



A SIGNIFICANT ASSESSMENT OF NANO-FERTILIZERS AND IT'S IMPORTANCE

Pooja Srishti

School of Allied Health Sciences (SOAHS), Noida International University (Plot 1, Yamuna Expy, Sector 17A, Uttar Pradesh, Email: poojasrishti05@gmail.com

V. Sankara Vel

Department of Botany, PSG College of Arts & Science, Coimbatore, Tamilnadu.
Email: sankarphdbot@gmail.com

Sajith. S

Department of Chemistry, Government Polytechnic College, Attingal, Thiruvananthapuram, Kerala, Email: sajiththattamala@gmail.com

R. Lakshmi

Department of Microbiology, Justice Basheer Ahmed Sayeed College for Women, Chennai, Tamilnadu, Email: lakshmi.r@jbascollege.edu.in

Summera Rafiq

Department of Microbiology, Justice Basheer Ahmed Sayeed College for Women, Chennai, Tamilnadu, Email: summerarafiq@jbascollege.edu.in

SK. Jasmine Shahina

Department of Microbiology, Justice Basheer Ahmed Sayeed College for Women, Chennai, Tamilnadu, Email: jasmine.shahina@jbascollege.edu.in

Abstract

One of the challenges faced by the agriculture sector is ensuring that plants have sufficient bioavailability of minerals. Therefore, it is crucial to have mechanisms in place that allow for the controlled release of nutrients during planting, as well as innovative procedures that avoid any negative consequences. The application of nanotechnology in agriculture offers numerous advantages, including enhanced nutrient utilization by plants and waste reduction. Nano-fertilizers are a burgeoning technology and a continuously growing category of agrochemicals, offering potential solutions to the advancement of sustainable agriculture. The objective of this study is to provide an updated and comprehensive analysis of several aspects related to nanomaterials. These include different methods of synthesizing nano-fertilizers, potential mechanisms by which plants absorb these materials, and the benefits and drawbacks associated with their use. Additionally, this paper provides a comprehensive review of the primary literature in the field, focusing on recent investigations that employ the principles of green chemistry.



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Introduction

Over the past two decades, agriculture has faced a multitude of recurring challenges. The frequent climatic instabilities are not caused by the lack of space or investment in technology, but rather by the exacerbation of global warming and the extensive deforestation. Due to this, sustainable agriculture principles have gained significance in agricultural research organizations. These principles include the advancement of green nano-materials, the enhancement of agricultural processes, breeding techniques, the judicious use of pesticides, and other related areas (Duhan *et al.*, 2017). Researchers worldwide are increasingly striving to find intelligent and environmentally friendly ways to address the expanding global food demands resulting from population expansion. In this situation, particular emphasis is placed on biodegradable materials which are created using environmentally friendly and secure methods. At present, a global phenomenon has emerged where nano-materials are being produced by environmentally friendly methods, such as utilizing water as a solvent, reducing the usage of harmful chemicals, and repurposing agricultural and industrial waste. Fertilizers (Usman *et al.*, 2020) are a significant category of agrochemicals affected by these principles.

Organic fertilizers play a crucial role in the success of crops by either significantly altering the physical characteristics of the soil or enhancing crop production, hence increasing the profitability of the farmer. Nevertheless, the use of this category of agrochemicals is constrained by its low efficacy (Zulfiqar *et al.*, 2019). This drawback is prevalent in traditional methods of applying fertilizer. Approximately 50% of the nitrogen which is applied is believed to be lost to the environment, resulting in increased production expenses and the pollution of rivers, lakes, and groundwater. Hence, the primary obstacles in utilizing these fertilizer elements lie in the strategic optimization of their use, which needs to be more sustainable and ensure the maintenance or enhancement of productivity and quality across various crops. The development of nano-fertilizers is being motivated by these obstacles, as they are perceived as prospective allies for advancing agriculture (Maghsoodi *et al.*, 2020).

Nano-fertilizers are composed of nano-materials which may contain a carrier matrix of mineral components. He *et al.* (2019) stated that these compounds can be generated by the process of nano-encapsulation of nutritional components or as nano-particulate nutrients themselves. Plants require nutrients for their growth and development (Jaafry *et al.*, 2020), and the availability of these nutrients in the soil is vital for the plants to absorb them. Another constraining aspect is the insufficient availability of these minerals in the soil in sufficient amounts (Asgari Lajayer *et al.*, 2019). In order to do this, the farmers apply the necessary soil fertilizer according to the particular crop. Plant nutrition is categorized into two main groups: micronutrients and macronutrients (Zhao *et al.*, 2021). Micronutrients are essential minerals required by plants in small quantities (Zhao *et al.*, 2020). This collection comprises iron (Fe), boron (B), chlorine (Cl), copper (Cu), zinc (Zn),

manganese (Mn), and molybdenum (Mo) (Nair & Augustine, 2018). The existence of minute quantities of these elements are crucial for the growth and development of plants as they play a key role in the control of enzymes, proteins, and carbohydrates (Briat *et al.*, 2020). Macronutrients are essential components which plants require in large numbers (Dwivedi *et al.*, 2023). These compounds, as described by Tuhy *et al.* (2015), have essential activities in the growth of plant tissues, production of fruits and flowers, development of roots, regulation of water levels in plants, and other important processes. The composition of this group includes nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulphur (S) (Lal, 2015).

There are three primary methods for producing nano-fertilizers: top-down, bottom-up, and biological (Parida *et al.*, 2017). Every synthesis method has its own set of pros and cons in terms of the necessary procedure, including factors such as particle size, economic feasibility, and required yield for a specific crop. In a study by Kah *et al.* (2018) found that the use of nano-fertilizers resulted in a 30% increase in nutrient absorption compared to conventional fertilizers across several plant species. Within the scientific realm, this category of nutritional agrochemicals is classified into three distinct groups: nanostructured micronutrients, nanostructured macronutrients, and nanostructures which facilitate nutrient transportation. Some examples of these categories are hydroxyapatite, zinc oxide (ZnO), and chitosan nanoparticles (Sampathkumar *et al.*, 2020).

The significant potential of nano-fertilizers in revolutionizing and eventually replacing conventional methods is noteworthy, given the addressed challenges. This paper will provide an analysis of nano-fertilizers, covering various methods of production, potential mechanisms for plant uptake of nano-fertilizers, and the benefits and drawbacks associated with their use. Figure 1 depicts nano-fertilizers in agriculture. The objective of this review is to encompass the primary studies in the field concerning the generation of these agrochemicals using green synthesis. These elements are indisputable in their ability to mitigate the environmental and human health problems associated with modern agriculture.

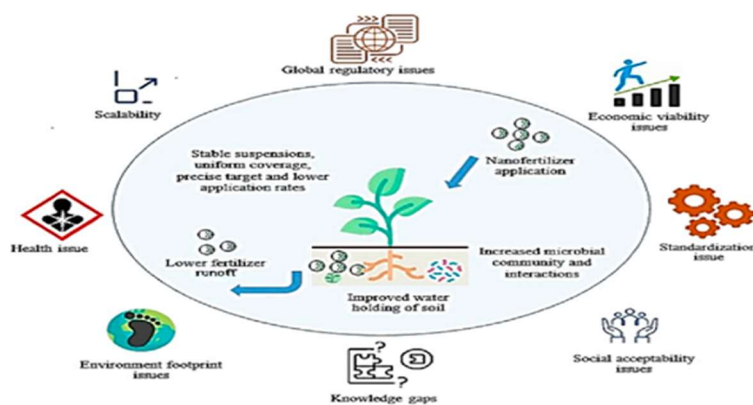


Figure 1. Nano-fertilizers in Agricultural Sustainability

Source: Yadav *et al.*, 2023

Production of nano-fertilizers

There are multiple methods for acquiring nano-fertilizers, including top-down, bottom-up, and biological approaches (Fig. 2). The top-down production process employs physical techniques, first with bigger particles and gradually reducing those to the nanometric scale (Feregrino-Pérez *et al.*, 2024). The techniques derived from this concept possess certain limitations, such as limited control over homogeneity and particle size. An alternative method for acquiring nano-fertilizers is through a bottom-up approach, which relies on chemical reactions (Abdel-Aziz *et al.*, 2019). Bottom-up approaches provide enhanced manipulation over the dimensions of the nanostructures and facilitate the minimization of contaminants. Another technique employed in the production of nano-fertilizers is the biological approach. Microorganisms, specifically bacteria and fungi, are employed for the process of biosynthesis. The benefit of acquiring nano-fertilizers through biosynthesis is in the little cytotoxicity exhibited by the end product (Cai *et al.*, 2020). Hence, it is evident that there exist several opportunities for the manufacturing of nano-fertilizers, accompanied by a wide range of obstacles, including the minimization of energy expenses, enhancement of crop yields, and the creation of a material possessing exceptional properties. By incorporating these attributes, it becomes feasible to produce agrochemicals that exhibit exceptional efficacy and sustained utility.

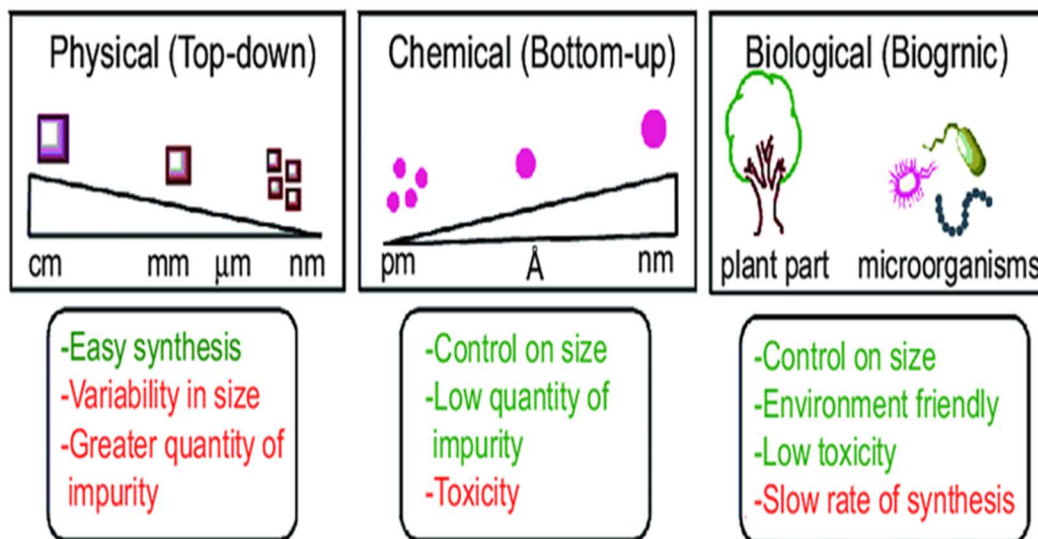


Figure 2. Representation of methods for the production of nano-fertilizers

Source: Manju Bernela *et al.*, 2020

Nano-fertilizers can be synthesized using either organic or inorganic substances. Inorganic nanostructures are primarily fabricated using metal oxides, including zinc oxide (ZnO), magnesium oxide (MgO), and silver oxide (AgO). Nanomaterials derived from organic chemicals, polymers, carbon, and other substances are utilized. Sharma *et al.* (2020) documented the impacts of nano-fertilizers containing copper and salicylic acid in a chitosan matrix on maize crops. The

nanoparticles were synthesized by encapsulating nutrients via chitosan ion gelation. The application of nano-fertilizer yielded positive outcomes, including enhanced antioxidant enzyme activities, decreased malondialdehyde content, and increased chlorophyll content in the leaves.

Shebl *et al.* (2020) synthesized ferrite nano-fertilizers by a microwave-assisted green hydrothermal method, utilizing hydrated zinc, manganese, and iron nitrates dissolved in water. Following the preparation of the suitable combinations and concentrations of each reagent, the medium was transferred to a 100 mL container and exposed to microwaves at a power of 750W. Following the application of microwave treatment, a total of five ferrite samples were subjected to testing at various temperatures ranging from 100 to 180°C. Eventually, the substance underwent a process of cleansing and dehydration at a temperature of 100°C for a duration of 6 hours. The various nanomaterials that were synthesized were utilized at varying concentrations (0, 10, 20, and 30 ppm) as leaf nano-fertilizers for pumpkin cultivation.

A method of cultivating *Cucurbita pepo* L, an experiment was conducted where nanoferrite was synthesized at a temperature of 160°C and then applied to a pumpkin culture which was growing. The nanoferrite was administered at a concentration of 10 parts per million (ppm). The results showed that the treated pumpkins had a higher yield compared to the pumpkins which were not treated. This increase in yield was observed for two consecutive seasons.

Madusanka *et al.* (2017) produced eco-friendly nanoparticles of urea transporters to serve as a nutrition for various cultures. The work demonstrated the ability to programme and utilize nanostructured materials as nano-fertilizers. Due to the significant solubility of the urea molecules, the authors integrated them into a hydroxyapatite matrix. The authors employed the bottom-up approach to produce the nanoparticles. This involved dispersing phosphoric acid in a mixture of calcium hydroxide and urea using mechanical agitation, with the acid being added drop by drop. Ultimately, purification processes were employed to obtain the nano-fertilizers from the material. The scientists conducted an assessment of nitrogen release in aqueous conditions utilizing the synthesized nanohybrid. This release was seen for a duration of one week. The study also investigated the effects of employing pure urea.

In a study by Kumar *et al.* (2018) devised a method to synthesize polyvinyl acetate (PVA) starch using polymers. This PVA starch serves as a substrate for the controlled release of copper and zinc nutrients, which are carried by carbon nanofibers. The researchers assessed the efficacy of nano-fertilizers by administering varying dosages to chickpea crops. According to their findings, the utilization of the created nanohybrid resulted in a significant rise in the crop yield of chickpea plants, from 46% to 96%.

Hence, it is evident that there exist multiple options for the manufacturing of nano-fertilizers, necessitating the selection of the most suitable technique for each specific scenario and intended use. The decision should be made considering the economic feasibility of the production, use, preparation, and ultimate implementation. Another crucial aspect to consider is the

performance of the end products. To assess this, it is essential to have knowledge about the mechanisms of nutrient absorption in the culture being analyzed.

Nutrient absorption by plants

Plants have numerous potential methods for absorbing macro and micronutrients. Once the nano-fertilizers are released into the environment near the crops, they can be absorbed through many pathways, including the root, leaf, endocytosis, and/or other methods. Figure 3 depicts a schematic representation illustrating the several pathways through which plants absorb nutrients. The absorption of nutrients by the roots can be significantly limited when they are handled in the soil, primarily due to the size of the pores and the specific elements that need to be absorbed. In a study conducted by Sartori et al. (2008), two forms of absorption were examined to see whether one had a greater impact on the orange crop (*Citrus sinensis* (L.) Osbeck). The researchers assessed the processes by which the plant absorbs nutrients through its roots and leaves during its growth over a period of five years. They used zinc as a vital micronutrient in their experimental solutions.

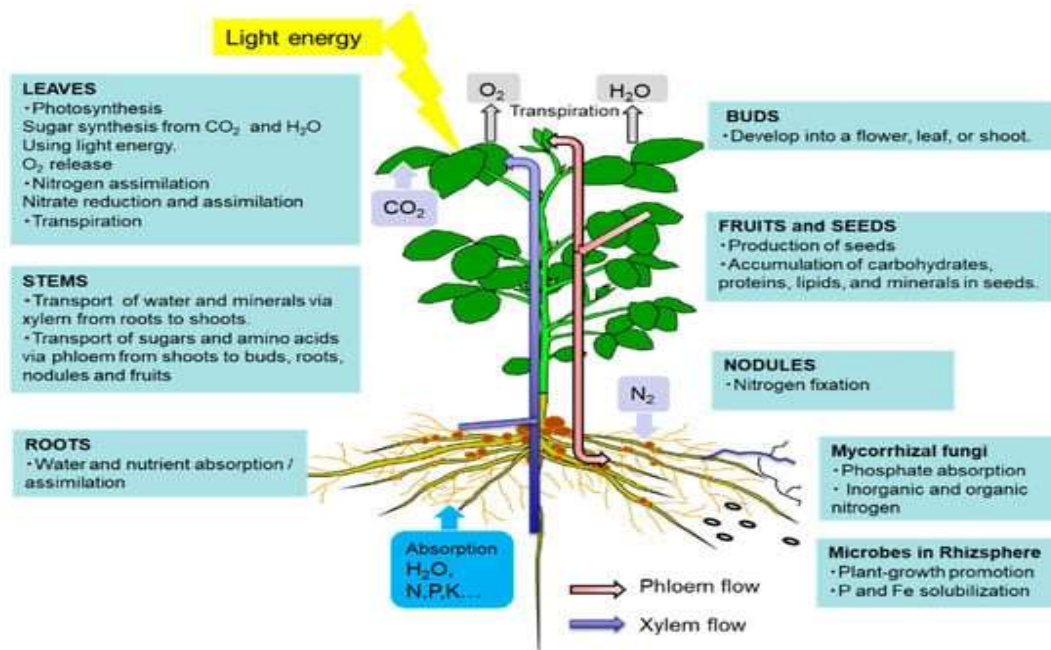


Figure 3. Routes of nutrient absorption by plants.

Source: Baslam *et al.*, 2020

Another significant pathway is through the leaf, which allows for the simultaneous application of insecticides, herbicides, and fertilizers in the plantation. Due to this factor, foliar fertilization is extremely effective and reduces pollution to a minimum. Nevertheless, it does have certain drawbacks, such as limited nutrient mobility and the difficulty of penetrating leaf cuticles. Rios, Garcia-Ibañez, and Carvajal (2019) assessed the application of Zn nanobiocarriers as a potential nano-fertilizer through the foliar route. The researchers utilized hydroponically cultured

broccoli and pak-choi plants (*Brassica rapa* subsp. *chinensis*) which were grown without the presence of zinc. The researchers conducted an experiment to evaluate the effectiveness of combining zinc nano-fertilizer with surfactant (PMP) and plant vesicles in enhancing the bioavailability of the nutrient. Following the experiments including the application of fertilizers paired with vesicles produced from broccoli and PMP, the researchers observed substantial variations in the analyzed crops. The absence of the surfactant during the administration of the fertilizer resulted in a marginal enhancement in the concentration of Zn in the leaves. Nevertheless, the concurrent application of the micronutrient and the surfactant significantly enhanced its leaf concentration, reaching about three times the concentration observed in the previous scenario. The treatment involving the use of vesicles and surfactants exhibited a significantly greater concentration compared to the other tests, reaching nearly four times the concentration observed in plants treated alone with zinc.

In a study by Abdel-Aziz *et al.* (2019) examined the potential impacts of utilizing chitosan nanoparticles and modified carbon nanotubes, either in their isolated form or when loaded with NPK (nitrogen, phosphorus, and potassium), as fertilizers for French bean plants. They investigated two methods of application: seed priming and leaf application. Consequently, the researchers found that application of fertilizer on the leaves was more effective than priming the seeds. Additionally, treating the leaves with chitosan nanoparticles resulted in a shorter time to harvest (80 days) without compromising the yield, compared to the control and seed priming treatment (110 days). The authors observed few alterations in the outcomes when carbon nanotubes were subjected to leaf treatment.

Nano-fertilizers primarily penetrate plants via the root and leaf channels, however they can also utilize additional mechanisms including endocytosis (Shinde *et al.*, 2020). Endocytosis is a biological mechanism that enables the transportation of substances from the external environment into the cell using membrane-bound vesicles (Fan *et al.*, 2015). In a study by Moghaddasi *et al.* (2015). Investigated the beneficial and detrimental impacts of utilizing rubber ash nanoparticles as a zinc fertilizer on plants. The researchers examined the uptake of Zn by the roots and the impact of these nanoparticles on the growth of cucumber. The scientists documented that the nanostructures were observed at the root through a Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The authors ascribed the introduction of zinc into the cucumber culture through the roots, facilitated by a potential subsequent mechanism of endocytosis.

Apodaca *et al.* (2017) employed bean plants (*Phaseolus vulgaris*) cultivated with copper (Cu) nanoparticles in conjunction with kinetin, a plant hormone. The study examined the crop's growth, nutrient absorption processes, copper levels in the roots and leaves, chlorophyll content, and enzymatic activity in beans that were roughly 2 months old. The researchers assessed the potential pathways for nutrient absorption, specifically focusing on copper, and discovered elevated levels of this element in the root tissue. The research findings indicated substantial

concentrations of copper in the leaves following treatment with kinetin. Therefore, the significance of the endocytosis pathway in plants for the uptake of nutrients is well-known.

The aforementioned studies have demonstrated that several variables have a direct impact on nutrient uptake. These variables include particle size, chemicals used, concentration, plant stage, external environmental conditions, duration of contact with the elements, and other factors. Hence, conducting comprehensive analyses of individual crops is vital when utilizing nano-fertilizers as a nutrient source.

Advantages and difficulties associated with the utilization of nano-fertilizers

Technology is continuously advancing quickly, especially in the area of contemporary agriculture. Environmental concerns must be a primary consideration, given the growing scarcity of natural resources and the exacerbation of climate consequences due to human-induced devastation. The pursuit of progress and population expansion has led to significant requirements, such as the need for more food production within limited areas and shorter timeframes. Hence, the utilization of nano-fertilizers in agriculture can act as a valuable asset in attaining sustainability.

Recently, the food industry has made significant progress in the advancement of technologies employed in crops to address vitamin deficiencies in the human diet. This deficiency is mostly caused by the rise of fast food and the insufficient consumption of vegetables and fruits. Therefore, recognizing the significance of employing nanotechnology in the advancement of agrochemicals resulted in the creation of nano-fertilizers. These nanoparticles have a role in controlling the nutrient levels in various plants (Hussain *et al.*, 2018) by employing regulatory mechanisms and gradually releasing critical components during the growth and germination of crops. For instance, certain studies have shown that nano-fertilizers can gradually release nutrients over a period of up to two months. This is a significant benefit compared to other fertilizers that release nutrients over a shorter time frame of up to 10 days. An additional advantage of using a nutrient management system is that it prevents the loss of these essential elements into the environment (Cyriac *et al.*, 2020).

One other benefit of employing nano-fertilizers is that they can be manufactured with consideration for the specific nutrients required by a particular crop due to the simplicity of producing these substances. In addition, the nanoparticles' large surface area, size, and reactivity contribute to the enhanced bioavailability of nutrients (Pullagurala *et al.*, 2018). Nanoparticles induce the elimination of several variables, including biotic and abiotic stressors, by ensuring a balanced distribution of components in cultures. Nevertheless, the extensive utilization of nano-fertilizers in agriculture can present several drawbacks and restrictions which require careful consideration (Younis *et al.*, 2021).

Excessive use of nano-fertilizers in agricultural practices might lead to undesirable and potentially irreversible ecological consequences. Furthermore, the safety of nanoparticles in plant development is a significant consideration, as nano-fertilizers may have distinct effects on crops.

Therefore, it is crucial to examine the hazards and identify the detrimental impacts of these nanostructures, including evaluating their life cycle. One further drawback of the uncontrolled application of nano-fertilizers is their environmental degradation caused by their great susceptibility to transformation.

Reactivity refers to the susceptibility of a substance to undergo undesired reactions and alterations in its properties (Iavicoli *et al.*, 2017). In a study by Ma *et al.* (2017) examined the use of CeO₂ nanoparticles in cucumber plants through the investigation of translocation and absorption. These processes are often undesirable as they might lead to heightened environmental toxicity when the nanoparticles undergo transformation into different forms. Around 15% of cerium underwent reduction from Ce⁴⁺ to Ce³⁺ in the cucumber roots, and the resulting chemicals were then transported through the phloem. This illustrates that the utilization of nano-fertilizers can have significant ramifications for human health. Therefore, it is imperative to thoroughly assess the safety of food cultivated with nano-fertilizers.

Conclusion

The review focused on nano-fertilizers, a rapidly evolving subject in research. The study conducted in this field, while demonstrating a greater number of benefits compared to drawbacks in the use of these nano-materials, remains at an early stage and highly specialized. Therefore, further research is necessary to support the integration of this technology as a feasible, secure, and environmentally-friendly option for widespread use in several societies. The multitude of synthesis methods utilizing renewable materials and environmentally friendly processes are advantageous factors. Furthermore, the lack of complicated equipment and ease of application offer promising paths for the effective integration of these nanostructures in the field. It is crucial to have a comprehensive understanding of both the drawbacks and advantages of using nano-fertilizers. These encompass a variety of topics, including the impact of a particular culture on performance and the changes that occur in chemical structure when they come in contact with plants throughout their life cycle. With an abundance of unexplored potential, research on the application of nano-fertilizers for plant nutrition is currently a promising topic.

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