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Effect of Nanoscale zinc oxide particles on post-harvest nutrient concentration of soils in Groundnut (*Arachis hypogaea* L.)

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Abstract
In the present experiment, application of Nanoscale zinc oxide particles on post-harvest nutrient concentration of soils has been reported. The zinc oxide nanoparticles (n-ZnO) used in the current study were majorly prepared especially for agriculture purpose by modified oxalate decomposition method. These n-ZnO particles were characterized by using transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), Dynamic light scattering (DLS) and X-ray diffraction analysis (XRD). Different sizes (mean size of 20, 25 and 30 nm) and concentrations (150, 200 and 400 ppm) of ZnO-nanoparticulates were applied (foliar spray) at 25 and 45 DAS to reveal their effects on groundnut crop in comparison to bulk $ZnSO_4$ and control. Recommended dose of N, P and K fertilizers are applied in all the treatments except in control. The results indicate that application of zinc nanoparticles did not influenced the macronutrients (N, P, and K) and micronutrient (Cu, Mn, Fe and Zn) concentration of soils even with the application of various sizes and concentrations.

Keywords: ZnO nanoparticles, synthesis, characterization, macronutrients, micronutrients

1. Introduction
The major factor that is shaping or changing modern agriculture is the improvement in agricultural technology. Among the innovative technologies currently, nanotechnology occupies a prominent role in transforming agriculture and food production. Nanotechnology includes designing and synthesis of materials whose size is less than 100 nm in at least one dimension. Nanotechnology plays a vital role in improving soil health, nutrient management, weed management, pest and disease control, through the new scientific approaches to increase production and productivity of crops. It helps to introduce new techniques through enabling slow and controlled release of fertilizers, efficient and targeted delivery of fertilizers coupled with enabling resistance, effective processing, storage and packing.
Nanoparticles have smaller particle sizes, higher specific surface area and an increased proportion of reactive surface atoms as compared to bulk particles (Wigginton *et al.*, 2007) [10]. Zinc nanoparticle is used in various agricultural experiments to understand its effect on growth, germination, and various other properties. Only limited studies have been reported on the promotory effects of nanoparticles on plants at low concentrations. This new area of research – application of nanoscale materials in agriculture as nutrients, is catching up in agricultural universities and ICAR institutes that will help to understand further processes of nanoscale fertilizer/nutrient transformations and availability in soil-cropping systems as well as their mechanisms of uptake, translocation and utilization in plants as well as in soils. Zinc nanoparticles are being used in various agricultural experiments by the researchers to understand its effect on growth, germination, and various other properties (Prasad *et al.*, 2012, Subbaiah *et al.*, 2016, Naseeruddin *et al.*, 2018 and Ramapuram *et al.*, 2018) [6, 8, 4,7] and reported encouraging results.

2. Materials and Methods
ZnO nanoparticles of mean size of 20, 25, 30 nm diameter were used in the study. Nanocrystalline zinc oxide has been prepared by using the oxalate decomposition technique. Zinc oxalate was prepared by mixing equimolar (0.2 M) solutions of zinc acetate and oxalic acid. The resultant precipitate was collected and rinsed extensively with double deionized water (DI-water) and dried in air. The oxalate was then ground and decomposed in air by placing it in a pre-heated furnace for 45 minutes at 500 °C.

The characterization of the samples was done by Dynamic Light Scattering analysis, Transmission Electron Microscopy. The TEM samples were prepared by drop casting the suspensions on carbon coated Cu grids.

The experiment was conducted at College farm, S. V. Agricultural College, Acharya N.G. Ranga Agricultural University, Tirupati during *Kharif*, 2018-19 with twelve treatments and three replications in RBD. The treatments were *viz.*, control *i.e.*, no application (T_1), Recommended Dose of Fertilizer RDF (T_2), RDF + Zinc sulphate @ 2000 ppm at 25 and 45 DAS (T_3), RDF + Nanoscale zinc oxide (20 nm) @ 400 ppm (T_4), RDF + Nanoscale zinc oxide (20 nm) @ 200 ppm (T_5), RDF + Nanoscale zinc oxide (20 nm) @ 150 ppm (T_6), RDF + Nanoscale zinc oxide (25 nm) @ 400 ppm (T_7), RDF + Nanoscale zinc oxide (25 nm) @ 200 ppm (T_8), RDF + Nanoscale zinc oxide (25 nm) @ 150 ppm (T_9), RDF + Nanoscale zinc oxide (30 nm) @ 400 ppm (T_{10}), RDF + Nanoscale zinc oxide (30 nm) @ 200 ppm (T_{11}) and RDF + Nanoscale zinc oxide (30 nm) @ 150 ppm (T_{12}). Laboratory analysis is done by following standard procedures given by Jackson, 1973 [3] and piper, 1966 [5].

3. Results and Discussion

The data on nutrient content (N, P, K, Cu, Fe, Mn and Zn) of soil after harvest of groundnut as influenced by the application of nano ZnO and bulk ZnO are presented in Table 1.

3.1 Nitrogen content (kg ha^{-1})

The soil nitrogen content in soil after harvest did not showed any significant difference between the treatments because in all the treatments micronutrients applied through foliar spray. Numerically higher content of N (282.9 kg ha^{-1}) was observed in observed in T_8 treatment n-ZnO of size (25 nm) @ 200 ppm and all treatments were on par with each other.

3.2 Phosphorus content (kg ha^{-1})

Numerically higher content of phosphorus content (45.50 kg ha^{-1}) was observed in T_6 treatment n-ZnO of size (20 nm) @ 150 ppm and all treatments are on par with each other.

3.3 Potassium content (kg ha^{-1})

The results revealed that there was no significant difference between the potassium concentrations in between the treatments. Numerically higher content of potassium content (198.8 kg ha^{-1}) was observed in T_2 treatment with 100 per cent RDF and all treatments are statistically similar.

3.4 Copper content (mg kg^{-1})

It has been observed that there was no significant difference between the treatments because all the treatments are foliar applied. Numerically higher content of Cu (1.57 mg kg^{-1}) was observed in T_5 treatment n-ZnO of size (20 nm) @ 200 ppm and all treatments are on par with each other.

3.5 Manganese content (mg kg^{-1})

No significant difference was observed between the treatments. Numerically higher content of Mn (26.94 mg kg^{-1}) was observed in T_1 treatment that is control with no application of fertilizers and all treatments are nonsignificant.

3.6 Iron content (mg kg^{-1})

The results proved that there was no significant difference between the treatments. Numerically higher content of Fe (10.59 mg kg^{-1}) was observed in T_1 treatment that is control and all treatments are on par with each other.

3.7 Zinc content (mg kg^{-1})

It has been observed that there was no significant difference between the treatments because all the n-ZnO treatments are foliar applied. Numerically higher content of Zn was observed in (16.91 mg kg^{-1}) was observed in T_9 treatment n-ZnO of size (25 nm) @ 150 ppm which is more than initial zinc content, indicating the translocation of zinc from the leaves to the soil through the plant body system and accumulating in the soils.

The results of the present experiment suggested that there was no significant change observed in soil chemical properties amongst control and treated with ZnO nanoparticles, after harvesting of the crop. Wang *et al*. (2010) [9] reported that ZnO nanoparticles and bulk particles have shown higher solubility in the soil environment. Similar findings were reported by Du *et al*. (2011) [1] on the effect of ZnO nanoparticles on wheat growth and suggested that ZnO nanoparticles were no longer retained in the soil for longer period of time and dissolved in the soil and they leave no significant changes in soil chemical properties. These results are in concordance with the findings of Fasil Mohmood *et al*. (2017) [2].

Table 1: Effect of nanoscale ZnO particles on concentration of macro and micronutrients in soil after harvest

Treatments	N (kg ha^{-1})	P (kg ha^{-1})	K (kg ha^{-1})	Cu (mg kg^{-1})	Mn (mg kg^{-1})	Fe (mg kg^{-1})	Zn (mg kg^{-1})
T_1: control	262^a	42.98^a	160.47^a	1.3^{ab}	26.94^a	10.59^a	15.53^a
T_2: RDF	261.5^a	33.28^a	198.80^a	1.08^{ab}	19.10^a	6.89^{ab}	13.78^a
T_3: RDF + $ZnSO_4$ @ 2000 ppm	282.3^a	35.59^a	197.03^a	1.07^{ab}	18.18^a	5.95^{ab}	11.89^a
T_4:RDF + Nano ZnO (20 nm) @ 400 ppm	276.3^a	41.58^a	183.13^a	0.89^b	14.55^a	6.73^{ab}	13.47^a
T_5: RDF + Nano ZnO (20 nm) @ 200 ppm	261.9^a	36.72^a	165.30^a	1.57^a	22.29^a	6.24^{ab}	12.47^a
T_6: RDF + Nano ZnO (20 nm) @ 150 ppm	258.4^a	45.50^a	173.50^a	1.12^{ab}	13.38^a	3.38^b	6.77^a
T_7: RDF + Nano ZnO (25 nm) @ 400 ppm	282^a	39.09^a	181.67^a	0.91^{ab}	16.8^a	5.06^b	10.14^a
T_8: RDF + Nano ZnO (25 nm) @ 200 ppm	282.9^a	39.43^a	181.97^a	1.04^{ab}	19.51^a	6.07^{ab}	12.15^a
T_9: RDF + Nano ZnO (25 nm) @ 150 ppm	273.9^a	33.87^a	192.77^a	1.22^{ab}	21.43^a	8.25^{ab}	16.51^a
T_{10}: RDF + Nano ZnO (30 nm) @ 400 ppm	272.7^a	34.75^a	172.07^a	1.23^{ab}	24.03^a	8.14^{ab}	16.27^a
T_{11}: RDF + Nano ZnO (30 nm) @ 200 ppm	272.1^a	39.07^a	153.33^a	1.26^{ab}	24.22^a	7.47^{ab}	14.93^a
T_{12}: RDF + Nano ZnO (30 nm) @ 150 ppm	275.7^a	37.56^a	196.03^a	1.28^{ab}	25.54^a	7.73^{ab}	15.46^a
SE(m)	8.59	4.5	15.9	0.196	4.08	1.58	3.17
CD	NS	NS	NS	NS	NS	NS	NS

*The mean values were separated by Duncan's Multiple Range Test (DMRT)

Conclusions

Application of nanoscale zinc oxide particles did not showed any influence on post-harvest nutrient concentration of soils because the n-ZnO 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.

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Competing interests

Authors declare that there is no competing interests exist.

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