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Soil Properties Influenced by the Foliar Application of Nano Fertilizers in Maize (*Zea mays* **L.) Crop**

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The aim of this present investigation is to study the effect of foliar application of nano fertilizers N, Zn and Cu on soil properties including chemical and biological properties after harvest of maize (*Zea mays* L.) crop. The field experiment was carried out during June-October 2020 season at Instructional Farm, Rajasthan College of Agriculture, MPUAT, Udaipur which lies in agro-climatic zone IV-a of Rajasthan, India. The field was designed in a randomized block design having 12 treatments which were replicated thrice. The treatments include the various combination of conventional and nano fertilizers of N, Zn and Cu. The result showed that the plots treated with nano fertilizers found better nutrient and biological status in post harvest soil. The foliar application of two sprays of Nano N + Nano Zn + Nano Cu at 21 and 42 days after sowing (DAS) plus 50% N and Zn through conventional fertilizers along with 100% PK (T_{12}) significantly (P=.05) increased the availability of macronutrients (N and K), micronutrients (Zn and Cu), microbial population (bacteria, fungi and actinomycetes) as well as the dehydrogenase and acid phosphatase enzyme activity in post harvest soil of maize over control. The result of this investigation shows that 50% recommended dose of conventional fertilizers can be reduced by 2 sprays of nano fertilizers which reduces the harmful effects of conventional fertilizers and maintained the soil health.

Keywords: Actinomycetes; bacteria; conventional fertilizers; fungi; macronutrients; maize; nano fertilizers; soil properties.

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1. INTRODUCTION

Soil is very valuable and sensitive resource of nation. Soil provides essential ecological services for life's nourishment and survival so maintaining soil health is crucial for ecosystem sustainability [1]. The soil physiochemical properties and soil microbial community is important factor influencing soil health. Soil microbes are recognized as early warning signs of soil health because of their rapid responsiveness and sensitivity to environmental changes [2]. Fertilization is important for increasing the soil fertility and crop production [3]. In order to meet the food demand for outbursting population the heavy use of chemical fertilizers practices. The excessive use of chemical fertilizers definitely increases the crop production but also deteriorate the soil physiochemical and microbial population of soil. The constant use of chemical fertilizers is responsible for decline in soil organic matter, alter the soil pH, acidification, crusting and pest infestation, thus totally disturb the soil ecosystem. The indiscriminate use of fertilizers pollutes the soil, water and air, thereby rendered serious environment hazards [4,5]. This is due to the fact that chemical fertilizers have low use efficiency it lost easily through leaching, runoff, seepage, fixation, atmospheric losses, therefore nutrient uptake and utilization by plants has been reduced [6]. The nutrient use efficiency of chemical fertilizers has been reduced to 30-40% for nitrogen, phosphorus, potassium and sulphur [7]. Therefore, this challenge demands the adoption of controlled and targeted delivery of nutrients, can be achieved by diversion from traditional way of crop production to the new innovation technology [8]. Nanotechnology can be a boon to a modern agriculture which aim at manipulating and transform material and structure at nanoscale level generally below 100 nm dimension which is called nanomaterials/ nanoparticles [9]. Nanoparticles, unlike conventional chemical fertilizers, which require a large dose $(80-140 \text{ kg} \text{ ha}^{-1})$ in intensive agriculture production systems, can be employed in much smaller quantities due to their unique chemical properties [10]. Nanoparticles posses unique properties due to their small size, large surface to volume ratio and optical properties can be employed in fertilizers, to processed the improve form of fertilizers called nanofertilizers [11]. These properties allow slow release and targeted delivery of nutrients that promote efficient uptake of nutrients by crop, thus minimizes the nutrients losses, environmental

hazard; hence, restored the soil fertility and plant health.

Maize is important cereal crop grown in more than 170 countries globally. It is third leading staple food crop after rice and wheat [12]. It is known as queen of cereals due to its high yield potential. Currently, over 170 nations produce roughly 1137 million MT of maize over an area of 197 million ha, with an average productivity of 5.75 t ha⁻¹, contributing 39% in global cereal production [13]. Feed accounts for 61% of worldwide maize consumption, followed by food (17%) and industrial (22%). It has risen to the status of an industrial crop, with 83 percent of worldwide output going to the feed, starch, and biofuel industries. In India, maize ranks fourth in terms of area and seventh in terms of output, accounting for around 4% of global maize area and 2% of total production. In India, the maize covers an area of 9.2 million hectares with a production of 27.8 million metric tonnes and having average productivity of 2965 kg ha⁻¹, during 2018-19 [14]. It is a nutritional staple food crop for more than 200 million people. This number is likely to rise when the world's population exceeds 8 billion people in 2025 [15,16]. It fulfills about 15% of the global protein and 20% of the global calories requirement of human population [17], indicating the maize importance in human nutrition. India's most dominant rice–wheat cropping system has encountered various problems, viz. low inputuse efficiency, nutrients imbalances, more groundwater depletion and irrigation water shortages, high energy and labour demands, high emissions of greenhouse gases, weed resistance [18]. Therefore maize can take place of rice in rice–wheat cropping system [19].

Nitrogen is an essential nutrient for maize and a key determinant of grain yield, because it is a important element in structural component of amino acids, nucleic acids, chlorophyll, ATP and phyto hormones. The nitrogen status influences the biological processes such as absorption of water and minerals, xylem transport, vacuole storage as well as photosynthesis, carbon and nitrogen metabolisms and protein synthesis [20]. Through leaching, runoff, volatization, it causes groundwater contamination [21], aquatic eutrophication, ammonia and nitrous oxide emission and soil acidification [22,23,24]. Globally, more than 50% to 75% of applied conventional nitrogen fertilizer is not taken up by crops [25,26] and recovery of applied nitrogen by maize hardly exceeds 50% [27,28]. In 2014, the global demand for nitrogen fertilisers was 112 million metric tons (MMt) [29] and is expected to increase to 240 million metric tons (MMt) by 2050 [30]. The low nitrogen use efficiency, negative effects to environment and need of nitrogen fertilizers demands the use of nanofertilizers over conventional nitrogen fertilizers.

Micronutrient deficiency has been a major problem in recent years, resulting in micronutrient malnutrition in people due to Zndeficient soils. After nitrogen, phosphorus and potassium, zinc is the fourth most yield-limiting nutrient in the globe, as well as in Indian soils [31]. Zn deficiency is expected to be present in 36.5 percent of Indian soils [32]. Zinc functions as a functional, structural or regulatory co-factor for a wide number of enzymes in plants [33]. It is important cofactor for about 200 enzymes, the most significant of which being carbonic anhydrase, alcoholic dehydrogenase, and Zn-Cu-super oxide dismutase [34]. It is important for the synthesis of tryptophan, a precursor of Indole Acetic acid [35]. It is crucial for germination and pollen production and is involved in fertilisation [36,37,38]. As a result, Zn fertilization is an effective way to enhance crop production as well as to overcome the zinc deficiency in the soil.

Copper is one of the essential micronutrients for plants and humans. The copper content in Indian soils ranges between 1.8 and 285 mg kg^{-1} [39] and 4.2 % of Indian soils are deficient in copper [32]. It act as transitional element which actively participate in physiological redox process. It is necessary element for many proteins like plastocyanin, Cu-Zn-SOD, cytochrome c oxidae, diamine oxidase and polyphenol oxidase which involved in the electron transfer system in photosynthesis, detoxification of superoxide radical in process of photosynthesis, respiration, lignification process, respectively [40].

Soil microbial communities play an important role in biological soil fertility and productivity management. They are harvested and processed in such a way that their beneficial effects on the soil are captured and the soil-biological relationship is improved. Soil microorganism involved in nitrogen fixation, hormonal homeostasis, siderophore and phytohormone production, phytopathogen resistance, nutrient availability, promotion of mycorrhizal functioning, and reduced pollutant toxicity. [41]. Plants and microorganisms interact in a variety of ways that stimulate each other directly or

indirectly. Phytohormones (auxin, gibberellin, and cytokinin), siderophores and enzyme production, as well as elicitation of systemic resistance are examples of direct stimulatory processes, whereas antibiotic and extracellular enzyme production are examples of indirect stimulatory processes [42].

Dehydrogenase is an enzyme found in all living microorganisms. These enzymes are used to assess the metabolic health of soil microorganisms [43]. Dehydrogenase activity (DHA) is one of the most useful, relevant and sensitive bioindicators for determining soil fertility [44]. By transferring hydrogen from organic substrates to inorganic acceptors, dehydrogenases play an important role in the biological oxidation of soil organic matter (OM).

The majority of P in the soils studied is organically bound, phosphatase activity is a significant element in maintaining and managing the rate of P cycling through soils, especially in soils with insufficient P [45]. Acid phosphatase activity (AcP) is predominant in acid soils. AcP that are responsible for organic P transformation in soil by hydrolyzing C–O–P ester bonds in organic P compounds and release inorganic P, might be originating from extracellular and intracellular enzyme activities. Plant roots, fungi, mycorrhizal fungi and bacteria all contribute to AcP activity in soil [46].

2. MATERIALS AND METHODS

2.1 Site, Soil and Climatic Conditions

This study was conducted at the Instructional Farm of Agronomy, Rajasthan College of Agriculture, MPUAT, Udaipur district, Rajasthan,
India during June-October 2020. The India during June-October 2020. The experimental location was located at 24° 35' north latitude, 72° 42' east longitude, and 579.5 meters above mean sea level. The area is part of Rajasthan's agro-climatic zone IVa (Sub-Humid Southern Plain and Aravalli Hills).

The composite soil sample was collected randomly before sowing of crop from the experimental field up to 15 cm depth. The composite sample was air dried under shade and passed through 2 mm sieve and then use for analysis. The soil of this area was clay loam (38.82%, silt 26.58% and clay 34.60 %). The soil having pH 8.40, electrical conductivity 0.81 dSm-1 , soil organic carbon 0.55% and available nitrogen 260.20 kg ha⁻¹, phosphorus

16.09 kg ha⁻¹, potassium 350.47 kg ha⁻¹, zinc 1.99 mg kg^{-1} and copper 1.58 mg kg^{-1} . The population of bacteria 54.33 x 10⁷ cfu g^{-1} soil, fungi 21.21 x 10^5 cfu g⁻¹ soil, actinomycetes 22.30 x 10 6 cfu g⁻¹ soil, dehyrogenase activity 9.88 μ g TPF g⁻¹ 24h⁻¹ soil and acid phosphatase activity 41.01 μ g PNP g⁻¹ h⁻¹ soil. The pH and EC both were estimated using method of The Richards [47]. The organic carbon, available N, P, K and micronutrients (Zn and Cu) were estimated using the method of Walkley and Black [48], Subbiah and Asija [49], Olsen et al. [50], Flame photometer method [81] and Lindsay and Norvell Merwin [51], respectively. The microbial population was determined by serial dilution [52].

The climate of Udaipur is sub-tropical having mild winters and moderate summers. The monsoon season begins in mid-June and ends in mid-September, total rainfall received during June to October 2020 crop growing period is 773.4 mm entirely from south- west monsoon. During June to October 2020, the maximum and minimum temperature vary from 33.3 to 28.5° C and 24.5 to 15.8° C.

2.2 Experimental Design and Treatments

The seed of PM 9 (Pratap Makka 9) maize variety was used for this experiment. The experiment was laid out in a randomized block design with three replication. The gross plot size was 21 m^2 (5 x 4.2 m). The twelve treatments viz, T₁ (100% PK (Control), T₂ (100% PKZn), T₃ (100% NPK), T_4 (100% PKZn + Two sprays of Nano N), T_5 (100% P K Zn + Two sprays of Nano N (2X)), T_6 (100% NPK + Two sprays of Nano Zn), T_7 (100% PK + Two sprays of Nano N + Nano Zn), T $_{8}$ (100% RDF (NPKZn), T $_{9}$ (100%) PKZn + 50% N + Two sprays of Nano N), T_{10} (100% NPK + 50% Zn + Two sprays of Nano Zn), T_{11} (100% PK + 50% NZn + Two sprays of Nano N + Nano Zn) and T_{12} (100% PK + 50% N $Zn + Two$ sprays of Nano N + Nano Zn + Nano Cu).

2.3 Application of Nano Fertilizers

The foliar application of nano fertilizer was given twice $1st$ at 21 days after sowing and $2nd$ at 42 days after sowing as per treatments with the help of a knapsack sprayer with flat fan nozzle. Foliar spray of nano N was applied $@$ 4 ml I^1 water while a double dose of nitrogen $@$ 8 ml $I⁻¹$ water was applied in T_5 . Nano Zn @ 2 ml I⁻¹ water was given in all zinc treatments except T_{10} , T_{11} and

 T_{12} in which nano zinc applied @ 1.25 ml I^1 water. Nano Cu was given $@2$ ml I^1 water as per the scheduled treatments.

2.4 Soil Microbial Properties

At crop harvest, soil samples (0-15 cm depth) from each treated plot were collected for analysis. The soil was sieved (2 mm mesh size), homogenised and kept at 4°C after being placed in plastic bags and transported to the laboratory. The population of fungi, bacteria and actinomycetes was assessed using the standard serial dilution method [52]. The number of cells per gram of soil was used to compute the microbial population. The dehyrogenase activity was determined by the 2-3-5-triphenyl tetrazolium chloride (TTC) reduction technique [53] and acid phosphatase activity by βnitrophenol phosphate [54].

2.5 Statistical Analysis

The obtained data were statistically analyzed with the techniques of analysis of variance as described by Steel and Torrie [55]. The comparison in the treatment mean was tested by critical difference (CD) at 5% (P=.05) level of significance.

3. RESULTS AND DISCUSSION

3.1 Chemical Properties

The available N K, Zn and Cu in soil were significantly altered due to the foliar application of nano fertilizers after harvest of maize crop over control (Tables 2 and 3). The significantly highest available nitrogen (350.29 kg ha⁻¹), potassium $(482.58 \text{ kg ha}^{\text{T}})$, zinc (3.27 mg kg⁻¹) and copper $(2.12 \text{ mg kg}^{-1})$ in soil was found under the application of T₁₂ (100% PK + 50% N Zn + Two sprays of Nano $N +$ Nano $Zn +$ Nano Cu) followed by T_{11} (100% PK + 50% N Zn + Two sprays of Nano N + Nano Zn), T_{10} (100% NPK + 50% Zn + Two sprays of Nano Zn) and $T₉$ (100% P K Zn + 50% N + Two sprays of Nano N) over control. It was found that there was no statistical difference between T₁₂ (100% PK + 50% N Zn + Two sprays of Nano $N +$ Nano $Zn +$ Nano Cu) and T_{11} (100% PK + 50% N Zn + Two sprays of Nano N + Nano Zn) in terms of available N, K, Zn and Cu in soil after harvest of maize crop. The maximum available phosphorus (23.53 kg ha $^{-1}$) was recorded with T_3 (100% NPK) followed by T_1 control (100% PK), T_6 (100% NPK + Two sprays

of Nano Zn) and $T₇$ (100% PK + Two sprays of Nano $N + Zn$). The combined application of conventional fertilizers and nano fertilizers increased the available amount of N, K, Zn and Cu in soil when tested at the harvest of the crop. The application of nano fertilizers enhances some biogeochemical process such as nitrification which increases the available nitrogen in soil. The nano fertilizers release some humic acid and root exudates during slow release of nutrients which increases the content of carbon and nitrogen which serves as a food of soil microorganism [56]. Rajonee et al. [57] reported that the due to slow release pattern of nano fertilizers showed better pH, moisture, CEC and higher available nitrogen in post harvest soil than conventional fertilizers in *Ipomoea aquatic* (Kalmi). Jassim et al. [58] found that the application of nano fertilizers increase the available micronutrients (Zn, Fe, Mn and Cu) content in the soil after the harvest of the rice crop. The available micronutrients were increased in soil with the application of nano NPK fertilizers [59]. The application of nano chelated nitrogen fertilizers increased the phosphorus and potassium content by 26% and 6% than conventional urea [60]. Thirunavukkarasu and Subramanian [61] also proved that the slow release mechanism of nano fertilizers is able to enhance the nutrient status of soil by reducing leaching loss, fixation, atmospheric losses and microbial conversion. Similar results were also observed by Rani et al. [62]; Li et al*.* [63]; Nibin et al. [64] and Meena et al. [65].

3.2 Biological Properties

The biological population (bacteria, fungi and actinomycetes) and enzymatic activity (dehydrogenase and acid phosphatase activity) were significantly increased in the soil after the harvest of maize crop with foliar application of nano fertilizers (Table 4). The significantly highest bacteria (67.17 x 10⁷ cfu g⁻¹ of soil), fungi (31.27 x 10⁵ cfu g⁻¹ of soil), actinomycetes $(27.72 \times 10^6 \text{ ctu g}^{-1} \text{ of soil})$ population, dehydrogenase activity (13.48 µg TPF g^{-1} 24h⁻¹ soil) and acid phosphatase activity (48.72 µg PNP g^{-1} h⁻¹ soil) in soil was recorded with T_{12} (100% PK + 50% N Zn + Two sprays of Nano N + Nano Zn + Nano Cu) followed by T_{11} (100% PK + 50% N Zn + Two sprays of Nano N + Nano Zn), T_{10} (100% NPK + 50% Zn + Two sprays of Nano Zn), T₉ (100% PKZn + 50% N + Two sprays of Nano N) and T_6 (100% NPK +Nano Zn)

over control. The T₁₂ (100% PK + 50% N Zn + Two sprays of Nano $N +$ Nano Zn + Nano Cu) and T_{11} (100% PK + 50% N Zn + Two sprays of Nano $N +$ Nano Zn) were found at par in the population of bacteria, fungi and actinomycetes as well as in activity of dehydrogenase and acid phosphatase enzyme. The minimum bacteria $(54.34 \times 10^7 \text{ c}$ fu g⁻¹ of soil), fungi (22.17 x 10⁵ cfu g^{-1} of soil), actinomycetes (20.77 x 10⁶ cfu g^{-1} of soil) population, dehydrogenase activity (10.20 μ g TPF g⁻¹ 24h⁻¹ soil) and acid phosphatase activity (48.72 µg PNP g^{-1} h⁻¹ soil) were observed under control T_3 . The impact of nano fertilizers on microbial communities depends on many factors including soil type and its properties such as pH, texture, ionic strength, organic matter content as well as on type, size and concentration of nanoparticles [66,67,68 and 69]. These factors influence their interaction with soil microorganism that causes the positive and toxicity effect of nano particles on the soil microbial community [70]. However, the use of nano fertilizers influenced the microbial population structure and function in the soil system. You et al. [71] concluded that soil type and type of nanoparticle used is a key component in affecting the microbial population, they found that nano-ZnO at low concentration (0.5-2 mg g^{-1}) significantly increases the enzymatic activity and microbial population in black soil. Simonin et al. [72] reported that the application of nano-CuO at low concentration $(0.1-100 \text{ mg kg}^{-1})$ improved the carbon and nitrogen cycling in soil, which cause an increase in the activity of ammonia-oxidizing bacteria in soil. The direct soil application of nano-ZnO (10 mg kg−1) showed stimulating effect on dehydrogenase activity and microbial population [73]. Nibin et al. [64] also reported the positive effect of foliar application of nano NPK on microbial population and enzyme activity in bhindi. Raliya et al. [74] also reported the positive effect of biosynthesized ZnO NPs in clusterbean crop significantly increasing the microbial population (bacteria, actinomycetes and fungi) and acid phosphatase activity in the soil. The combined application of conventional and nano fertilizers influenced the microbial population after the harvest of the wheat crops (Meena et al. 2020). Sharifi and Khoramdel [75] found that the activity of nitrogen fixing bacteria in the rhizosphere was increased due to foliar application of nano ZnO in soyabean crop. Similar findings were recorded by Tarafdar et al. [76]; Li et al. [63]; Tondey et al. [77] and Yusefi-Tanha et al. [78].

Table 1. Physio-chemical and biological properties of experimental soil (0-15 cm)

Table 2. Effect of foliar application of nano fertilizers on available macronutrients (N, P and K) in soil after harvest of maize

Table 3. Effect of foliar application of nano fertilizers on available micronutrients (Zn and Cu) in soil after harvest of maize

 T1 T2 T3 T4 T5 T6 T7 T8 T9 T10 T11 T12 Bacteria Fungi Actinomycetes

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Fig. 1. Effect of foliar application of nano fertilizers on microbial population in soil after harvest of soil

4. CONCLUSION

From the forgoing result, it was concluded that the combined application of the conventional and nano fertilizers significantly alter the chemical and biological properties of soil. The application of 50% conventional and 2 sprays of nano fertilizers as in T₁₂ (100% PK + 50% NZn + two sprays of Nano N+Zn+Cu) significantly increased the available macronutrients (N and K), micronutrients (Zn and Cu), microbial population (bacteria, fungi and actinomycetes), enzyme activity (dehydrogenase and acid phosphatase activity) which is at par with T_{11} (100% PK + 50% NZn + two sprays of Nano N + Nano Zn) over control. The nano fertilizers application reduced the toxic effects of conventional fertilizers and maintained soil health by reducing the 50% recommended dose of conventional fertilizers by 2 sprays of nano fertilizers.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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