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Unveiling the combined effect of nano fertilizers and conventional fertilizers on crop productivity, profitability, and soil well-being

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It is widely accepted that deficiency of macro (nitrogen) and micronutrients (zinc, copper etc.) affects the plant growth and development which cause a significant threat to crop production and food security. The Indian Farmers Fertilizer Cooperative (IFFCO) developed nano-urea (nano-N), nano-zinc (nano-Zn), and nano-copper (nano-Cu) liquid fertilizer formulations to enhance the crop yields, simultaneously addressing the nutrient deficiency, without causing toxicity. Therefore, this study was formulated to evaluate the effectiveness of nano-N (nano-urea), nano-Zn, and nano-Cu at varying N levels [0, 50, 75, and 100% of the recommended rates of nitrogen (RRN)] on maize-wheat and pearl millet-mustard systems during 2019–20 and 2020–21. The results exhibited that the application of nano-N + nano-Zn with 100% RRN exhibited significantly higher grain yields in maize (66.2–68.8%), wheat (62.6–61.9%), pearl millet (57.1–65.4%), and mustard (47.2–69.0%), respectively, over absolute control plots and combinations of three nano-fertilizers like nano-N + nano-Zn + nano-Cu applied plots. This was mainly attributed to the higher N and Zn uptake by the crops. However, 75% RRN with nano-N + nano-Zn also produced comparable yields. Thus, applying nano-N and nano-Zn via foliar applications, in conjunction with conventional urea, has the potential to reduce the required nitrogen fertilizer amount by up to 25%, while simultaneously maintaining equivalent yield levels. Similarly, 100% RRN and 75% RRN + nano-N + nano-Zn registered comparable profitability, soil mineral N, dehydrogenase activity (DHA), and soil microbial biomass carbon (SMBC), during both the study years. However, further research and field trials on nano fertilizers alone or in combination with conventional fertilizers are essential to fully unlock its benefits and ascertain its long-term effects which may offer a pathway to more efficient and eco-friendly crop nourishment.

KEYWORDS
energy efficiency, maize, mineral nitrogen, mustard, nano-urea, nano-Zn, pearl millet, wheat

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1. Introduction

Macro and micronutrient deficiency in crop and soil have risen significantly over the past few years in India as well as globally (Shukla et al., 2021). The major reason behind the upsurge these deficiencies are growing of high-yielding crop varieties (Shukla et al., 2018), increased cropping intensity (Behera et al., 2021), and decreased or no usage of organic manures (Shukla et al., 2021). With the increasing demand of food for growing population, a disproportionate reliance on the excessive use of chemical fertilizers, specifically nitrogen (N) (Wen et al., 2017; Upadhyay et al., 2022) in agricultural practices has been evident in the recent past. Due to the injudicious use of conventional chemical fertilizers, the environment is polluted in terms of deteriorating soil quality (Oenema et al., 2014; Krasilnikov et al., 2022), eutrophication (Liu et al., 2021), groundwater pollution (Norton et al., 2015; Ye et al., 2020), and air pollution (Kumar et al., 2021) as well as diminished soil macro and micronutrient-supplying capacity (Babu et al., 2022). The most deficient among the micronutrients in Indian conditions is Zn (Shukla and Behera, 2020). The lack of micronutrients in the soil reduces grain nutritional quality in addition to crop yield (Fageria et al., 2002; Phattarakul et al., 2012; Dapkekar et al., 2018; Shukla et al., 2021). Micronutrient insufficiency occurs when animals and humans consume food (obtained from crops) with low micronutrient concentrations (Shukla et al., 2021). Insufficient dietary intake of zinc (Zn), which poses a significant health issue (Kihara et al., 2020), remains a pressing concern, especially in the underdeveloped countries, affecting both crop production and human nutrition (Manzeke et al., 2019). However, the foliar application of novel nano fertilizers (macro and micronutrients) in crops can reduce the nutrient deficiency in plants and animals.

Improved crop yields and grain quality can be achieved by the use of nano-fertilizers (Hu and Xianyu, 2021) which are built on nano-scale (1–100 nm) substrates (Peters et al., 2014; Babu et al., 2022). Many people believe that the use of these novel nano-fertilizers (Bartolucci et al., 2022) could lead to a shift in the agricultural practices (Verma et al., 2022). The adoption of nano-fertilizer (Jha et al., 2023) could be a big step toward the objective of sustainable agriculture (Mahapatra et al., 2022) in India and around the world, through curtailing of fertilizer dosages (Kumar et al., 2021; Upadhyay et al., 2023) and reducing runoff, leaching, and emission of gas in the atmosphere (Manjunatha et al., 2016). Indian Farmers Fertiliser Cooperative (IFFCO) has developed and patented three nano-fertilizer formulations *viz.* nano-urea/nano-N (Indian patent application number 201921044499), nano-Zn (Indian patent application number 201921044497) and nano-Cu (Indian patent application number 201921044498). Many researchers have found that spraying crops with nano-urea improves the crop yield under the field conditions (Das et al., 2016; Manikandan and Subramanian, 2016; Raliya et al., 2017; Du et al., 2019; Rathore et al., 2019; Kumar et al., 2021; Upadhyay et al., 2023).

Concurrently, nanoparticles, such as urea hydroxyapatite nanohybrid (Kottegoda et al., 2017), nano potassium (Al-Juthery et al., 2019), Zn nanoparticles (Drostkar et al., 2016), nano zinc oxide (ZnO) (Du et al., 2019), nano-micronutrients (Fe, Mn, Zn, Cu, Mo, and B) (Kanjana, 2020), silver nano particles (Mosa et al., 2021), nano copper oxide (CuO) (Dimkpa et al., 2019) etc. have been found to increase the plant growth in agricultural crops (Ahmed et al., 2021). However, most of this research has only been conducted in the lab or in pots. Although nanoparticles have been shown to be highly toxic to many plant species (Chen et al., 2015; Khan et al., 2019), they also play an important role in reducing heavy metal stress (Noman et al., 2020; Zhou et al., 2020) and promoting plant development (Salam et al., 2022). Plants can easily absorb excessive amount of Cu^{2+} and Zn^{2+} (Dong et al., 2022), leading to a wide range of structural and cellular abnormalities (Rizvi and Khan, 2018). Therefore, non-toxic nano-fertilizers are required to enhance the grain nutrient content as well as the crop yields.

Among micronutrients, zinc (Zn) plays a role in improving photosynthesis (Arough et al., 2016; Cabot et al., 2019), chlorophyll content (Sakya et al., 2018), grain yield (Ibrahim et al., 2017; Mahmood et al., 2019), relative water content (Pavia et al., 2019), the body's antioxidant defense system (Olechnowicz et al., 2018), and disease resilience etc. Therefore, for efficient utilization of N, Zn, Cu etc. their nano formulation is urgently needed (Ali et al., 2019). Nano fertilizers are gaining significant popularity and recognition as one of the most valuable nanomaterials (Salam et al., 2022) due to their small size, unique shape, and intriguing physicochemical properties (Selim et al., 2020). Increasing crop yield while using less conventional fertilizer on the environment is possible with nano-enabled agriculture (Milani et al., 2012; Sabir et al., 2020). A detailed study exploring the impact of the application of nano fertilizers or their judicious integration with traditional fertilizers on growth, yield and economics of crops under field condition is lacking (Kah et al., 2018; Mullen, 2019; Hu and Xianyu, 2021). Keeping these facts in view, the present study was planned to investigate the positive effect of nano-urea (nano-N), nano-Zn and nano-Cu on crop productivity, uptake, soil nutrient and biological health status under maize-wheat and pearl millet-mustard systems.

2. Materials and methods

2.1. Site description

The field trials were conducted at the experimental farm of ICAR-Indian Agricultural Research Institute, located in New Delhi. The specific coordinates for the trials were as follows: maize-wheat trials were conducted at N 28.38.0838 and E 077.09.1441, while pearl millet-mustard trials took place at N 28.38.1146 and E 077.09.1405. Table 1 provides detailed information about the soil properties of the location.

2.2. Experimental details

During *rabi* and *kharif* seasons of 2019–20 and 2020–21, field experiments on wheat, maize, mustard and pearl-millet under maize-wheat and pearl millet-mustard systems were established.

A total of 14 treatments were evaluated in a randomized complete block with three replications. The four rates of applied N as [0, 50, 75, and 100% of recommended rates of nitrogen (RRN)] were tested with different combinations of Nano-urea, Nano-Zn, and Nano-Cu application. The other major nutrients, *viz.* phosphorus and potassium were applied uniformly per the prescription. Table 2 shows the details of the treatments.

2.3. Nutrient management

The recommended fertilizer doses for the different crops were as follows: for maize, 150 kg N per ha, 75 kg P_2O_5 per ha, and 75 kg K_2O per ha; for pearl millet, 60 kg N per ha, 60 kg P_2O_5 per ha, and 30 kg K_2O per ha; for mustard, 80 kg N per ha, 40 kg P_2O_5 per ha, and 30 kg K_2O per ha; and for wheat, 120 kg N per ha, 60 kg P_2O_5 per ha, and 60 kg K_2O per ha. The recommended sources for nitrogen (N), phosphorus (P), and potassium (K) were prilled urea, single superphosphate, and muriate of potash, respectively. According to the treatment plan, mustard and pearl millet were provided with half of the nitrogen (N) requirement and the full doses of phosphorus (P) and potassium (K) at the time of sowing. The remaining half of the nitrogen (N) requirement was supplied as top-dressing later. Similarly, wheat and maize were supplied with half of their nitrogen (N) requirement and the full doses of phosphorus (P) and potassium (K) at the time of sowing, with the remaining half of the nitrogen (N) applied as top-dressing. Two sprays of Nano-urea were applied to the crops. The first spray occurred 30 days after sowing, followed by another spray one week before flowering. The rate of Nano-N spray was 4 mL/L, while Nano-Zn and Nano-Cu were sprayed at a rate of 2 mL/L. These sprays were applied using hand-operated knapsack sprayers with flat fan nozzles to ensure optimal foliage coverage. During harvesting, sickles were used to harvest the crops from the designated net plot area. Precautions were taken during spraying, including repeating the spray after rain and applying the spray in the afternoon when the dew had disappeared.

TABLE 1 Initial soil physico-chemical properties.

Soil properties	Value	Rating
Soil texture	Sandy loam	–
pH	8.22	Mildly alkaline
EC	0.24 dS m^{-1}	Non-saline
Organic carbon	0.58%	Medium
Available N	272 kg ha^{-1}	Low
Available P	22.3 kg ha^{-1}	Medium
Available K	311 kg ha^{-1}	High
DTPA-extractable Zn	0.84 mg kg^{-1}	Medium
DTPA-extractable Fe	4.72 mg kg^{-1}	Medium
DTPA-extractable Mn	19.9 mg kg^{-1}	High
DTPA-extractable Cu	1.91 mg kg^{-1}	High

2.4. Collection and processing of soil samples

Soil samples were collected at the flowering stage of each crop from the 0–15 cm depth using a core sampler with a diameter of 3.9 cm and a volume of 179.2 cm^3. Additionally, soil samples were obtained from the given plots for analysis of mineral nitrogen (N), microbial biomass carbon (MBC), and dehydrogenase activity (DHA). The collected soil samples from each plot were air dried, ground using a mortar and pestle, and passed through a 2-mm sieve. Subsequently, the samples were stored for further analysis. Similarly, another round of sampling was conducted after the harvest of each crop for nutrient estimation.

TABLE 2 Treatments details of experiments undertaken in maize-wheat and pearl millet-mustard systems.

S. No.	Treatment	Treatment details
T1	RRN_0PK	Recommended P and K (no-N)
T2	RRN $_{100}$PK	Recommended N, P and K
T3	RRN $_0$PK + Nano-Zn	Recommended P and K (no-N) and nano Zn sprays (2 times at the rate 2 mL/L)
T4	RRN $_{50}$PK+ Nano-Zn	50% of recommended N, recommended P and K, and nano Zn sprays (2 times at the rate 2 mL/L)
T5	RRN $_{75}$PK+ Nano-Zn	75% of recommended N, recommended P and K (no-N), and nano Zn sprays (2 times at the rate 2 mL/L)
T6	RRN $_{100}$PK+ Nano-Zn	Recommended N, P and K, and nano Zn sprays (2 times at the rate 2 mL/L)
T7	RRN $_0$PK + Nano-N+ Nano-Zn	Recommended P and K (no-N), and nano-N (2 times at the rate 4 mL/L) and nano Zn sprays (2 times at the rate 2 mL/L)
T8	RRN $_{50}$PK+ Nano-N+ Nano-Zn	50% of recommended N, recommended P and K, and nano-N (2 times at the rate 4 mL/L) and nano Zn sprays (2 times at the rate 2 mL/L)
T9	RRN $_{75}$PK+ Nano-N+ Nano-Zn	75% of recommended N, recommended P and K, and nano-N (2 times at the rate 4 mL/L) and nano Zn sprays (2 times at the rate 2 mL/L)
T10	RRN $_{100}$PK+ Nano-N+ Nano-Zn	Recommended N, P and K, and nano-N (2 times at the rate 4 mL/L) and nano Zn sprays (2 times at the rate 2 mL/L)
T11	RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	Recommended P and K (no-N), and nano-N (2 times at the rate 4 mL/L), nano Zn sprays (2 times at the rate 2 mL/L) and nano Cu sprays (2 times at the rate 2 mL/L)
T12	RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	50% of recommended N, recommended P and K, and nano-N (2 times at the rate 4 mL/L), nano Zn sprays (2 times at the rate 2 mL/L) and nano Cu sprays (2 times at the rate 2 mL/L)
T13	RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	75% of recommended N, recommended P and K, and nano-N (2 times at the rate 4 mL/L), nano Zn sprays (2 times at the rate 2 mL/L) and nano Cu sprays (2 times at the rate 2 mL/L)
T14	RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	Recommended N, P and K, and nano-N (2 times at the rate 4 mL/L), nano Zn sprays (2 times at the rate 2 mL/L) and nano Cu sprays (2 times at the rate 2 mL/L)

*Recommended fertilizer doses were 150 kg N ha^{-1}, 75 kg P_2O_5 ha^{-1}, 75 kg K_2O ha^{-1} for maize; 60 kg N ha^{-1}, 60 kg P_2O_5 ha^{-1}, 30 kg K_2O ha^{-1} for pearl millet; 80 kg N ha^{-1}, 40 kg P_2O_5 ha^{-1}, 30 kg K_2O ha^{-1} for mustard, and 120 kg N ha^{-1}, 60 kg P_2O_5 ha^{-1}, 60 kg K_2O ha^{-1} for wheat crop.

2.5. Soil and plant analysis

The estimation of dehydrogenase activity (DHA) in the soil samples followed the standard protocol, which involved measuring the production rate of triphenyl formazan (TPF) from triphenyl tetrazolium chloride (TTC) under anaerobic conditions (Casida, 1977). For the extraction of mineral nitrogen (N), undisturbed soil samples collected at different growth stages were treated with 2 M KCl and estimated using the steam distillation method (Kjeldahl, 1883). Estimation of available zinc (Zn) and copper (Cu) were performed following the method described by Lindsay and Norvell (1978), and the analysis was conducted using an atomic absorption spectrophotometer. Similarly, the micro-Kjeldahl method described by Jackson (1973) was used to estimate the nitrogen (N) content in grain/seed and straw/stover samples. To ensure result accuracy, each plant and soil sample were analyzed thrice, and the mean values were utilized for the statistical analysis.

2.6. Nitrogen uptake

The estimation of nitrogen (N) uptake by the grain/seed and straw/stover of different crops was done based on the dry matter production per hectare using the equation provided by Rowell (1994).

$$\text{N uptake}\left(\text{kg ha}^{-1}\right) = \frac{\text{N content}\,(\%) \times \text{Grain yield}\left(\text{kg ha}^{-1}\right)}{100}.$$

2.7. Soil microbial biomass carbon

The method (fumigation-extraction) as described by Vance et al. (1987) was used for the estimation of soil microbial biomass carbon (SMBC)

$$\text{SMBC}\left(mg\ kg^{-1}\right) = 2.64 \times \left(\text{C1} - \text{C2}\right)$$

Where,
C1 = extractable C in fumigated soil.
C2 = extractable C in non xlix fumigated soil.
2.64 = Kc factor.

2.8. Profit analysis

The economic assessment encompassed an examination of cultivation expenses, net profits, and the benefit-to-cost ratio (B: C), across different experimental conditions. The cost of cultivating each treatment was determined using current market rates for inputs, factoring in all expenses associated with crop cultivation. This encompassed all costs incurred throughout the crop growth cycle, aggregated alongside shared expenses for various operations and inputs. The benefit–cost ratio (B: C) was derived by dividing gross profits by the cost of cultivation for each specific treatment combination.

$$\text{B}:\text{C} = \frac{\text{Gross return}}{\text{Cost of cultivation}}.$$

2.9. Statistical analysis

The standard analysis of variance (ANOVA) was conducted using SPSS 21.0 statistical software (IBM Corp, 2012) to compare the treatment means (Tables 3–11). The treatment means were compared at the 5% level of significance ($p \leq 0.05$) using the critical difference method. For Figures 1, 2, the standard error (SE ±) of the treatment means was computed as

$$SE = SD\left(\sqrt{N}\right)^{-1}$$

Where, SD: standard deviation of the mean, and N: number of observations on which the mean is based. Contrast analysis (Supplementary Table 2) was done using SAS 9.4 (SAS Institute Inc, 2013) with generalized linear model procedure.

3. Results

3.1. Productivity

Nano-fertilizers like N, Zn and Cu exerted a strong influence on both the grain and straw yield of maize-wheat and pearl millet-mustard systems during 2019–20 and 2020–21 crop seasons (Table 3). Nano-N + nano-Zn with 100% RRN applied plots recorded significantly higher grain yields of 6.55 and 6.43 t ha^{-1}, 5.48 and 5.39 t ha^{-1}, 3.52 and 3.59 t ha^{-1}, and 2.40 and 2.45 t ha^{-1} in maize, wheat, pearl millet and mustard crops during first and second years, respectively over control (N_0PK or N_0PK+ nano-N or N_0PK+ nano-N+ nano-Zn or N_0PK+ nano-N+ nano-Zn + nano-Cu). The percentage increase in yield under N_{100}PK+ Nano-N+ Nano-Zn treatment was 72.1–84.1% in maize, 73.8–77.1% in wheat, 55.5–62.8% in pearl millet, and 50.3–73.3% in mustard over control plots (N_0PK+ nano-N+ nano-Zn). Likewise, there was 66.2–68.8%, 62.6–61.9%, 57.1–65.4%, and 47.2–69.0% yield enhancement was noted in maize, wheat, pearl millet and mustard crops, respectively under N_{100}PK+ Nano-Zn treatment over N_0PK + nano-Zn. Similarly, combination of all the three nano fertilizers like, nano-N + Zn + Cu with 100% RRN enhanced maize grain yield by 64.4–73.7%, wheat yield by 58.2–63.7%, pearl millet yield by 61.3–66.2%, and mustard yield by 50.0–72.9% over control plots (N0PK + Nano-N+ Nano-Zn + Nano-Cu). Therefore, sole application of nano-Zn or in combination with nano-N had higher yield advantage in all the crops compared to combination of all the three nano-fertilizers. However, in all the crops during both the study years, treatment with100% RRN with sole application of nano-Zn or a combination of nano-N+ Nano-Zn was found to be at par with 75% RRN + Nano-N + Nano-Zn. Likewise, the percentage yield enhancement with 75% RRN + nano-N + nano-Zn was 51.0–56.2% in maize, 53.7–54.7% in wheat, 50.0–51.6% in pearl millet, and 41.1–57.2% in mustard crops over control (N_0PK + Nano-N+ Nano-Zn) during both the study years. The application of RRN_{100}PK+ nano-N+ nano-Zn + nano-Cu led to slightly lower yields in all crops compared

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TABLE 3 Effect of nano-fertilizers on productivity (t ha^{-1}) of maize, wheat, pearl millet, and mustard systems.

Treatment	Maize		Wheat		Pearl millet		Mustard	
	2020	2021	2019–20	2020–21	2020	2021	2019–20	2020–21
RRN$_0$PK	3.35	3.24	2.81	2.75	1.90	1.78	1.28	1.23
RRN $_{100}$PK	5.98	6.01	5.02	5.14	3.33	3.35	2.28	2.31
RRN $_0$PK + Nano-Zn	3.69	3.46	3.05	2.97	2.18	2.07	1.55	1.35
RRN $_{50}$PK+ Nano-Zn	5.03	4.94	4.20	4.17	2.85	2.65	2.00	1.81
RRN $_{75}$PK+ Nano-Zn	5.35	5.30	4.85	4.61	2.91	2.83	2.25	1.93
RRN $_{100}$PK+ Nano-Zn	6.35	6.37	5.30	5.26	3.39	3.37	2.33	2.34
RRN $_0$PK + Nano-N+ Nano-Zn	3.94	3.81	3.37	3.33	2.24	2.17	1.63	1.45
RRN $_{50}$PK+ Nano-N+ Nano-Zn	5.30	5.19	4.66	4.59	2.90	2.88	2.15	1.93
RRN $_{75}$PK+ Nano-N+ Nano-Zn	5.95	5.95	5.18	5.15	3.36	3.29	2.30	2.28
RRN $_{100}$PK+ Nano-N+ Nano-Zn	6.55	6.43	5.48	5.39	3.52	3.59	2.40	2.45
RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	3.79	3.69	3.42	3.25	2.17	2.13	1.60	1.40
RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	5.23	5.15	4.60	4.53	2.86	2.85	2.20	1.91
RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	5.77	5.74	5.09	5.05	3.27	3.21	2.25	2.21
RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	6.23	6.41	5.41	5.32	3.50	3.54	2.40	2.42
Sem±	0.20	0.21	0.22	0.19	0.16	0.12	0.13	0.13
CD ($p \leq 0.05$)	0.58	0.61	0.64	0.55	0.46	0.36	0.39	0.39

to $RRN_{100}PK$+ nano-N and nano-Zn, although these results were statistically comparable (Table 3). Furthermore, a contrast analysis (between RRN_0PK + Nano-N+ Nano-Zn Vs. RRN_0PK + Nano-N+ Nano-Zn + Nano-Cu; $RRN_{75}PK$+ Nano-N+ Nano-Zn Vs. $RRN_{75}PK$+ Nano-N+ Nano-Zn + Nano-Cu; $RRN_{100}PK$+ Nano-N+ Nano-Zn Vs. $RRN_{10}PK$+ Nano-N+ Nano-Zn + Nano-Cu) was performed to elucidate the individual effect of nano-Cu from that of nano-N and nano-Zn, aiming to understand any potential antagonistic interactions (Supplementary Table 2). It was observed that the effect on nano-Cu in all the treatment combinations was non-significant in all the crops.

3.2. Profitability

Across various crop types, the highest cultivation costs were recorded in plots treated with 100% recommended rate of nitrogen (RRN) along with nano-N + nano-Zn + nano-Cu application, with values of 570, 507, 379, and 397 US\$ ha^{-1} for maize, wheat, pearl millet, and mustard crops, respectively (Supplementary Table 1). Furthermore, the maximum net returns were observed in plots treated with 100% RRN along with nano-N + nano-Zn application for all crops, amounting to 996, 866, 898, and 1,209 US\$ ha^{-1} for maize, wheat, pearl millet, and mustard crops, respectively. Notably ($p \leq 0.05$), maize exhibited significantly higher net returns (996 US\$ ha^{-1}) and a Benefit–Cost ratio (B: C) of 2.77 under the 100% RRN along with nano-N + nano-Zn treatment, compared to the control (net return of 314 US\$ ha^{-1} and B: C of 1.65). This performance remained comparable to the $RRN_{75}PK$ + Nano-N + Nano-Zn, $RRN_{100}PK$, $RRN_{100}PK$ + Nano-Zn, and $RRN_{100}PK$ + Nano-N + Nano-Zn + Nano-Cu treatments (Supplementary Table 1).

Wheat demonstrated a notably elevated net return of 866 US\$ ha^{-1} under the $RRN_{100}PK$ + Nano-N + Nano-Zn treatments, in stark contrast to the control group's net return of 272 US\$ ha^{-1}. This performance remained on par with other treatments: $RRN_{75}PK$ + Nano-N + Nano-Zn (804 US\$ ha^{-1}), $RRN_{100}PK$ (816 US\$ ha^{-1}), $RRN_{100}PK$ + Nano-Zn (843 US\$ ha^{-1}), and $RRN_{100}PK$ + Nano-N + Nano-Zn + Nano-Cu (841 US\$ ha^{-1}) (Supplementary Table 1). Additionally, the statistical analysis unveiled a higher B: C of 2.76 under the $RRN_{100}PK$ treatment, surpassing the control's B: C of 1.63. This performance was consistent with the B: C observed under $RRN_{75}PK$ + Nano-N + Nano-Zn (2.63), $RRN_{100}PK$ + Nano-N + Nano-Zn (2.73), and $RRN_{100}PK$ + Nano-N + Nano-Zn + Nano-Cu (2.66) treatments.

The treatment involving $RRN_{100}PK$ + Nano-N + Nano-Zn exhibited significantly elevated net returns in pearl millet, reaching 898 US\$ ha^{-1}, in contrast to the control's net return of 374 US\$ ha^{-1}. This performance remained consistent with the net returns observed under $RRN_{75}PK$ + Nano-N + Nano-Zn (816 US\$ ha^{-1}), $RRN_{100}PK$ (863 US\$ ha^{-1}), $RRN_{100}PK$ + Nano-Zn (841 US\$ ha^{-1}), and $RRN_{100}PK$ + Nano-N + Nano-Zn + Nano-Cu (877 US\$ ha^{-1}) treatments (Supplementary Table 1). Furthermore, the analysis revealed a statistically higher B: C of 3.41 under the $RRN_{100}PK$ treatment, surpassing the control's B: C of 2.18. This B: C performance remained consistent with the ratios observed under $RRN_{100}PK$ + Nano-Zn (3.36), $RRN_{75}PK$ + Nano-N + Nano-Zn (3.21), and $RRN_{100}PK$ + Nano-N + Nano-Zn + Nano-Cu (3.31) treatments.

Net return in mustard was registered higher under $RRN_{100}PK$+ Nano-N+ Nano-Zn treatments (1,209 US \$ ha^{-1}) over control (509 US \$ ha^{-1}) and it was remained at par with $RRN_{75}PK$+ Nano-N+ Nano-Zn (1,120 US \$ ha^{-1}), $RRN_{100}PK$ (1,156 US \$ ha^{-1}), $RRN_{100}PK$+ Nano-Zn (1,157 US \$ ha^{-1}) and $RRN_{100}PK$+ Nano-N+ Nano-Zn + Nano-Cu (1,183 US \$ ha^{-1}) (Supplementary Table 1). Significantly higher B: C was noticed under $RRN_{100}PK$ treatment (4.28) over control (2.54) and it was remained at par with $RRN_{75}PK$+ Nano-N+ Nano-Zn (3.90), $RRN_{100}PK$+ Nano-Zn (4.09), $RRN_{100}PK$+ Nano-N+ Nano-Zn (4.10), and $RRN_{100}PK$+ Nano-N+ Nano-Zn + Nano-Cu (3.98).

3.3. Nitrogen uptake

In all crop seasons, maize, wheat, pearl millet and mustard grains exhibited significantly higher N uptake during the study years. In general, nano-N + nano-Zn with 100% RRN had higher N uptake [(87.8 and 86.8 kg ha^{-1} in maize during first and second year, respectively), (68.3 and 66.8 kg ha^{-1} in wheat during first and second year, respectively), (59.7 and 62.0 kg ha^{-1} in pearl millet during first and second year, respectively) and (67.6 and 70.2 kg ha^{-1} in mustard during first and second year, respectively)] over control (N_0PK). However, sole or combination of nano-fertilizers had similar grain N-uptake in mustard crop during both the study years (Table 4). In maize and wheat crops, maximum N uptake of 86.8–87.8 kg ha^{-1}, and 68.3–66.8 kg ha^{-1}, respectively was recorded with 100% RRN + nano-N + nano-Zn plots over other combinations. However, superior treatment was at par with other treatments as compared to N_0PK + Nano-Zn, N_0PK + Nano-N + Nano-Zn, and N_0PK + Nano-N + Nano-Zn + Nano-Cu during both the cropping seasons. Likewise, application of 100% RRN + Nano-Zn recorded significantly higher grain N uptake of 60.5 kg ha^{-1} in pearl millet during 2019–20, while it was comparatively higher in 100% RRN + Nano-N + Nano-Zn (62.0 kg ha^{-1}) during 2020–21 than other nano-fertilizer applied plots. Furthermore, the treatments with 75% RRN + Nano-N+ Nano-Zn, and 75% RRN + Nano-N + Zn + Cu with 100% RRN + nano fertilizers applied plots registered the slightly lesser but similar grain N uptake in all the crops during all the study years. In mustard, the treatment 100% RRN + nano-N + nano-Zn + nano-Cu registered the higher grain N uptake by 67.9–70.2 kg ha^{-1} over other treatments during both the study years.

Total N uptake (grain + stover/straw) in maize, wheat, pearl millet and mustard crops were significantly influenced by nano fertilizer application. Application of nano-N + nano-Zn along with 100% RRN had higher total N uptake by 174–181 kg ha^{-1} in maize, ~123 kg ha^{-1} in wheat, 114–172 kg ha^{-1} in pearl millet, and 195–204 kg ha^{-1} in mustard over other combinations of nano-fertilizers with 100% RRN plots as well as in lower levels of fertilizer application, but it was at par with 75% RRN levels (Table 5).

3.4. Zn uptake

In comparison to the other combinations of nano-fertilizers with 100% RRN plots, the Zn uptake with nano-N + nano-Zn was greater than 1,100 mg ha^{-1} in maize, wheat and pearl millet crops, while it was >900 mg ha^{-1} in mustard (Table 6). Zinc uptake was significantly higher with 100% RRN + Nano-N + Nano-Zn plots, and the Zn uptake was higher by 1,435–1,508 mg ha^{-1} in maize, 1,626–1,195 kg ha^{-1} in wheat, 1,144–1,195 mg ha^{-1} in pearl millet, and 962–972 mg ha^{-1} in mustard over other treatments. However, application of 75% RRN

TABLE 4 Effect of nano-fertilizers on grain N uptake (kg ha^{-1}) under maize-wheat and pearl millet-mustard systems.

Treatment	Maize		Wheat		Pearl millet		Mustard	
	2020	2021	2019–20	2020–21	2020	2021	2019–20	2020–21
RRN_0PK	47.9	45.7	38.2	37.3	34.6	32.3	37.8	36.4
RRN $_{100}$PK	80.5	81.0	63.0	64.5	59.3	62.0	64.7	66.5
RRN $_0$PK + Nano-Zn	52.8	49.3	40.7	38.0	39.7	38.0	46.9	40.4
RRN $_{50}$PK+ Nano-Zn	72.0	70.7	56.2	54.1	52.7	49.2	58.6	53.6
RRN $_{75}$PK+ Nano-Zn	74.1	73.0	63.1	59.1	52.7	52.6	65.1	56.3
RRN $_{100}$PK+ Nano-Zn	86.7	84.7	67.7	67.4	60.5	60.6	67.5	67.4
RRN $_0$PK + Nano-N+ Nano-Zn	56.7	54.8	45.5	43.2	41.2	40.6	48.9	43.2
RRN $_{50}$PK+ Nano-N+ Nano-Zn	74.0	70.2	61.1	59.3	51.3	51.7	62.1	56.8
RRN $_{75}$PK+ Nano-N+ Nano-Zn	79.0	78.5	63.4	63.2	57.9	58.1	66.6	65.0
RRN $_{100}$PK+ Nano-N+ Nano-Zn	87.8	86.8	68.3	66.8	59.7	62.0	67.6	70.2
RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	55.6	53.2	47.2	44.2	40.0	39.5	49.0	42.3
RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	77.6	74.2	63.3	61.3	52.2	52.9	64.7	57.4
RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	78.2	76.3	65.0	63.7	58.6	58.1	64.3	63.9
RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	80.4	82.8	65.4	64.5	59.7	61.8	67.9	68.2
Sem±	5.3	4.6	4.3	4.6	3.6	3.5	2.8	4.1
CD ($p \leq 0.05$)	15.7	13.5	12.5	13.3	10.5	10.1	8.2	12.0

TABLE 5 Effect of nano-fertilizers on total (grain + straw/stover) N uptake (kg ha^{-1}) under maize-wheat and pearl millet-mustard systems.

Treatment	Maize		Wheat		Pearl millet		Mustard	
	2020	2021	2019–20	2020–21	2020	2021	2019–20	2020–21
RRN_0PK	102	97	71	66	102	95	104	104
RRN $_{100}$PK	163	163	115	120	164	172	178	186
RRN $_0$PK + Nano-Zn	106	101	75	71	69	106	129	114
RRN $_{50}$PK+ Nano-Zn	139	134	101	97	77	134	154	141
RRN $_{75}$PK+ Nano-Zn	150	144	117	107	84	140	178	159
RRN $_{100}$PK+ Nano-Zn	172	172	124	123	100	168	185	186
RRN $_0$PK + Nano-N+ Nano-Zn	115	112	82	79	70	114	132	122
RRN $_{50}$PK+ Nano-N+ Nano-Zn	151	141	113	109	87	137	171	159
RRN $_{75}$PK+ Nano-N+ Nano-Zn	164	158	121	116	100	154	186	183
RRN $_{100}$PK+ Nano-N+ Nano-Zn	181	174	123	123	114	172	195	204
RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	116	108	84	79	70	109	130	116
RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	158	151	111	108	94	144	182	169
RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	165	160	117	115	103	163	179	181
RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	172	167	119	119	99	158	180	183
Sem±	10	7	75	5	7	6	12	10
CD ($p \leq 0.05$)	28	21	101	16	21	18	37	30

along with nano-N + nano-Zn was at par with Zn uptake of 100% RRN + nano-N + nano-Zn applied plots. Interestingly, all the three combinations of nano-fertilizers like nano-N + nano-Zn + nano-Cu exhibited lower Zn uptake in grains of all the crops as compared to combination of nano-N + nano-Zn during the study years.

When applied to maize, wheat, pearl millet and mustard, nano fertilizers dramatically increased total Zn uptake (grain + straw/stover) and irrespective of crops, >52–62% of that Zn was retained in the straw over grain/seed (Table 7). Likewise, Zn uptake was significantly higher with 100% RRN+ Nano-N+ Nano-Zn plots in all the tested crops like maize (5636–5,670 mg ha^{-1}), wheat (2753–2,843 kg ha^{-1}), pearl millet (4386–4,603 mg ha^{-1}), and in mustard (4520–4,635 mg ha^{-1}; Table 7). However, it was at par with 75% RRN+ Nano-N+ Nano-Zn applied plots in all the crops.

3.5. Cu uptake

Over the years, harvests of maize, wheat, pearl millet, and mustard have all seen considerable increases in grain Cu consumption with 100% RRN applied plots (Table 8). However, application of nano-N + Zn + Cu either in alone or in combination had little effect in Cu uptake in maize, wheat and mustard crops, while slight variation in Cu uptake was observed in pearl millet crop. The variation of only about 2–4 mg ha^{-1} was observed in all the crops with respect to nano-fertilizer application. However, the uptake of Cu in pearl millet plant was 3–4 times higher than maize, wheat and mustard crops. Similarly, total Cu uptake by all the crops also followed the same trend as that of grain Cu uptake during the study years (Table 9). However, total plant Cu uptake was significantly higher in 100% RRN + nano-N + nano-Zn

TABLE 6 Effect of nano-fertilizers on grain Zn uptake (mg ha^{-1}) under maize-wheat and pearl millet-mustard systems.

Treatment	Maize		Wheat		Pearl millet		Mustard	
	2020	2021	2019–20	2020–21	2020	2021	2019–20	2020–21
RRN$_0$PK	713	695	792	775	685	670	543	520
RRN $_{100}$PK	1,310	1,348	1,588	1,656	1,165	1,180	963	916
RRN $_0$PK + Nano-Zn	839	776	941	971	754	734	617	515
RRN $_{50}$PK+ Nano-Zn	1,135	1,151	1,280	1,257	944	868	793	718
RRN $_{75}$PK+ Nano-Zn	1,331	1,238	1,571	1,420	955	935	935	792
RRN $_{100}$PK+ Nano-Zn	1,245	1,373	1,482	1,443	1,100	1,134	957	980
RRN $_0$PK + Nano-N+ Nano-Zn	787	804	953	920	747	721	650	587
RRN $_{50}$PK+ Nano-N+ Nano-Zn	1,234	1,262	1,450	1,450	1,029	992	898	847
RRN $_{75}$PK+ Nano-N+ Nano-Zn	1,399	1,303	1,605	1,662	1,099	1,180	893	874
RRN $_{100}$PK+ Nano-N+ Nano-Zn	1,508	1,435	1,663	1,626	1,195	1,144	962	972
RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	882	838	1,051	992	686	710	635	552
RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	1,200	1,089	1,396	1,413	993	953	855	724
RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	1,198	1,228	1,405	1,430	1,006	1,097	864	820
RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	1,306	1,386	1,599	1,591	1,192	1,147	963	901
Sem±	97	118	95	93	99	63	68	76
CD ($p \leq 0.05$)	283	345	280	272	290	184	201	222

TABLE 7 Effect of nano-fertilizers on total (grain + straw) Zn uptake (mg ha^{-1}) under maize-wheat and pearl millet-mustard systems.

Treatment	Maize		Wheat		Pearl millet		Mustard	
	2020	2021	2019–20	2020–21	2020	2021	2019–20	2020–21
RRN$_0$PK	2,973	2,855	1,411	1,358	2,875	2,840	2,883	2,820
RRN $_{100}$PK	5,040	5,068	2,731	2,923	4,395	4,550	4,483	4,536
RRN $_0$PK + Nano-Zn	3,245	3,148	1,652	1,650	2,890	2,850	3,040	2,614
RRN $_{50}$PK+ Nano-Zn	4,179	4,199	2,244	2,206	3,566	3,459	3,904	3,510
RRN $_{75}$PK+ Nano-Zn	5,099	4,747	2,706	2,520	3,666	3,647	4,531	4,020
RRN $_{100}$PK+ Nano-Zn	4,549	5,036	2,593	2,544	3,979	4,339	4,540	4,585
RRN $_0$PK + Nano-N+ Nano-Zn	3,189	3,215	1711	1,646	3,071	2,990	3,271	3,168
RRN $_{50}$PK+ Nano-N+ Nano-Zn	4,708	4,687	2,481	2,446	4,027	3,916	4,435	4,124
RRN $_{75}$PK+ Nano-N+ Nano-Zn	5,385	5,134	2,781	2,802	4,221	4,481	4,204	4,480
RRN $_{100}$PK+ Nano-N+ Nano-Zn	5,670	5,636	2,843	2,753	4,603	4,386	4,520	4,635
RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	3,722	3,402	1823	1728	2,787	2,839	3,059	2,759
RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	4,850	4,607	2,430	2,391	3,941	3,737	4,155	3,733
RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	4,837	5,076	2,499	2,509	3,930	4,163	4,123	4,050
RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	5,217	5,305	2,816	2,871	4,564	4,273	4,478	4,522
Sem±	334	308	153	133	403	228	379	204
CD ($p \leq 0.05$)	981	904	449	391	1,182	669	1,110	598

applied plots in maize, wheat and mustard crops as compared to other combinations. Whereas, 100% RRN + nano-N + nano-Zn + nano-Cu applied plots had significantly higher total Cu uptake in pearl millet than other combination of fertilizers.

3.6. Soil mineral nitrogen

The data presented in Table 10 indicated that the soil mineral nitrogen in maize, wheat, pearl millet and mustard crops was significantly influenced by nano-fertilizer application at different sampling times during both the study years. Soil mineral nitrogen ranged from 16.4–30.1 μg g^{-1} of soil during flowering and post-harvest stages in maize crop. Application of 100% RRN + Nano-Zn, and 100% RRN + Nano-N + Nano-Zn exhibited significantly higher values for soil mineral N uptake at flowering (30.8–31.0 μg/g of soil) and post-harvest soils (30.0–31.1 μg/g of soil) than other combinations, and it was at par with 100% RRN+ Nano-N+ Nano-Zn + Nano-Cu. While the variation in soil mineral N was slightly higher in wheat than maize. Mineral N in soil varied significantly from 17.1 to 31.6 μg/g of soil in wheat (Table 10). Among growth stages of wheat, application of 100% RRN+ Nano-N+ Nano-Zn recorded significantly higher mineral N at flowering (31.0 μg/g) and at post-harvest soils (30.3 μg/g) over other plots during 2019–20. During 2020–21, application of 100% RRN+ Nano-N+ Nano-Zn + Nano-Cu (31.6 and 28.6 μg/g of soil at flowering and post-harvest stages, respectively) noted maximum values for mineral nitrogen and remained at par with almost all the other treatments except treatments N$_0$PK + Nano-Zn and N$_0$PK + Nano-N+ Nano-Zn + Nano-Cu.

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TABLE 8 Effect of nano-fertilizers on grain Cu uptake (mg ha^{-1}) under maize-wheat and pearl millet-mustard systems.

Treatment	Maize		Wheat		Pearl millet		Mustard	
	2020	2021	2019–20	2020–21	2020	2021	2019–20	2020–21
RRN$_0$PK	65	61	62	56	312	294	87	82
RRN $_{100}$PK	119	117	113	106	552	588	160	157
RRN $_0$PK + Nano-Zn	67	61	62	63	389	378	107	94
RRN $_{50}$PK+ Nano-Zn	95	92	90	92	499	456	140	126
RRN $_{75}$PK+ Nano-Zn	102	98	115	107	519	509	153	133
RRN $_{100}$PK+ Nano-Zn	120	125	121	125	588	612	162	163
RRN $_0$PK + Nano-N+ Nano-Zn	75	68	68	71	440	411	113	102
RRN $_{50}$PK+ Nano-N+ Nano-Zn	99	99	99	95	517	495	153	135
RRN $_{75}$PK+ Nano-N+ Nano-Zn	111	109	123	119	552	596	160	156
RRN $_{100}$PK+ Nano-N+ Nano-Zn	126	120	124	121	624	686	168	166
RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	71	68	76	74	393	388	114	99
RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	97	95	107	99	526	551	151	129
RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	105	106	118	114	598	615	152	146
RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	115	117	123	122	644	662	165	165
Sem±	7	5	13	9	49	36	10	10
CD ($p \leq 0.05$)	20	16	37	26	145	104	29	30

TABLE 9 Effect of nano-fertilizers on total Cu (grain + straw/stover) uptake (mg ha^{-1}) under maize-wheat and pearl millet-mustard systems.

Treatment	Maize		Wheat		Pearl millet		Mustard	
	2020	2021	2019–20	2020–21	2020	2021	2019–20	2020–21
RRN$_0$PK	564	504	321	300	1,632	1,524	1,327	1,372
RRN $_{100}$PK	948	950	559	549	2,662	2,698	2,230	2087
RRN $_0$PK + Nano-Zn	544	547	318	310	1870	1760	1,646	1,417
RRN $_{50}$PK+ Nano-Zn	717	719	453	447	2,245	2,138	2,328	1817
RRN $_{75}$PK+ Nano-Zn	808	792	578	546	2,604	2,379	2,375	2040
RRN $_{100}$PK+ Nano-Zn	874	911	591	599	2,651	2,901	2086	2052
RRN $_0$PK + Nano-N+ Nano-Zn	616	618	355	349	1900	1912	1884	1766
RRN $_{50}$PK+ Nano-N+ Nano-Zn	792	757	500	490	2,159	2,321	2,441	2006
RRN $_{75}$PK+ Nano-N+ Nano-Zn	891	892	613	589	2,611	2,562	2,518	2,267
RRN $_{100}$PK+ Nano-N+ Nano-Zn	974	955	625	616	2,893	2,939	2,418	2,569
RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	632	592	378	365	1879	1819	1,686	1,568
RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	819	779	511	496	2,385	2,263	2,253	2,136
RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	877	861	575	560	2,725	2,735	2,305	2086
RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	951	917	603	570	2,920	2,915	2,134	2,209
Sem±	61	46	52	32	118	104	231	169
CD ($p \leq 0.05$)	180	136	152	94	346	304	678	496

Mineral nitrogen in pearl millet during 2019–20 and 2020–21, at flowering and post-harvest stages ranged from 17.7 to 32.3 µg/g of soil (Table 11). Application of 100% RRN + Nano-Zn and 100% RRN+ Nano-N+ Nano-Zn + Nano-Cu noted the highest values for soil mineral N of 32.0 and 31.0 µg/g, 32.3 and 30.7 µg/g soil at flowering and post-harvest stages, respectively during the studied seasons and recorded comparable values of mineral nitrogen with treatments 75% RRN + Nano-Zn, 75% RRN+ Nano-N + Nano-Zn, 100% RRN + Nano-N + Nano-Zn and 75% RRN + Nano-N + Nano-Zn + Nano-Cu in both the years, respectively. Significant variation in soil mineral nitrogen in mustard crop was recorded and ranged from 20.1 to 33.3 µg/g of soil (Table 11). Adoption of 100% RRN + Nano-Zn registered highest value for soil mineral N at flowering (~33.1 µg/g soil) and 100% RRN+ Nano-N + Nano-Zn + Nano-Cu at post-harvest stages (~32.3 µg/g soil), respectively during both the study years and it was at par with 75% RRN + Nano-N + Nano-Zn, 100% RRN + Nano-N + Nano-Zn and 75% RRN + Nano-N + Nano-Zn + Nano-Cu.

3.7. Dehydrogenase activity

Dehydrogenase activity (DHA) of soil under different treatments was measured in maize-wheat and pearl millet-mustard systems (Figure 1). In maize, maximum DHA activity was recorded under treatment of 100% RRN + nano-N + nano-Zn (35.5 µg TPF g^{-1} 24 h^{-1}, average of 2 years) which remained at par with 100% RRN+ Nano-N + Nano-Zn + Nano-Cu and 75% RRN + Nano-N + Nano-Zn. The treatment 100% RRN + Nano-Zn registered similar dehydrogenase activity (34.7 µg TPF g^{-1} 24 h^{-1}, average of 2 years) and also remained at par with treatment 100% RRN+

TABLE 10 Effect of nano-fertilizers on soil mineral nitrogen (µg/g of soil) at flowering and post-harvest stages of maize and wheat crops.

Treatment	Maize				Wheat			
	2020		2021		2019–20		2020–21	
	Flowering	Post-harvest	Flowering	Post-harvest	Flowering	Post-harvest	Flowering	Post-harvest
RRN_0PK	19.5	16.5	19.1	15.5	20.7	17.6	20.8	17.8
RRN $_{100}$PK	30.7	28.5	31.9	28.0	30.8	28.6	30.9	27.8
RRN $_0$PK + Nano-Zn	20.2	17.4	19.5	16.4	21.3	18.0	23.3	18.1
RRN $_{50}$PK+ Nano-Zn	22.7	22.5	21.8	21.4	23.4	20.6	25.0	24.6
RRN $_{75}$PK+ Nano-Zn	25.1	24.2	25.9	24.0	25.9	24.7	27.6	25.6
RRN $_{100}$PK+ Nano-Zn	30.8	29.6	29.9	29.7	30.8	30.2	31.8	28.4
RRN $_0$PK + Nano-N+ Nano-Zn	19.7	19.3	19.0	18.1	21.9	18.9	21.1	17.1
RRN $_{50}$PK+ Nano-N+ Nano-Zn	21.4	19.9	22.5	21.4	22.2	19.2	24.5	18.9
RRN $_{75}$PK+ Nano-N+ Nano-Zn	26.2	25.3	26.0	25.5	27.0	26.2	26.6	24.9
RRN $_{100}$PK+ Nano-N+ Nano-Zn	30.3	30.0	31.0	30.1	31.0	30.3	29.4	26.7
RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	20.7	19.4	19.9	18.3	23.5	20.7	23.2	19.1
RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	23.4	21.7	23.1	21.6	24.1	21.5	24.3	23.9
RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	24.7	24.3	27.0	25.8	25.4	24.3	26.1	26.0
RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	30.3	29.6	30.7	29.2	30.9	30.4	31.6	28.6
Sem±	1.46	1.43	1.75	1.73	1.36	2.15	2.70	2.01
CD ($p \leq 0.05$)	4.28	4.18	5.13	5.09	4.00	6.30	7.93	5.90

TABLE 11 Effect of nano-fertilizers on soil mineral nitrogen (µg/g of soil) at flowering and post-harvest stages of pearl millet and mustard crops.

Treatment	Pearl millet				Mustard			
	2020		2021		2019–20		2020–21	
	Flowering	Post-harvest	Flowering	Post-harvest	Flowering	Post-harvest	Flowering	Post-harvest
RRN_0PK	20.8	19.0	20.2	17.9	22.3	19.6	22.3	19.3
RRN $_{100}$PK	32.4	29.7	32.0	29.4	33.3	30.7	33.9	31.1
RRN $_0$PK + Nano-Zn	21.3	20.9	20.0	19.4	22.8	21.6	22.0	20.8
RRN $_{50}$PK+ Nano-Zn	26.2	24.7	25.4	24.6	26.8	25.3	27.1	24.9
RRN $_{75}$PK+ Nano-Zn	28.8	27.0	28.0	26.2	29.6	28.0	29.7	27.6
RRN $_{100}$PK+ Nano-Zn	32.0	29.5	31.7	29.9	33.1	32.0	33.3	33.1
RRN $_0$PK + Nano-N+ Nano-Zn	20.5	19.9	19.7	18.6	22.7	20.6	20.9	20.1
RRN $_{50}$PK+ Nano-N+ Nano-Zn	25.7	24.8	25.1	23.8	26.5	25.6	26.1	24.9
RRN $_{75}$PK+ Nano-N+ Nano-Zn	29.1	28.2	28.7	27.0	30.1	29.3	29.6	28.7
RRN $_{100}$PK+ Nano-N+ Nano-Zn	30.7	30.0	31.0	30.0	32.1	31.1	32.6	32.0
RRN $_0$PK + Nano-N+ Nano-Zn + Nano-Cu	21.2	18.9	19.7	17.7	22.1	19.9	21.4	20.3
RRN $_{50}$PK+ Nano-N+ Nano-Zn + Nano-Cu	27.0	23.9	25.9	22.7	29.0	24.7	28.1	24.4
RRN $_{75}$PK+ Nano-N+ Nano-Zn + Nano-Cu	31.0	28.9	30.5	27.4	31.4	30.3	30.8	29.4
RRN $_{100}$PK+ Nano-N+ Nano-Zn + Nano-Cu	31.9	31.0	32.3	30.7	32.8	32.3	33.0	32.8
Sem±	2.34	1.85	2.43	2.63	2.03	1.62	1.94	1.78
CD ($p \leq 0.05$)	6.87	5.43	7.14	7.71	5.95	4.76	5.69	5.23

Nano-N + Nano-Zn. The maximum dehydrogenase activity was recorded under 100% RRN + nano-Zn treatment (39.3 µg TPF g^{-1} 24 h^{-1} for wheat, 42.2 µg TPF g^{-1} 24 h^{-1} for pearl millet, 46.1 µg TPF g^{-1} 24 h^{-1} for mustard, average of 2 years) and it remained at par with 100% RRN + nano-N + nano-Zn (38.2 µg TPF g^{-1} 24 h^{-1} for wheat, 40.2 µg TPF g^{-1} 24 h^{-1} for pearl millet, 41.3 µg TPF g^{-1} 24 h^{-1} for mustard, average of 2 years) and 100% RRN + nano-N + nano-Zn + nano-Cu (36.7 µg TPF g^{-1} 24 h^{-1} for wheat, 42.4 µg TPF g^{-1} 24 h^{-1} for pearl millet, 40.3 µg TPF g^{-1} 24 h^{-1} for mustard, average of 2 years).

Furthermore, the treatments 75% RRN + Nano-Zn (32.1 µg TPF g^{-1} 24 $h^{-1}$for wheat, average of 2 years), 75% RRN + Nano-N + Nano-Zn (34.9 µg TPF g^{-1} 24 $h^{-1}$for wheat, 36.3 µg TPF g^{-1} 24 $h^{-1}$for pearl-millet, average of 2 years) and 75% RRN + Nano-N + Nano-Zn + Nano-Cu (36.0 µg TPF g^{-1} 24 h^{-1} for wheat, 36.1 µg TPF g^{-1} 24 h^{-1} for pearl-millet, average of 2 years) also remained at par with 100% RRN + Nano-N + Nano-Zn during the 1st and 2nd years, respectively.

3.8. Soil microbial biomass carbon

A significant effect on soil microbial biomass carbon was recorded under various treatments of maize-wheat and pearl millet-mustard

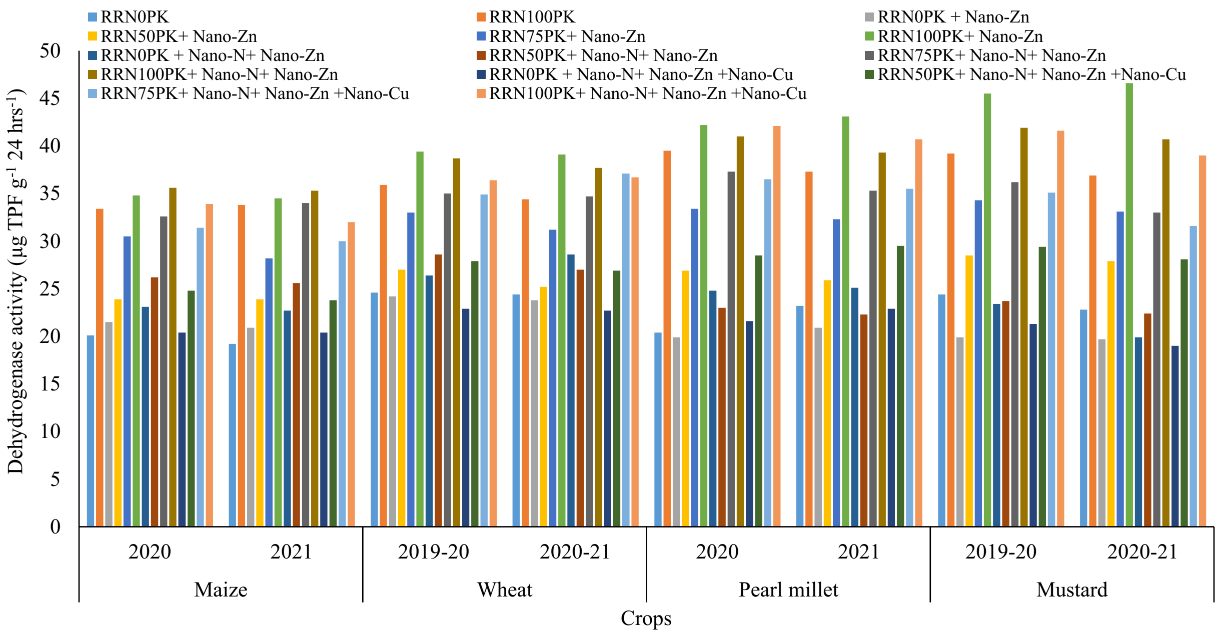

FIGURE 1
Effect of nano-fertilizers on dehydrogenase activity (µg TPF g^{-1} 24 h^{-1}) under maize-wheat and pearl millet-mustard systems.

system (Figure 1). Application of 100% RRN + Nano-N + Nano-Zn recorded maximum value for microbial biomass carbon for maize (282–316 µg g^{-1} of soil), wheat (291–296 µg g^{-1} of soil), pearl-millet and Mustard (289–349 µg g^{-1} of soil) during first as well as second year, while application of 100% RRN + Nano-Zn recorded maximum value for microbial biomass carbon during first year in wheat crop (293 µg g^{-1} of soil) (Figure 2). The treatments 100% RRN + Nano-Zn and 100% RRN + Nano-N + Nano-Zn + Nano-Cu recorded comparable values for microbial biomass carbon for maize, wheat and pearl millet during 2019–2020 and 2020–2021. In mustard, during 2019–2020 and 2020–2021, application of 100% RRN + Nano-N + Nano-Zn and 100% RRN + Nano-N + Nano-Zn + Nano-Cu recorded the highest and same values (300 µg g^{-1} of soil) for soil microbial biomass but did not show any significant difference (Figure 1). Both the treatments remained at par among themselves and with treatments 100% RRN + Nano-Zn (298 µg g^{-1} of soil), 75% RRN + Nano-N+ Nano-Zn (252 µg g^{-1} of soil), and 75% RRN+ Nano-N+ Nano-Zn + Nano-Cu (259 µg g^{-1} of soil) during both the years.

4. Discussion

4.1. Productivity of crops

Overuse of conventional fertilizers is a globally followed practice to meet plant nutrient needs. However, the efficiency of fertilizer use in crops rarely exceeds 30–35%, which is due to the loss of nutrient through leaching, evaporation and fixation (Mahmud et al., 2021). Therefore, nano-fertilizers have gained momentum over the decade to make fertilizer use more efficient and facilitate fertilizer application. However, research has evolved over a decade from laboratory studies and concentric pot experiments. Few systematic studies have been conducted so far to demonstrate the effects of nano-fertilizers or the combination of nano-fertilizers with conventional fertilizers on crop yield and economics under the field conditions (Kah et al., 2018; Hu and Xianyu, 2021; Upadhyay et al., 2023).

The application of 100% RRN in conjunction with nano-N + nano-Zn increased grain yields by 66.2–68.8% in maize, 62.6–61.9% in wheat, 57.1–65.4% in pearl millet, and 47.2–69.0% in mustard compared to control plots. However, for maize, wheat, pearl millet, and mustard, 75% RRN combined with two sprays of Nano-urea + nano-Zn produced statistically equivalent yields to 100% RRN + nano-N + nano-Zn (Table 3). This increase in crop yield with the application of nano-N + nano-Zn could be attributed to increased uptake of applied nano-fertilizers in addition to the basal application of traditional fertilizers. Foliar use of nano-fertilizers at important crop growth stages in various crops, either alone or in conjunction with fertilizers, boosts the crop yield (Kumar et al., 2021). According to Al-Juthery et al. (2019), foliar spraying of nano-fertilizers considerably increased plant growth parameters and yield of maize and wheat crops. Nano-urea, nano-Zn, and nano-Cu were sprayed on leaves in the current investigation, resulting in direct penetration through stomatal holes, and transfer through plasmodesmata (Kumar et al., 2021). Similarly, 75% RRN alone or in conjunction with nano-N + Nano-Zn was determined to be equivalent to 100% RRN+ Nano-N + Nano-Zn. Although maize, wheat, pearl millet, and mustard yields were statistically equal during the first year, yield was significantly lower under 75% RRN than 100% RRN during the second study year. This could be related to a deterioration in the soil's intrinsic fertility state, which contributed N nutrition to both crops during the first year (the year the experiment began). These nano-fertilizers release N and Zn in a regulated manner after entering plant systems. The absorption efficacy of nano-urea by plants is 80% greater than that of regular urea (Kumar et al., 2021). However, the efficiency of these nano-fertilizers is dependent on their concentration, application method, and also on the weather conditions. According to

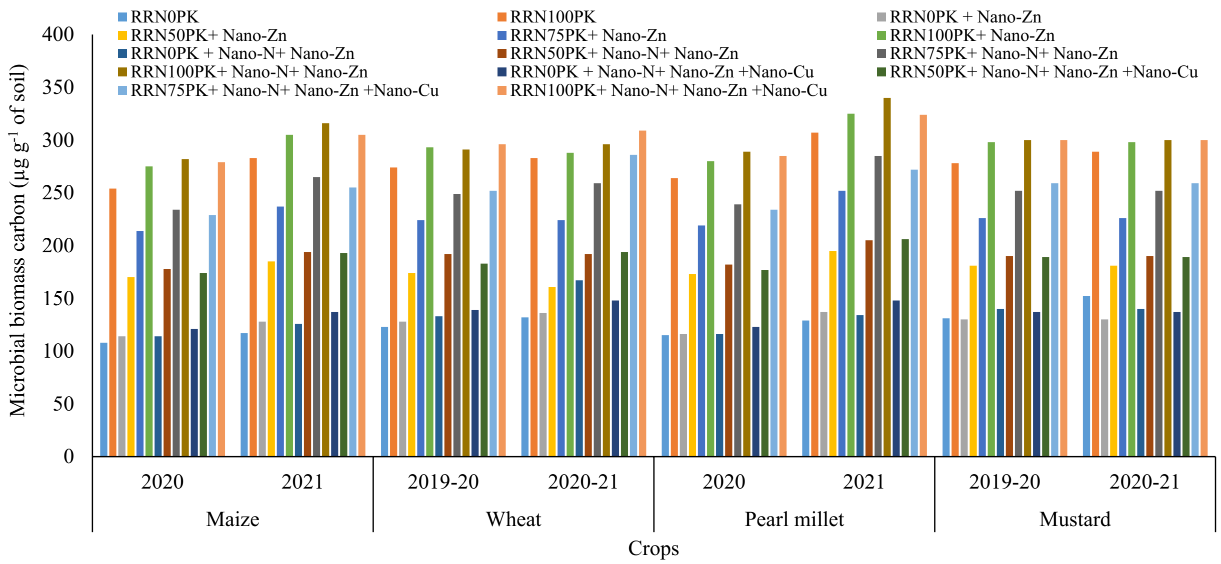

FIGURE 2
Effect of nano-fertilizers on Microbial biomass carbon (μg g^{-1} of soil) under maize-wheat and pearl millet-mustard systems.

Babu et al. (2022), in warm weather better acquisition and translocation of nano-urea results in achieving higher efficiency of nano-urea by plants. Interestingly, the use of ZnO nano particles (NPs) enhanced gas exchange parameters and chlorophyll concentration, leading to a better photosynthetic rate (Srivastav et al., 2021). As a result, either alone or in combination with nano-N, nano-Zn delivered a higher yield advantage. Zn has already been shown to improve chlorophyll synthesis by stimulating chlorophyll pigment formation and protochlorophyllide development, which ultimately improve photosynthesis (Sadak and Bakry, 2020; Del-Buono et al., 2021; Salam et al., 2022).

4.2. Uptake of nutrients

Regardless of crop, the application of nano-fertilizers with 100% RRN + Nano-N + Nano-Zn plots increased N and Zn uptake (Tables 4–7). However, the use of 75% RRN in conjunction with nano-N + nano-Zn produced comparable N and Zn uptake to that of 100% RRN + nano-N + nano-Zn plots. This was mostly attributable to the statistically same level of productivity noticed in all crops under mentioned treatments compared to statistically at par N and Zn levels. It implies that the application of nano-urea as a foliar spray additionally stimulates the uptake mechanism. Nano-N absorption is dependent on the leaf surface area (Babu et al., 2022), plant nutritional needs (Tarafdar et al., 2012), applied N (Grillo et al., 2021), and usage efficiency of native soil N (Tarafdar et al., 2014). In this work, Zn nano fertilizers and nano-N dramatically increased Zn uptake in all crops. As a result, our research enables us to decipher the Zn nano-fertilizer, allowing it to be used as an effective growth regulator to boost crop output under stress situations. Salam et al. (2022) discovered that adding ZnO NPs to maize plants decreased Co stress by lowering its uptake and bioaccumulation, boosting critical nutrient intake, and improving photosynthetic efficiency. Interestingly all the three combinations of nano-fertilizers like nano-N + nano-Zn + nano-Cu had similar Cu uptake with no nano-Cu applied plots (Tables 8, 9).

4.3. Mineral nitrogen and biological activities

Soil mineral nitrogen (Tables 10, 11), dehydrogenase activity (DHA) (Figure 1), and soil microbial biomass carbon (SMBC) (Figure 2) in maize, wheat, pearl millet, and mustard crops were significantly higher with the application of 100% RRN + Nano-N + Nano-Zn at flowering and post-harvest soils than other combinations. As a result, using Zn nano-fertilizers in conjunction with nano-N in addition to traditional fertilizers provided a greater advantage in terms of increasing DHA and SBMC. Zinc (Zn) is an essential element which involved in photosynthesis, the antioxidant defense system, and disease resistance (Olechnowicz et al., 2018; Cabot et al., 2019). Post-flowering applications of ZnO NPs had a larger effect on grain Zn content and a relatively lesser impact on grain yield was reported by Dapkekar et al. (2018) and Srivastav et al. (2021). In the current study, the applications of 100% RRN and 75% RRN + Nano-N + nano-Zn yielded statistically similar mineral N values throughout the seasons, implying that nutrient mining did not occur. The superior plots' increased root biomass frequently serves as a substrate for microbial development and metabolism. The addition of nano-urea increased root development and activity, which favored soil enzymatic activity. Nevertheless, the recommended N applications, along with Nano-N and Nano-Zn spray, produced the highest soil mineral N levels. However, lesser or no application of conventional fertilizers resulted in significantly lower mineral N, DHA, and SMBC levels across the seasons. Therefore, to avoid nutrient mining, at least 75% of the recommended nitrogen along with 2 sprays of nano-urea or nano-urea and nano-Zn should be applied. Further, it is observed from the study that maintaining ecological balance between aboveground (in terms of plant growth and yield) and underground (soil mineral N, DHA, SMBC etc.) the conjoint use of conventional fertilizers and nano-fertilizer (nano-N and nano-Zn) could be one of the best option.

5. Conclusion

The use of nano-N and nano-Zn in combination with traditional nitrogen fertilizers has immense scope to improve crop yields, nutrient uptake, soil mineral N, dehydrogenase activity, and soil microbial biomass carbon in wheat-maize and mustard-pearl millet cropping systems. Maximum grain yield of maize, wheat, pearl millet and mustard crops was observed under RRN $_{100}$PK+ Nano-N+ Nano-Zn treatments. The alone application of nano-Zn or nano-N+ nano-Zn or nano-N+ nano-Zn + nano-Cu could not suffice the requirement of the crops. Basal N application (75% of recommended) through prilled urea with full dose of P_2O_5 and K_2O along with nano-urea (2,500 mL ha^{-1} $spray^{-1}$) + nano-Zn (1,250 mL ha^{-1}) sprays recorded on par grain yield (wheat, mustard, maize and pearl millet) over 100% N + full dose of P_2O_5 and K_2O (recommended dose of fertilizer). Furthermore, the application of nano-Cu did not produced any significant results concerning crops yield. Overall, continued exploration demands a rigorous pursuit of additional research and expansive field trials concerning nano fertilizers, both in isolation and in tandem with conventional counterparts. It is imperative to carry out these endeavors across diverse crops and varied locations, a vital undertaking aimed at unraveling the true scope and potential of this innovative approach.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

PU: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Writing – original draft, Writing – review & editing. VS: Conceptualization, Methodology, Writing – original draft. GR: Data curation, Formal analysis, Methodology, Writing – review & editing. BD: Investigation, Methodology, Project administration, Writing – review & editing. AD: Data curation, Formal analysis, Methodology, Supervision, Writing – original draft. RS: Data curation, Validation, Writing – review & editing. SR: Data curation, Formal analysis, Writing – review & editing. KS: Data curation, Formal analysis, Writing – original draft, Writing – review & editing. SB: Data curation, Formal analysis, Validation, Visualization, Writing – review & editing. TS: Funding acquisition, Resources, Writing – review & editing. YK: Funding acquisition, Resources, Writing – review & editing. CS: Data curation, Resources, Writing – review & editing. MR: Data curation, Methodology, Writing – review & editing. AK: Resources, Writing – review & editing. SS: Formal analysis, Writing – review & editing. SD: Formal analysis of data. SR: Writing – review & editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fsufs.2023.1260178/full#supplementary-material

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