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# Nano technology based P fertilizers for higher efficiency and agriculture sustainability

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## ABSTRACT

*Nutrient use efficiency (NUE) is a critical parameter for determining sustainability of crop production systems. Under the current fertilization practices involving conventional fertilizers, the NUE ranges 30–40% for N-fertilizers and 18–20% for P-based fertilizers. Apparently, only a fraction of these nutrients is available for crop growth and yield formation. In contrast, a relevant amount of fertilizers is released into the environment annually, resulting in eutrophication and groundwater contamination that threatens environmental resources, public health, and economic investments. Thus, it will be essential to introduce agro technological innovations and revolutionary agri inputs. Nanotechnologies have the potential to produce a significant boost in crop yield along with improvement of food production systems. This innovation can lead to more precise application of nutrients along with saving of the nutrients. This review provides a critical view of the latest advances in nano fertilizer research, mainly referring to nano-hydroxyapatite based nanoparticles and other alternative nanotech based nanofertilizers.*

**Keywords:** ***S**ustainable agriculture; nanotechnologies; nano-enabled agriculture; fertilizer delivery; nano-hydroxyapatite, nano DAP*

## INTRODUCTION

According to Organization for Economic Cooperation and Development (FAO), about 85% of the growth in global agricultural production over the next ten years is expected from the improvement in crop yield resulting from more intensive use of inputs and investments in production technology and best farming practices. The intensification of land use through more crops per year will represent another 10%. At the same time, the expansion of the cultivated area is predicted to represent only 5% playing a marginal role compared to the previous decade, improving the sustainability of agriculture. The requirements for N-based and P-based fertilizers are expected to reach 137.4 million tons (Mt) of N and 52.9 Mt of P fertilizers in 2030 (OECD-FAO 2020). The nutrient use efficiency (NUE) is a valuable parameter in the evaluation of sustainable crop production systems. The maximum crop dry matter produced per unit of that particular nutrient taken up by plants is called NUE. Thus, it measures how well plants use the available nutrients. The current fertilization practices involving conventional fertilizers, the NUE comprises 30–40% for N-fertilizers and 18–20% for P-based fertilizers. Apparently, only a fraction of these nutrients help in crop growth and yield formation. In contrast, a relevant amount of fertilizers is released into the environment annually, resulting in eutrophication and groundwater contamination that threaten environmental resources, public health, and economic investments. A nutrient leaching causes environmental pollution and water eutrophication, while nutrient excess favors spread of pests and weeds. Since the excess of nutrients in the environment is a major source of water, soil, and air pollution, negatively impacting biodiversity and climate, all efforts should be made to reduce nutrient losses by at least 50%, while ensuring no deterioration on soil fertility. At the same time, a reduction in fertilizer use by at least 20% is expected by 2030 (Seck *et al.,* 2012). This review aims at analyzing the perspective of P nutrition of plants through different P carrying engineered nanomaterials (ENMs) with particle dimensions in the range 1–100 nm and high surface area to mass ratio to ensure based different properties in comparison to the corresponding conventional bulk fertilizers.

Phosphorus is an essential element for plants required for their development and reproduction, and it is one of the main components of the fertilizers necessary to sustain modern agriculture. In soils, the concentration of inorganic P (available to plants) ranges from 35 to 70% of the total P. This form of P shows low diffusion and high fixation rates in soils through ligand exchange by 1: 1 clay minerals, Fe and Al oxides and hydroxides, and is thus precipitated as Fe, Al, and Ca phosphates (Almeida *et al.*, 2018). Increasing population, growing preferences towards meat-based diets and rising demands for bio-energy crops will increase the future demand for P fertilizers. (Childers *et al.*, 2011). However, application of P fertilizers exacerbates eutrophication problem in surface waters. Therefore, numerous regulations, best managements practices (BMPs) and remediation technology have been proposed to reduce P fertilizer application and to prevent the applied P from entering water bodies (Buda *et al.*, 2012). To this end, it is expected that use of nano-P fertilizer, as an alternative to the regular P fertilizers on agricultural lands, would enhance agricultural production, use efficiency of P, and improve the surface-water quality. Agriculture is the major user of mined phosphorus (P), accounting for 80–90% of the world demand for P (Childers *et al.*, 2011). Additionally, phosphate fertilizers are obtained from phosphoric rock, a nonrenewable resource, and whose reserves are running out. Due to multiple problems associated with traditional phosphate fertilizers, nanofertilizers could be a suitable alternative.

## Nano technologies for P fertilizers

Currently, the development and utilization of the potential of nanotechnologies in crop fertilization is a high priority in fertilizer research with the target to prevent or minimize nutrient losses (Chhipa 2016) and increase crop productivity through target delivery or slow release of nutrients, thereby limiting the rate of fertilizer application through significant increase in the NUE (Kah *et al.*, 2019). This controlled release of nutrients is exactly synchronized with the nutritional needs of the crops (Zuverza-Mena *et al.*, 2017). It has been already demonstrated that the size reduction by physical or chemical methods increased the surface mass ratio of fertilizers, which allows a significant increase of nutrient absorption. In that way, slow, targeted, and more efficient nutrient release becomes possible, allowing: (i) reduction of dosages and application costs, (ii) significant reduction of nutrient losses, and therefore (iii) increase of NUE. It is estimated that the gain in NUE when using nano-fertilizers instead of conventional fertilizers could be 20–30% (Kah *et al.*, 2018).

## Nano-Hydroxyapatite as Source of Phosphorus

Needless to say, most research on nanofertilizers has been done with metallic nutrients like Cu, Mn, Zn, and Fe . Also, Al, Ce, La, and Ti among other beneficial elements (Chen 2018*)* have been tested as nanoparticles in plants. Consequently, during the last decade, metal nanoparticle production has grown exponentially, with a global production expected to reach 58,000 metric tons by the year 2020 (United Nations Environment Programme). In contrast, research on macronutrients is limited, although these elements drive global crop production (Vazquez-Nunez *et al.*, 2018). Among macronutrients, phosphorus (P) deficiency is a common factor hindering yield and crop quality globally (Aziz *et al.*, 2013). The most used P fertilizers are NP (diammonium phosphate (DAP, $(NH_3)_2H_2PO_4$), ammonium monophosphate (MAP, $NH_3H_2PO_4$), NPK complexes and single super phosphate. The P fertilizers are applied to soil, and P is released in water-soluble forms, highly mobile, and readily available to crops. However, there is significant P losses by leaching or surface run-off. The use of poorly soluble forms of P, such as phosphate rocks and apatite, on the one hand, reduces P losses, but on the other, it makes more difficult the P supply to plants. Among the critical factors associated with food security and environmental sustainability is P shortage. Herein, the potential of using Nano-Hydroxyapatite as source of phosphorus nano-CaP for the controlled delivery of P is being reported.

Crystalline and nanocrystalline calcium phosphate compounds (CaP) are found (i) in biological system after precipitation in mild conditions of pressure and temperature, and (ii) in the environment as mineral deposits formed in thousands of years under heavier conditions of pressure and temperature. Calcium phosphates are also the most important inorganic constituents of biological hard tissues in living systems. Owing to their peculiar properties (hosting of a variety of cations, eg., K, Mg, Zn, anionic substitutions, adsorption of organic molecules, and pH-responsive solubility) CaP, under several crystal forms, has been widely used for a broad range of applications (Epple 2018).

Liu and Lal (2014) synthesized hydroxyapatite ($Ca_5(PO_4)_3OH$) nanoparticles (NPs), approximately 19 nm in size, and evaluated their effect on soybean (*Glycine max*) in a substrate (50% perlite and 50% peat) in the greenhouse to assess the fertilizing effect of synthetic apatite nanoparticles on soybean (*Glycine max*). This is the first report on synthesis and application of nHA as nano P fertilizer for increasing soybean yields. The data showed that application of the nanoparticles increased the growth rate and seed yield by 32.6% and 20.4%, respectively, compared to those of soybeans treated with a regular P fertilizer ($Ca(H_2PO_4)_2$). Biomass productions were enhanced by 18.2% (above-ground) and 41.2% (below-ground). Apparently, using apatite nanoparticles as a new class of P fertilizer can potentially enhance agronomical yield and reduce risks of water eutrophication. It is likely that the retention time of nHA was longer in the porous medium than that of the soluble phosphate, and thus the former had supplied more P to the plants than the latter. There might be two reasons for the difference in P retention time in the medium (Childers *et al.*, 2011): (1) Soluble phosphates are more easily removed from the solution phase through precipitation when solution chemistry changes (pH increased or more cations introduced) or being absorbed by iron/manganese minerals or other clay minerals (Fageria 2009) while nHA may remain relatively stable in the suspension and be affected less by the solution pH, co-existing ions, or solids. The aqueous solution containing soluble P may leach out of the soil column faster than the nHA solution because the latter contained the macromolecular CMC and had higher viscosity. Thus, there was much more P remaining in the growing medium for plant roots to absorb in the case of nHA. Nevertheless, NPs may increase reactive oxygen species (ROS) levels in plants, which cause cytotoxic effects. The enhanced ROS levels triggered by NPs may lead to the activation of defense pathways to combat the oxidative stress. When plants achieve an efficient control of ROS, these molecules can be used as signals to regulate growth, development, and responses to environmental cues (Rawat *et al.*, 2018).

An assessment of nHA toxicity by lettuce seed germination test indicated that nHA did not exhibit any acute toxic or inhibitory effect on the germination and that application of engineered nHA in the field should be safe to the environment and the ecosystem. This research indicated that nHA could be used as a P fertilizer in enhancing crops' yields and biomass production (Liu and Lal, 2014). They also emphasized that more research is needed to systematically elucidate the interaction of nHA with plants and soil. Field studies also needed to confirm the fertilizing effect of nHA on various plants and in various soil environments. The eutrophication potential of nHA needs to be specially addressed.

Rane *et al.* (2015) reported that calcium phosphate nanoparticles supplemented calcium and phosphate, the essential macronutrients required for profuse root proliferation. Calcium phosphate nanoparticles may help in the formulation of new nano growth promoter and nanofertilizers for agricultural use. Therefore, it could potentially help in reduction of the quantity of fertilizer applied to crops and contributing to precision farming, as it reduces fertilizer wastage and in turn environmental pollution due to agricultural malpractices. The study conducted by Marchiol *et al.*, (2019) tested the potential of *n*HAP to be used as both a P supplier and carrier of other elements or molecules in a germination trial carried out on *Lycopersicum esculentum* (Table1). The fate of P in soil is strongly influenced by the properties of the soil itself, such as temperature, moisture, aeration, and pH (Shen *et al.*, 2011). For this reason, studies on the behavior of nHAP in soil columns were conducted (Montalvo *et al.*, 2015). In this case, the potential of *n*HAP was evaluated at two levels. At first, bulk HAP and *n*HAP were compared in saturated soil column experiments using two Andisols (from Chile and New Zealand, respectively) and two Oxisols (from Australia). Subsequently, the P availability to *Triticum aestivum* fertilized with bulk HAP, TSP, and *n*HAP was evaluated. The results showed that in the experimental conditions, the P uptake and the percentage of P in the plant that was derived from the fertilizer followed the order: TSP > *n*HAP > bulk HAP (Table1). A second experiment dedicated to studying the behavior of nHAP in soil was carried out by Xiong *et al.*, (2018) wherein three forms of *n*HAP having different surface charges (positive, neutral, and negative) were administered to *Helianthus annuus* grown in P deficient Ultisol and Vertisol, respectively. Conventional P fertilizers (TSP and rock phosphate) were tested, as well. In the acid

Ultisol (pH 4.7), the addition of TSP or any of the *n*HAPs increased plant biomass, whereas, in basic Vertisol (pH 8.2), none of the *n*HAPs significantly increased the plant growth. Both studies confirmed the potential of *n*HAP, but the fertilizing effect was lower than conventional TSP. On the other hand, likely, the nanofertilizers that will be used on a large scale in the future will be different from the nano-forms studied at this time. New design criteria for nanofertilizers will be developed based on the results of the studies conducted in this still exploratory phase. On the other hand, several workers found nanohydroxyapatite to be such an alternative phosphate fertilizer, thereby showing that nanofertilizers help minimize the quantity of added fertilizer while reducing fertilizer loss and pollution due to agricultural malpractice (Liu and Lal 2015, Tulsi *et al.*, 2015 and marzouk *et al.*, 2019).

Table 1: Nano hydroxyapatite as a source of P

| Material | Species | Treatment | Experimental Conditions | Results |
|---|---|---|---|---|
| *n*HAP, 16 nm | *Glycine max* | 21.8 mg L$^{-1}$ as P | Perlite-peat moss (1:1), nutrient solution, greenhouse. | Increased growth rate (+32.6%), aerial biomass (+18.2%) and seed yield (+20.4%) than control. |
| *n*HAP, 94–163 nm | *Solanum lycopersicum* | 0, 2, 20, 200, 500, 1000, 2000 mg L$^{-1}$ | Germination, hydroponics. | Stimulation of root elongation; no plant toxicity. |
| *n*HAP, primary size 22 nm | *Triticum aestivum* | 0–150 mg kg$^{-1}$ P *n*HAP, | Soil columns; glasshouse pot experiment; Andisol and Oxisol. | Increased shoot dry matter and P uptake than bulk-HA but less than the conventional P fertilizer. |
| *n*HAP $^{(+)}$, *n*HAP $^{(0)}$, *n*HAP $^{(-)}$, average size 25.7 nm | *Helianthus annuus* | bulk-HA, triple superphosphate (TSP) 150 kg ha$^{-1}$ *n*HAP $^{(+)}$;*n*HAP $^{(0)}$; *n*HAP $^{(-)}$; triple superphosphate (TSP); rock phosphate (RS), | Glasshouse pot experiment; P-deficient Ultisol (pH 4.2) and Vertisol (pH 8.2). | In Ultisol *n*HA $^{(-)}$ more effective in supplying P than TSP; in Vertisol nHAP did not increase plant growth. |
| *n*HAP, rod shaped 59.5 × 10.6 nm | *Adansonia digitata* | Control (unfertilized); MAP; DAP; *n*HAP. | Pot experiment; sandy soil. Foliar application of 20 mL of different P sources weekly. | Increased plant growth (plant height, leaf area, plant fractions dry matter) compared to other P sources. |
| Urea–*n*HAP nanohybrid, <100 nm | *Camellia sinensis* | 50% NPK 4 Splits; 50% NPK 2 Splits; 100% N (HA-urea nanohybrid) + 100% K MOP (2 Splits); 100% N (Urea-*n*HAP) + 100% K MOP (4 Splits); 50% N (Urea-*n*HAP) + 100% K MOP (4 Splits); 50% N (Urea-*n*HAP) + 100% K MOP (2 Splits); 100% conventional NPK fertilizer (4 Splits). | Field experiments in three different locations; Urea-*n*HAP nanohybrid provided as ground fertilizer. | Enhancement of NUE; increased quality parameters of tea leaves (e.g., total polyphenols and total amino acids). |
| *n*HAP with natural and synthetic humic substances (HA) | *Zea mays* | *n*HAP-natural HA; *n*HAP-synthetic HA; Superphosphate; *N*ha. | Growth chamber; pot experiment | Early growth, better salt stress tolerance and yield. |

***Adopted from: Fellet et al. (2021)***

More recently, Nano calcium phosphate (NCaP) was successfully synthesized, characterized and applied by and a pot experiment was carried out in two successive seasons in 2016 and 2017 on (*Phaseolus vulgaris* L.) plants to obtain the best phosphorus treatments. The results were applied in a field experiment during the 2018–2019 seasons. Single superphosphate (SSP) at 30 and 60 kg $P_2O_5$ ha$^{-1}$ and NCaP at 10%, 20% and 30% from the recommended dose were applied to the soil. Foliar application involved both monoammonium phosphate (MAP) at one rate of 2.5 g L$^{-1}$ and NCaP at 5% and 10% from the MAP rate. The results of all experiments showed that NCaP significantly increased the shoot and root dry weights, the nutrient content in the shoot and root, the yield components, the nutrient concentration and crude protein percentage in pods of the snap bean plants compared with traditional P. The greatest increase was obtained from a 20% NCaP soil application in combination with a 5% NCaP foliar application. This study recommends using NCaP as an alternative source of P to mitigate the negative effects of traditional sources. These results are in agreement with those of Dhansil *et al.* (2018) who found that the nutrient content of a pearl millet crop increased significantly when using both Nano-P and traditional phosphorus fertilizers. The highest nutrient and crude protein contents were obtained from the application of a 2.5 times reduction in the recommended dose of phosphorus through NP fertilizer. The slow and steady release of nutrients from nanofertilizer regulated the release of nutrients from the fertilizer and minimized losses resulting in the increased uptake of nutrients. Because phosphorus is critical for root growth, density and length (Desnos 2008), its further acquisition improves the symbiotic relation between rhizobium and legume roots (Hussain *et al.*, 2017); hence, it causes increased nodulation, nitrogen fixation and, therefore, nitrogen content (Singh *et al.*, 2011). In this context, Hagagg *et al.* (2018) recommended nano NPK supplements to increase fertilizer efficiency. They ascribed that nanofertilizers promote the uptake of water and nutrients, which is reflected in plant growth. Moreover, nano-fertilizers have a huge surface compared to conventional fertilizers, and this increases the plant's metabolic efficiency. The small diameter of the nanoparticles (25–50 nm) results in increased total surface area and decreased phosphorus fixation. The controlled release of nutrients and increased phosphorus uptake allow more P to be available for a longer time (Dhansil *et al.*, 2018) reported that foliar application of NCaP had a significant positive effect on the leaf and N, P and K content compared with traditional P fertilizer. Table 1 summarizes the state of the art of the studies related to this perspective.

### Cryo-milled Nano P fertilizer

Singh *et al.* (2021) demonstrated a novel, easy, effective, and environmentally benign physical method, namely cryo-milling, to prepare nano-diammonium phosphate (n-DAP) from commercial DAP (c-DAP). Cryo-milling involves milling at liquid $N_2$ temperatures and therefore helps in brittle fracture of coarser DAP particles into n-DAP particles. Cryo-milled n-DAP, with particle size ~5000 times smaller but specific surface area ~14 000 times greater than that of c-DAP enhanced efficacy of n-DAP on the growth of monocot (wheat) and dicot (tomato) plants even for a far lower input than c-DAP. The shoots of n-DAP treated seedlings were found to be significantly longer than their respective c-DAP counterparts at each concentration, with a maximum increase of 34.57% recorded at 25% (quarter-strength) dosage of supplementation. The supplementation of n-DAP at half-strength (50%) or higher dosage produced seedlings with at least 51.48% heavier shoots than the full-strength c-DAP supplemented seedlings. The first true leaf on n-DAP treated seedlings had larger surface area over their respective c-DAP counterparts. Even quarter-strength n-DAP treated seedlings had 13.11% more surface area than the full-strength c-DAP treated seedlings. They concluded that n-DAP supplemented seedlings, starting from the quarter-strength dosage, had ~9% higher $F_v/F_m$ values over the full-strength c-DAP controls. The shoot samples of 25% n-DAP grown seedlings even had 12.28% higher total soluble Pi content than the 100% c-DAP treated seedlings. Similarly, the P content of 50% n-DAP seedlings had a tremendous 93.38% increase over their c-DAP counterparts. Similarly, both quarter-strength and half-strength n-DAP supplementation resulted in 23.47% and 27.63% higher root total soluble P over their respective c-DAP supplemented counterparts. Then they tested the inverse effect of P content and anthocyanin accumulation in shoot tissues. The n-DAP supplemented seedlings accumulated at least 28.28% lower anthocyanin than their respective c-DAP treated counterparts. Furthermore, the shoot total carbohydrate content in n-DAP treated seedlings was significantly lower than their respective c-DAP controls. Through a series of morphological, physiological, and biochemical assays, they have provided evidence on the superior agronomic use efficiency of n-DAP over c-DAP. Improved biomass, pronounced P content, and reduced anthocyanin at the quarter-strength (in tomato) and half-strength (in wheat) n-DAP supplemented seedlings support the improved agronomic use efficiency of the developed nano-P fertilizer. Such a surge in plant total soluble P content is often associated with better P uptake efficiency, in this case primarily from the supplemented n-DAP that outsmarts its granular counterpart for this trait. Besides the potential better agronomy of n-DAP over c-DAP, the use of n-DAP in reduced quantities while meeting the plants' optimum P nutrient requirement is preferred for better soil health and agricultural sustainability. It is thus concluded that nano DAP enhanced the growth of monocot (wheat) and dicot (tomato) plants due to improved bioavailability of Pi even for a far lower input than c-DAP. Phenotypic observations such as higher leaf biomass, longer shoots, shorter roots, and less anthocyanin pigmentation manifested the extraordinary efficacy of cryo-milled n-DAP for 75% lower input than c-DAP.

Studies were also conducted on cultivated species of regional interest. For example, a study was carried out on *Adansonia digitata* (baobab) where the effectiveness of the foliar application of MAP, DAP, and *n*HAP was investigated (Soliman *et al.*, 2016). Baobab plants sprayed with *n*HAP showed a significant increase in several growth traits (plant height, stem diameter, number of leaves per plant, leaf area, root length, total dry weight) compared to conventional P fertilizers. A conceptually similar study was conducted on *Camelia sinensis* (Raguraj *et al.*, 2020). Different P fertilization strategies were tested, which included comparing conventional fertilizers and *n*HAP, and a different fractionation of doses. However, the most relevant aspect of this study was that it was carried out for three years in different locations in Sri Lanka characterized by different climatic and pedological conditions, thus also introducing environmental variables. Overall, the results demonstrated that the application of slow-release fertilizer significantly increased soil P, leaf N, and P concentration, particularly in unfavorable climatic conditions.

Herein, we cite a recent study concerning the synthesis of hybrid nanostructures (Yoon *et al.*, 2020). In this case, the possibility of associating natural or synthetic humic substances with *n*HAP, exploiting the interaction between the polyphenolic groups of humic substances (HA) and the surface charge of *n*HAP. *Zea mays* were grown in a pot trial and fertilized with commercial P fertilizer, bare *n*HAP, and *n*HAP-HA. The synergistic co-release of P ions and humic substances resulted in a significant increase in plant growth, corn yield, and resistance to salt stress (Table1). Saleem *et al.*, (2021) studied the effect of coated nanoparticles (NPs) of potassium ferrite ($KFeO_2$ NPs) on di-mmonium phosphate (DAP) fertilizer with three rates (2, 5, 10%) of $KFeO_2$ NPs and were evaluated for release of N, P, K and Fe supplementation in clay loam and loam soil up to 60 days. In India, IFFCO has recently brought Nano DAP to cater to the needs of the farmers. Field trials started from *Kharif* 2021 to study the relative potential of Di-ammonium Phosphate sources (DAP and Nano DAP) have shown very encouraging results. Nano DAP developed in India ranges in size from 10 to 30 nanometers and has 8 percent nitrogen and 16 percent phosphorus content. Nano DAP, will not only save money but would be economical for the farmers in terms of low cost and higher nutrient use efficiency. Nano DAP would play an important role in self-reliance in terms of DAP.

## FUTURE RESEARCH

(1). One of the great technical challenges to be overcome in the future is the fact that protocols to quantify nanoparticles within plant tissues are not well established yet. Furthermore, nanoparticle absorption, translocation, and accumulation processes depend on plant species, as well as size, type, chemical composition, functionalization, and stability of the nanoparticles (Gonzalez-Gomez *et al.*, 2017).

(2). Many efforts have yet to be undertaken for optimization of nanoparticles delivery, aiming to minimize risks from over-dosage and accumulation. For these reasons, the use of highly biodegradable biopolymers that reduce the persistence of nanostructures in the soil and on the plants is promising (e.g., cellulose, lignin, zein, chitins) (Grillo *et al.*, 2021).The risk of undesired effects must therefore lead to find technological solutions able to optimize the interaction between nanomaterials and plant, thus enabling agronomical treatments with a low environmental impact, which is exactly what nanotechnologies are applied for in agriculture. These considerations imply an accurate design and customization of the nanoparticles concerning their charge, as well as morphology for a specific interaction with different plant species. The choice of spherical particles might not be the best technological solution in the case of foliar distribution, where rod- and platelet-like carriers provide a more efficient adhesion due to their high contact surface area. Therefore, the aspect ratio and morphology of nanoparticles has to be considered in the future for the best assessment of field applications (Grillo *et al.*, 2021).

3. More research is needed to systematically elucidate the interaction of nano P fertilizers with plants and soil. Field studies are needed to confirm the fertilizing effect of nano P fertilizers/ nHA on various plants and in various soil environments. The eutrophication potential of nano P fertilizers needs to be specially addressed.

4. The positive prospects related to nanomaterials in agriculture cannot make us underestimate the precautionary principle. The deliberate introduction of nano-sized materials within agricultural activities raises questions and concerns over the possible human and environmental health implications. Nanomaterial residues in soil and crops are expected to increase with exposure routes, including possible bioaccumulation in the environment and food chain. In this perspective, the purpose of achieving sustainable agriculture overlaps the need to balance the benefits provided by nano-products in solving environmental challenges. Thus, the assessment of environmental, health, and safety risks, potentially posed by nanoscale materials in agriculture, will become very soon of paramount importance (Lavicoli *et al.*, 2017). However, the fact remains that most of the literature data come from studies carried out in artificial conditions (laboratory and hydroponic experiments, or pot experiments with commercial potting soil or other artificial substrates). Since they do not predict the results under natural soil conditions, more experiments with natural soil and field conditions are strongly requested. Field trials are necessary to develop more applicative knowledge relating to the open field handling of nano-agrochemicals, the use of specific operating machines, and precautions for operators and consumers. Such information is also essential to provide the elements necessary to structure the rules, standards, prescriptions, and precautions to develop nano-enabled agriculture and reap the expected benefits fully.

## EPILOGUE

The Second Green Revolution requires a profound transformation of the agricultural sector, which will have to become more sustainable and ensure universal access to healthy food. Thus, there is a consensus on the need to introduce significant innovations into the global agricultural system for sustainable intensification to ensure food security and protect natural capital. Within this context, in the next years, a strong challenge will need to be faced regarding developing new and more efficient uses of nutrients in agriculture, being the nutrient use efficiency (NUE) paramount in sustaining high crop productivity without depleting biodiversity, and altering both the natural and agricultural systems. With global population anticipated to surpass 9 billion in the next few decades (United Nations 2013). In order to maintain sufficient crop production, the demand for phosphate fertilizers is also expected to rise. Elemental phosphorus (P) is obtained by plants in the form of plant-accessible water-soluble P salts, which are normally applied to fields as triple super P (TSP), and mono and diammonium P (MAP, DAP). However, only about 20% of the P applied to fields is actually used by the crops during a growing season. Some of the applied P forms complexes with soil aluminum, calcium, and iron oxides, resulting in plant-inaccessible forms. However, much of the soluble P is lost to agricultural run-off into local water bodies, where it contributes to eutrophication and may cause algal blooms, with their devastating effects on the aquatic ecosystems. Little P actually reaches target crops and mineral rock P is a limited, non-renewable, and increasingly costly resource. In the future, plant P acquisition and use efficiency might be improved but in the short term alternative fertilizing technologies are worth examining. Recently, nanofertilizers are being tested as a new technology, either for soil or foliar applications, to improve food production and with a reduced environmental impact due to improved nutrient delivery for a more finely tuned, accurate, and saving-resources distribution of nutrients. Knowledge in the field of nano fertilisers is developing very rapidly. The literature highlights the high potential of nanomaterials in crop fertilization in terms of more accurate delivery of nutrients. The physico-chemical characteristics of the nanostructures influence their behavior (e.g., solubility, stability, nutrient release rate). Nonetheless, uptake and use efficiency, as well as the effects of the nanoparticles on growth and metabolic functions in plants, vary between genotypes. For this reason, the design and development of nanofertilizers requires close collaboration between researchers in the field of nanochemistry, crop nutrition and agronomy.

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