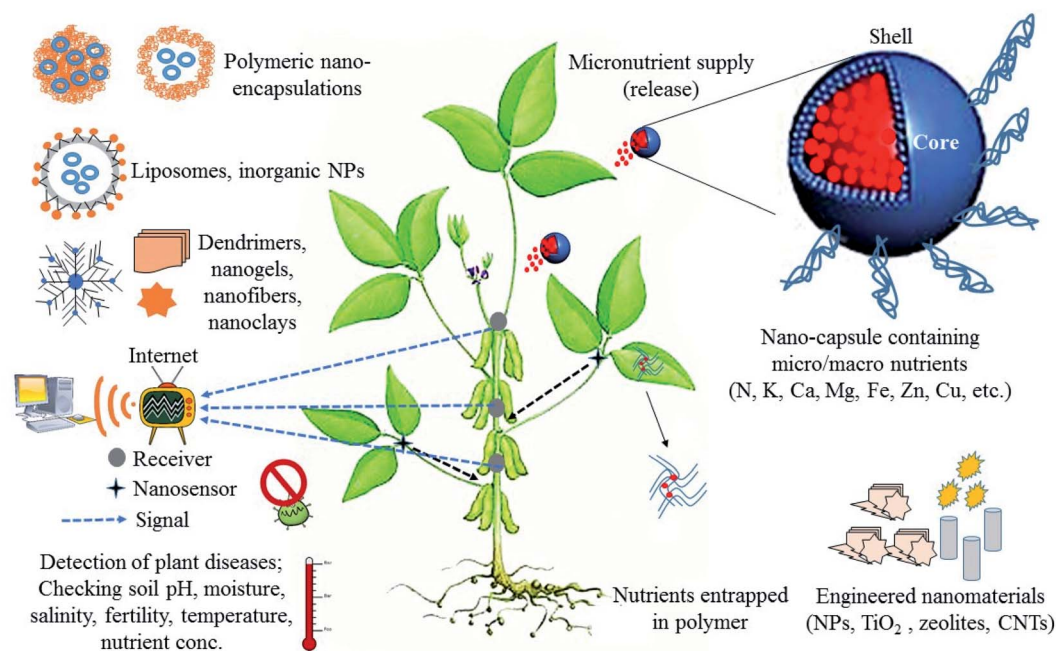


Fig. 2 Role of various nanomaterials as agrochemicals in enhancing crop productivity and providing sustainable agricultural practices.

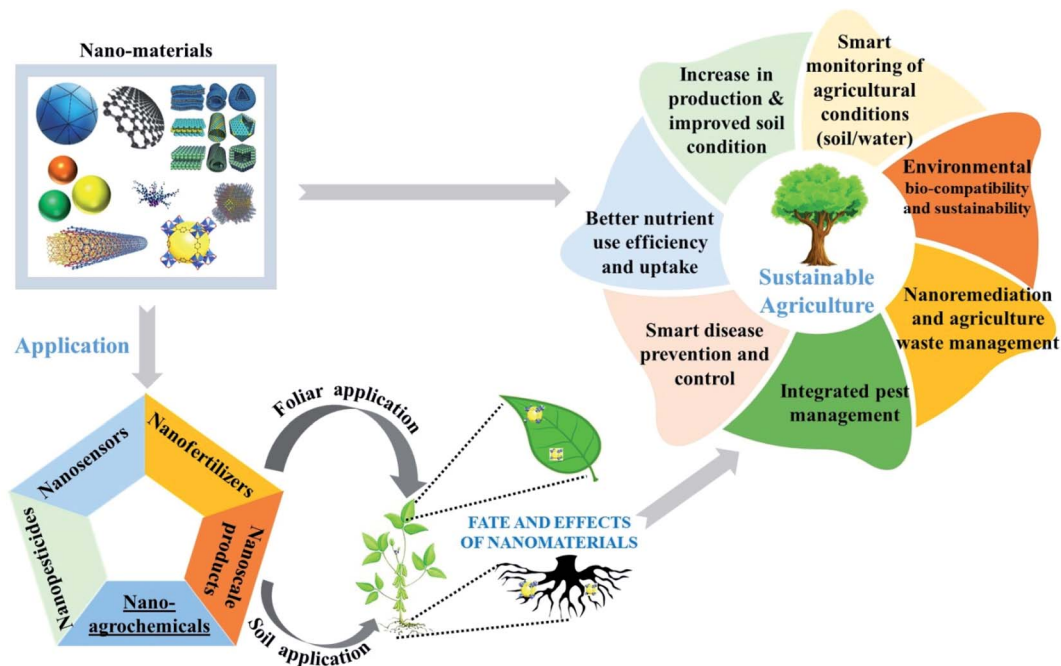


Fig. 3 The applications of nano-agrochemicals for sustainable agriculture.

accessibility and reach of the active components to the plant parts, which subsequently leads to increased crop yields and better vegetation. For example, the macronutrients (such as nitrogen, potash, phosphorus, calcium, and magnesium) and micronutrients (such as zinc, copper, iron, and manganese) can be encapsulated within the NPs coated by nano-films or agents and can be directly delivered in the form of nano-emulsions.^{56–58}

Nanofertilizers promote agriculture sustainability by reducing the production costs of conventional fertilizers. In addition to delivering multiple nutrients at the same time, thereby preventing nutrient loss, the nanolayers on the particles can help in holding the nutrients strongly due to greater surface tension.^{29,59} The protected nutrients are delivered to the targeted regions of the plant, hence preventing nutrient

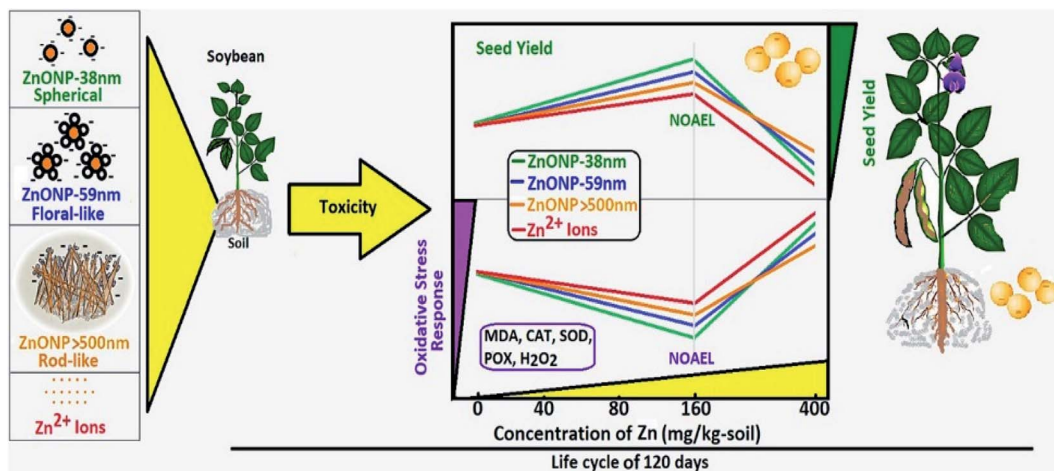


Fig. 4 The applications of zinc oxide nanoparticles (ZnONPs) as a novel nanofertilizer to improve the crop yield and food quality of soybean.⁸⁵

losses.^{58,60,61} The most common engineered materials used in nano-enabled fertilizers for the targeted release and delivery of nutrients are hydroxyapatite, mesoporous silica, chitosan, calcite, carbon nanotubes, metal oxide NPs (zinc oxide NPs, copper oxide NPs, titanium dioxide NPs), magnetite, zeolites, and nanoclays for foliar and soil application.^{62,63} These materials have shown great potential in the slow release of nutrients and can replace conventional chemical fertilizers. For instance, the primary macronutrients (nitrogen, phosphorus, and potassium, collectively called NPK) along with calcium and magnesium, which are required in essential amounts by the plants, are provided with urea hydroxylapatite NPs.^{64,65} Several reports have published the slow and sustained delivery of nitrogen in the urea-hydroxyapatite NPs to increase the plant nitrogen agronomic efficiency (NAE) of the plants several times.^{66–68} Nitrogen can be delivered to the plants by encapsulating urea-hydroxyapatite NPs in the cellulose matrix as a green nano fertilizer strategy.⁶⁹ Besides, the application of phosphatic fertilizers in the form of hydroxyapatite NPs and phosphorus-loaded nanozeolites improved the phosphorus availability in soybean and kankong plants, respectively.^{70,71} Chitosan-based materials have emerged as one of the best nanometric agrochemicals in agriculture for the efficient delivery of nutrients.^{72,73} Along with NPK, calcium is an essential plant nutrient required by plants. In a study, the application of nano calcium carbonate (CaCO_3) to *Vigna mungo* seeds was shown to accelerate the seed germination process with an increase in the root and shoot height, water content, as well as dry and fresh weight of plants.⁷⁴ Recent studies have also reported calcium phosphate NPs doped with urea and NPK nutrients for nutrient delivery.^{75,76} Some other groups have also reported calcium supply through NMs to different varieties of plants.^{77–80} The foliar treatment of the nano forms of magnesium has also been demonstrated to enhance the plant yield in different plants.^{81,82}

Micronutrient nanofertilizers containing zinc, iron, manganese, copper, and molybdenum are generally packed in the NMs such as zinc oxide NPs (ZnO NPs), copper oxide NPs (CuNPs), magnetite NPs, and manganese NPs.^{83,84} For instance,

nanoparticulate ZnO has an increasingly positive influence on plant growth as compared to bulk Zn chemicals presented in Fig. 4.⁸⁵ For instance, ZnO NPs have been shown to increase plant yields, germination rates, and root and shoot length, and biofortification in various plants such as maize, mung bean, chickpea, and peanuts.^{86,87} ZnO NPs have myriad physiological advantages to plants such as chlorophyll biosynthesis, total protein activity, increase in seed vigor, increase in photosynthesis rates, and biomass production.^{88–90} In addition to ZnO NPs, iron oxide NPs are alternatives for conventional iron-based fertilizers as the source of providing iron to plants.^{91–93} The plants utilized iron NPs as the source of iron and as a result, their enzymatic and biochemical efficiency in photosynthetic processes improved considerably.⁹⁴ For instance, a study reported that corn seeds (*Zea mays*) exposed to 20 ppm Fe_2O_3 NPs promoted root elongation by 11.5% and an increase in seed germination indices such as germination rate, germination energy, and vigor index.⁹⁵ Numerous other studies have reported the positive effects of iron NPs on plant growth and yield.^{96,97} The applications of nano copper and nano manganese in agricultural systems have also shown good potential in enhancing the crop yield compared to their bulk counterparts CuSO_4 and MnSO_4 .^{88,98,99} For example, Cu nanowires were reported to improve the plant morphology and agronomical parameters in alfalfa plants.¹⁰⁰ In another study, the application of manganese zinc ferrite NPs was shown to increase the vegetable yield, mineral content, and plant yield in aquash (*Cucurbita pepo* L.) plants.⁸¹

In addition to macro- and micro-nutrients, nano-enhanced fertilizers contain NMs such as zeolites, titanium oxide (TiO_2) NPs, silicon NPs, graphene oxide (GO), and multi-walled carbon nanotubes (MWCNTs) augmented with one or multiple plant nutrients (macro/micro). These fertilizers help the plants in nutrient uptake without themselves providing any nutrient element.^{101–103} Zeolites are nano-porous materials that possess high surface area and high cation exchange capacity, and are highly selective towards plant macronutrients (usually K or NH_4). In a greenhouse experiment, a zeolite augmented with

Table 1 A summary of some of the important studies of different nanomaterials used as agrochemicals and their applications in promoting sustainability in agriculture

(A) Nanofertilizers					
S. no.	Nanomaterial as fertilizer	Nutrient	Test plant/soil	Agronomic findings/application	Reference
1	Hydroxyapatite NPs-urea	Macronutrient (N)	<i>Oryza sativa</i>	<ul style="list-style-type: none"> ■ Slow-release of nitrogen (35% less) ■ Increased plant NAE ■ Increased N and K content in leaves 	66
2	Urea-hydroxyapatite-montmorillonite nanocomposites	Macronutrient (N)	<i>Oryza sativa</i>	<ul style="list-style-type: none"> ■ Slow and sustained release of urea into the soil ■ Higher crop yield 	67
3	Hydroxyapatite NPs-urea	Macronutrient (N, P)	Red-yellow oxisol soil	<ul style="list-style-type: none"> ■ Higher sustained P availability ■ Decreased phosphorus immobilization 	68
4	Nano zeolites	Macronutrient (P and K)	<i>Ipomoea aquatica</i>	<ul style="list-style-type: none"> ■ Increased release time ■ High accumulation of P and K ■ Better pH and moisture ■ More nutrient availability 	71
5	Nano-chitosan	Macronutrient (NPK)	<i>Triticum aestivum</i>	<ul style="list-style-type: none"> ■ Increase in harvest and crop index ■ Increase in root and shoot length 	321
6	Chitosan nanoparticles	Macronutrient (NPK)	<i>Coffea</i> seedlings	<ul style="list-style-type: none"> ■ Enhanced leaf number, plant height, and leaf area of the coffee seedlings ■ Increased nutrient uptake, better photosynthesis 	322
7	Calcium phosphate nanoparticles (CaP)	Macronutrient (NPK)	<i>Triticum durum</i>	<ul style="list-style-type: none"> ■ Enhanced the efficiency of fertilization ■ Precision agriculture 	75 and 76
8	Calcium nanoparticles (CaNPs)	Macronutrient (Ca)	<i>Moringa oleifera</i>	<ul style="list-style-type: none"> ■ Increased efficiency of N uptake ■ Enhanced nutritional quality of fruits ■ Essential nutrients in plants fruits 	77
9	Calcium borate nanoparticles	Macronutrient (Ca) and boron	Lettuce (<i>Lactuca sativa</i>) and zucchini (<i>Cucurbita pepo</i>)	<ul style="list-style-type: none"> ■ Physiological and biochemical features ■ Boosted plant productivity ■ B availability 	79
10	Nano-Mg	Macronutrient (Mg)	<i>Vigna unguiculata</i>	<ul style="list-style-type: none"> ■ Increased plant yield ■ Increased stem Mg content 	91
11	Chitosan nanofertilizer	Micronutrient (Cu)	<i>Zea mays</i>	<ul style="list-style-type: none"> ■ Higher seedling vigor index ■ Increased chlorophyll contents 	323
12	Zinc oxide nanoparticles (ZnONPs)	Micronutrient (Zn)	Soybean (<i>Glycine max</i>)	<ul style="list-style-type: none"> ■ Improvement in crop yield ■ Better food quality 	85
13	Zn and Cu nanoparticles (NPs)	Micronutrient (Zn and Cu)	Basil plant	<ul style="list-style-type: none"> ■ Total chlorophyll and carotenoid in the leaves increase ■ Highest phenolic and flavonoid content ■ Better quantity and quality in basil 	88
14	ZnO nanoparticles	Micronutrient (Zn)	<i>Triticum aestivum</i>	<ul style="list-style-type: none"> ■ Enhances Zn uptake under drought stress ■ Grain nutrient accumulation 	90 and 324
15	Magnetite (Fe ₂ O ₃) NPs	Micronutrient (Fe)	Coriander plant	<ul style="list-style-type: none"> ■ Growth regulator and antimicrobial agent ■ Antimicrobial activity 	97
16	Zeolite/Fe ₂ O ₃ nanocomposites	Micronutrient (Fe)	—	<ul style="list-style-type: none"> ■ Smart iron nanofertilizer ■ Slow-release of iron ions 	96
17	Manganese zinc ferrite NPs	Micronutrient (Mn, Zn)	Squash plant (<i>Cucurbita pepo</i> L)	<ul style="list-style-type: none"> ■ Vegetative growth, ■ Good mineral content ■ The better yield of squash plant 	81
18	Copper nanoparticles	Micronutrient (Cu)	Sandy loam soil	<ul style="list-style-type: none"> ■ Slow-release of micronutrient fertilizer ■ Better soil nitrification kinetics ■ Control the bioavailability of Cu to soil bacteria 	98
29	Nano zeolite	Nano-enhanced fertilizers (NPK)	Sage plant	<ul style="list-style-type: none"> ■ Better vegetative growth ■ Increase in fresh and dry weight ■ Better photosynthesis ■ phenols, tannins, total flavonoids, oil constituents, macro, and micro-elements 	102
20	Urea-loaded mesoporous nanofertilizers	Nano-enhanced fertilizers	<i>Oryza sativa</i>	<ul style="list-style-type: none"> ■ Controllable release of nutrients ■ High yield ■ High nitrogen recovery efficiency (NRE) 	101

Table 1 (Contd.)

S. no.	Nanomaterial/active ingredient	Nature	Host plant/crop	Target	Reference
(B) Nanopesticides					
21	Nanostructured alumina	Nanoinsecticide	<i>Oryza sativa</i>	■ <i>Sitophilus oryzae</i> ■ <i>Oryzaephilus surinamensis</i> ■ <i>Ceratitidis capitata</i> ■ Leaf-cutting ants	129 and 130
22	Nanostructured alumina	Nanoinsecticide	—	■ <i>Oryzaephilus surinamensis</i> ■ <i>Stegobium paniceum</i> (L.) ■ <i>Tribolium confusum</i>	133
23	Nano silica	Nanoinsecticide	<i>Zea mays</i>	■ <i>Sitophilus oryzae</i> ■ <i>Rhizopertha dominica</i> ■ <i>Tribolium castaneum</i> ■ <i>Orizaephilus surinamensis</i>	134
24	ZnO and SiO ₂ NPs	Nanoinsecticide	<i>Triticum aestivum</i>	■ <i>Sitophilus oryzae</i> L ■ <i>Tribolium castaneum</i> Herbst F	136
25	ZnO NPs	Nanoinsecticide	—	■ White grubs (<i>Holotrichia</i> sp.)	139 and 142
26	Chitosan NPs loaded with permethrin and spinosad	Nanoinsecticide	—	■ <i>Drosophila melanogaster</i>	325
27	AgNPs/silver-chitosan nanocomposite	Nano bactericides	Bacterial canker disease of fruit trees	■ <i>Pseudomonas syringae</i>	155
28	AgNPs	Nano bactericides	Bacterial blight disease of pomegranate	■ <i>Xanthomonas axonopodis</i>	326
29	TiO ₂ /Cu ₂ (OH) ₂ CO ₃ NPs	Nano bactericides/nano fungicides	—	■ <i>E. coli</i> ■ <i>F. graminearum macroconidia</i>	157
30	CuNPs	Nano fungicides	Various crops	■ <i>Fusarium solani</i> ■ <i>Neofusicoccum</i> sp. ■ <i>Fusarium oxysporum</i>	151
31	Cobalt and nickel ferrite nanoparticles	Nano fungicides	Various crops	■ <i>Fusarium oxysporum</i> ■ <i>Colletotrichum gloeosporioides</i> ■ <i>Dematophora necatrix</i>	152
32	CuNPs and AgNPs	Nano fungicides	Woody trees	■ <i>Rhizoctonia solani</i> ■ <i>Phytophthora cactorum</i> ■ <i>Fistulina hepatica</i> ■ <i>Grifola frondosa</i>	164
33	Aluminum, silver, titanium oxide NPs	Nano fungicides	<i>Oryza sativa</i>	■ <i>Ustilaginoidea virens</i>	150
34	ZnO NPs and SiO ₂ NPs	Viricide	<i>Nicotiana tabacum</i>	■ Tobacco mosaic virus (TMV)	169
35	Titanium NPs, magnetite NPs, MWCNTs, C60	Viricide	<i>Nicotiana benthamiana</i>	■ Turnip mosaic virus	170
36	Nanoencapsulation of atrazine in polycaprolactone	Nanoherbicides	—	■ <i>Brassica juncea</i> plants	178
37	Polycaprolactone nanocapsules with atrazine	Nanoherbicides	—	■ <i>Amaranthus viridis</i> ■ <i>Bidens pilosa</i>	179
38	Chitosan NPs loaded with imazapic and imazapy	Nanoherbicides	<i>Allium cepa</i>	■ <i>Bidens pilosa</i>	327
39	Nanoencapsulation of savory (<i>Satureja hortensis</i> L.) essential oil	Nanoherbicides	—	■ Tomato (<i>Lycopersicon esculentum</i> Mill.) ■ Amaranth (<i>Amaranthus retroflexus</i> L.)	181
40	Metsulfuron methyl-loaded pectin (polysaccharide) nanoparticles	Nanoherbicides	—	■ <i>Chenopodium album</i> plant	174

Table 1 (Contd.)

(C) Nanosensors					
S. no.	Nanomaterial used	Analyte	Detection method	Application	Reference
41	AuNPs	Urea, nitrate, nitrite, ammonium, and urease	Colorimetry	■ Detection of soil nutrients and nitrogenous compounds	195 and 196
42	Graphene oxide (rGO) nanosensors	Nitrate (NO ₃ ⁻)	Impedimetric	■ Detection of soil/water nitrate	198
43	Polypyrrole/electrochemically reduced graphene/glassy carbon	Nitrate (NO ₃ ⁻)	Potentiometric	■ Detection of soil nitrate	197
44	AgNPs	Ammonium	Colorimetry	■ Detection of NH ₄ ⁺ in soil	199
45	Porphyrin-based nano metal-organic framework (NMOF)	Phosphate	Ratiometric fluorescence	■ Detection of phosphate in soil	204
46	GQDs	Soil moisture	Electrochemical	■ Detection and quantification of soil moisture and humidity	201
47	Quantum dots, carbon nanomaterials (MWCNTs and graphene), polymers, AuNPs	Atrazine, neonicotinoids, carbamates, glyphosates, and organophosphates	Optical/electrochemical	■ Detection of pesticide residues	209, 210 and 328
48	AuNPs, AgNPs, QDs, CNTs, and graphene	Toxic metal ions	Fluorescence/colorimetry/electrochemical	■ Detection of heavy metals (Pb ²⁺ , Cd ²⁺ , etc.)	329

KCl, called 'MesoLite', was applied at different concentrations on wheat plant seedlings and was shown to increase the potassium availability to plants.¹⁰⁴ In another report, a naturally-obtained zeolite (clinoptilolite) augmented with ammonium nitrate was able to increase the crop yield from 96 kg ha⁻¹ to 1.4 t ha⁻¹ in corn crops.¹⁰⁵ Silicon NPs have also been known to improve seed germination rates, photosynthetic rates, mesophyll conductance, chlorophyll content, better water uptake, and biomass production.^{106,107} There are various studies available on the positive impacts of silicon dioxide NPs on plant growth and development.^{108,109} Another important NM, TiO₂ NPs, promoted growth in different plants by improving the chlorophyll content, straw yield (barley plants), and plant growth.^{60,110,111} Carbon nanotubes (CNTs) are known to improve the germination of crop plants, thereby covering the utility of the emergent nano-biotechnology field to crop science. There have been numerous reports of improvement in plant growth by carbon uptake, especially in the form of MWCNTs.^{112,113} To describe the possible toxicological effects of the nanofertilizers, more research should be conducted to explore the NM-plant interaction. Moreover, the economic viability of nanofertilizer needs to be investigated for sustainable agriculture. A list of some important studies on plants to evaluate the potential of nano-agrochemicals on plant growth are presented in Table 1.

3.2 Nanopesticides: protection against pests, pathogens, and weeds

The use of pesticides is a common practice in agriculture for the control of pests and weeds. Conventionally-used pesticides and crop protection techniques show inefficiency towards environmental safety and sustainable development.¹¹⁴⁻¹¹⁷ The worldwide usage of pesticides on crops has shown a significant

increase of about 79% from 2 285 881 metric tonnes in 1990 to 4 113 591 tonnes in 2017.⁵² However, the excessive use of pesticides in the agricultural sector faces numerous challenges such as disease resistance, targeting of non-threatening and even beneficial species, nitrogen fixation, destruction of soil biodiversity, accumulation of pesticides in the environment, and adverse effects on human health.^{32,118} Nanopesticides include nanoinsecticides, nanoweedicides, nanofungicides, and nanobactericides that are used for efficient delivery systems, low cost, availability, and easier application.^{119,120} Nano-encapsulation is the finest method to improve the pesticide value of the active ingredient ligated by protective coverings.¹²¹⁻¹²³ Nanocarriers, being biocompatible, safe to use, and eco-friendly, help in enhancing the solubility of active compounds and give better protection from volatilization and degradation. They possess amazing properties such as controlled and slow-release, enhance stability and permeability, and prevention from premature degradation. Nanoscale engineering has developed pesticide delivery systems that can enormously decrease pesticide production costs and usage as well. This will greatly help in pesticide development and use for sustainable agricultural practices.¹²⁴ Different formulations such as polymeric NPs, solid lipid NPs, inorganic NPs (silica, alumina, silver, copper, titanium dioxide), carbon materials (MWCNTs, graphene, etc.), nanogels, and nanoemulsions have been demonstrated as effective nanopesticides (Fig. 5) due to their insecticidal, bactericidal, and fungicidal properties.^{33,125,126} Polymeric NPs, metallic NPs, and nanoalumina-silicates have been used to boost plant growth by employing them as nanocarriers for pesticides and herbicides.¹²⁷ Currently, nanoemulsions/nanodispersions (consisting of an oil phase, surfactant, and water, being optically isotropic and kinetically

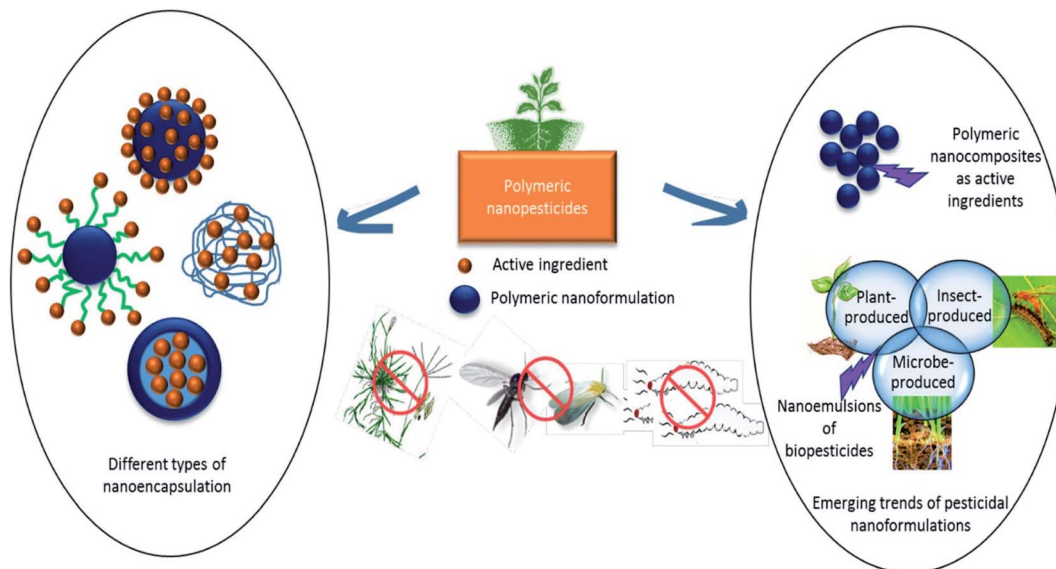


Fig. 5 Nanopesticides for effective pest management: Nanocarriers for pesticides include polymers, lipid, clay nanomaterials, metal–organic frameworks, and greener formulations.³²⁰

stable colloidal solutions with 20–200 nm droplet size range) have gained attention as potential carriers for targeted pesticide delivery.¹²⁸

One of the most important strategies for increasing the crop productivity is the protection against insects. Nano-insecticides (particularly nanosilicate–alumina and inorganic NPs) can pave the way for the development of sustainable strategies for pest management. For example, nanostructured alumina (NSA) exhibited strong insecticidal properties against pests belonging to families Coleoptera (*Sitophilus oryzae*, *Oryzaephilus surinamensis*), Dipteran (*Ceratitis capitata*), and leaf-cutting ants.^{129–132} NSA is known to possess non-toxicity, biocompatibility, lesser costs, and environment-friendly nature. Recently, NSA was effectively investigated as a seed protectant against seed-eating insects belonging to Coleoptera such as *Oryzaephilus surinamensis*, *Stegobium paniceum* (L.), and *Tribolium confusum*.¹³³ In another study, nano-silica applied through soil treatment was evaluated as an effective pesticide against storage insects such as (*Sitophilus oryzae*, *Rhizopertha dominica*, *Tribolium castaneum*, and *Oryzaephilus surinamensis*) in maize plants.¹³⁴ Several studies have also reported the insecticidal potential of nano-silica against many insect families.^{135–137} Inorganic NPs such as titanium NPs, zinc oxide NPs, and AgNPs have been extensively used as insecticidal agents for crop protection.^{138–141} These inorganic NPs have shown activity against white grubs, pulse beetles, and mosquito vectors. Most importantly, AgNPs have been found to be more effective in agricultural pest management.^{142–144}

In addition to insecticidal properties, NMs with specific antimicrobial activity against plant pathogens (phytopathogenic fungi, bacteria, and viruses) can greatly help in preventing crop losses. Some excellent reviews giving an overview of the applications of NMs in plant disease management have been published.^{145–147} Several studies have established the antimicrobial

activity of inorganic NPs against pathogenic bacteria and fungi.^{148–150} For example, copper NPs were used as an efficient fungicide against several phytopathogenic fungi such as *Fusarium solani*, *Neofusicoccum* sp., and *Fusarium oxysporum*.¹⁵¹ Similarly, the activities of cobalt and nickel ferrite NPs were tested against *Fusarium oxysporum*, *Colletotrichum gloeosporioides*, and *Dematophora necatrix*.¹⁵² Silver NPs (AgNPs) have always been known for their antibacterial characteristics and can significantly affect the bacterial growth in crop environments.^{153–156} Also, the antibacterial properties of titanium NPs have been well investigated for crop protection against diseases in several reports.^{157–160} The activity of inorganic nanoformulations of copper and aluminum has also been elucidated for both insecticidal and antibacterial activity in crop plants.^{161–164} Along with bacterial and fungal infections, viruses are known to cause large losses in crop production.^{165,166} The influence of NMs can be used for a novel anti-viral strategy against viral infestations.^{35,167,168} For instance, ZnO NPs and SiO₂ NPs were used as foliar sprays due to their activity against the tobacco mosaic virus in tobacco plants both *in vivo* and *in vitro*.¹⁶⁹ Several studies have reported engineered NMs including magnetite NPs, TiO₂ NPs, C₆₀, MWCNTs, and chitosan NMs for infusing resistance against viral infections during plant growth.^{170–173}

Nano-weedicide and nano-herbicide development is specifically aimed at targeting specific weeds/herbs that enter the crop environment and cause nutrient exhaustion in the crops. Weed management with encapsulated NMs (nanocarriers) can reduce the phytotoxicity of herbicides in crops.^{119,147,174} Nanoactive herbicides can decrease the requirement for synthetic herbicides, thus increasing the harvest profits. The encapsulation of herbicides (namely, atrazine, ametryn, simazine, and paraquat) in polymers such as poly(epsilon-caprolactone), chitosan, and alginate has shown high efficacy against the target weeds.^{175–177}

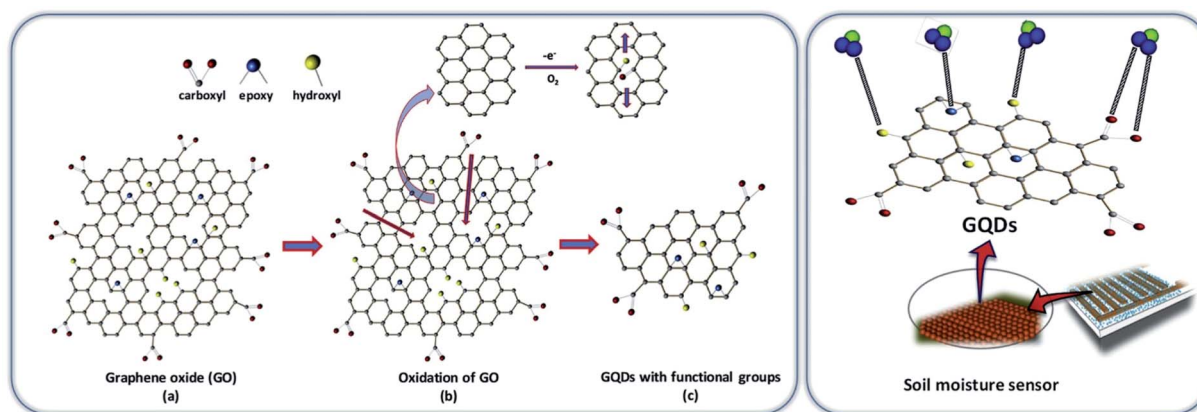


Fig. 6 Electrochemical synthesis of graphene quantum dots from graphene oxide and its application in sensing of soil moisture.²⁰¹

Recently, a study reported the herbicidal potential of nanoformulations and nanocapsules of atrazine when applied through the foliar spray on Indian mustard plants.^{178,179} They were found to be effective against slender amaranth (*Amaranthus viridis* L.) and hairy beggarticks (*Bidens pilosa* L.). The controlled release of herbicides can be achieved by loading them in the nanocomposites to prevent the degradation and sorption of the active ingredients (AI) in soil.^{180,181} Various support materials such as clays, polymeric microparticles, and NPs have been recently investigated for the formulations of herbicides.^{182–185} To conclude, nanopesticides play a significant role in the efficient and sustainable elimination of pests by minimizing the use of synthetic chemicals and their hazardous risks. For their wider applications, it is required to gain knowledge of the mechanism of the action of nanopesticides at the cellular level and their toxic effects on the target organisms. For a safe and sustainable approach, it is of fundamental importance to verify the risks associated with nanopesticides. This will help in ensuring proper and significant awareness and usage of better and correct management practices among farmers. Moreover, extensive research assessment of the risks associated with their use must be carried out to check their environmental fate.

3.3 Nanosensors: detection of pathogens and contaminants

Nanotechnology-based sensing approaches have gained considerable momentum as they provide a wide range of applications in agriculture and food-related sectors. Nanosensors can greatly help in improving the crop yields by the management of agricultural water and soil, and detecting the presence of chemical fertilizers and pesticides, soil nutrients, moisture content, and contaminants such as excess fertilizers, pesticide residues, plant pathogens (bacteria, fungi, and viruses), and heavy metals.^{186–188} Nanosensors possess certain benefits over conventional sensors, namely, large surface to volume ratio, real-time detection, compact size, high stability, selectivity, and, sensitivity.^{189–191} Nanobiosensors are the next generation detection devices that comprise of a biological sensing element and a transducer that measures the

physicochemical signal. This signal (optical, electrochemical, or mechanical) is obtained with even ultra-low concentration of the selected analyte or a parameter.^{29,192} Numerous types of NMs including GO, CNTs, AuNPs, magnetic NPs, and quantum dots (QDs) have been exploited for designing a variety of nanobiosensors. NMs can be used to detect the soil nutrients such as urea, nitrate, nitrite, ammonium, and urease, which can cause toxicological implications in soils when present in excessive amounts.^{193,194} Many studies are available in which nanobiosensors have been utilized for the detection of these nitrogenous nutrients in soil/water matrices employing AuNPs.^{195,196} Similarly, soil nitrate has been detected using electrochemically-reduced GO nanosensors based on the ion-selective membrane of polypyrrole-doped with nitrate.^{197,198} AgNPs have also been investigated for their potential as colorimetric sensors for the detection of ammonium in water samples.¹⁹⁹ There is a considerable amount of literature demonstrating the detection and quantification of soil moisture and humidity (Fig. 6).^{200–202} Also, NM-based sensors have been used to quantify the total carbon content, organic matter, phosphates, *etc.*, for soil analysis.^{203–205} The excessive use of pesticides such as atrazine, neonicotinoids, carbamates, glyphosates, and organophosphates can have toxicological implications on the environment and human health.^{206,207} The detection of pesticide residues in soil and water using nanobiosensors is a hot topic of research.^{208–210} The potential of NMs such as QDs, carbonaceous NMs (MWCNTs and graphene), polymers, AuNPs, and their derived composites in the nanosensors for pesticide detection have been investigated in several reports.^{211–213} For example, pesticides such as atrazine, methyl parathion, acetamiprid, and glyphosate were detected in soil samples using a different variety of NMs such as TiO₂ nanofilms, MWCNTs-chitosan nanocomposite, and AuNPs.²¹⁴ Numerous studies have been proposed for the detection of organophosphates and carbamates in vegetables and other food samples.^{215–217} Recently, the detection of triazophos, parathion, chlorpyrifos, carbofuran, carbendazim, and carbamates such as carbofuran was achieved using QDs, AuNPs, and molecularly imprinted polymers.^{218–221} Carbon NMs including graphene and CNTs have also shown potential as sensing tools for

chlorpyrifos and atrazine, respectively.^{222,223} In addition to soil and water samples, the pesticide residues can be efficiently detected in food samples as well.^{224–226}

Nanobiosensors have also been used for the determination of microbial pathogens and toxins in agricultural systems and food. These sensors play a significant role in 'smart' agriculture as they may detect infectious plant diseases even before the appearance of symptoms.^{227–229} Metal oxide NPs, QDs, and polymeric NPs have been studied for their role in plant disease control by sensing microbial pathogens in the environment near the plants. For instance, optical nanobiosensors have been developed for the detection of waterborne and foodborne pathogens.^{191,230,231} In addition, metal NPs such as AuNPs, AgNPs, and magnetic NPs have been exploited for the optical detection of bacteria such as *E. coli*, *S. typhimurium*, *S. aureus*, *S. enterica*, and *L. monocytogenes*.^{191,232,233} There are certain reviews on the electrochemical detection of pathogens and food toxins in food products.^{234–238}

The presence of toxic metal ions in the environment above the critical limits proves harmful to crop growth. Various types of NMs such as graphene, AuNPs, AgNPs, QDs, CNTs, and their nanocomposites have been employed in fluorescent, colorimetric, surface-enhanced Raman scattering (SERS), and electrochemical sensors for the recognition of a variety of toxic heavy metals ions (*e.g.* Pb^{2+} , Hg^{2+} , and Cd^{3+}) in soil and water samples.^{239–241} Along with these analytes, nanobiosensors have been successfully employed for the detection of hyaluronidase, hydrogen peroxide, and environmental stress.^{242–244} These optical nanosensors can identify the initial stress signals and can thus be considered as a unique tool for precision agriculture. Unmanned aerial vehicle (UAV)-based gateway nanosensors have been employed for various monitoring aspects for the management of the soil state in agricultural activities and the monitoring of environmental pollution.²⁴⁵ NMs coupled with paper/microfluidics has further helped in the development of compact and portable biosensors for industrial applications.^{246–248} In short, nanosensor technology has made the way for smart agriculture based on sustainable development, environmental safety, management of fertilizers, reduction in input costs, and enhancement in crop productivity, and prevention of water overuse. Despite these unique advantages, most of the nanosensors have been developed at the laboratory scale and further efforts are required to design these sensing systems for on-field agricultural applications.

3.4 Nanoscale products: remediation of contaminated water and soils

Nanotechnology has been providing potential solutions to global challenges such as pollution caused in the agricultural environment. Soil and groundwater have been at great risk due to toxic organic and inorganic pollutants, and the improper use of agricultural wastes. Nanotechnology provides cost-efficient methods for the removal of heavy metals, dyes, biphenyls, polycyclic aromatic hydrocarbons, volatile organic compounds, and other organic contaminants from wastewater released from the fields.^{249–251} This section particularly focuses on the applications

of NMs in biotic and abiotic strategies to eliminate contaminants from soil and water. Nano-remediation techniques possess certain advantages such as the reduction in the clean-up time procedures, elimination of the complex procedures required for the treatment and disposal of contaminated soil, decrease in the cleaning costs of the contaminated soils, and reduction in the concentrations of certain contaminants to near-zero low levels.^{43,252} The commonly employed NMs for agricultural water are metal and metallic oxide NPs, carbon nanotubes (CNTs), fullerenes, nanofibers, magnetic NPs, nano zero-valent-iron (nZVI) QDs, and polymeric NPs.²⁵³ The most common mechanism of remediation of contaminated water and soils is the removal of contaminants through adsorption, photocatalysis, reduction, and chemical oxidation.^{159,254,255} Water polluted by agricultural chemicals can be purified using nanofiltration using CNT membranes, alumina fibers, TiO_2 , thin-film nanocomposite membranes, and biomimetic membranes. These NMs have been utilized for the removal of bacteria and pathogenic parasites from the surface as well as groundwater.^{256–258} In addition to water remediation, NMs have been found to treat contaminated soils. The mobility and toxicity of toxic soil pollutants can be affected by their adsorption onto organic ligands, minerals, and NMs surface through ion exchange/coordination interactions.^{259,260} The reuse and recyclability of the adsorbent NMs play an important role in cutting down the remediation costs. In this context, magnetic iron oxide NPs offer good advantages such as superparamagnetism, environment friendliness, quick separation after adsorption, and ease of synthesis.^{31,261} For example, a recent study reported a decrease in soil erosion and arsenate leaching using magnetic NPs.²⁶² Another important material, nanoscale zerovalent iron particles (n-ZVI), has gained a lot of attention for the removal of pollutants such as heavy metals, drug residues, and pesticides from agricultural soil remediation.^{263–265} NMs can also be used for the catalytic degradation and mineralization of organic pollutants, and antibiotics in contaminated soils *via* the oxidation process.^{266–268} Apart from these advancements, NMs have achieved a breakthrough by the effective biodegradation of organic pollutants such as triclosan, lindane, polychlorinated biphenyls (PCBs), DDE, and polybrominated diphenyl ethers (PBDEs) in soil and water.^{269–271}

Another important application of NMs in promoting environmental sustainability is the effective management of agricultural wastes.²⁷² It should be the top priority of researchers to develop novel technologies that can attain full sustainability in agriculture. The advancement of nanotechnology has helped in the exploitation of agricultural wastes and residues to prevent their dumping into the environment.^{273,274} Different types of crop residues such as wheat straw, rice crop residues, grasses, soy hulls, potato pulp, tea wastes, and cotton wastes have been considered as the best raw materials for the production of nanocellulose.^{275,276} Nanocellulosic materials can be extracted from these plant resources as fibers or nanocrystals. These materials exhibit several properties such as high strength, high surface area, bio-degradability, low toxicity, and a wide range of applications in food science and environmental remediation.^{277,278} Apart from nanocellulose, several useful products

such as super-adsorbent hydrogels,^{279,280} bio-nano-composites,²⁷⁴ bioethanol,²⁸¹ silica,²⁸² detergents,²⁸³ and bio-fuels^{284–286} have been reported. Moreover, nanotechnology engineering has been used to develop agro-machinery, tracking of agricultural products, and barcode technology *via* nano-devices, storage, and distribution of agricultural produce.²⁸⁷ Despite enough information about the beneficial applications of NMs in environmental remediation, there is still a lack of knowledge about their large-scale and real-world application in contaminated soils and water. A proper evaluation system for the employment of NMs in the agricultural sector must be established to provide practical information so as to prevent damaging exposure.^{288,289}

4. Nanomaterial safety and regulations

The advancements of nanotechnology in agriculture has led to the entry of NMs into the environment and soil systems. Upon entering the soil, NMs may undergo physical/chemical/biological transformations depending upon their nature and the presence of organic/inorganic constituents of the soil. The transformation or aggregation of the NMs may alter their stability, reactivity, toxicity, and selectivity against their target. Detailed investigations are required to access the fate of NMs in the soil.^{290,291} NMs may enter human food chains through the consumption of plant-derived products obtained *via* delivery systems or processed foods. The main risk arises due to the extremely small particle size and large surface area of the NMs, which is comparable to our biomolecules (*e.g.* DNA, RNA, and proteins). They may cross cellular barriers, showing toxicity to humans and livestock as well.^{292,293} Improper handling of nano-agrochemicals by untrained workers further poses a risk of their solubility and dispersion in water and soil. Moreover, industrial exposure will also increase with the growing manufacturing and usage of NMs in society (Fig. 7). These worries have created apprehensions about the harmful effects of the engineered NMs on human health and environment.^{294,295} A complete knowledge of NMs as products in agriculture and food processing, NP-plant interactions, bio-distribution, entrance in food chains, and toxicological implications must be carefully obtained before their application in agriculture. Different factors before NP exposure must be understood, which may raise concerns about their toxicity.^{296,297}

Although NM-enabled technologies have provided many opportunities to fuel the growth of sustainable agriculture, certain challenges prevent their overall development and commercialization in agriculture. The most important technological barriers in realizing the full potential of NMs include the lack of information regarding the plant–NM interactions and nanomaterial uptake, limited routes of delivery of NMs into plant architecture, incomplete understanding of the NMs' fate in the environment, and human health risks arising from NMs entering the food chain.³¹ Currently, the underlying mechanisms of nano-enabled solutions are mainly focused on the phenomenological and theoretical observations, which need to

be explored more. In the context of nano-agrochemicals for enhancing plant function, the biophysics relating to the interaction of NMs with the leaf cuticle and chloroplast cells must be elucidated. The properties of NMs including size, dose, exposure time, surface chemistry, structures, immune response, accumulation, retention time, and other effects should be accessed carefully. There is a need for more *in situ* investigations for the determination of the range of mechanisms responsible for providing the beneficial effects. Such information will help to customize smarter designs for NMs to improve photosynthesis and to manage plant stress.^{298,299} Also, the delivery of the NMs at the right target place and the calculation of appropriate dose in plants is a big challenge. Tuning charge and size, or coating NMs with guiding biomolecules, may increase the uptake efficiency and enable the targeting of specific plant cell compartments and organelles. NMs should be applied to plants when the environmental conditions (such as temperature, pH, salinity, water content, and moisture) are favorable to overcome any climatic stress. NM exposure should be critically measured in assessing and managing the risks in the nano-agricultural field. Concerns regarding human health, safety, and ecological implications have not been addressed properly to date. The combination of disciplines including plant biology, nanochemistry, and plant pathology is necessary to realize the full potential of nanotechnology in agriculture.²⁹⁹ In addition to all these scientific challenges, the successful deployment of this technology within the profit margins of crop agriculture mainly depends on their ability to balance system costs and benefits. The commercial use of NMs requires thorough investigations into screening and their optimization for different plant species. The performance and fate of NMs can be altered by tuning the properties and stability of NMs. Further developments in innovative and improved synthetic methods will result in better product composition with improved efficiency. More knowledge at the field level will be highly useful for the large-scale industrial implementation of nano-based solutions. There should be more collaborative research among different stakeholders exploring efficient, multifunctional, stable, cost-effective, and environment-friendly NMs. Another important aspect of commercialized nano-agro products is the public perception regarding the safety concerns during the application of these products in agricultural practices. Excessive inputs of NMs into the agriculture system will raise questions on the ultimate fate and translocation of these materials into the environment.²⁹ To ensure the positive implications of nanotechnology in agro products, a comprehensive and responsive strategy must be developed along with coordinated risk management. In this context, the toxicological assessment of NMs is viewed as the basic step towards the identification of hazards related to applications of NMs in the agro-food sector.

With the development of numerous nano-products in the commercial market (Table 2), there are efforts worldwide to address and regulate the production and use of NMs either by legislation or by recommendations and guidance. Various governments and scientific organizations have realized the significance of NM-risk management in the agri-food sector. The regulation of engineered NMs is well defined from the

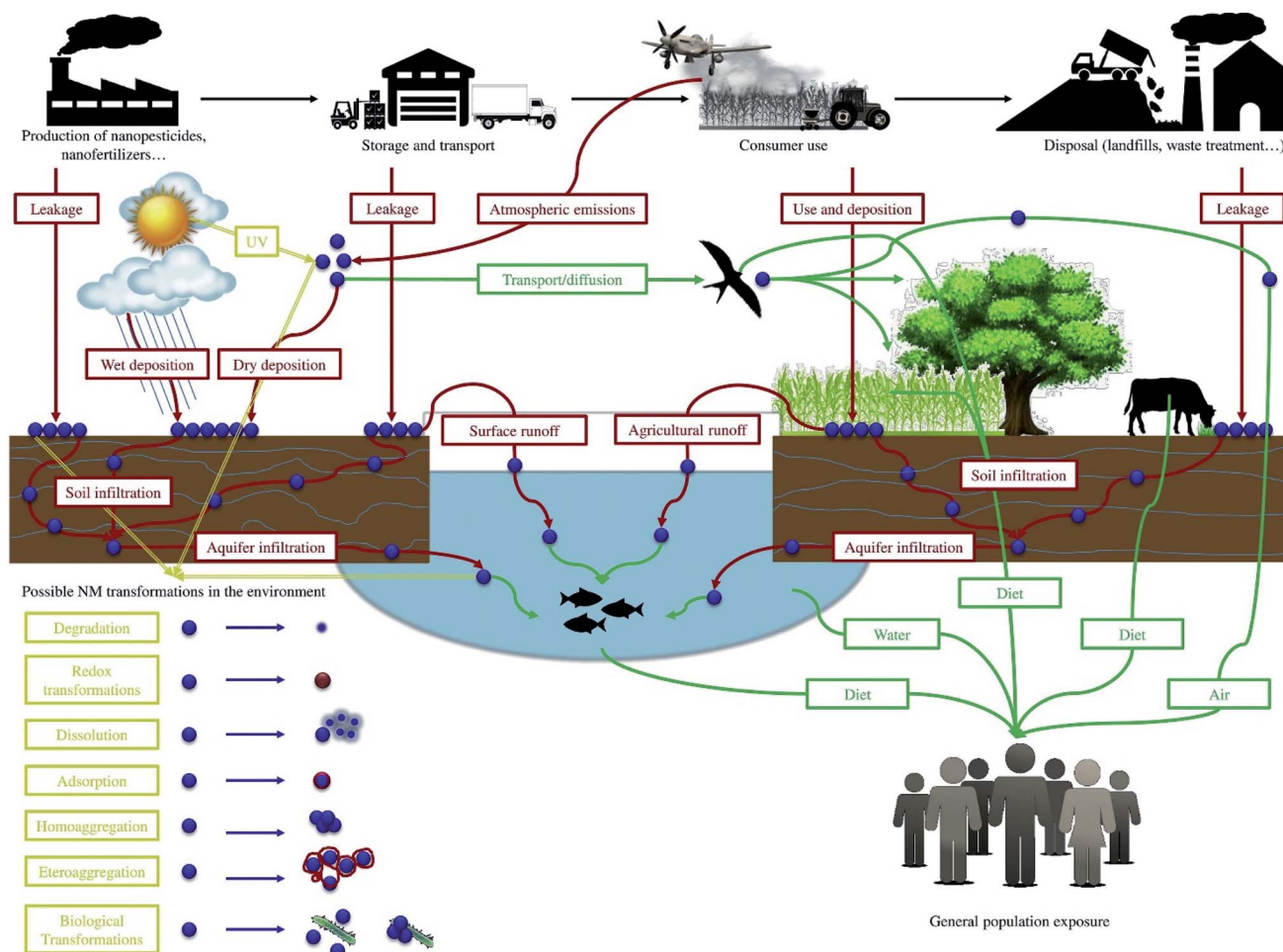


Fig. 7 Life-cycle of nano-agrochemicals used in agriculture. The increased use of nanomaterials in the agriculture sector has caused a risk to human health and the environment.²⁹

perspective of Environment, Health, and Safety (EHS).^{300,301} Different government, industry, and standards organizations have proposed different definitions for NMs. A legal definition of NMs is essential to implement specific risk assessment and risk management measures for them. Regulatory agencies such as USEPA, USFDA, European Commission (Recommendation on the Definition of NMs), and others have given advisory definitions of NMs.³⁰² Also, Health Canada published a 'Policy statement on Canada working definition of nanomaterials' for the regulatory framework of NMs.³⁰³ NMs are either indirectly or directly declared unsafe by various sections of legislation for safety assessment. In the UK, the Royal Academy of Engineering in its 2004 report 'Nanoscience and Nanotechnologies: Opportunities and Uncertainties' treated NMs as the new materials under their new substances regulation and recommended fresh registration, evaluation, authorization, and testing of NPs.³⁰⁴ The 'Joint Statement on Nanomaterials Toxicology' issued by the Committee on Toxicity, Carcinogenicity, and Mutagenicity of Chemicals in food, consumer products, and environment, has identified the risk assessment and management related to NMs used in the UK.³⁰⁵ In the European Union (EU), the important

legislation regulating the use of NMs in the food industry is Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) regulation (1907/2006).³⁰⁶ The main aim of the REACH regulations is to protect human health and the environment from chemical substances including NMs. The substances used as plant protection products, biocides and NMs (including SAS, TiO₂, and nano-silver), is registered under REACH provisions. Also, according to Regulation on Classification, Labelling, and Packaging (CLP), products containing hazardous substances or NMs have to be labeled depending on the concentration limit. Also, European Biocidal Products Regulation (EU 528/2013) contains provisions for specific testing and risk assessment for the NM form of a biocidal substance.³⁰⁷ In addition to REACH and CLP legislation, EU legislation asks for a market authorization of NM applications in foods based on the safety assessment by the European Food Safety Authority (EFSA) to take care of the potential health risks.³⁰⁸ EFSA has become one of the most important part of EU food-related legislation that ensures food safety and protects consumers from food-related risks. In Switzerland, nano-products' safety is regulated by the Swiss Ordinance of 2010 under

Table 2 Commercialized nanoscale products available in the market

S. no.	Type of nanomaterial	Type of polymer	Trade/commercial name	Modified functions
1	Nanoclay	Nylon 6	Aegis® OXCE Barrier Nylon Resin, a product from the USA, Honeywell International Inc.	The better barrier as compared to the glass bottle's performance. Well-suited to the co-injection process because its processing temperature is similar to that of PET
2	Nanoclay	Nylon 6	Imperm® Nylon nanocomposite, a product from the USA, Mitsubishi Gas Chemical Company, Inc.	Replacement of EVOH with a better cost-effective material. Easy processing and maintaining the barrier features. Elimination of the requirement of tie-layers
3	Nanoclay	Starch	Plantic® Plastic Tray, a product from Australia, Plantic Technologies Limited	Developed from renewable and sustainable resources. Non-toxic to the environment. Biodegradable after use. Better mechanical & rheological properties.
4	Nanosilver (25 nm)	Polypropylene (PP)	FresherLonger™ Plastic Storage Bags, FresherLonger™ Miracle Food Storage, a product from USA, Sharper Image® Company	Less sensitivity to moisture. Fresh foods by a factor of 3 or 4 for fruits, vegetables, herbs, breads, cheeses, soups, sauces, and meats. 98% reduction of bacterial growth after 24 hours
5	Nanosilver	Polypropylene (PP) silver	Sina Antibacterial Food Storages, product from Vietnam, Dai Dong Tien Corporation	Dirt and fungal protection. Bad smell removal. Germ prevention. Fresh food for a longer time
6	Nanosilver	Copolyester (Tritan™)	e.Window® Nano Silver Airtight Container, product from South Korea	No odor. Better sterilization of food containers. Less bad smell. USFDA approved
7	Nanosilver	—	Everin Food Containers Nano Silver Airtight, product from South Korea NewLife Co., Ltd.	Antibacterial activity. Fresh food for long times
8	Nanosilver (20–70 nm)	Polyethylene	Fresh Box Nano Silver Food Container, product from South Korea, FinePolymer, Inc.	Antimicrobial food container. Antifungal. Fresh food for longer times
9	Nanosilver	Polypropylene (PP) Polyethylene (PE)	Anson Nano Freshness-Keeping Film, Anson Nano Freshness-Keeping Storage Bag, Anson Nano Silver Fresh Containers, product from China, Anson Nano-Biotechnology (Zhuhai) Co., Ltd.	Fresh food for longer times. Safe food storage. American FDA standard
10	Nanosilver	Silicon	Double handle nanosilver baby bottle, product from China, Shenzhen Ibecare Commodity Limited Company	Antibacterial. Bisphenol A (BPA) free

the Federal Office of Public Health (FOPH). In the USA, the USEPA (the United States Environmental Protection Agency) has emphasized the responsible role of nanotechnology in society and the consequences of NPs exposure on humans.³⁰⁹ USFDA (United States Food and Drug Administration) is chiefly responsible for the safety of food and feed additives, food

coloring agents, and other food products present in the market under Federal Food, Drug, and Cosmetic Act (FFDCA).^{310,311} FFDCA does not contain any specific regulations for nano-based products in the food sector. USA and Canadian agencies are working together towards the regulation of NMs under the US-Canada Regulatory Cooperation Council (RCC) Nanotechnology

Initiative. In India, food safety is ensured by the Food Safety and Standards Act, 2006, wherein the risks associated with nanotechnology are assessed but there is no strategy to manage the risks.^{312,313} In China, food safety is regulated under the Food Safety Law. However, it does not contain any specifications regarding the usage of NMs. The NCNST (National Centre for Nanoscience and Technology) is responsible for developing standards in the nanotechnology area in China.³¹⁴ Many countries (US, Australia, New Zealand) have accepted a wide approach dealing with the regulation and use of NPs in the agro-food sector including non-mandatory provisions and current frameworks to deal with NMs. Appropriate risk assessment methods and standards can be coordinated with risk management strategies to formulate the policies. FAO and WHO have formed CAC (*Codex Alimentarius Commission*) that creates international food standards and guidelines for food products and their safety.^{315,316} U.S. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Scientific Advisory Panel, consulted by USEPA, regulates the current procedures for hazard evaluation and exposure-related with nanopesticides.³¹⁷ Proper safety and adequate regulatory frameworks should be adopted towards the products of nanotechnology. The applications of NMs in the agro-food sector should be carefully administered while following existing regulations and policies. Multilateral collaborations between countries can ensure high levels of safety against NMs exposure. For instance, Organization for Economic Co-operation and Development (OECD) assists different countries in the implementation of national policies that guarantee the responsible development of nanotechnology and address the safety of NMs under the project “Working Party on Manufactured Nanomaterials (WPMN)”.^{318,319} The OECD Environment Directorate has published the “Series on the Safety of Manufactured Nanomaterials” under OECD Environment, Health, and Safety Publications in the Joint meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides, and Biotechnology. In this project, various national voluntary reporting schemes and regulatory programmes have been analyzed to assess the safety of manufactured NMs and to develop risk assessment approaches. Overall, planned research and policy formulation must be framed by inter-governmental organizations after the collection of relevant scientific information.

5. Conclusion and future outlook

Sustainable agriculture has become essential for promoting food safety and protection of the environment. Agriculture needs modernization and innovation to meet the increasing demands of food for the growing global population and to maintain environment sustainability simultaneously. As a basic principle of sustainable agriculture, minimum agrochemicals should be used with low production costs but higher outputs. The production and application of nano-agrochemicals in the agricultural sector have developed confidence among researchers and scientists regarding the reliability of nanotechnology in agriculture. Nanosized delivery systems and sustained release are the smartest tools for modern agriculture.

Nanotechnology can contribute to the agro-food sector with novel tools such as the delivery of nanofertilizers and micronutrients, agrochemical encapsulated nanocarrier systems, and nanopesticide delivery including green pesticides and biopesticides. Management of agricultural wastes, water and soil remediation, agro-products processing and storage, detection of plant diseases, and monitoring plant growth with nanosensors have tremendously benefited agricultural workers. However, these nanoproducts must be carefully assessed before implementation. The research outcomes of this field are mostly restricted to the laboratories and the related rules and regulations are also not well documented. Farmers and industrial personnel are quite unwilling to invest in this field due to high-product investments and poor cost benefits. These technologies may not be commercially very profitable and are unable to cope up with the ongoing demands of food production and distribution. Examples of available commercial products in the market are few and need urgent attention. The effects of NMs on human health, safety, and ecological implications are also not well understood. There should be a clear analysis of the physical and chemical characteristics of the soil of the fields for the application of NPs to reduce the associated risks concerning the plant. Human and eco-toxicological research can pave the way for understanding the complex relationship between agro-environment, nanoscale agrochemicals, exposure levels, and human beings. A detailed investigation is needed for assessing the mechanistic application of NMs and their agro-ecological toxicity.

Conflicts of interest

There are no conflicts to declare.

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