

# Nanotechnology in Plant Nutrients Fortification

Subjects: Plant Sciences

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Nutrient deficiency in food crops is seriously affecting human health, especially those in the rural areas, and nanotechnology may become the most sustainable approach to alleviating this challenge. There are several ways of fortifying the nutrients in food such as dietary diversification, use of drugs and industrial fortification. However, the affordability and sustainability of these methods have not been completely achieved. Plants absorb nutrients from fertilizers, but most conventional fertilizers have low nutrient use and uptake efficiency. Nanofertilizers are, therefore, engineered to be target oriented and not easily lost.

Keywords: nanotechnology ; nanofertilizer ; biofortification ; nutrient security ; plant improvement

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## 1. Introduction

The quest to apply nanotechnology in agriculture arises from the fact that human population is constantly on the rise, which necessitates the need for more food. Population survey has estimated about 9.6 billion people by the end of 2050 <sup>[1]</sup>. Farm lands are losing their fertility due to human activities on them and societal change in lifestyle. This invariably affects the production of crops and could lead to famine and hunger, thus concerted efforts are necessary to improve plants for enhanced production. Nanotechnology serves as the latest technology for precision agriculture, whereby strategies are formulated and channeled towards meeting with food demands of the increasing human population.

There is a diversion from the traditional ways of crop production to technologies that could increase agricultural productivities with required nutrients, cost effective and efficient resource use that guarantees nutrient security, uplifts the value of production, boosts farmers' economy, delivers agri-value chain to rural partakers and supports pollution free environment <sup>[2]</sup>. This technology uses improved materials to add value to agriculture, by exploiting the nanoscale properties. Nanotechnology, as applied to agriculture, is bridging the gap in nutrient loss and fortification of crops. Farmers are using this science in the nano-regime to boost the quality and quantity of agricultural produce. The application of nanotechnology in agriculture includes nanobiotechnology, livestock, nanotoxicology, agrochemicals, hydroponics, biotechnology, etc.

Urban agriculture that makes use of recent nanotechnologies has the potential to contribute immensely to food security and healthy nutrition. Although there are associated risks from chemicals which may have emanated from soils, water or air <sup>[3]</sup>, the ultimate goals for application of nanomaterials in agriculture spans reducing hazard chemicals, nutrient losses, pest control and crop yield improvement <sup>[4]</sup>.

The nutrients needed by the plants are fortified in the fertilizers, with the belief that they could be absorbed by the plants. The lack of the micronutrients is manifested by abnormal growth of the plant parts; however, sometimes the soil may not be deficient of the micronutrient, rather the roots are unable to absorb and translocate the nutrients due to small root pore size. It is, therefore, imperative to explore the strategies of improving crop quality and their essential nutrients to meet the food demands of the growing populace.

The use of chemical fertilizers is an age long practice and has tremendously increased crop yields. However, they lead to soil mineral imbalance, destroy the soil structure, soil fertility and general ecosystem, which are serious impediments in the long term. To deal with the situation, it is pertinent to develop smart materials that can release nutrients to targeted areas and contribute to clean environment. Recent studies have shown that graphene is a promising material that could serve as a carrier for plant nutrients. It is capable of slow and controlled release of nutrient for the plants benefit, and ultimately increases the amount of crop production with low environmental impact <sup>[5]</sup>.

Nanotechnology seems to be the alternative that could revolutionize this field of agriculture as the entire nanotechnology industry had grown to \$1 trillion in 2015 <sup>[6]</sup>.

Plants remain the primary source of nourishment for humans, and food quality determines the health of majority of the people. Staple foods are usually high calorific foods, consumed regularly in high quantity, which becomes dominant part of a standard diet in a community. As a result, there is high correlation between staple foods and nutrition of its consumers, especially among the rural and poor communities who rarely have other sources of nutrient supplementation. Lack of essential micronutrients in food is common in such areas. These have become a global issue with serious adverse effects [7][8][9][10][11]. About 50% of children do not get the necessary vitamins and minerals and they become vulnerable, thus impairing their intelligence and mental capabilities. According to Clemens [12], high percentage of child death and global disease concern are traced to iron and zinc deficiencies. Several methods have been postulated to combat nutrient deficiencies such as dietary diversification, use of drugs and industrial fortification [13]. However, Sharma et al. noted that these interventions have not been fully successful owing to economic level of the people, social content or some technicalities in the method adopted [14]. Consumption of diverse food sources, although recommended as a sustainable solution, is unaffordable to the poor populace, who are at risk of malnutrition. The use of industries for the fortification of food nutrients has not been very successful, except for iodized salt. Biofortification is a concept of increasing the nutrient content of food crops during their cultivation [15]. The uniqueness of biofortification over other interventions for combating micronutrient deficiencies is that it is affordable and available for everyone. This is because these fortified crops are staple foods widely consumed by many people. As a result, it neither incurs extra cost nor is affected by the social behavior of the people. Non-staple foods such as animal products and vegetables, although high in vitamins and minerals, are very expensive. Significant number of the poor spend their income on staple foods for provision of energy, with little left for fruits and vegetables and animal-based proteins [14].

Biofortification strategies exist in enhancing nutritional content of crops and these strategies, according to Stein et al. (2007), include agronomic and breeding methods [16]. Under agronomic interventions, the use of fertilizers including inorganic, organic and biofertilizers are highlighted. Inorganic fertilizers usually with sizes more than 100 nm are easily lost due to leaching and volatilization, while organic matter utilization is hampered by its low mineral content and long-period of nutrient release. Numerous attempts to increase the efficiency of nutrient uptake of crops and thus biofortify them have not been so successful. Thus, the time is ripe to apply nanotechnology in solving some of these problems.

## **2. Nutrient Fortification, Its Relevance and Types**

Humans derive their nutrition from food, and require over 20 minerals and 40 nutrients for healthy living. Unfortunately, human diets most often contain less of the required essential nutrients, thus leading to malnutrition [17]. A fortified food reduces incidence of heart disease, anemia, blindness, incidence of cancer and early death [7]. Poor maternal health, low intellectual capacity and stumpy educational ability are consequences of micronutrient deficiencies. It also leads to reduced work ability and earning power, with untold consequences for sustainable national development [15].

To tackle this global menace, there is need to fortify the crops. According to Smith and Bouis et al. [18][19], several options to tackle micronutrient deficiencies exist: supplementation, dietary variation, industrial fortification, and biofortification. Dietary variation or diversification can be seen as consumption of different dietary sources (including fruits, vegetables and animal and animal-based products) at the community or household level, targeted at addressing micronutrient deficiencies [20]. Arimond and Ruel [21] noted that children's nutritional status and growth is positively influenced by dietary diversification. The problem with dietary diversification is that foodstuffs containing high micronutrients are not easily accessible because the affordability and availability in rural communities is low. Notwithstanding, these animals and animal products also rely on nutrients in plants for their nourishment [12]. thus, if these plants are not enriched in micronutrients, it becomes a vicious cycle of deficiency in humans [22].

Supplementation, however, involves the intake of micronutrients in the form of capsules, tablets or syrup. In fortification and supplementation, manufacturing and/or distribution infrastructure is required, which in the long run may not benefit many, especially those in rural communities. Vitamin A capsules intervention, which started in the 1990s, is an example of supplementation [23]. Moreover, supplementation can easily lead to overdose. Murgia et al. opined that overdose of iron can exacerbate diseases [24][25]. To be effective supplementation, as seen during some immunization, requires annually costly campaigns and these drugs or fortified foods do not always reach the most targeted and most affected rural community [26].

Gibson and Hotz [27] noted that staples and other food sources can be modified or altered to improve the micronutrient content or bioavailability. In most resource poor settings, starch-based diets with limited access to animal-based products or fruits and vegetables are predominant. Strategies such as plant breeding, agricultural biofortification and genetic engineering during food processing are means of dietary diversification. This is because sustainable availability of staple

food supplies preconditions food security at household or community level. In addition, increased and sustainable yields from agricultural production will increase the potential access to adequate food and food diversification.

Industrial fortification of food materials has been practiced for a number of years, such as iodized salt or vitamin D enriched milk. The crucial goal of the fortification strategy is to reduce diseases and death rates associated with micronutrient malnutrition. In commercial food fortification, micronutrients are introduced during the processing of the foods, which provides the appropriate nutritional levels to humans when consumed. However, those concerned do not necessarily need to change their diet. According to Pandav et al., only 29% of the populace has no access to iodized salt globally; and, since 2003, the number of iodine-sufficient countries has increased from 46% to 68% [28]. Other forms of fortification may include enrichment of wheat flour with zinc, iron, vitamin B and folic acid and introduction of vitamin A to edible oils and sugar. To avoid micronutrient deficiencies in preschool and breastfeeding children, it is recommended that they take adequate breast milk, powder and other food formula rich in micronutrient. Supplementation with vitamin A, according to Edejer et al. [29], is one of the most efficient strategies for improving children survival. Vitamin A is known to be associated with a reduced risk of diarrhea and causes of mortality [30].

Fortified foods may only be accessible to urban consumers, who can easily see and buy them. It is also very essential at crisis period, where food supply is inadequate and unbalanced. Thus, these fortified diets rich in minerals and vitamins are distributed to avoid malnutrition. However, it may be difficult to get to the rural consumers who cannot afford or have access to them. Thus, the need for biofortification of crops is conceived as a strategy for nutrient fortification in crops or staples while in the field. Dubock [31] noted that the primary priority in fortification should constitute fortification of locally available food sources, while food supplementation should be an interim measure. Biofortification is intended to cater to the poor populace, low-income earners and everyone at large.

### **3. Biofortification of Crops**

Malnutrition increase has resulted from consuming specific type of food without diversifying them, especially consumption of staples high in calories [13]. Biofortification is a novel technique to address this. Biofortification means growing varieties that are rich in minerals and vitamins. A typical example is the development of new variety of sweet potatoes rich in vitamin A. With biofortification, mass accessibility to better nutrient rich food is guaranteed. The target in biofortification is to produce staple crops at low cost that are sustainable and have high nutritional value, able to reduce the consequential side effects of micronutrient deficiencies. Although biofortified staple crops deliver low level of essential nutrients and vitamins per day compared to supplements or industrially enriched foods, they can satisfy the individual daily requirement of micronutrients [15]. They offer the rural consumers the ability to obtain rich nutrient foods within the community, unlike with industrial or commercial fortified foods. There are different biofortification techniques: agronomic biofortification, conventional breeding, and nutritional genetic modification [16].

### **4. Inorganic Fertilizers**

The need for inorganic fertilizers arises in order to supplement the soil nutrients needed for crop production. The soil could be deficient in some nutrients because, e.g. constant use of the soil, which negates recycling; post-harvest practices, which may take away the nutrients with the harvested crops; etc. However, for sustainability and excellent crop production, there is need for plant supplements, which could be in form of organic manure or inorganic fertilizers. Inorganic fertilizers are synthetic fertilizers made from petroleum, the formulation of which could either be single nutrients or combination of different nutrients. In the case of different nutrients, they are referred to as multi-nutrient fertilizers and they contain majorly nitrogen, phosphorus and potassium among other nutrients and can be complete or balanced. They are balanced when they are of the same ratio and complete when they are needed in a particular formula. The soil supplies most of the nutrients needed for plant growth, but sometimes the nutrients are depleted during harvest and need to be replaced using fertilizers.

Fertilizers help plants to grow and absorb the appropriate nutrients required in crops. Most conventional fertilizers contain the macronutrients, namely nitrogen, phosphorus and potassium, with little calcium, sulfur and magnesium. Other micronutrients such as zinc, iron, copper and manganese become lacking, making the crops deficient. A typical fertilizer with all nutrients should have the following: N (2–4%), P (0.3–1%), K (1.5–5%), S (0.15–0.8%), Ca (0.2–1.5%), Mg (0.15–1%), Zn (10–100 ppm), Fe (20–500 ppm), Mn (15–250 ppm), Cl (4–50 ppm), Co (2.5–50 ppm), Cu (5–75 ppm), and Mo (0.03–10 ppm) [32]. The confronting issues are: How much of the nutrients are absorbed by the plants? Are they in a manner that could be absorbable? Do the crops get the complete nutrients that fulfils the human requirement when consumed?

There is no doubt that inorganic fertilizers are made having full knowledge of the necessary ingredients needed by the plants. With this complete formula of ingredients, when applied to the soil, they are dispersed by water molecules and the nutrients are broken down into various forms that are needed by the plants. There are various soil reactions and mechanisms that determine the quantity absorbed by the plants.

Soil test is a preliminary operation that must be done before application of fertilizers. If the soil is acidic, using urea fertilizer, for example, the  $\text{NH}_3$  released from the reaction of the urea fertilizers with sufficient water molecules is absorbed in the form of ammonium ions and, when they are basic, there is no change. In neutral or near neutral pH (7–8), the ammonia may escape into the environment, causing pollution such as greenhouse gases. These are the challenges that need to be addressed.

## **5. Biofertilizers**

Continuous farming and use of agricultural lands, over a period of time, lead to depletion of the nutrients contained in the soil. Hence, the frequent resuscitation of the lands using fertilizers is necessary. When the soil is impoverished, there is low crop production, which leads to poor harvest, hunger and malnutrition. Farmers find it easy and convenient to use chemical fertilizers for crop improvement, but their cost and inherent environmental pollution calls for urgent attention. Biofertilizers or green fertilizers are natural ways of enriching the soil by using dead plant materials or animal wastes, which are fed on by microbes to give the required nutrients for efficient crop production.

The microorganisms are key in this process of natural fertilization because, without them, the plant or animal materials are not in the absorbable form by the growing crops and therefore are of no use to the soil [33]. Alternatively, biofertilizers can be microorganisms that activate the soil and plant natural processes for efficient nutrient uptake, high crop yield and quality, and tolerance to abiotic stress. Such microorganisms are majorly bacteria that are contained in the soil and are called plant growth-promoting rhizobacteria, including blue-green algae, phosphorus-potassium solubilizing organisms, azotobacter, and *Rhizopium* [33]. They fix the atmospheric nitrogen and interact with the decaying organic matter to make available nutrients for the plant growth. They are symbiotic in behavior, as plants cannot grow well without them, and they also depend on plants for existence. Apart from making nutrients available for plants, they also get involved in protecting the plants against some pathogenic attack.

Other methods of the biofertilization involve the rotational practice of cereal–legume with combined crop–livestock agricultural system. This method works to enhance the soil nutrients through fixing of the atmospheric nitrogen by legumes and the livestock wastes combines with the cereal–legumes to improve the soil texture and provide appropriate environment for the action of the microbes. Organic farming or biofertilization generally gives high-value crops but can be practiced in a small way, especially by rural farmers and the prices of the produce are high.

## **6. Nanofertilizers**

According to recent research works, nanotechnology has the possibility to revolutionize agricultural systems [34][35][36]. It enables the platform for the use of elegant delivery structure for agrochemicals which is safe, target bound and has easy mode of delivery. Nanofertilizers, due to their high surface area to volume ratio, are more effective than most of the latest polymeric type conventional fertilizers. Their nature could also allow slow release and promote efficient nutrient uptake by the crops. This technology, therefore, offers the platform for sustainable and novel nutrient delivery systems, which will exploit the nanoporous surfaces of the plant parts on plant surfaces. With encapsulated nanoparticles, nanoclays and zeolites, there is increase in the efficiency of applied fertilizer, restoration of soil fertility and plant health and reduction of environmental pollution and agroecology degradation [35].

The components of nanofertilizers may include zinc oxide nanoparticles (ZnONPs), silica, iron and titanium dioxide, ZnS/ZnCdSe core–shell quantum dots (QDs), InP/ZnS core–shell QDs, Mn/ZnSe QDs, gold nanorods,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ , and FeO [37]. The success of using nanomaterials as fertilizers in plant growth depends on the species of the plants and some other factors such as the size, concentration, composition and chemical properties of nanomaterials [4]. The vast knowledge of the fields of biology, biotechnology, material science, and engineering is key to development of new technologies needed to expand the field on nano-agriculture for efficient crop production.

There are shortcomings associated with the conventional fertilizers, as most of the nutrients are lost through leaching and they go further to pollute the underground water aquifers. In other words, chemical fertilizers lead to environmental consequences such as greenhouse gas emissions and hypoxia and these problems need urgent attention; hence, the

search for alternatives such as the nanofertilizers [38]. With nanofertilizer, there is slow release of the nutrients, which minimizes leaching of the nutrients among other interesting properties.

Nanomaterials are of unique properties resulting from their low particle size, large surface to volume ratio and excellent optical properties. Such properties, among others, afford nanofertilizers the opportunities in plant development, nutrient security and diverse farm practices. Since the great revolution of nanotechnology applications in the early 21st century, several fields of endeavor are making use of this novel science in creating novel products. Human population is growing and likewise crop production should also grow. Fertilizers have helped in making crops abundant for human consumption; and taking advantage of nanoscience, improved varieties of fertilizers in form of nanofertilizers can be processed. They get easily absorbed by the soil and enhance the quality of the soil, thereby improving the growth of the plant. The mainstream application of nanotechnology concentrates on electronics, optical devices, water purification, and health care with little awareness on agriculture. Conventional fertilizers do not possess all the nutrients required for plant growth and nutritional composition; on that premise and owing to the active nature of nanoparticulate materials, it becomes an interesting venture to engineer materials to give nanofertilizers that can address nutrient problems and environmental issues associated with fertilizers [39].

Nanofertilizers are more advantageous to the conventional fertilizers because they can triple the effectiveness of the nutrients, reduce the requirement of chemical fertilizers, make the crops drought and disease resistant and are less hazardous to the environment. They can easily get absorbed by plants due to their high surface area to volume ratio. The sizes and morphologies of nanoparticles are however strong factors that determine the level of bio-accessibility by the plants from the soil. The nanoparticles may not be activated instantly to be taken up by plants, rather series of reactions ranging from oxidation and recombination may take place to provide the plants with the right micronutrients. Since the nutrients are in nanoscale, the fortification of the plant with such nanonutrients seems to be an interesting option. The plants not only grow but also accumulate such nutrients, which bridges the gap of nutrient deficiency. Moreover, nanofertilizers could be engineered in such a way as to address particular deficient nutrients in plants. This is possible because the atoms on the surfaces of nanomaterials could be structured to obtain characteristic different properties.

Li et al. [40] reported that metals and anionic nanoparticles are highly adsorbed by porous materials, or the soil, which makes them overly available as food nutrients or even contaminants when not desirable. In addition, in recent times, some researchers have developed and patented a nanofertilizer called “Nano-Leucite Fertilizer”, which is eco-friendly and could reduce nutrient loss in food, with overall increase in crop and food production [41]. In a nutshell, nanofertilizers might be the best thing that could happen in agricultural revolution, as they have the potentials of enhancing soil fertility in nutrient deficient soil. However, it may be seen as “one more tool in the toolkit”. Table 1 shows some approved nanofertilizers currently used around the world [37][42].

**Table 1.** Some approved nanofertilizers used in the world today and their compositions. Data from [37][42].

Nanofertilizers	Constituents	Name of Manufacturer
Nano Ultra-Fertilizer (500) g	organic matter, 5.5%; Nitrogen, 10%; P <sub>2</sub> O <sub>5</sub> , 9%; K <sub>2</sub> O, 14%; P <sub>2</sub> O <sub>5</sub> , 8%; K <sub>2</sub> O, 14%; MgO, 3%	SMTET Eco-technologies Co., Ltd., Taiwan
Nano Calcium (Magic Green) (1) kg	CaCO <sub>3</sub> , 77.9%; MgCO <sub>3</sub> , 7.4%; SiO <sub>2</sub> , 7.47%; K, 0.2%; Na, 0.03%; P, 0.02%; Fe-7.4 ppm; Al <sub>2</sub> O <sub>3</sub> , 6.3 ppm; Sr, 804 ppm; sulfate, 278 ppm; Ba, 174 ppm; Mn, 172 ppm; Zn, 10 ppm	AC International Network Co., Ltd., Germany
Nano Capsule	N, 0.5%; P <sub>2</sub> O <sub>5</sub> , 0.7%; K <sub>2</sub> O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.8%; Fe, 2.0%; Mn, 0.004%; Cu, 0.007%; Zn, 0.004%	The Best International Network Co., Ltd., Thailand
Nano Micro Nutrient (EcoStar) (500) g	Zn, 6%; B, 2%; Cu, 1%; Fe, 6%+; EDTA Mo, 0.05%; Mn, 5%+; AMINOS, 5%	Shan Maw Myae Trading Co., Ltd., India

Nanofertilizers	Constituents	Name of Manufacturer
PPC Nano (120) mL	M protein, 19.6%; Na <sub>2</sub> O, 0.3%; K <sub>2</sub> O, 2.1%; (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , 1.7%; diluent, 76%	WAI International Development Co., Ltd., Malaysia
Nano Max NPK Fertilizer	Multiple organic acids chelated with major nutrients, amino acids, organic carbon, organic micro nutrients/trace elements, vitamins, and probiotic	JU Agri Sciences Pvt. Ltd., Janakpuri, New Delhi, India
TAG NANO (NPK, PhoS, Zinc, Cal, etc.) fertilizers	Proteino-lacto-gluconate chelated with micronutrients, vitamins, probiotics, seaweed extracts, and humic acid	Tropical Agrosystem India (P) Ltd., India
Nano Green	Extracts of corn, grain, soybeans, potatoes, coconut, and palm	Nano Green Sciences, Inc., India
Biozar Nano-Fertilizer	Combination of organic materials, micronutrients, and macromolecules	Fanavar Nano-Pazhoohesh Markazi Company, Iran

## 7. General Synthesis of Nanomaterials

There are two major ways of synthesizing nanomaterials: the top-down and bottom-up approaches. Top-down methods are physical means, which are expensive and consume a lot of energy and time, whereas bottom-up approaches are wet-chemical or biological means and are preferred by most researchers. Top-down methods are physical means and include the mechanical/ball milling, photolithography, sputtering, chemical etching, etc., while bottom-up approaches involve physical, chemical and biological means and include sonochemical, microwave, photochemical, vapor deposition, sol-gel, chemical and electrochemical deposition, atomic and molecular condensation, spray, laser pyrolysis, etc. <sup>[43]</sup>.

The biological method is one of the emerging green methods of synthesis because it uses eco-friendly materials and aqueous solvents, saves time and energy, and is cost effective, sustainable and non-toxic. The ultimate objectives of using biological means of synthesis, phytonanotechnology or green nanotechnology is to reduce the environmental and human risks associated with other methods of engineering nanomaterials. They provide nanomaterials that serve the essential needs of the present century. Biological means of synthesis consist of the microorganism-mediated method and plant-assisted green nanotechnology. More focus and interest have been give to the use of the plant method, as all plant parts ranging, including the roots, barks, leaf, stem, fruits, sap, and even fruit wastes, are applied in fabricating nanomaterials for various uses. Plants are considered as natural reservoirs for various components such as flavonoids, phenolics, terpenoids, carbohydrates, proteins, saponins, and acids that have potentials for reducing, stabilizing and capping metal or metal oxide nanoparticles as well as functionalizing carbon-based nanomaterials. Since these biocomponents in plants have functional groups that can act as organic ligands, they serve as electron donors and effectively reduce the bulk metal or metal oxides to their nanoparticulate forms. This method provides nanoparticles that have interesting characteristics including small sizes, eco-friendly nature, biocompatibility, low toxicity, simple reaction procedures and enhanced surface morphologies with unlimited applications.

In the application of the biological method of synthesis, the plant-assisted method in particular is seriously gaining attention because it is cost effective, easily manipulated, of high purity, sustainable, parametric efficient and greens. It has thus far outweighed other options. For instance, in a typical synthesis of SeNPs, sodium selenite, selenous acid or selenium oxide can be used as the precursor compound and plants substrates from *Vitis vinifera* fruits, *Bougainvillea spectabilis* wild flower, etc. have been used <sup>[44][45]</sup>. The synthesis involves different concentrations of the precursor compound and the plant extract. The solution is mixed and stir-heated at a temperature the plant biocomponents can withstand—not too high as to render them inactive. After a period, there could be observable color changes, indicative of nanoparticles formation and the solution is centrifuged, washed and dried to get the nanoparticles. Surega reported different positive influences of silver nanoparticles synthesized by different plant extracts on improving crop production <sup>[46]</sup>.

From the results, there was interesting development on the root and shoot and the fruit yield, among others. Although there are many reports on plant-mediated synthesis of nanoparticles, some gaps still exist on their application in crop improvement.

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