Original Research Article

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

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 chemical 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

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 (Liao *et al*., 2018). 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 (Xu *et al*., 2017). Fertilization is important for increasing the soil fertility and crop production (Tao *et al*., 2017). 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 pH soil, 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 (Geisseler *et al*., 2014; Adnan *et al*., 2020). 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 (Seleiman *et al*., 2021).The nutrient use efficiency of chemical fertilizers has been reduced to 30-40% for nitrogen, phosphorus, potassium and sulphur (Guo *et al*., 2018). 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 (Subramanian and Tarafdar, 2011). 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 (Verma and Kapoor, 2020). Nanoparticles, unlike conventional chemical fertilizers, which require a large dose (80–140 kg ha^{-1}) in intensive agriculture production systems, can be employed in much smaller quantities due to their unique chemical properties (Raliya *et al*., 2017). 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 (Li *et al*., 2016). 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 (Sandhu *et al*., 2007). 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, contributing 39% in global cereal production (FAOSTAT, 2021). 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 (FAI, 2020). 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 (Lutz *et al*., 2001; USDA 2009). It fulfills about 15% of the global protein and 20% of the global calories requirement of human population (Brown *et al*., 1988), indicating the maize importance in human nutrition. India’s most dominant rice–wheat cropping system has encountered various problems, viz. low input-use efficiency, nutrients imbalances, more groundwater depletion and irrigation water shortages, high energy and labour demands, high emissions of greenhouse gases, weed resistance (Humphreys *et al*., 2010). Therefore maize can take place of rice in rice–wheat cropping system (Ladha *et al*., 2009).

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 (Crawford and Forde, 2002). Through leaching, runoff, volatization, it causes groundwater contamination (Schröder *et al*., 1998), aquatic eutrophication, ammonia and nitrous oxide emission and soil acidification (Guo *et al*., 2010; Hoang *et al*., 2010; Ju *et al*., 2011). Globally, more than 50% to 75% of applied conventional nitrogen fertilizer is not taken up by crops (Asghari *et al*., 2011; Modolo *et al*., 2018) and recovery of applied nitrogen by maize hardly exceeds 50% (Abbasi *et al*., 2013; Conant *et al*., 2013). In 2014, the global demand for nitrogen fertilisers was 112 million metric tons (MMt) (FAO, 2015) and is expected to increase to 240 million metric tons (MMt) by 2050 (Tilman, 1999). 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 Zn-deficient soils. After nitrogen, phosphorus, and potassium, zinc is the fourth most yield-limiting nutrient in the globe, as well as in Indian soils (Arunachalam *et al*., 2013). Zn deficiency is expected to be present in 36.5 percent of Indian soils (Arvind *et al*., 2019). Zinc functions as a functional, structural, or regulatory co-factor for a wide number of enzymes in plants (Barak and Helmke, 1993). It is important cofactor for about 200 enzymes, the most significant of which being carbonic anhydrase, alcoholic dehydrogenase, and Zn-Cu-super oxide dismutase (Auld, 2001). It is important for the synthesis of tryptophan, a precursor of Indole Acetic acid (Brown *et al*., 1993; Alloway, 2008). It is crucial for germination and pollen production and is involved in fertilisation (Kaya and Higgs, 2002; Pandey *et al*., 2006; Cakmak, 2008). As a result, Zn fertilization is an effective way to for 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} (Singh, 2008) and 4.2 % of Indian soils are deficient in copper (Arvind *et al*., 2019). 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 (Yruela, 2009).

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. (Jacoby *et al*., 2017). 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 (Mishra *et al*., 2019).

Dehydrogenase is an enzyme found in all living microorganisms. These enzymes are used to assess the metabolic health of soil microorganisms (Watts *et al*., 2010). Dehydrogenase activity (DHA) is one of the most useful, relevant, and sensitive bioindicators for determining soil fertility (Wolinska and Stepniewska 2012). 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 (Eichler *et al*., 2004). 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 (Kumar *et al*., 2011).

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY

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 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 10^{7} 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 µg TPF g^{-1} 24h^{-1} soil and acid phosphatase activity 41.01 µg PNP g^{-1} h^{-1} soil. The pH and EC both were estimated using method of The Richards (1954). The organic carbon, available N, P, K and micronutrients (Zn and Cu) were estimated using the method of Walkley and Black (1934), Subbiah and Asija (1956), Olsen *et al.,* (1954) and Lindsay and Norvell Merwin (1978), respectively. The microbial population was determined by serial dilution (Allen, 1959).

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 ^{o}C and 24.5 to 15.8^{o}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, T_1 (100% PK (Control), T_2 (100% PKZn), T_3 (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 l^{-1} water while a double dose of nitrogen @ 8 ml l^{-1} water was applied in $T_{5.}$ Nano Zn @ 2 ml l^{-1} water was given in all zinc treatments except T_{10}, T_{11} and T_{12} in which nano zinc applied @ 1.25 ml l^{-1} water. Nano Cu was given @2 ml l^{-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 (Allen, 1959). 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 (Casida *et al.,* 1964) and acid phosphatase activity by β-nitrophenol phosphate (Tabatabai and Bremner, 1969).

2.5 Statistical analysis:

The obtained data were statistically analyzed with the techniques of analysis of variance as described by Steel and Torrie (1960). 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, P, K, Zn and Cu in soil were significantly altered due to the foliar application of nano fertilizers after harvest of maize crop over control (Table 2 and 3). The significantly highest available nitrogen (350.29 kg ha^{-1}), potassium (482.58 kg ha^{-1}), zinc (3.27 mg kg^{-1}) and copper (2.12 mg kg^{-1}) in soil was found under the application of 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 + Zn), T_{10} (100% NPK + 50% Zn

+ Two sprays of Nano Zn) and T_9 (100% P K Zn + 50% N + Two sprays of Nano N) over control. It was found that there was no statistical difference between T_{12} (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 + 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 T_7 (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 (Vande Voort and Arai, 2019). Rajonee *et al*., 2016 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*., 2019 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 (Sahar *et al*., 2020). The application of nano chelated nitrogen fertilizers increased the phosphorus and potassium content by 26% and 6% more than conventional urea (Astaneh *et al*., 2021). Thirunavukkarasu and Subramanian 2015 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*., 2019; Li *et al.,* (2013); Nibin *et al*., (2019) and Meena *et al*., (2021).

3.2 Biological properties

The biological population (bacteria, fungi, 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 population (67.17 x 10^7 cfu g^{-1} of soil) fungi population (31.27 x 10^5 cfu g^{-1} of soil), actinomycetes (27.72 x 10^6 cfu g^{-1} of soil), dehydrogenase activity (13.48 µg TPF g^{-1} $24h^{-1}$ soil) 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 + Zn), T_{10} (100% NPK + 50% Zn + Two sprays of Nano Zn), T_9 (100% PKZn + 50% N + Two sprays of Nano N) and T_6 (100% NPK +Nano Zn) over control. The T_{12} (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 + Zn) were found at par in the population of bacteria, fungi, actinomycetes as well as in activity of dehydrogenase and acid phosphatase enzyme. The minimum bacteria population in soil (54.34 x 10^7 cfu g^{-1} of soil), fungi (22.17 x 10^5 cfu g^{-1} of soil),

actinomycetes (20.77 x 10^6 cfu g^{-1} of soil), dehydrogenase activity (10.20 µg 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 (Shoultswilson *et al*., 2011; Ben-Moshe *et al*., 2013; Frenk *et al*., 2013 and Vaishnavee *et al*., 2021). These factors influence their interaction with soil microorganism that causes the positive and toxicity effect of nano particles on the soil microbial community (Kalwani *et al*., 2022). However, the use of nano fertilizers influenced the microbial population structure and function in the soil system. You *et al*., 2018 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*., 2018 reported that the application of nano-CuO at low concentration (0.1–100 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 (Jośko *et al*., 2019). Nibin *et al*., 2019 also reported the positive effect of foliar application of nano NPK on microbial population and enzyme activity in bhindi. Raliya *et al*., 2013 also reported the positive effect of biosynthesized ZnO NPs in clusterbean crop significantly increasing he 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 2016 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*., (2014); Li *et al.,* (2013); Tondey *et al*., (2021) and Yusefi-Tanha *et al*., 2020.

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

Particulars	Value	Methods
A. Mechanical properties		
Sand (%)	38.47	
Silt (%)	26.46	
Clay (%)	34.57	
Textural class	Clay Loam	International pipette method by Piper (1960)
B. Physical properties		
Bulk density (Mg m^{-3})	1.40	Core sampler method by Singh (1980)
Particle density (Mg m^{-3})	2.45	Richards (1954)

Porosity (%)	41.50	Richards (1954)
C. Chemical properties		
pH (1:2, soil : water suspension)	8.40	Potentiometeric method using pH meter Richards (1954)
EC (dSm^{-1}) (1:2, soil: water suspension)	0.81	Using solubridge method (Conductivity meter) Richards (1954)
Organic carbon (%)	0.55	Walkley and Black wet oxidation method (Walkley and Black (1934))
Available nitrogen ($kg\ ha^{1}$)	260.20	Alkaline permanganate method (Subbiah andAsija, 1956)
Available phosphorus ($kg\ ha^{-1}$)	16.09	Olsen's method (Olsen (1954))
Available potassium ($kg\ ha^{-1}$)	350.47	Flame photometer method (Mervin and peach 1951
Available Zn ($mg\ kg^{-1}$)	1.99	DTPA extractable method
Available Cu ($mg\ kg^{-1}$)	1.58	DTPA extractable method
D. Biological properties		
Bacterial population (10^{7} cfu g^{-1} soil)	54.33	Serial dilution technique Allen, (1959)
Fungi population (10^{5} cfu g^{-1} soil)	21.21	Serial dilution technique Allen, (1959)
Actinomycetes (10^{6} cfu g^{-1} soil)	22.30	Serial dilution technique Allen, (1959)
Dehyrogenase activity (µg TPF g^{-1} $24h^{-1}$ soil)	9.88	2-3-5-Triphenyl tetrazolium chloride (TTC) reduction technique
Acid phosphatase activity (µg PNP g^{-1} h^{-1} soil)	41.01	β-nitrophenol phosphate

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 T_{12} (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+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.

REFERENCES

1. Abbasi MK, Tahir MM, Rahim N. 2013. Effect of N fertilizer source and timing on yield and N use efficiency of rainfed maize (*Zea mays* L.) in Kashmir-Pakistan. Geoderma. 2013;195:87–93.
2. Adnan N, Nordin SM, Anwar A. Transition pathways for Malaysian paddy farmers to sustainable agricultural practices: an integrated exhibiting tactics to adopt Green fertilizer. Land Use Pol. 2020;90:104255.
3. Allen ON. Experiments in soil bacteriology (3rd ed.). Burgess Publishing Co. Minnea Polis, Minnesota;1959.
4. Alloway BJ. Zinc in soils and crop nutrition. Brussels, Belgium: Online book published by the International Zinc Association; 2008.
5. Arunachalam P, Kannan P, Prabukumar G, Govindaraj, M. Zinc deficiency in Indian soils with special focus to enrich zinc in peanut. African Journal of Agriculture Research. 2013;8(50):6681-6688.
6. Arvind KS, Sanjib KB, Satyanarayana T, Majumdar K. Importance of micronutrients in Indian agriculture. Better Crops -South Asia. 2019;1-10.
7. Asghari HR, Cavagnaro TR. Arbuscular mycorrhizas enhance plant interception of leached nutrients. Funct Plant Biol. 2011;38:219–226.
8. Astaneh N, Bazrafshan F, Zare M, Amiri B, Bahrani A. Nano-fertilizer prevents environmental pollution and improves physiological traits of wheat grown under drought stress conditions. 2021;12:005.
9. Auld DS. 2001. Zinc coordination sphere in biochemical zinc sites. Biometals. 2001;14:271-313.
10. Barak P, Helmke PA. The chemistry of zinc. In: Robson AD, editor. Zinc in soils and plants. Dordrecht: Kluwer Academic Publishers. 1993:90–106.
11. Ben-Moshe T, Frenk S, Dror I, Minz D, Berkowitz B. Effects of metal oxide nanoparticles on soil properties. Chemosphere. 2013;90:640–646.
12. Brown, WL, Bressani R, Glover DV, Hallauer AR, Johnson VA, Qualset CO. Quality-protein maize: report of an ad hoc panel of the advisory committee on technology innovation, Board on Science and Technology for International Development, National Research Council, in cooperation with the Board on Agriculture, National Research Council. Washington, D.C.: National Academy Press; 1988.
13. Cakmak, I. Enrichment of cereal grains with zinc: Agronomic or genetic biofortification. Plant Soil. 2008;302:1-17.
14. Casida IE, Klein DA, Santore T. Measurement of dehydrogenase activity by incubating the soil with TTC method. Soil Science. 1964;98:373.
15. Conant RT, Berdanier AB, Grace PR. Patterns and trends in nitrogen use and nitrogen recovery efficiency in world agriculture. Glob Biogeochem Cycles. 2013;27:558–566.
16. Crawford NM, Forde BG. Molecular, and developmental biology of inorganic nitrogen nutrition. Arabidopsis Book; 2002.
17. Eichler B, Caus M, Schnug E, Köppen D. Soil acid and alkaline phosphatase activities in regulation to crop species and fungal treatment. Landbauforschung Völkenrode. 2004;54(1):1-5.
18. FAI. Fertiliser Statistics. The Fertiliser Association of India, New Delhi;2020.
19. FAO. World Fertilizer Trends and Outlook to 2018; Food and Agriculture Organization of the United Nations-Rome: Rome, Italy; 2015.
20. FAOSTAT. Food and Agriculture Organization Corporate Statistical Database, FAO, Rome, Italy;2021.
21. Frenk S, Ben-Moshe T, Dror I, Berkowitz B, Minz D. (2013) Effect of metal oxide nanoparticles on microbial community structure and function in two different soil types. PLoS One. 2013;8:e84441.

22. Geisseler D, and Scow K.M. Long-term effects of mineral fertilizers on soil microorganisms – A review. Soil Biol Biochem. 2014;(75):54–63.
23. Guo JH, Liu XJ, Zhang Y, Shen JL, Han WX, Zhang WF. Significant acidification in major Chinese croplands. Science, 2010;327:1008–1010.
24. Guo H, White JC, Wang Z, Xing B. Nano-enabled fertilizers to control the release and use efficiency of nutrients. Curr Opin Environ Sci Health. 2018;6:77–83.
25. Hoang VN, Alauddin M. Assessing the eco-environmental performance of agricultural production in OECD countries: The use of nitrogen flows and balance. Nutr Cycl Agroecosyst.2010;87:353–368.
26. Humphreys E, Kukal SS, Christen EW, Hira GS, Singh B, Yadav S, Sharma RK. Halting the ground water decline in North-West India – which technologies will be winners? Advances in Agronomy, 2010;109:155–217.
27. Jassim RA, Jabar AK, Fzaa AK. 2019. Evaluation of foliar application with nano fertilizer (super micro plus) in different times on availability and uptake of some micronutrients and some quality properties of rice (*Oriza sativa* L.). Plant Archives. 2019;19(1):1434-1438.
28. Jacoby R, Peukert M, Succurro A, Koprivova A, Kopriva S. The Role of Soil Microorganisms in Plant Mineral Nutrition-Current Knowledge and Future Directions. Front Plant Sci. 2017;8(19):1617.
29. Jośko I, Oleszczuk P, Dobrzyoska J, Futa B, Joniec J, Dobrowolski R. Long-term effect of ZnO and CuO nanoparticles on soil microbial community in different types of soil. Geoderma. 2019;352:204-212.
30. Ju X, Lu X, Gao Z, Chen X, Su F, Kogge M. 2011. Processes and factors controlling N_2O production in an intensively managed low carbon calcareous soil under sub-humid monsoon conditions. Environ Pollut. 2011;159:1007–1016.
31. Kaya C, Higgs D. Response of tomato (*Lycopercsicon esculentum* L.) culture at low zinc. Scientific Horticulture. 2002;93:53-64.
32. Kalwani M, Chakdar H, Srivastava A, Pabbi S, Shukla P. Effects of nanofertilizers on soil and plant-associated microbial communities: Emerging trends and perspectives. Chemosphere. 2022;287:132107.
33. Kumar S, Chaudhuri S. Maiti SK. Soil Phosphatase Activity in Natural and Mined Soil – A Review. Ecology and Environment. 2011;31(11):1-11.
34. Ladha JK, Kumar V, Alam MM, Sharma S, Gathala MK, Chandna P, Saharawat YS. Balasubramanian V. Integrating crop and resource management technologies for enhanced productivity, profitability and sustainability of the rice–wheat system in South Asia. (In) Integrated Crop and Resource Management in the Rice–Wheat System of South Asia. Ladha J.K. et al. (Eds.). IRRI, Los Banos, Philippines. 2009:69–108.
35. Li H, Shan C, Zhang Y, Cai J, Zhang W, Pan B. Arsenate adsorption by hydrous ferric oxide nanoparticles embedded in cross-linked anion exchanger: Effect of the host pore structure. ACS Appl Mater Interfaces. 2016;8:3012–3020.
36. Li J, Wee C, Sohn B. Effect of ammonium- and potassium loaded zeolite on Kale (*Brassica alboglabra*) growth and soil property. American Journal of Plant Sciences. 2013;4:1976-1982.
37. Liao H, Liao H, Zhang Y, Zuo Q, Du B, Chen W, Wei D, Huang Q. Contrasting responses of bacterial and fungal communities to aggregate-size fractions and long-term fertilizations in soils of northeastern. China Sci Total Env. 2018;635:784–792.
38. Lindsay WL, Norvell WA. Development of DTPA soil test for zinc, iron, manganese and copper. Soil Science Society of America Journal. 1978;42:421-442.

39. Lutz W, Sanderson W, Scherbov S. The end of world population growth. Nature, 2001;412:543–5.
40. Meena RH, Jat G, Jain D. Impact of foliar application of different nano-fertilizers on soil microbial properties and yield of wheat. Journal of Environmental Biology. 2021;42: 302-308.
41. Merwin HD, Peech M. Exchange ability of soil potassium in the sand, silt and clay fractions as influenced by the nature and complementary exchangeable cations. Soil Science American Proceedings. 1951;15:125-128.
42. Mishra P, Singh, PP, Singh, SK, Verma H. Sustainable agriculture and benefits of organic farming to special emphasis on PGPR. Role of Plant Growth Promoting Microorganisms in Sustainable Agriculture and Nanotechnology. 2019:75-87.
43. Modolo LV, Da-Silva CJ, Brandão DS, Chaves IS. A mini review on what we have learned about urease inhibitors of agricultural interest since mid-2000s. J Adv Res. 2018;13:29–37.
44. Nibin PM, Ushakumari K, Ishrath PK. Organic nano NPK formulations on soil microbial and enzymatic activities on post harvest soil of Bhindi. International Journal of Current Microbiology and Applied Sciences. 2019;8:1819-1814.
45. Olsen SR, Cole CV, Frank SW, Dean LA. Estimation of available Phosphorus by extraction with sodium bicarbonate, United States Development of Agriculture Circular number. 1954;939.
46. Pandey N, Pathak GC, Sharma CP. Zinc is critically required for pollen function and fertilization in lentil. Journal of Trace Elements in Medicine and Biology. 2006;20:89-96.
47. Piper C, Piper CS. Soil and Plant Analysis. Inter Science Publishers, New York. 1960:128-136.
48. Rajonee AA, Nigar F, Ahmed S, Imamul Huq SM. Synthesis of nitrogen nano fertilizer and its efficacy. Canadian Journal of Pure and Applied Sciences. 2016;10:3913-3919.
49. Raliya R, Saharan V, Dimkpa C, Biswas, P. 2017. Nanofertilizer for precision and sustainable agriculture: current state and future perspectives. J Agric. Food Chem. 66 (26), 6487–6503.
50. Raliya R, Tarafdar JC. ZnO nanoparticle biosynthesis and its effect on phosphorous-mobilizing enzyme secretion and gum contents in clusterbean (*Cyamopsis tetragonoloba* L.) Agricultural Research. 2013;2(1):48-57.
51. Rani B, Nirali B, Bahu D. Effect of chemical and nano nitrogenous fertilizers on availability of major nutrients (N, P, K) in soil after harvest of the sorghum crop. Int J Chem Stu. 2019;7(4):2940-2942.
52. Richards LA. Diagnosis and improvement of saline- alkali soils. Agriculture Handbook No. 60, USDA, Washington;1954.
53. Sahar A El-Sayed, Awad A Algarni, Khaled AH Shaban. Effect of NPK nano-fertilizers and compost on soil fertility and root rot severity of soybean plants caused by *Rhizoctonia solani.* Plant Pathol J. 2020;19:140-150.
54. Sandhu KS, Singh N, Malhi NS. 2007. Some properties of corn grains and their flours I: Physicochemical, functional and chapati-making properties of flours. Food Chemistry. 2007;101:938–946.
55. Schröder JJ, Neeteson JJ, Withagen JCM, Noij IGAM. 1998. Effects of N application on agronomic and environmental parameters in silage maize production on sandy soils. Field Crop Res. 1998;58:55–67.
56. Seleiman MF, Almutairi KF, Alotaibi M, Shami A, Alhammad BA, Battaglia ML. Nano-Fertilization as an emerging fertilization technique: why can modern agriculture benefit from its use? Plants. 2021;10(1):2.
57. Sharifi R, Khoramdel R. Effects of Nano-zinc oxide and seed inoculation by plant growth promoting rhizobacteria (PGPR) on yield, yield components and grain filling period of soybean (*Glycine max* L). Iran J Field Crop Res. 2016;13(4):738–753.

58. Shoultswilson WA, Reinsch BC, Tsyusko OV, Bertsch PM, Lowry GV,Unrine JM. Role of particle size and soil type in toxicity ofsilver nanoparticles to earthworms. Soil Sci Soc Am J. 2011;75:365–377.
59. Simonin M, Cantarel Amélie AM, Crouzet A, Gervaix J, Martins Jean MF, Richaume A. Negative effects of copper oxide nanoparticles on carbon and nitrogen cycle microbial activities in contrasting agricultural soils and in presence of plants. Frontiers in Microbiology. 2018;9:03102.
60. Singh MV. Micronutrient deficiencies in crops and soils of India. Micronutrient Deficiencies in Global Crop Production. 2008;93-125.
61. Singh RA. Soil Physical Analysis. Kalyani Publisher, New Delhi. 1980:163.
62. Steel RGD, Torrie JH. Principles and procedures of statistics with special reference to the biological sciences, McGraw Hill, New York. 1960:187-287.
63. Subbiah BV, Asija GL 1956. A rapid procedure for determination of available nitrogen in soil. Current Science. 1956;25:259-260.
64. Subramanian KS, Tarafdar JC. Prospects of nanotechnology in Indian farming. Indian J Agric Sci. 2011;81:887–893.
65. Tabatabai M, Bremner J. Use of p-Nitrophenyl Phosphate for Assay of Soil Phosphatase Activity. Soil Biology and Biochemistry. 1969;1:301-307.
66. Tao R, Wakelin SA, Liang Y, Chu G. Response of ammonia-oxidizing archaea and bacteria in calcareous soil to mineral and organic fertilizer application and their relative contribution to nitrification. Soil Biol Biochem. 2017;114:20–30.
67. Tarafdar JC, Raliya R, Mahawar H. Development of zinc nanofertilizer to enhance crop production in Pearl Millet (*Pennisetum americanum*). Agricultural Research. 2014;3(3):1-6.
68. Thirunavukkarasu M, Subramanian KS. Synthesis and characterization of surface modified nano-zeolite fortified with sulphate and its sulfate sorption and desorption pattern. Journal of Scientific and Industrial Research . 2015;74(12):671–675.
69. Tilman D. Global environmental impacts of agricultural expansion: The need for sustainable and efficient practices. Proc. Natl. Acad. Sci. USA. 1999;96:5995–6000.
70. Tondey M, Kalia A, Singh A, Singh Dheri G, Taggar MS, Nepovimova E, Krejcar O. Kuca K. Seed priming and coating by nano-scale zinc oxide particles improved vegetative growth, yield and quality of fodder Maize (*Zea mays* L.). Agronomy. 2021;11:2-16.
71. USDA (United States Department of Agriculture). World agricultural production: world wheat area down, corn steady, soy up. Foreign Agricultural Service/USDA Office of Global Analysis. 2009:1–7.
72. Vaishnavee T, Dagade-Gadale S, Kalyankar V, Waghmode S. Interaction between Nanoparticles and Soil Microflora. Research & Reviews in Biotechnology and Biosciences. 2021;8(1):140-147.
73. Vande Voort AR, Arai Y. 2019. The role of nanotechnology in the fortification of plant nutrients and improvement of crop production. Applied Sciences. 2019:9:499.
74. Verma H, and Kapoor A. Agronanotechnology: an agricultural paradigm. 2020;1-24.
75. Walkley AJ, Black IA. 1934. Estimation of soil organic carbon by chromic acid titration method. Soil Science. 1934;37:29-38.
76. Watts DB, Torbert HA, Feng Y, Prior SA. Soil microbial community dynamics as influenced by composted dairy manure, soil properties, and landscape position. Soil Science. 2010;175:474–486.

77. Wolinska A, Stepniewska Z. Dehydrogenase activity in the soil environment. In: Canuto R.A. (ed.): Dehydrogenases. Intech, Rijeka. 2012. Available at http://www.ebook3000.com/
78. Xu L, Yi M, Yi H, Guo E, Zhang A. Manure and mineral fertilization change enzyme activity and bacterial community in millet rhizosphere soils. World J Microbiol Biotechnol. 2017;34:8.
79. You T, Liu D, Chen J, Yang Z, Dou R, Gao X, Wang L. Effects of metal oxide nanoparticles on soil enzyme activities and bacterial communities in two different soil types. J Soils Sediments. 2018;8(1):211–221.
80. Yruela I. 2009. Copper in plants: acquisition, transport and interactions. Functional Plant Biology. 2009;**36**:409-430.
81. Yusefi-Tanha E, Fallah S, Rostamnejadi A, Pokhrel LR. Zinc oxidenanoparticles (ZnONPs) as a novel nanofertilizer: influence on seed yield and antioxidant defense system in soil grown soybean (*Glycine max* cv. Kowsar). Sci Total Environ. 2020;738:140240.

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

Treatments		Available Nitrogen (kg ha^{-1})	Available Phosphorus (kg ha^{-1})	Available Potassium (kg ha^{-1})
T_1	100% PK (Control)	266.01	22.33	364.81
T_2	100% PKZn	275.01	17.08	374.79
T_3	100% NPK	289.02	23.53	390.73
T_4	100% PKZn + Two sprays of Nano N	305.33	18.26	418.55
T_5	100% P K Zn + Two sprays of Nano N (2X)	306.66	18.26	419.89
T_6	100% NPK + Two sprays of Nano Zn	320.67	21.15	442.74
T_7	100% PK + Two sprays of Nano N + Nano Zn	309.78	21.11	425.20
T_8	100% RDF (NPKZn)	299.00	17.13	406.48
T_9	100% PKZn + 50% N + Two sprays of Nano N	324.67	19.36	447.81
T_{10}	100% NPK + 50% Zn + Two sprays of Nano Zn	336.33	19.91	462.53
T_{11}	100% PK + 50% NZn + Two sprays of Nano N + Nano Zn	349.44	19.84	481.23
T_{12}	100% PK + 50% NZn + Two sprays of Nano N + Nano Zn + Nano Cu	350.29	19.82	482.58
S Em±		3.61	0.36	4.28
CD (P= .05)		10.59	1.08	12.57

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

Treatments		Available Micronutrients (mg kg $^{-1}$)	
		Zn	Cu
T_1	100% PK (Control)	2.04	1.63
T_2	100% PKZn	2.18	1.65
T_3	100% NPK	2.10	1.70
T_4	100% PKZn + Two sprays of Nano N	2.38	1.76
T_5	100% P K Zn + Two sprays of Nano N (2X)	2.39	1.77
T_6	100% NPK + Two sprays of Nano Zn	2.61	1.85
T_7	100% PK + Two sprays of Nano N + Nano Zn	2.40	1.80
T_8	100% RDF (NPK Zn)	2.36	1.71
T_9	100% PKZn + 50% N + Two sprays of Nano N	2.67	1.89
T_{10}	100% NPK + 50% Zn + Two sprays of Nano Zn	2.88	1.92
T_{11}	100% PK + 50% NZn + Two sprays of Nano N + Nano Zn	3.21	1.95
T_{12}	100% PK + 50% NZn + Two sprays of Nano N + Nano Zn + Nano Cu	3.27	2.12
S Em±		0.04	0.03
CD (P= .05)		0.13	0.10

Table 4: Effect of foliar application of nano fertilizers on soil microbial population, dehydrogenase and acid phosphatase enzyme activity after harvest of maize

Treatments		Microbial Population (cfu g^{-1} of soil)			Dehydrogenase (µg TPF g^{-1} 24 h^{-1} soil)	Acid Phosphatase (µg of PNP g^{-1} h^{-1}soil)
		Bacteria (1 x 10^7)	Fungi (1 x 10^5)	Actinomycetes (1 x 10^6)		
T_1	100% PK (Control)	54.34	22.17	20.77	10.20	42.10
T2	100% PKZn	54.84	22.22	20.80	10.30	42.13
T3	100% NPK	57.17	23.73	21.61	10.79	43.96
T_4	100% PKZn + Two sprays of Nano N	60.87	26.02	23.18	11.52	44.68
T_5	100% PKZn + Two sprays of Nano N (2X)	60.88	26.05	23.19	11.55	44.69
T_6	100% NPK + Two sprays of Nano Zn	63.22	27.65	24.67	12.42	46.05
T_7	100% PK + Two sprays of Nano N + Nano Zn	61.62	26.15	23.78	11.84	44.62
T_8	100% RDF (NPK Zn)	58.77	25.44	22.56	10.94	43.99
T_9	100% PKZn + 50% N + Two sprays of Nano N	63.25	27.81	24.85	12.72	46.53
T_{10}	100% NPK + 50% Zn + Two sprays of Nano Zn	65.06	29.29	25.81	12.93	46.98
T_{11}	100% PK + 50% NZn + Two sprays of Nano N+Nano Zn	67.14	31.26	27.71	13.46	48.68
T_{12}	100% PK+50% NZn+Two sprays of Nano N+Nano Zn + Nano Cu	67.17	31.27	27.72	13.48	48.72
S Em±		0.53	0.45	0.31	0.16	0.46
CD (P= .05)		1.57	1.33	0.92	0.48	1.35

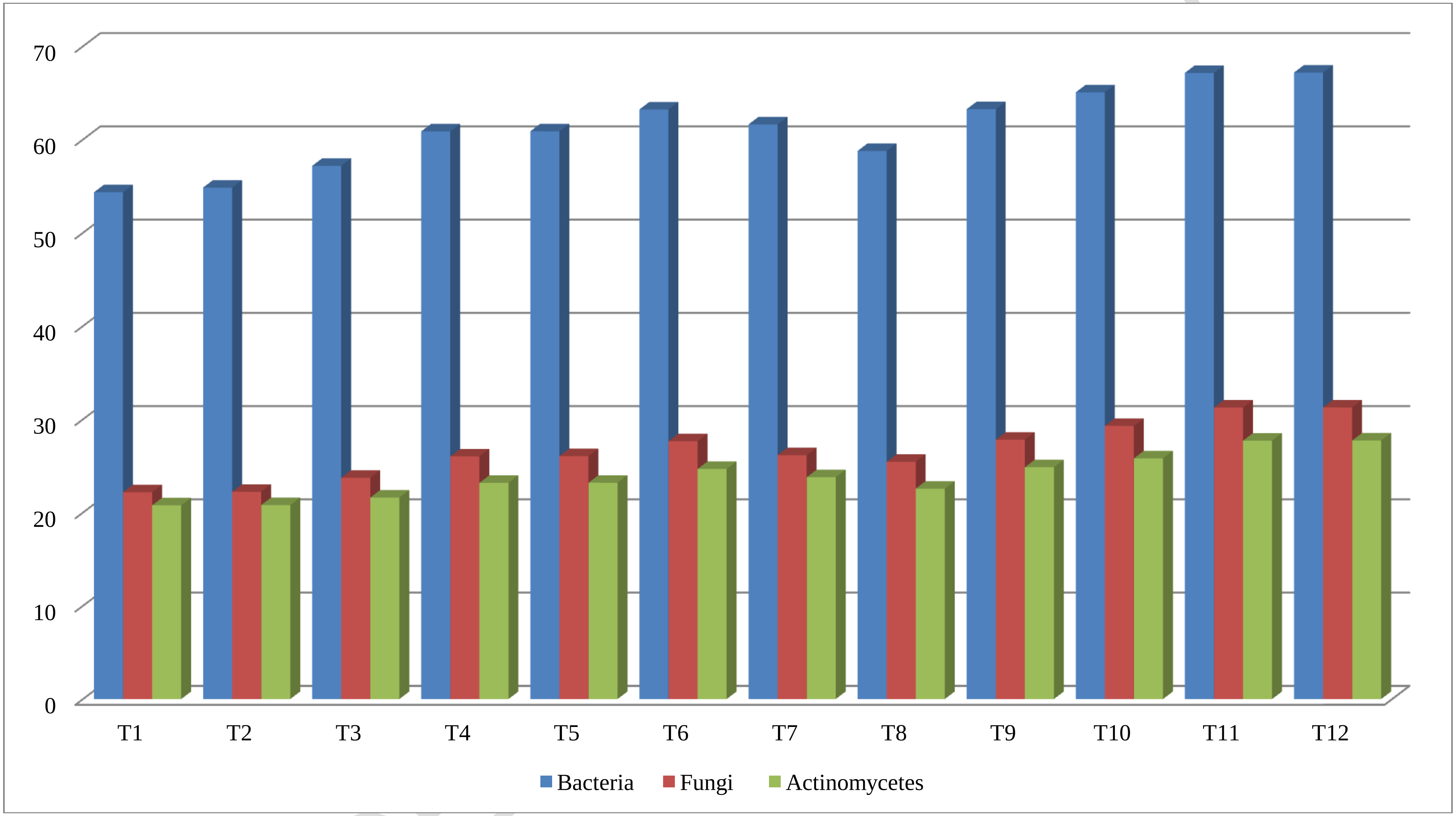

Fig. 1: Effect of foliar application of nano fertilizers on microbial population in soil after harvest of soil