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RESPONSE OF GROUNDNUT TO FOLIAR APPLICATION OF NANO ZNO AND NANO CAO ON BIO-CHEMICAL PARAMETERS, SOIL CHEMICAL PROPERTIES AND AVAILABLE NUTRIENTS STATUS

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ABSTRACT

A field experiment was conducted during *kharif* 2023-24 on groundnut in *vertisol* at AICRP on Groundnut, MARS, UAS, Dharwad to assess the effect of nano ZnO and nano CaO on bio-chemical parameters of groundnut and soil nutrient status. The experiment was laid out in randomized block design with twelve treatments with three replications which includes foliar spray of nano ZnO, nano CaO at different doses and at different days after sowing by using GPBD-4 genotype. The study revealed that, treatment T_4: T_1 + nano zinc oxide @ 2 g 10 l^{-1} of water (Foliar spray at 25 and 45 DAS) recorded higher zinc content in leaf (36.02 ppm) and kernel (34.64 ppm) and it also recorded higher SPAD values at 60 and 90 DAS, treatment T_6: T_1 + nano calcium oxide @ 2 g 10 l^{-1} of water (Foliar spray at 30 and 60 DAS) recorded higher calcium content in leaf (1.99 %) and in kernel (1.89 %). The lower zinc content of leaf (23.56 ppm) and kernel (21.33 ppm) and lower calcium content (1.32 %) in leaf (1.32 %) and kernel (1.21 %) was recorded in treatment T_1: RDF (only NPK) (18:46:25 kg N: P_2O_5:K_2O ha^{-1}). After harvest higher available nitrogen (295.06 kg ha^{-1}), phosphorous (54.08 kg ha^{-1}), potassium (325.20 kg ha^{-1}), zinc (0.67 mg kg^{-1}) and exchangeable calcium (18.0 meq 100 g^{-1} of soil) was recorded under the treatment T12: RPP (FYM @ 7.5 t ha^{-1} + 18:46:25 kg N: P_2O_5:K_2O ha^{-1}+ 25 kg $FeSO_4$ + 25 kg $ZnSO_4$ + 500 kg Gypsum ha^{-1}).

***Keywords* :** Groundnut, nano ZnO, nano CaO, Foliar spray, Available nutrient status.

Introduction

Groundnut (*Arachis hypogea* L.), often referred as the “king of oilseeds’’, is a self-pollinating, vital edible oilseed crop known as the wonder nut and poor man’s cashewnut. It holds great importance as both staple food and a cash crop in India, serving as a rich source of several vitamins, nutrients, contain 25 to 30 per cent digestible protein, 45 to 50 per cent oil, 20 per cent carbohydrates and 5 per cent fiber and ash. In India groundnut contribute about 37 per cent of total oilseed production; however, the crop’s productivity falls significantly short of its potential yield. It is an important oilseed crop of India which is cultivated in nearly 5.7 m ha area with production of 10.24 mt and productivity of 17.77 q ha^{-1} (Anonymous 2022). Though India ranks first in the world under groundnut area, there is a need to import 84 per cent of edible oil. This is due to lower productivity.

Zinc is crucial for plants playing a vital role in various metabolic processes. It is essential for synthesizing proteins and carbohydrates and contributes to the growth of stems and roots (Kabata and Pendias, 1999). Additionally, zinc serves a significant function in protecting cells against oxidative stress, acting as a defence against various forms of oxidation such as those affecting membrane lipids, proteins, chlorophyll, enzymes containing sulfhydryl groups and DNA (Cakmak, 2000). Furthermore, zinc is necessary for pollen function, fertilization and germination (Kaya and Higgs, 2002; Pandey *et al*., 2006; Cakmak, 2008). Calcium, classified as a secondary nutrient is indispensable for the cultivation of groundnut. Groundnut plants need calcium from the emergence of pegs through fruit formation until pod maturation. A deficiency in calcium results in a notable increase in the proportion of undeveloped seeds (empty pods), inadequately filled pods and various issues such as aborted or shrivelled fruits, darkened plumules and the formation of seedless pods (Kabir *et al*., 2013). When it comes to groundnut plants, their roots may encounter difficulty in absorbing adequate amounts of essential nutrients like zinc and calcium. This challenge can arise due to a range of factors including soil quality issues, nutrient fixation in the soil, leaching of 3 nutrients, cold soil temperatures, inadequate soil moisture, root damage and overall nutrient deficiencies. In such situations, employing foliar fertilization can prove advantageous for promoting optimal growth and development.

Nanotechnology presents a promising new avenue for agricultural applications, offering precise detection and delivery of nutrients and pesticides to enhance productivity while maintaining environmental safety and improving resource efficiency. This technology can be integrated into various stages of the agricultural production process, as highlighted by Tarafdar *et al*. (2012). Nanotechnology has made it possible to utilize nanostructured materials at the nanoscale as carriers for fertilizers or controlled-release agents, leading to the development of "smart fertilizers". This innovation offers a novel approach to improving nutrient utilization efficiency and lowering the expenses associated with environmental conservation, as discussed by Chinnamuthu and Boopathi (2009). Zinc and calcium content in groundnut is very important as these nutrients are essential for growth and production. By considering these facts, this study aims to know the effect of foliar applications of nano ZnO and nano CaO on the biochemical parameters of groundnut and also to know the effect on soil fertility status.

Material and Methods

A field experiment was conducted to study the effect of foliar applications of nano ZnO and nano CaO on the biochemical parameters of groundnut and the soil fertility status at Main Agricultural Research Station, University of Agricultural Sciences, Dharwad during 2023-24. It is located at 15^0 26' North latitude, 75^0 07' East longitude and 678 m above mean sea level (MSL). The soil type of the experimental site was *Vertisol*. The soil had a normal electrical conductivity (EC) of 0.17 dS m^{-1} and was somewhat alkaline in reaction (8.20) with medium organic carbon content of 0.50 %. The soil had a low available nitrogen content (270.8 kg ha^{-1}), medium phosphorus content (41.4 kg ha^{-1}), medium available potassium content (310.2 kg ha^{-1}), sufficient zinc content (0.65 mg kg^{-1}) and sufficient exchangeable calcium content (17.2 meq 100 g^{-1} of soil). The groundnut variety used for the study was GPBD-4 during *kharif* 2023. The seed rate was 150 kg per hectare with spacing of 30 x10 cm. The crop was provided with basal application of $N:P_2O_5:K_2O$ @ 18:46:25 kg ha^{-1}. The fertilizers used were urea, SSP ana MOP. The mean annual rainfall during the experimental year from January 2023 to December 2023 was 507.0 mm. The rainfall received during the crop growth period (July to November) was 377.0 mm. As the rainfall received the cropping period is not sufficient for normal growth and development of groundnut hence irrigation was provided at flowering and pegging stage of groundnut which favoured the normal growth of the plant.

The experiment was laid out in randomized block design with twelve treatments replicated three times. Treatments comprised of, T_1- RDF (only NPK) (18:45:25 kg $N:P_2O_5:K_2O$ ha^{-1}), T_2- T_1 + Zinc sulphate @ 2 g l^{-1} of water (Foliar spray at 25 and 45 DAS), T_3- T_1 + Nano zinc oxide @ 2 g 15 l^{-1} of water (Foliar spray at 25 and 45 DAS), T_4- T_1 + Nano zinc oxide @ 2 g 10 l^{-1} of water (Foliar spray at 25 and 45 DAS), T_5- T_1 + Nano calcium oxide @ 2 g 15 l^{-1} of water (Foliar spray at 30 and 60 DAS), T_6- T_1 + Nano calcium oxide @ 2 g 10 l^{-1} of water (Foliar spray at 30 and 60 DAS), T_7- T_1 + Gypsum @ 500 kg ha^{-1} (Soil application at pegging stage), T_8- T_1 + Nano zinc oxide @ 2 g 15 l^{-1} of water (Foliar spray at 40 and 60 DAS), T_9- T_1 + Nano zinc oxide @ 2 g 10 l^{-1} of water (Foliar spray at 40 and 60 DAS), T_{10}- T_1 + Nano calcium oxide @ 2 g 15 l^{-1} of water (Foliar spray at 40 and 60 DAS), T_{11}- T_1 + Nano calcium oxide @ 2 g 10 l^{-1} of water (Foliar spray at 40 and 60 DAS) and T_{12}- RPP (FYM @ 7.5 t ha-1 + 18:45:25 kg $N:P_2O_5:K_2O$ ha^{-1}+ 25 kg $FeSO_4$ + 25 kg $ZnSO_4$ + 500 kg Gypsum ha^{-1}).

SPAD values were measured by using SPAD meter. It is a hand-held device that is widely used for the rapid, accurate and non-destructive measurement of leaf chlorophyll concentration. The second leaf from terminal bud of the main stem of each plant was measured. At harvest the leaf samples, kernels, soil samples were collected and analysed zinc, calcium content and soil nutrients status.

Zinc content in groundnut leaf and kernels were estimated by di-acid method. Estimation of zinc content in the groundnut leaf and kernels was done by Atomic Absorption Spectroscopy to know the association of zinc in the leaf and kernel with nutritional quality and other productivity traits. This estimation is performed by the following procedure: Digestion of plant samples with di-acid mixture Powdered plant sample of 0.5 g was pre-digested with concentrated Nitric acid overnight and then digested with a di-acid mixture containing HNO3 and HClO4 in the 36 proportion of 9:4 till a snow-white residue was obtained (Piper, 1966). The volume of the digest was made to 100 ml with distilled water, stored and used for total element analysis. Micronutrient (Zn) concentration in the di-acid extract of the sample was determined using atomic absorption spectrophotometer (AAS). Calcium content (%) in groundnut leaf and kernel. Estimation of Ca percent in the groundnut leaf and kernel was done by titration against 0.01 N EDTA after it's extraction to know the association of calcium in leaf and kernel with nutritional quality and other productivity traits. The above digest was used in calcium estimation.

Soil samples were analyzed in the laboratory for soil pH, electrical conductivity (EC), soil organic carbon (SOC), available nitrogen (N), phosphorus (P_2O_5), potassium (K_2O), zinc and calcium following standard procedures. Soil pH was measured by potentiometric method, electrical conductivity (EC) was measured by conductometric method, soil organic carbon (SOC) was measured by Walkley and Black's wet oxidation method (Sparks, 1996), available N was measured by modified alkaline permanganate oxidation method (Sharawat and Burford, 1982), available P_2O_5 was determined following the Olsen's method, available K_2O was determined using NH_4OAC extraction method and available zinc was estimated by atomic absorption spectrophotometer as described by Lindsay and Norvell (1978). The exchangeable calcium was estimated by using the titration method. The data recorded was analysed statistically by following the analysis of variance for randomized block design as suggested by Gomez and Gomez (1984). Statistical significance was tested with 'F' test at 5 per cent level of probability and compared the treatment means with critical difference. Means followed by the same alphabet (s) in a column do not differ significantly by DMRT (P=0.05).

Results and Discussion

SPAD values

The data prevailing to SPAD values of groundnut as affected by foliar application of nano fertilizers was presented in the figure 1, 2 and 3. At 30 DAS, treatment T_{12}: RPP (FYM @ 7.5 t ha^{-1} + 18:45:25 kg N:P_2O_5:K_2O ha^{-1} + 25 kg $FeSO_4$ + 25 kg $ZnSO_4$ + 500 kg Gypsum ha^{-1}) recorded significantly higher SPAD value (43.10) compared to T_1: RDF (only NPK) (18:46:25 kg N:P_2O_5:K_2O ha^{-1}). Among the different foliar application of fertilizer treatments, no significant difference is observed in other treatments. At 60 DAS, SPAD value differed significantly due to foliar application of nanoparticles. Maximum SPAD value (46.98) was recorded in treatment T_4: T_1 + nano zinc oxide at 2 g 10 l^{-1} of water (Foliar spray @ 25 and 45 DAS) compared to T_1 treatment and which was on par with Treatment T_{12}: RPP (FYM @ 7.5 t ha^{-1} + 18:46:25 kg N:P_2O_5:K_2O ha^{-1} + 25 kg $FeSO_4$ + 25 kg $ZnSO_4$ + 500 kg Gypsum ha^{-1}) (45.41). At 90 DAS, treatment T_4: T_1 + nano zinc oxide @ 2 g 10 l^{-1} of water (Foliar spray at 25 and 45 DAS) recorded maximum SPAD value (45.45) compared to treatment T_1: RDF (only NPK) (18:46:25 kg N:P_2O_5:K_2O ha^{-1}) and which was on par with treatment T_6: T_1 + nano calcium oxide @ 2 g 10 l^{-1} of water (Foliar spray at 30 and 60 DAS) (45.22) and T_{12}: RPP (FYM @ 7.5 t ha^{-1} + 18:46:25 kg N:P_2O_5:K_2O ha^{-1} + 25 kg $FeSO_4$ + 25 kg $ZnSO_4$ + 500 kg Gypsum ha^{-1}) (43.60). The lower SPAD value (38.67) was observed in treatment T_1: RDF (only NPK) (18:46:25 kg N:P_2O_5:K_2O ha^{-1}).

Zinc is associated with enzyme activation, structural and catalytic components of proteins. As a co-factor for normal development of pigment biosynthesis its deficiency disrupts the chlorophyll synthesis. The mechanism at the back of increased chlorophyll content is the role of Zn as the important nutrient for the plant. Zn plays important role on plant metabolism via changing the action of vital enzymes, such as carbonic anhydrase. In the present study, carbonic anhydrase activity was also increased by foliar application of nano ZnO. It is in agreement of the other studies where ZnO-NPs application enhanced chlorophyll content These findings were in accordance with Mahmood *et al*. (2017), Mukherjee *et al*. (2016), Raliya and Tarafdar (2013) and Prasad *et al*. 2012).

Calcium plays a crucial role in maintaining photosynthesis by regulating the expression of genes involved in chlorophyll synthesis in leaves. The improved photosynthetic efficiency observed with nanoparticles may also be attributed to the up-regulation of essential photosynthetic enzymes, including Rubisco and Rubisco activating enzyme. These findings were in accordance with Mazhar *et al*. (2023), Gao *et al*. (2023) and Mohsen *et al*. (2017).

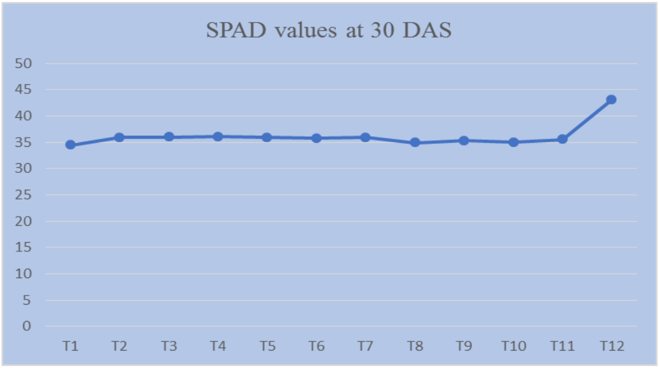

Fig. 1: SPAD values of groundnut at 30 DAS as influenced by nano ZnO and nano CaO

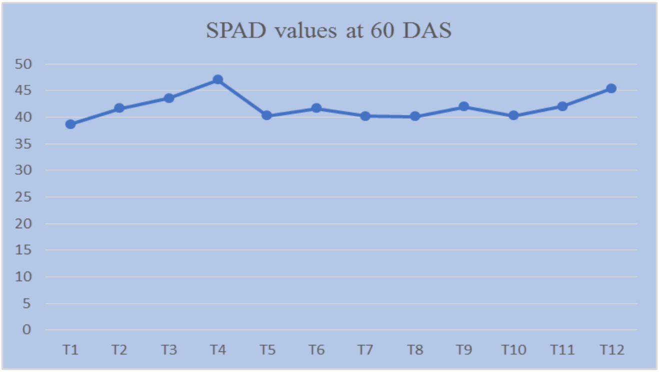

Fig. 2 : SPAD values of groundnut at 60 DAS as influenced by nano ZnO and nano CaO

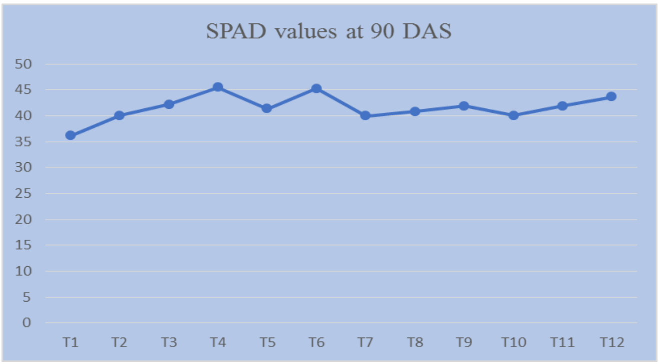

Fig. 3 : SPAD values of groundnut at 60 DAS as influenced by nano ZnO and nano CaO.

Zinc content in leaf and kernel

Notable differences in the zinc content of leaf and kernel among various treatments was depicted in figure 4 & 5. Among all the treatments, after the post-harvest leaf sample analysis, treatment T_4: T_1 + nano zinc oxide @ 2 g 10 l^{-1} of water (Foliar spray at 25 and 45 DAS) recorded higher zinc content in leaf (36.02 ppm) followed by the treatment T_3: T_1 + nano zinc oxide @ 2 g 15 l^{-1} of water (Foliar spray at 25 and 45 DAS) zinc content (32.67 ppm) of leaf. The lower zinc content of leaf (23.56 ppm) was recorded in treatment T_1: RDF (only NPK) (18:46:25 kg $N:P_2O_5:K_2O$ ha^{-1}). Among the different treatments, kernel sample analysis revealed that treatment T_4: T_1 + nano zinc oxide @ 2 g 10 l^{-1} of water (Foliar spray at 25 and 45 DAS) recorded higher zinc content in kernel (34.67 ppm) followed by the treatment T_3: T_1 + nano zinc oxide @ 2 g 15 l^{-1} of water (Foliar spray at 25 and 45 DAS) zinc content of kernel (30.60 ppm) The lower zinc content of kernel (21.33 ppm) was recorded in treatment T_1: RDF (only NPK) (18:46:25 kg $N:P_2O_5:K_2O$ ha^{-1}).

Foliar spray is more effective than soil application. Foliar zinc application significantly increased zinc concentration of groundnut indicating high mobility of zinc within plants. The total Zn content of groundnut leaf increased compared to the control, suggesting that ZnO nanoparticles penetrated plant cells, thereby enhancing the uptake of Zn^{2+} ions. Zinc acts as an activator of enzymes in plants and is directly involved in the biosynthesis of auxin, which promotes cell production and dry matter accumulation. This dry matter is subsequently stored in seeds as a sink, leading to a higher zinc content in kernels. The probable reason might be because of the high uptake and translocation efficiency of nano zinc oxide than bulk zinc form. These findings are in conformity with Venkataramana *et al*. (2022), Poornima and Koti (2019) and Prasad *et al*. (2012).

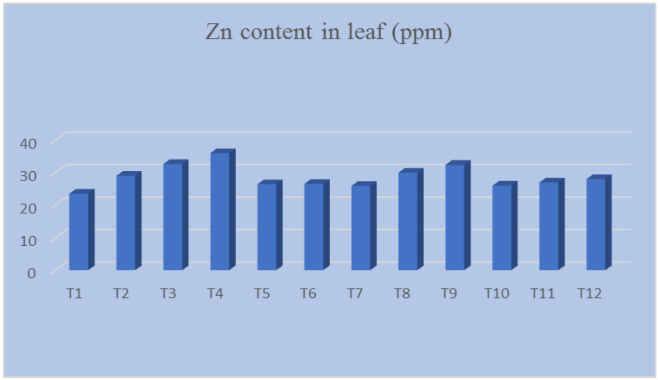

Fig. 4 : Zinc content (ppm) of groundnut leaf as influenced by nano ZnO and nano CaO

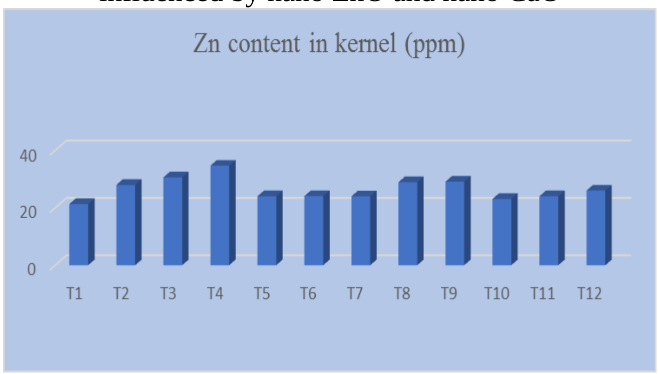

Fig. 5 : Zinc content (ppm) of groundnut leaf as influenced by nano ZnO and nano CaO

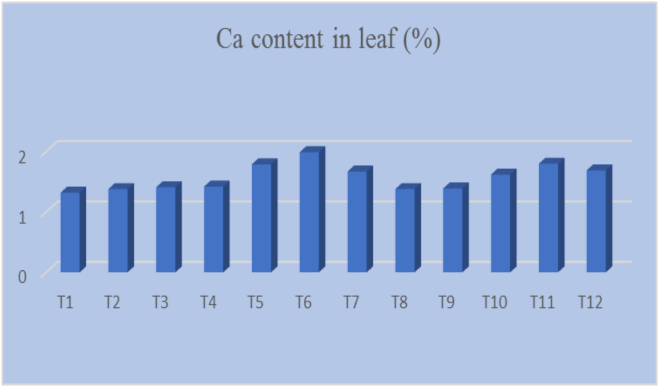

Fig. 6 : Ca content (%) of groundnut leaf as influenced by nano ZnO and nano CaO

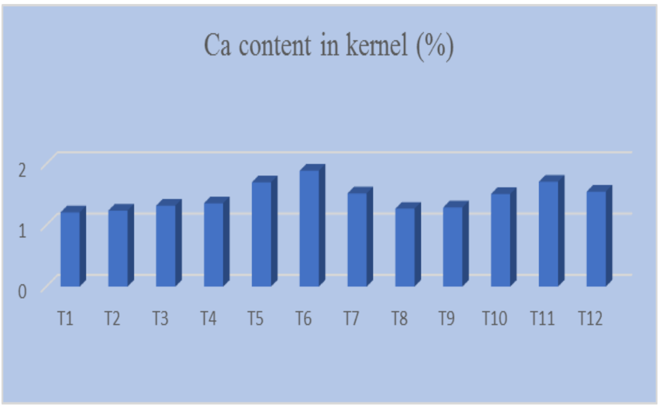

Fig. 7 : Ca content (%) of groundnut kernel as influenced by nano ZnO and nano CaO

Calcium content in leaf and kernel

The notable changes in calcium content of groundnut leaf and kernel was represented in Figure no. 6 & 7. Calcium content varied significantly among the treatments. Higher calcium content of leaf (1.99 %) was found in treatment T_6: T_1 + nano calcium oxide @ 2 g 10 l^{-1} of water (Foliar spray at 30 and 60 DAS) followed by T_5: T_1 + nano calcium oxide @ 2 g 15 l^{-1} of water (Foliar spray at 30 and 60 DAS) (1.79 %). The lower calcium content (1.32 %) in leaf was observed in treatment T_1: RDF (only NPK) (18:46:25 kg $N:P_2O_5:K_2O$ ha^{-1}). Higher calcium content (1.89 %) in kernel was found in treatment T_6: T_1 + nano calcium oxide @ 2 g 10 l^{-1} of water (Foliar spray at 30 and 60 DAS) followed by T_5: T_1 + nano calcium oxide @ 2 g 15 l^{-1} of water (Foliar spray at 30 and 60 DAS) (1.70 %). The lower calcium content (1.21 %) in kernel was observed in treatment T_1: RDF (only NPK) (18:46:25 kg $N:P_2O_5:K_2O$ ha^{-1}).

Nano forms of calcium proved to be more effective than chelated forms, resulting in greater nutrient acquisition in leaves following the application of foliar nano calcium oxide. These findings were in accordance with El-temsah *et al*. (2023), Kumara *et al*. (2017) and Liu *et al*. (2005). Nanoscale calcium oxide particles are transported through the phloem in groundnut plants more quickly than bulk calcium forms. This allows for more efficient movement of nutrients to specific plant parts, particularly the grains. These results are consistent with the findings of Kumara *et al*. (2017) and Deepa *et al*. (2015).

Chemical properties of soil and available soil nutrient status

Soil reaction (pH), Electrical conductivity (EC) and Organic carbon

The soil fertility status is presented in the Table 3. Regarding soil pH, EC and OC, there is no significant difference was observed among the different treatments after the harvest of the groundnut. These results are consistent with the findings of Uma (2019), Gnanesh (2018) and Chaitra (2015).

Available Nitrogen, Phosphorous and Potassium

At harvest higher available nitrogen (295.06 kg ha^{-1}), Phosphorous (54.08 kg ha^{-1}) and potassium (325.20 kg ha^{-1}) was recorded under the treatment T_{12}: RPP (FYM @ 7.5 t ha^{-1} + 18:46:25 kg $N:P_2O_5:K_2O$ ha^{-1} + 25 kg $FeSO_4$ + 25 kg $ZnSO_4$ + 500 kg Gypsum ha^{-1}). There was no significant differences in available nitrogen, Phosphorous and potassium observed in nanoparticles treatments because in all the treatments nutrients are applied through foliar spray. Nanoparticles did not remain in the soil for an extended period; instead, they dissolved and did not cause any significant alterations to the soil's chemical properties. The results were in conformity with the findings of Jayashree *et al.* (2023), Venkataramana *et al*. (2022), Mahmood *et al*. (2017) and Du *et al*. (2011).

Available Zinc and Exchangeable calcium

At harvest significantly higher available zinc (0.67 mg kg^{-1}) was recorded under the treatment T_{12}: RPP (FYM @ 7.5 t ha^{-1} + 18:46:25 kg $N:P_2O_5:K_2O$ ha^{-1} + 25 kg $FeSO_4$ + 25 kg $ZnSO_4$ + 500 kg Gypsum ha^{-1}) and higher exchangeable calcium (18.0 meq 100 g-1 of soil) was recorded under the treatment T_{12}: RPP (FYM @ 7.5 t ha^{-1} + 18:46:25 kg $N:P_2O_5:K_2O$ ha^{-1} + 25 kg $FeSO_4$ + 25 kg $ZnSO_4$ + 500 kg Gypsum ha^{-1}) followed by treatment T_7: T_1 + Gypsum @ 500 kg ha^{-1} (Soil application at pegging stage). There was no significant differences in available zinc and calcium observed in the remaining treatments as the nano particles are applied through foliar spray.

The results of the present experiment suggested that there was no significant change The observed in soil chemical properties amongst RDF and treatments with ZnO and CaO nanoparticles, after harvesting of the crop. Application of nanoscale zinc oxide and calcium oxide particles did not showed any influence on post-harvest nutrient concentration of soils because the nano particles were applied through foliar spray but not soil application and the nanoparticles dissolved in the soil quickly leaving no significant changes in soil nutrient concentration. These findings were in accordance with Jayashree *et al*. (2023), Venkataramana *et al*. (2022), Mahmood *et al*. (2017) and Du *et al*. (2011).

Table 1: Chemical properties and available nutrient status of the soil as influenced by foliar spray of nano ZnO and nano CaO

	pH	**EC (dSm^{-1})**	**Organic carbon (%)**	**Available Nitrogen ($kg\ ha^{-1}$)**	**Available Phosphorous ($kg\ ha^{-1}$)**	**Available potassium ($kg\ ha^{-1}$)**	**Available zinc (ppm 10 kg^{-1} soil)**	**Available Ca (meq/100 g of soil)**
T_1	8.12^a	0.15^a	0.44^a	281.10^b	45.02^b	312.01^b	0.61^b	15.9^b
T_2	8.08^a	0.16^a	0.46^a	284.63^b	46.03^b	314.24^b	0.62^b	16.1^b
T_3	8.06^a	0.18^a	0.47^a	284.37^b	48.02^b	313.90^b	0.62^b	16.2^b
T_4	8.07^a	0.16^a	0.48^a	285.50^b	48.87^b	312.26^b	0.63^b	16.2^b
T_5	8.04^a	0.15^a	0.47^a	284.67^b	47.01^b	314.63^b	0.61^b	16.3^b
T_6	8.06^a	0.17^a	0.48^a	283.30^b	46.03^b	315.51^b	0.62^b	16.6^b
T_7	8.01^a	0.18^a	0.48^a	285.91^b	48.03^b	313.24^b	0.63^b	17.8^a
T_8	8.05^a	0.16^a	0.47^a	282.40^b	47.28^b	311.92^b	0.62^b	16.2^b
T_9	8.03^a	0.16^a	0.46^a	280.52^b	46.04^b	315.02^b	0.63^b	16.2^b
T_{10}	8.06^a	0.18^a	0.47^a	284.90^b	48.45^b	312.91^b	0.61^b	16.4^b
T_{11}	8.08^a	0.17^a	0.48^a	283.98^b	47.52^b	314.12^b	0.62^b	16.6^b
T_{12}	8.10^a	0.18^a	0.51^a	295.06^a	54.08^a	325.20^a	0.67^a	18.0^a
S.Em $\pm$	0.17	0.014	0.03	2.27	1.25	1.89	0.01	0.35

Note: Values are Means followed by the same alphabet (s) in a column do not differ significantly by DMRT (P=0.05).

Conclusion

NPK + foliar spray of nano zinc oxide @ 2 g 10 l^{-1} of water at 25 and 45 DAS has increased the zinc content in groundnut leaf and kernel compared to RPP and NPK + foliar spray of nano calcium oxide @ 2 g 10 l^{-1} of water at 30 and 60 DAS has increased the calcium content in groundnut leaf and kernel compared to RPP. Foliar spray of nanoparticles has no effect on chemical properties of the soil.

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