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A Comprehensive Study of the Effects of Engineered Nanomaterials and Nanoparticles on the Poaceae (Grass) Family Plants

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***Abstract*: Plants of Poaceae, otherwise known as the Grass family, are the world's single most important food source. Of all the human-produced food items worldwide, almost 4.51 billion tons come from the plants of this family like sugarcane, corn, rice, barley, wheat, etc., contributing to over 50% of the 8.9 billion tons of food produced annually. It is believed that around 30-40% of the landmass on earth is covered by grass. Given their diversity and the dependence of the animal kingdom on this family of plants, it is no wonder that any change in the environment and ecology would impact them, subsequently impacting all the living beings dependent on them. Over the last decade, the synthesis and use of engineered nanoparticles and nanomaterials have dramatically risen in many aspects of human life and civilization. Industries, agricultural, and daily consumer products are some of those, so to speak. After the end of their useful life, in one way or the other, they will end up in the environment, where they would most likely come in contact with the crops as well. Their effect caused to the environment and ecosystem is still not much known as the research on this aspect is comparatively new. However, we must explore this sector to take necessary and suitable measures to prevent the misuse of this technology caused by the lack of our consciousness as it happened in the past for plastic and fossil fuels, which were meant to be a blessing for us to begin with. This study focuses on the response of the plants in the grass family to the exposure of a few types of engineered nanoparticles to various degrees, as we are heavily dependent on the plants of this family in many aspects, primarily for food and agriculture.**

***Keywords*: Crop, Grass, Growth, Nanomaterial, Poaceae.**

1. Introduction

Nanotechnology is a new concept, but nanomaterials and nanoparticles are not. They have existed in nature for a long time, and even the ancient human civilization has exploited some of their benefits, only unknowingly. They occur in three broad ways, through natural processes like fire, industrial by-products, or particularly engineered for their nanoscale properties. The second and third ones are solely anthropogenic, and this study would be focusing on them. With the rapid advancement in processing and analysis in the last few decades, the technology to synthesize engineered nanomaterials has boomed, and they have been rapidly replacing or simply making their way into the conventional materials in our day-to-day life. In modern days the nanomaterials could be classified based on dimensions such as zero dimension (quantum dots), one dimension (nanowires), two dimensions (nanofilm), and three dimensions, and so on.

Some Prominent Inorganic Applications of Nanomaterials:

Although this paper focuses solely on the biological effects of the nanomaterials, not all the nanomaterials are sourced for organic uses. As such, a brief description of the present research trend in the inorganic field where extensive usage of nanomaterial is seen is presented here.

Efficient energy harnessing and improving structural strength are a few of the many fields where recent research has witnessed the extensive use of nanomaterials.

Although replacing combustion engines with solely electrical power is the most effective means to reduce emissions, it is still a far-fetched goal. Meanwhile, much research is focusing on making the existing manufacturing processes[1], [2] and use of combustion engines less adverse to the environment and nature by reducing emissions using biofuels instead of fossil fuels [3]. Nevertheless, more of a long-term goal is to eliminate the combustion engines as much as possible by switching to renewable energy. Although many of the technologies for renewable energies have seen a drastic improvement in the past two decades, researchers are still working on fine-tuning them through their work on individual components constituting the technologies. Energy storage, microelectronics [4]-[7] and batteries, for example, are receiving significant attention. Novel nanomaterials such as carbon nanofibers are making their way to this field, aiming to improve the modern and next-gen batteries [8] by increasing storage efficiency and durability.

Heat transfer[9, 10] is another field where introducing nanomaterials has made a significant difference. Nanoparticles such as Al_2O_3[11] and TiO_2 [12], coupled with clever designing of the flow channels[13, 14], have improved the convection process, also improving the processeses dependant on heat transfer, such as refrigeration [15], [16].

Solar energy is the most abundant and promising out of all renewable energy sources [17]. Studies show that even rudimentary technologies can completely resolve the power crises [18], [19] in many South Asian and African countries as these parts of the world receive a very high solar influx year-

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round. Yet ironically, these places are also home to a largely energy-deprived population on earth. It is safe to say that the ongoing research to obtain better performance out of the existing technologies by using nanomaterials [20] would drastically improve the future of this technology by improving its performance [21], efficiency, and feasibility.

It is a well-established fact that composite materials have shown superior structural properties to many high-end conventional metals such as steel and aluminum. The composite materials provide flexibility in terms of shape and size of the mold and directionality of the fiber layup commonly seen in the resin transfer molding (VARTM). The conventional methods of molding, such as hot press, injection molding [22], etc., lack the controllability of VARTM and often pose challenges when molding complicated designs and shapes. The structural and mechanical properties of the already strong composite materials could be further improved using nanomaterials. Carbon nanotubes and electrospun glass nanofibers, as opposed to the commercially available glass and carbon fibers, provide similar or better structural performance at a fraction of the added weight compared to the latter [23]. Even repairing the composite panels is proven more effective with the introduction of nanomaterial. The repaired product also shows better toughness and resilience compared to the repairs made without nanomaterials [24].

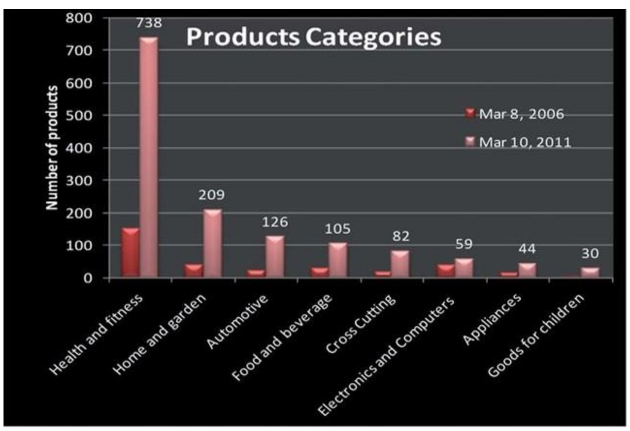

Fig. 1. Nanomaterial Production Pace from 2006 to 2011 [25]

With the technology becoming more cost-effective, we are producing them at an exponentially higher amount, which could be seen from the trend of just a few years, as presented in Fig. As stated by Graves in 2014 [26], global production of NMs is predicted to be 10^4–10^5 tons annually in structural applications by 2020, 10^3 tons of skin care products, information communications technology industries $>10^3$ tons, biotechnology 10 tons, and environmental industry 10^3–10^4[26]. According to Inshakova et al. (2017) [27] about one-fourth of the nanoproducts of the markets are incorporated by TiO_2, Ag, or SiO_2 nanoparticles. The first two are the most consumed metal and non-metal oxide-based nanomaterials. Consumption of SiO_2 was 198-kilo tons in 2015 and is projected to reach 786-kilo tons by 2022, at a CAGR of 21.8%. If these few nanomaterials were produced in such massive amounts, it is obvious how much the total production of nanomaterials would rise. These are just some examples to illustrate the rapid increase in the consumption of nanomaterials. With the increased rate of their usage, they are making their way into nature more than ever before, and their properties like high surface-area-to-mass ratio, tiny size, the tendency to agglomerate, optical sensitivity, high reactivity, etc. make them concern in the environment and ecology. As mentioned previously, grass accounts for a massive portion of the natural environment on earth. So, it is evident that they would be affected by our actions and studying them would give us an impression of how they interact when exposed to the environment and how that might affect us. While speaking of nanomaterials, we are considering a vast domain of materials that could be classified based on their compositions, size, shape, structure, etc. The effects on the environment caused by them could significantly differ not only based on these facts alone, but also, we need to consider the variables like the concentration, exposure, and effects of the environment, for example, the presence of light, moisture, individual plant types, etc. In this paper, however, we would solely focus on different types of nanomaterials based on the chemical composition and their interaction with the plants of the "Grass" family. Being the plants of the same family, their similarities in morphology[28], tissue arrangement, and the way of reacting to the nanomaterials would be able to give us an impression of how these tiny materials might affect the other species in this family, including the common crops, as over half of all the food we consume, comes from this family alone. Although the study attempted to confine within the interest of grass, drawing a specific boundary throughout the investigation hasn't been possible because of their multifaceted effects, so some other aspects like their use in fungicides, results on a few soil-dwelling organisms, etc. have been pertinently incorporated.

2. Sources of Synthetic Nanomaterials and their Migration to the Nature

The presence of synthetic or engineered nanomaterials in the environment has surpassed their naturally occurring counterparts long ago and is now overwhelmingly increasing with technological progress. According to a United Nations Environment Programme Division report, the engineered nanomaterials' production rate would reach 58 thousand tons per annum [29].

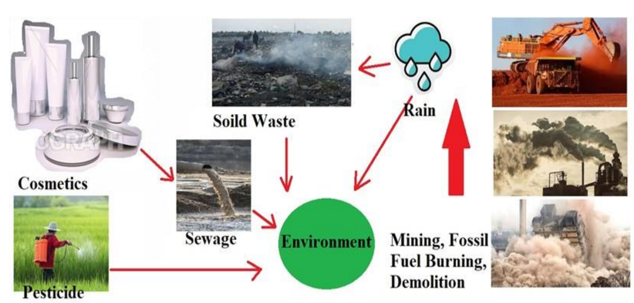

Fig. 2. A few possible ways nanoparticles end up in the environment

One of the examples of the source is the consumer products like the sunscreen contain a huge proportion of TiO_2 and ZnO nanoparticles which eventually ends up in the nature in ways that might seem insignificant, but they are raising concerns. For example, 25% of all the sunscreens are released in the reef areas [30]. According to a report by National Geographic, each year, 14,000 tons of sunscreen are assumed to be ending up in the oceans. Even during the showers, these sunscreens are washed up from our skin, mixing with wastewater in the sewage system and thus making their way to the environment [31], [32]. A recent study shows that the nanoparticles like TiO_2 and Ag used in UV-protecting clothing can make their way to the sweat during physical activities by the people wearing them [33]. So, nothing is surprising about the fact that this is just one of the many ways possible for the materials to enter the environment. Besides, studies and reports prove that countless industries worldwide release their wastewater and effluent into nature, sometimes into the natural streams. In some areas, the effluent stream from the sectors is directly used for irrigation due to water scarcity [34]. Even though many of the effluent streams are treated and filtered before releasing to nature, most treatment systems aren't specifically designed to filter and prevent the release of nanomaterials into the environment [35].

3. Effects Observed

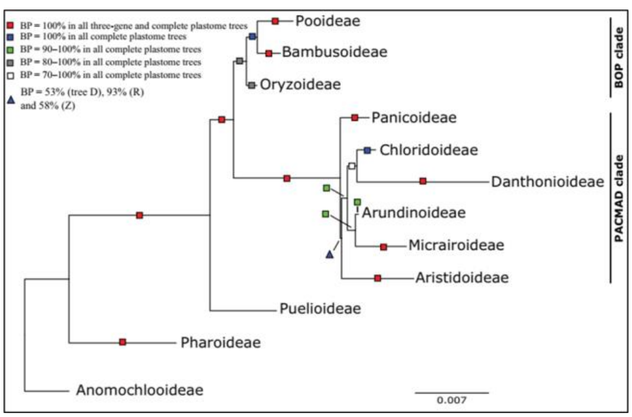

Fig. 3. Relationship among major lineages of Poaceae [36]

The Poaceae family could again be classified into several sub-families. Panicoideae (the sub-family of maize, sorghum, and switchgrass), Oryzoideae, Puelioideae, and Bambusoideae are some of them to mention, as shown in Fig. Given their similarities in terms of genomic sequences, it is likely that the way a specific nanoparticle would affect one plant in this family, the same might happen to the plants of another family in a more or less similar way.

Buell et al., (2005) [37] analyzed three different grass chromosomes and, based on the studies, concluded that, rice could be used as an "anchor" for the comparative cereal genomics. This supports the assumption that nanoparticles' effects would be closely related within this family.

A. Seed Gemination and Overall Growth

Chadchawan et al., (2014) have found in their study that Ag nanoparticles (AgNP) of 20nm can inhibit rice germination rate (Oryza sativa L.) depending on the dose. At the concentrations of 100 and 1000 mg/L, it strongly inhibited the shoot and root growth in dry weight; among them, inhibition of the shoot growth was more prominent [38]. In a different study, Velicogna et al., (2016) observed that the development of northern wheatgrass (E. lanceolatus) was more susceptible to the Ag (both nanoparticle and ionic) in comparison to the red clover (T. pratense) and the effects of the AgNO3 were more pronounced than that of AgNP [39], where plants exhibiting adverse effects on growth in the soils containing AgNP had stunted roots (primary and lateral) with lighter colored (green-yellow) leaves compared to control plants. In another study of the phytotoxicity effect of AgNP on Oryza sativa, it was found from the TEM micrograph that nanoparticles of different sizes could make their way inside the root cell. Among them, the average size of 25 nm was predominantly recorded [40].

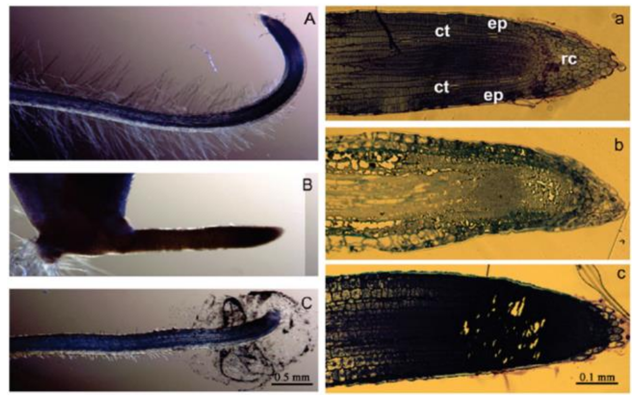

Fig. 4. Light microscopic observation of *Lolium multiflorum* root hairs (A-C) and primary root tips (a-c) after five days exposure of to DDI water control (A and a), 40 mg/L, 6 nm GA-coated AgNPs (B and b), and Ag+ (C and c). RC: root cap; ep: epidermis, ct: cortex [41]

The degree to which these might affect the root might be evident from the light microscopic observation by Berhardt et at., (2011) in the study of the effects of AgNPs on Italian Ryegrass (*Lolium multiflorum*), as shown in Fig.

Another study found a significant gradual decrease in germination percentage with an increase in CuO concentration[42]. Azimi R et al., (2013) found that a lower controlled concentration of TiO_2 nanoparticles enhances wheatgrass (*Agropyron desertorum*) seed germination[43]. However, at some higher concentrations, the rate decreases than the control specimen without nanoparticles. In the same study, shoot, root, and seedling elongation were found to be significantly affected by bulk and nanosized TiO_2 treatments, where nano-TiO_2 at 5 and 60 ppm showed the best result. Still, the growth was seriously disrupted at 80 ppm. However, the maximum biomass of roots was achieved from concentrations of 40 ppm nanoTiO_2. Lahiani et al., (2013) studied the growth of soybean, corn (*Zea mays*), and barley (*Hordeum vulgare*) in an ager medium upon exposure to Multi-walled Carbon Nanotube (MWCNT) for a period of 10-11 days and found out that the germination rate significantly increased in comparison to the untreated samples of plants [44]. Pure Single-walled Carbon Nanotube (SWCNT), when dispersed into THF (Tetrahydrofuran), causes the lowest rate of germinations among the studied common wheat (*Triticum aestivum*).

Compared to the other types of media, the pure-SWCNT sample with water had the highest growth rate of other control groups[45]. This demonstrates that although pure SWCNT are suitable for plants at specific concentrations, it can still be hazardous as it can act as a medium to carry harmful solvents like THF. Another study showed that Graphene and CNT at a concentration of 50 µg/mL could significantly improve the germination rate of switchgrass and sorghum seeds. Also, the total fresh biomass of 10-day-old seedlings increased when CBNs (Carbon-Based Nanomaterials) were added to the media [46]. ZnO has been found to play a role in germinating the root of Buckwheat (*Fagopyrum esculentum*). CeO_2 nanoparticle has been found to reduce corn's germination rate but significantly promote root growth [47]. Feizi et al., (2014) found SiO_2 nanoparticles, along with the prechilling process, to be a good alternative in breaking the dormancy of tall wheatgrass (*Agropyron elongatum L.*) [48]. Mitotic Index, another indicator of growth, has been sharply reduced with the uptake of nano-TiO_2 concentrations even with the dose as low as for *Zea mays* [49]. In a study of the impact of nano-CuO on rice (*Oryza sativa L.*), the maximum reduction in root growth was observed under 1.5 mM nano-copper treatment. After seven

Table 1
Effect of nanomaterials on plants in grass family

Nanomaterial	Plant	Effects	
		Beneficial	**Harmful**
AgNP[38-41]	Rice (*Oryza sativa L.*)[38, 40]		Inhibition in germination
			Deposition of particles inside root cell
			Inhibition in root (23-26%) and shoot (35-78%) growth [38]
	E. lanceolatus (northern wheatgrass)		Reduced growth, stunted roots [39]
	Lolium multiflorum		Significant reductions in root growth rate, more detrimental for smaller size nps[41] Cell structure and root morphology change
	Folsomia candida and *Eisenia Andrei*		- Significant affect on reproduction and dry biomass. - Organisms avoid the contaminated soil [39]
Nano-CuO[42, 55]	Rice	Remediation of as toxicity in plants Mitigating the effects on next-generation	Impedance in germination root growth reduction and root cell death Severe lipid damage [42]
TiO_2 np	Wheatgrass (*Agropyron desertorum*)	Enhanced germination at 5ppm Enhanced shoot and seedling growth at 40 ppm	Reduction in germination at 80 ppm Reduced shoot and seedling growth at 80 ppm [43]
	Zea mays		Declined Miotic Index[49]
Modified TiO_2 NM[56, 57]		reduce half-lives of pesticides without compensating their effectiveness	
(Ce)-doped TiO_2 nm[58]	cucumber (*Cucumis sativus L.*)	Controls powdery mildew of cucumber	
MWCNT[44]	corn (*Zea mays*) barley (*Hordeum vulgare*)	Improved germination rate	
THF dispersed pure-SWCNT	common wheat (*Triticum aestivum*)		Reduced Germination Rate at 43%
Graphene and CNT (carbon nanomaterial- CNM)[46]	Switchgrass and Sorghum	Improved Germination Rate	
CNM[59]			Inhibition of absorption of plant nutrients
CNM[46]	switchgrass	Reduced salt stress on seed germination	
CNT[60]			phytotoxic effects on plant cells causing cell death
ZnO np[61]	Buckwheat (*Fagopyrum esculentum*)		agglomeration in root
ZnO np[46]	Wheat, Green gram		inhibition on shoot and root growth
CeO_2 np[62]	Corn	Promoted root growth	Reduced germination
SiO_2 np[48]	Tall Wheatgrass	Breaking dormancy	
SWCNT[45]	Wheatgrass	13% Enhanced growth in water dispersed medium	Reduced grass growth in THF dispersed medium indicates the hazardous effect of SWCNT upon interaction with organic pollutants
carbon-based nanomaterials (CBN) Graphene and CNT[46]	Sorghum and Switchgrass	Increased biomass in seedlings Increase in Sorghum shoot upon exposure to Graphene	
CeO_2[54]	*Oryza sativa*	Increased K, Ca and phenolic content	Decreased Fe and reduction of S in the grains affecting protein synthesis and the antioxidant capacity Reduced Starch and Fatty Acid Concentration
hydroxyapatite (NHAP)[63]	Perennial ryegrass (*Lolium perenne L.*)	Increased soil pH, Pb fixation resulting in biomass increase, and growth	
Fe_3O_4[64]	Wheat (*Triticum aestivum L.*)	Enhanced antioxidant enzyme activity	

Table 2
Table title comes here

Nanomaterial	Pest	Effects
AgNP [65]	*Bipolaris sorokiniana* and *Magnaporthe grisea* (Pathogen of *Hordeum vulgare*, *Zea mays* and *Oryza sativa*)	AgNP shows five times higher value of EC50 than $AgNO_3$
Nanocid L2000 (AgNP) [66] (Product of AgNP)	*Pseudoperonospora cubensis* (responsible for downy mildew)	Highly effective against the mildew at 100 ppm
Silica np [67]	Rice weevil (*Sitophilus oryzae L.*)	Prevents weevil infestation in rice treated with SNP for a prolonged time. Conventional milling process can be used to remove nanocides
Al_2O_3 [68]	*Sitophilus oryzae* and *Rhyzopertha dominica* (Rice and Wheat Weevil)	Very small amount of the nanoparticle resulted in pest mortality rates comparable to commercially recommended pesticides

days of stress treatment, no further significant root growth was evident [42]. Death of cells in the exposed roots was also eminent. Not only is nano-CuO harmful to the seedling, but it is also significantly detrimental to the microbial community, as found from the studies [50]-[53].

B. Crop Quality

Gardea-Torresdey et at., (2013) have investigated the effect nano-CeO_2 has on the quality and nutrition content of the rice [54]. The increase in K and Ca in grains is beneficial for human nutrition. Conversely, reduction of Iron content could intensify the Fe deficiency of the people dependent on rice for their diet. Protein (reduced in MA, enhanced in LA), starch (reduced quantity in HA and LA), and Fatty Acid (significant decrease in MA) contents of various types of rice-based on their Amylose content have been changed at various degrees. This might be a problem for the population living on one specific rice type if the land is exposed to Cerium oxide nanoparticles.

C. Soil Dwelling Organisms

G. Velicogna et al., (2016) studied the effects of AgNPs on two soil-dwelling animals. Behaviors of springtail (*Folsomia candida*) and tiger worm (*Eisenia Andrei*) have been closely observed in this case to the exposure to AgNP and Ag^+ ions. It has been found that the presence of silver ions in much less amounts can make them avoid the area, and a concentration of 15 mg/kg of $AgNO_3$ in the soil would effectively reduce the juvenile mass into half [39].

All these effects described have been tabulated along with the outcomes found in some other studies. Here, the effects that enhanced the plants' growth, such as the root growth, mass and germination rates, were considered beneficial. Also, the effects caused to the pathogens and pests harmful to these plants of the family, which resulted in their death, reduction in population, reproduction, and other activities, were considered to be beneficial for the plants since the growth of these pathogens means the plants and the crops would be affected otherwise. There are also some soil-dwelling organisms that are at least harmless, if not beneficial to the crops and their presence in the soil indicates a healthy soil ecosystem. So, the reduction in the population of these organisms was considered harmful. In Table 2 the effects have been shown where the nanoparticles contributed to controlling the harmful organisms.

4. Conclusion

An important observation here is that all the effects found to be beneficial to the plants are all done in a controlled manner. Whether such strict control is possible on the agricultural land is still a big question. To this day, probably the best options to apply these effects on the plants are hydroponics and aeroponics, as more control is possible in that environment. Given the beneficial sides of these nanomaterials as the fertilizer and pesticide actually raises some questions that eventually need to be answered.

If these nanomaterials are used in the field as fertilizer and pesticide, would it be safe to apply them just the way we apply the conventional fertilizers and pesticides? Or does a new way of application need to be mastered? If it needs to be mastered, how it would be possible to ensure that the personnel using these new types of materials have the appropriate training to handle these, as the amounts applied in this case would be way more sensitive and as the tables show, an excess dosage of one material could reduce the desired growth in the plant instead of enhancing.

Since they would be used as fertilizer and pesticide, it could be taken for granted that they would be washed up by rain, flood, irrigation water, etc., and would make way to both the land and aquatic life. How can we ensure that these materials then won't cause trouble for the microbial biomass? There is evidence that it is possible to affect those environments, for example, for Ag [68].

The leftovers of the nanomaterials during the previous generation of plants would be there. Now, when the next generations of plants would be cultivated in the same piece of land where the nanomaterials were previously applied for the cultivation, how would the re-application of the same dose of nanomaterials over and over affect the plants?

Another question is how the exposure could be controlled as more prolonged exposure might make the nanomaterials rather detrimental than useful? Fe_3O_4 showed positive effects on wheat [64], while Want et al., (2011) studied the same material and found out that significantly induced oxidative stress due to prolonged exposure to the Fe_3O_4 NPs can pose toxicity risks to ryegrass. Another example is the Au nanoparticle, which, being an effective antibacterial agent, has been extensively used in biocide coating, soap, toothpaste, and shampoo and is the most prevalent nanoparticle in over 25 consumer products. TEM studies showed that Au nanoparticles when come in contact with rice roots, get deposited inside the root cells in the form of vacuoles and damage to the cells occurs due to penetrations of large Au nanoparticles entering via small pores [69].

As the trend suggests, it will be speeding up in the coming days. So, it is high time to carry on extensive study to find effective means to control their exposure to the environment and thus make clean use of this technology.

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