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RESEARCH PAPER

Long-term Effects of Zinc, FYM, and their Combination on Soil Chemical Properties in Rice-based Cropping Systems

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ABSTRACT

This study examines the long-term effects of zinc (Zn), farmyard manure (FYM), and their combination with NPK fertilizers on soil chemical quality in rice-based cropping systems (RBCS) on calcareous soils in Northern Bihar. Initiated in *Kharif* 1985 at RPCAU Experimental Farm, Pusa Bihar, the experiment involved four fertility levels (control, 50%, 100%, and 150% recommended dose of fertilizers, RDF) and six replications in a randomized block design (RBD). Two cropping systems were tested: Rice-Wheat-Sorghum (R-W-S) and Rice-Mustard-Moong (R-M-M). Recommended NPK doses were 120:60:40 for rice and wheat, 60:50:30 for mustard and sorghum, and 20:50:30 for moong. After ten cropping cycles, zinc deficiency was noted in treatments with 150% RDF. Thus, Zn and FYM amendments were superimposed on four replications, leaving two untreated. Superimposed treatments included application of 10 kg Zn/ha, 10 kg Zn/ha + 5 t FYM/ha, 10 t FYM/ha, and 10 kg Zn/ha + 10 t FYM/ha, applied in alternate years. Using paired t-test for analysis, soil chemical parameters were assessed in the 36th crop cycle after the 106th rice harvest in 2020. The combination of 10 kg Zn/ha and 10 t FYM/ha significantly improved soil chemical parameters, including organic carbon and available N, P, K, S, Zn, Cu, Fe, Mn, and B, while soil pH and EC remained unchanged. The study concludes that integrated use of NPK fertilizers with FYM enhances soil quality in long-term RBCS, with 10 kg Zn/ha crucial for maintaining Zn balance in calcareous soils.

HIGHLIGHTS

- It was a long-term experiment, after 10th cycle of cropping, superimposition treatments applied over the replication of initial treatments
- We have taken the soil samples after the harvest of only rice cop from both the cropping sequences
- The integration of NPK fertilizers with FYM proved to be beneficial with regards to soil quality and health.
- Integration nutrition management strategy is viable approach to restore soil chemical attributes.
- The micronutrients deficient calcareous soil particularly Zn, can be optimize with the use of Zn fertilizer sources integration with FYM.

Keywords: Cropping system, long-term, organic carbon, superimposition, zinc

Soil chemical properties play a crucial role in maintaining soil fertility and soil quality (SQ). The balance of these parameters is essential for supporting long-term crop cultivation and sustaining SQ. Soil quality refers to the soil's

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ability to function within its ecological boundaries to maintain biological productivity, protect the environment, and support plant and animal health (Doran and Parkin, 1994). It encompasses both intrinsic and dynamic soil properties, with chemical properties being the most variable in terms of quantity and availability.

Certain chemical parameters, such as cation exchange capacity (CEC), total nitrogen (N), phosphorus (P), pH, and extractable nutrients like P, sulphur (S), calcium (Ca), magnesium (Mg), and potassium (K), are critical measures of soil quality (Reganold *et al.* 1995). Long-term use of mineral fertilizers and organic manures significantly affects soil pH, organic matter (OM) content, and macronutrient availability, which in turn influences the availability of micronutrients to plants (Rutkowska *et al.* 2014). Integrated nutrient management (INM) strategies have emerged as a viable approach to restore soil chemical attributes while increasing soil organic matter (Rudrappa *et al.* 2006; Nayak *et al.* 2012).

Continuous application of NPK fertilizers, along with Zn and FYM, improves yield sustainability and soil quality. Long-term use of fertilizers reduces the risk of soil quality degradation compared to short-term application. Therefore, the judicious application of inorganic and organic nutrients in an integrated manner is essential for sustaining crop productivity and soil quality in long-term rice-based cropping systems (Nagar, 2017). Organic matter application enhances the availability and exchangeability of micronutrients, which vary within soil systems (Zhao *et al.* 2007; Zu *et al.* 2010).

Long-term integrated application of organic nutrient sources, particularly farmyard manure and green manure, along with optimal doses of chemical fertilizers, substantially enhances the micronutrient status of the soil and crops, facilitating the transfer of micronutrients from shoot to grain (Singh *et al.* 2022). Long-term fertility experiments help determine whether INM with organic amendments sufficiently meets plant micronutrient needs in specific agro-climatic regions (Saha *et al.* 2019). Including secondary and micronutrients like S, Zn, and boron (B) in long-term trials is useful for managing soil health and sustaining productivity in rice-rice cropping systems (Majhi *et al.* 2019).

Incorporating manures into the soil improves soil health by enhancing physicochemical properties and increasing the availability of macronutrients and micronutrients (Dhaliwal and Walia, 2008). In India, long-term fertilizer experiments established in the early 20th century, based on the "Rothamsted Classical Experiments," have shown that modern agriculture's emphasis on productivity often leads to micronutrient deficiencies due to the heavy use of NPK fertilizers. Continuous use of chemical fertilizers, especially nitrogenous ones, poses environmental hazards such as nitrate leaching, which can harm human and animal health (Pimentel, 1996).

Calcareous soils, like those in the present ongoing long-term experiment, are particularly prone to zinc deficiency. This deficiency is prevalent in rice-growing areas and can reduce lowland rice yields by up to 50% (White & Zasoski, 1999; Dobermann & Fairhurst, 2000). Continuous cropping with chemical fertilizers deteriorates soil health, whereas the use of organic manure alongside chemical fertilizers improves yield sustainability and soil properties (Bhatt *et al.* 2019). Therefore, long-term trials are essential for understanding nutrient imbalances and soil chemical properties, aiding in the development of sustainable soil health and SQ strategies. This study aims to address these issues through long-term integrated nutrient management in rice-based cropping systems.

MATERIALS AND METHODS

Field site and experimental design

The current study is part of an ongoing field experiment on Micro-Secondary and Pollutant Elements in Soil and Plants under the AICRP at RPCAU Pusa, Bihar. Initiated in Kharif 1985, the experimental plot is located at 25.9807988°N, 85.6676792°E, and 52 meters above sea level. The experimental field lies in the subtropical zone. The region receives 80% of its total annual rainfall (1300 mm) during July to September. The mean maximum temperature ranges from 34°C to 37°C, while the minimum temperature ranges from 9°C to 11°C. The experiment consisted of four fertility levels: 0%, 50%, 100%, and 150% of the recommended dose of fertilizers (RDF) for NPK for each crop

(RDF of 120:60:40 kg/ha for rice and wheat). The design used was a randomized block design (RBD) with six replications. Two cropping systems were studied: Rice-Wheat-Sorghum (R-W-S) and Rice-Mustard-Moong (R-M-M). Zinc sulfate was applied before the experiment began. The soil was allowed to equilibrate with Zn for one month (Zn content 3.2 ppm) before transplanting the rice crop, with soil samples taken beforehand. After completing 10 cropping cycles (30 crops in each rotation), sub-treatments were superimposed in alternate years. The sub-treatments included: 10 kg Zn/ha, 10 kg Zn/ha + 5 t FYM/ha, 10 kg Zn/ha + 10 t FYM/ha, and no superimposition in replications R1, R2, R3, R4, and R5 & R6, respectively.

The current research focuses on the 36^{th} crop cycle, specifically after the harvest of the 106^{th} rice crop. Rice variety 'Rajshree' was used for the R-W-S system and 'Prabhat' for the R-M-M system. On July 15^{th}, 22-day-old rice seedlings (20 cm × 20 cm spacing) were transplanted. Urea, DAP, and MOP were applied at rates of 211 kg/ha, 130 kg/ha, and 100 kg/ha, respectively, in treatment T3. For treatments T2 and T4, 50% and 150% of these fertilizer rates were applied. Half of the urea was applied basally, with the remainder top-dressed at the tillering, panicle initiation, and flowering stages. DAP and MOP were applied entirely at the basal stage.

Soil sampling

Soil sampling was conducted at four randomly selected locations within each plot immediately after the rice crop harvest, targeting a depth of 0-15 cm (surface soil). Approximately 500 grams of soil from each of the 48 plots were carefully blended and quartered before being placed in labelled, clean polythene bags. These samples were then air-dried in shaded conditions to preserve their integrity. Once dried, the soil samples were finely ground using a wooden roller on a clean surface and passed through a 2mm sieve. The prepared samples were securely stored in polythene bags for subsequent chemical analysis using standard procedure (Table 2).

Data processing

Correlation and regression analyses were carried out to examine the relationships between soil quality parameters, rice yield, and nutrient uptake using SPSS 16. Additionally, a Paired T-test was employed to compare means of two treatments at a significance level of 5%.

RESULTS

Soil PH, EC and Organic Carbon

The pH values ranged from 8.72 to 8.64 in the R-W-S rotation and from 8.74 to 8.63 in the R-M-M rotation. These values slightly decreased with higher fertility levels in both rotations (Table 3a). When different additional treatments were applied, pH values ranged from 8.50 to 8.78 in R-W-S and from 8.58 to 8.87 in R-M-M rotations. The lowest pH values were observed in plots treated with 10 kg Zn/ha and 10

Table 1: Initial soil properties at the start of the experiment

Properties	Content	Method used
Textural Class	Sandy loam	International Pipette method (Page *et al.* 1982)
pH	8.59	1:2 soil water suspension
EC (dS m^{-1})	0.24	1:2 soil water suspension
Organic carbon (%)	0.57	Dichromate oxidation method (Walkley and Black, 1934)
Available N (kg ha^{-1})	181.7	(Subbiah & Asija, 1956)
Available P_2O_5 (kg ha^{-1})	7.37	0.5 M $NaHCO_3$ pH 8.5 extraction (Olsen *et al.* 1954)
Available K_2O (kg ha^{-1})	215.0	1 M NH_4OAC, pH 7.0 extraction (Chapman and Prat, 1961)
Available S (ppm)	7.49	0.15% $CaCl_2$ extraction (Tabatabai, 1996)
Available B (ppm)		Hot water soluble (Berger and Trough, 1939)
Available (Zn, Cu, Fe, & Mn) ppm	(3.2, 1.86, 12.8 & 6.0)	DTPA-$CaCl_2$-TEA extractable, pH 7.3 (Lindsay and Norvell, 1978)
Free $CaCO_3$ (%)	32.8	Black *et al.* (1965)

Table 2: Methodology used to find the soil quality parameters during present investigation

Sl. No.	Soil Parameters	Standard Protocol Followed
1	Soil pH	(Jackson, 1978)
2	Electrical Conductivity (EC)	(Jackson, 1978)
3	Available N	(Subbiah & Asija, 1956)
4	Available P_2O_5 and K_2O	(Jackson, 1978)
5	Available sulphur	(Chesnin and Yien, 1951)
6	Available micronutrient cations (Zn, Cu, Fe and Mn)	(Lindsay and Norvell, 1978)
7	Available B	(Berger and Truog, 1939)

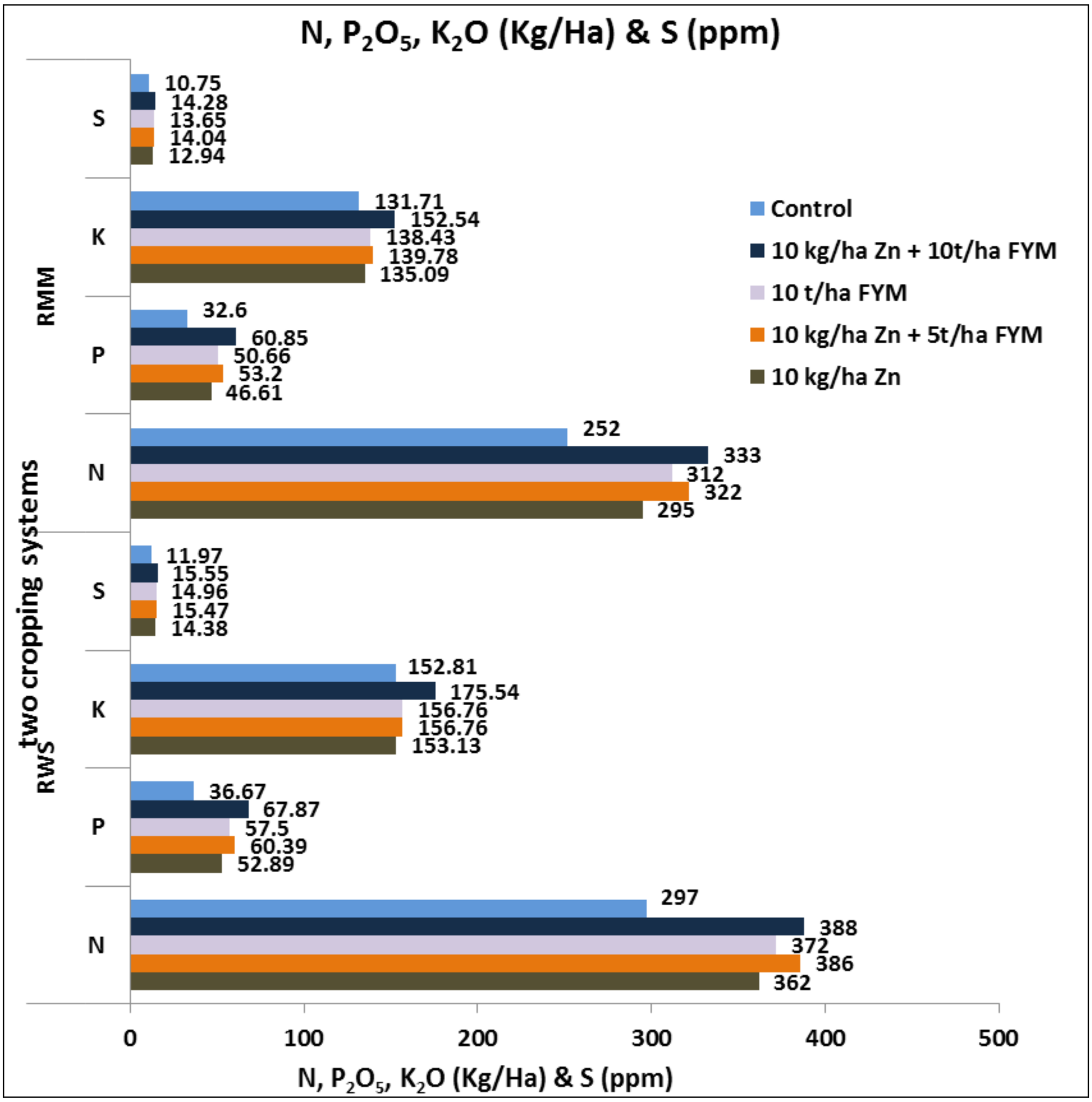

Fig. 1: Effect of long-term application of Zn, FYM and their combination on soil N, P_2O_5, K_2O (Kg/Ha) & S (ppm), under R-W-S and R-M-M cropping system

t FYM/ha in both rotations (8.65 in R-W-S and 8.67 in R-M-M), while the control plots had the highest pH (8.72 in R-W-S and 8.70 in R-M-M). All paired treatments showed statistically similar pH values, with a slight decreasing trend overall (Table 3b).

In the R-W-S cropping system, electrical conductivity ranged from 0.26 to 0.28 dS/m, and with different additional treatments, it ranged from 0.24 to 0.29 dS/m (Table 3a). Changes in fertility levels and additional treatments did not significantly affect electrical conductivity based on paired t-tests (Table 3b).

The organic carbon (OC) content increased from 0.69% to 0.80% in R-W-S and from 0.54% to 0.67% in R-M-M crop rotations with increased fertility levels. In superimposed treatments, OC content ranged from 0.65% in control to 0.80% with the combined application of 10 kg Zn/ha + 10 t FYM/ha in R-W-S. R-W-S showed greater variation in OC compared to R-M-M. Paired t-test analysis (Table 3b) indicated that all superimposed treatments significantly increased OC compared to the control, with the highest values observed with 10 kg Zn/ha + 10 t FYM/ha in both rotations. The application of 10 t FYM/ha was notably effective in increasing OC in both rotations compared to 10 kg Zn/ha, although it was comparable to 10 kg Zn/ha + 5 t FYM/ha in effectiveness.

Soil available Nitrogen, Phosphorous and potassium (N, P, K & S)

The results for available nitrogen (N), phosphorus (P), and potassium (K) content are presented in Table 4a. In the R-W-S cropping sequence, available N ranged from 308 kg/ha in the control to 394 kg/ha in the high fertility level, while P ranged from 26 kg/ha to 76 kg/ha, and K ranged from 120 kg/ha to 198 kg/ha. Similar trends were observed in the R-M-M rotation. The superimposed treatments also significantly influenced available N, P, and K, with ranges of 247-425 kg/ha for N, 13.2-81.5 kg/ha for P, and 115-208 kg/ha for K in R-W-S, and 213-376 kg/ha for N, 12.5-60.85 kg/ha for P, and 104-182 kg/ha for K in R-M-M. Higher fertility levels generally resulted in increased nutrient availability in both cropping sequences, with R-W-S showing higher levels of N, P, and K compared to R-M-M. Statistical analysis indicated that all superimposed treatments significantly increased N, P, and K compared to the control, particularly treatments involving 10 kg Zn/ha, 10 t FYM/ha, or their combination (Fig. 1). Combining 10 kg Zn/ha with 10 t FYM/ha consistently provided the highest available nitrogen content. The effectiveness of 10 t FYM/ha alone was comparable to combinations involving 5 t/ha FYM alongside 10 kg Zn/ha.

The increase in available sulfur (S) content in high fertility treatments over the control was 29.3% and 31.4% in R-W-S and R-M-M rotations, respectively. Superimposed treatments showed available S ranging from 9.9 ppm to 17 ppm in R-W-S and from 8.7 ppm to 15.8 ppm in R-M-M rotations, with the highest levels observed with the combined application of 10 kg Zn/ha and 10 t FYM/ha. Statistical tests confirmed that all superimposed treatments significantly enhanced soil available sulfur content compared to the control in both cropping systems. Additionally, 10 t FYM/ha was more effective than 10 kg Zn/ha alone in increasing available sulfur levels.

Available Micronutrients cations (Zn, Cu, Fe &Mn) and Boron

The available micronutrient cations (DTPA extractable Zn, Cu, Fe, and Mn) content of soil from our study is summarized in Table 5a and Fig. 2, covering both the R-W-S and R-M-M cropping sequences. In the R-W-S rotation, available Zn ranged from 1.40 ppm to 2.60 ppm, Cu from 1.50 ppm to 2.02 ppm, Fe from 14.28 ppm to 16.09 ppm, and Mn from 2.44 ppm to 3.04 ppm. For R-M-M, these values were 1.55 ppm to 2.86 ppm for Zn, 1.46 ppm to 1.97 ppm for Cu, 10.09 ppm to 13.97 ppm for Fe, and 2.64 ppm to 3.25 ppm for Mn, showing increases with higher fertility levels.

Across different superimposed treatments in R-W-S, Zn ranged from 0.63 ppm to 4.50 ppm, Cu from 1.30 ppm to 3.25 ppm, Fe from 13.6 ppm to 16.4 ppm, and Mn from 2.29 ppm to 3.25 ppm. In R-M-M, the ranges were 0.69 ppm to 4.94 ppm for Zn, 1.27 ppm to 2.46 ppm for Cu, 8.9 ppm to 13.7 ppm for Fe, and 2.48 ppm to 3.48 ppm for Mn. The combined application of 10 kg Zn/ha with 10 t FYM/ha consistently showed superior results for Zn, Cu, Fe, and Mn in both cropping sequences (Table 5a, Fig. 2). Statistical analysis confirmed significant improvements over control and other treatments without Zn in both rotations, highlighting the efficacy of combining Zn with FYM. FYM alone did not show significant improvements, underscoring the synergistic effect of Zn and FYM when applied together. These findings underscore the impact of alternate-year application of superimposed treatments on soil micronutrient availability.

Available boron content ranged from 0.67 ppm to 0.77 ppm in R-W-S and from 0.53 ppm to 0.65 ppm in R-M-M with increasing fertility levels. The highest value of 0.77 ppm was recorded in R-W-S at high fertility compared to 0.65 ppm in R-M-M at the highest fertility. Superimposed treatments,

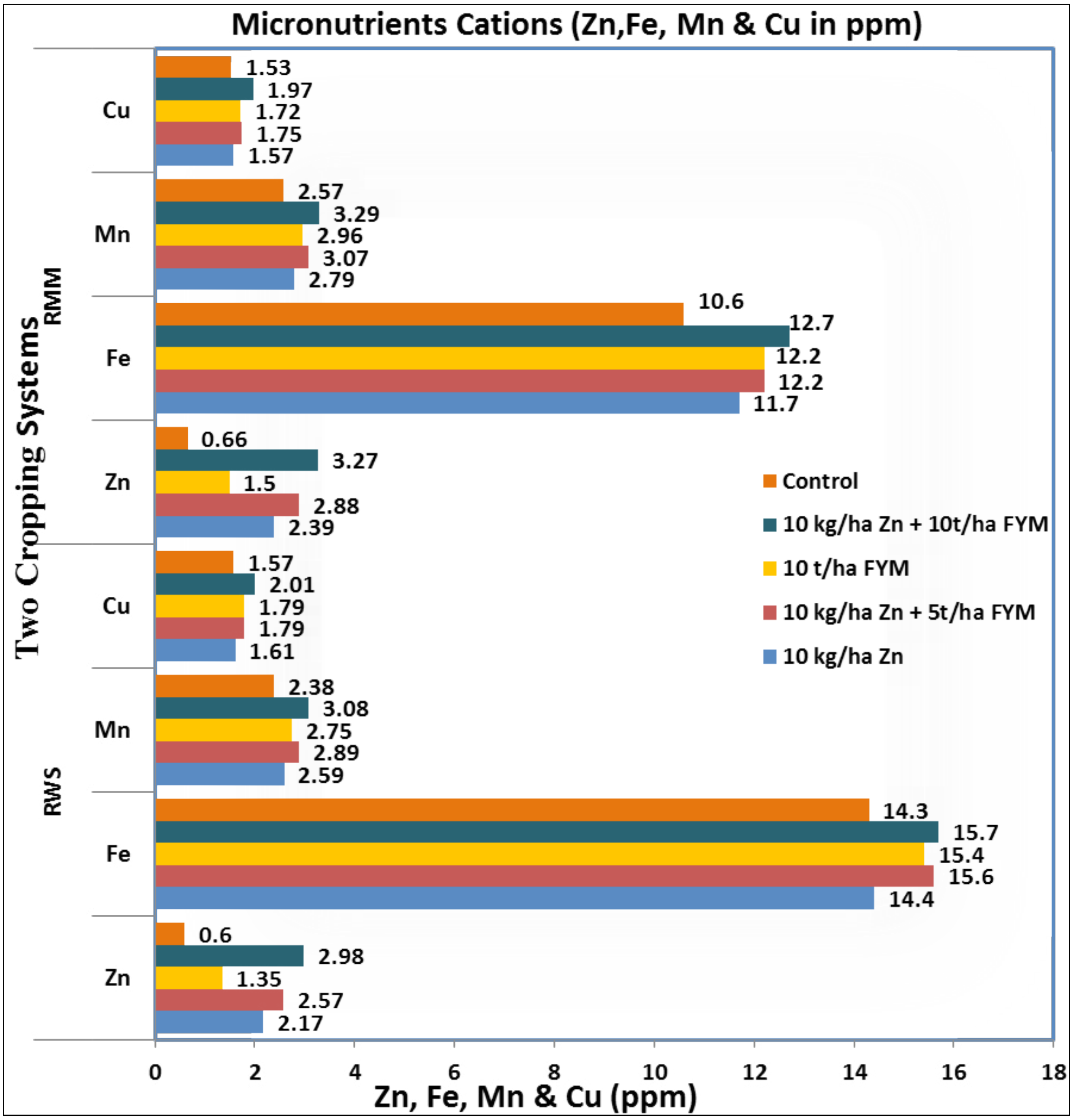

Fig. 2: Effect of long-term application of Zn, FYM and their combination on soil Micronutrients Cations (Zn,Fe, Mn & Cu in ppm), under R-W-S and R-M-M cropping system

especially the combination of 10 kg Zn/ha with 10 t FYM/ha, significantly increased boron content in both rotations, as indicated by paired t-tests against control values. Overall, 10 t FYM/ha was more effective than 10 kg Zn/ha alone in enhancing available boron levels in the soil.

DISCUSSION

Soil PH, EC and OC

In our 36-year study of a rice-based cropping system on calcareous soil, we observed a consistent decrease in soil pH with increasing fertility levels, likely due to acid-forming fertilizers such as urea and ammonium phosphate (Dhillon *et al.* 2018). These fertilizers release hydrogen ions during hydrolysis and nitrification processes, contributing to the pH decline. However, calcium carbonate in the soil acted as a buffer, mitigating substantial pH changes (Nayak *et al.* 2017). The addition of organic manures also influenced pH, potentially from organic acid and carbon dioxide released during decomposition (Moharana *et al.* 2017). Continuous cropping in the same field also contributed to a slight pH decrease (Dhaliwal *et al.* 2019). Despite these influences, none of the combined fertilizer treatments significantly altered soil pH. Long-term application of fertilizers

Table 3a: Effect of long-term application of Zinc, FYM, NPK fertilizers and their combination on Soil pH, EC (dS/m) and OC (%), under R-W-S and R-M-M cropping system

Treatments	10 kg Zn/ha		10 kg Zn/ha + 5 t FYM/ha		10 t FYM/ha		10 kg Zn/ha + 10 t FYM/ha		Control		Mean	
	pH											
	RWS	**RMM**	**RWS**	**RMM**	**RWS**	**RMM**	**RWS**	**RMM**	**RWS**	**RMM**	**RWS**	**RMM**
Control	8.78	8.87	8.74	8.78	8.70	8.78	8.70	8.70	8.78	8.75	**8.74**	**8.78**
Low Fertility	8.70	8.66	8.68	8.71	8.69	8.75	8.68	8.68	8.74	8.71	8.70	8.70
Medium Fertility	8.65	8.64	8.62	8.64	8.67	8.57	8.65	8.62	8.69	8.69	**8.66**	**8.63**
High Fertility	8.53	8.58	8.60	8.57	8.56	8.62	8.56	8.68	8.68	8.66	8.59	8.62
Mean	8.67	8.69	8.66	8.68	8.66	8.68	8.65	8.67	8.72	8.70		
	EC dS/m											
Control	0.26	0.30	0.26	0.31	0.23	0.29	0.33	0.31	0.20	0.22	**0.26**	**0.29**
Low Fertility	0.25	0.24	0.27	0.26	0.25	0.26	0.34	0.25	0.24	0.27	0.27	0.26
Medium Fertility	0.25	0.27	0.32	0.23	0.29	0.24	0.22	0.25	0.23	0.24	**0.26**	**0.24**
High Fertility	0.27	0.22	0.26	0.32	0.30	0.31	0.26	0.30	0.29	0.21	0.28	0.27
Mean	0.26	0.26	0.28	0.28	0.27	0.27	0.29	0.28	0.24	0.23		
	OC (%)											
Control	0.70	0.52	0.74	0.59	0.71	0.57	0.74	0.60	0.58	0.43	**0.69**	**0.54**
Low Fertility	0.71	0.59	0.80	0.65	0.73	0.60	0.78	0.63	0.60	0.49	0.72	0.59
Medium Fertility	0.77	0.62	0.80	0.68	0.79	0.67	0.81	0.70	0.68	0.53	0.77	0.64
High Fertility	0.79	0.64	0.82	0.69	0.82	0.68	0.85	0.76	0.72	0.59	0.80	0.67
Mean	0.74	0.59	0.79	0.65	0.76	0.63	0.80	0.67	0.65	0.51		

Table 3b: Paired t-test statistics for the effect of long-term application of Zinc, FYM and their combination on Soil pH, EC and OC, under R-W-S and R-M-M cropping system

Sl. No.	Pair Member	pH		EC		OC	
		t-value	Sig.	t-value	Sig.	t-value	Sig.
	Rice-Wheat-Sorghum (RWS)						
1	Control – 10 kg Zn/ha	-4.88	0.016	-0.91	0.432	-0.17	0.879
2	Control – (10 kg Zn + 5t FYM/ha)	-6.64	0.007	-3.39	0.043	-3.65	0.035
3	Control – 10t FYM/ha	-2.62	0.079	-21.06	0.000	-3.58	0.037
4	Control – (10 kg Zn + 10t FYM/ha)	-4.33	0.023	-3.33	0.045	-6.64	0.007
5	10 kg Zn/ha – (10 kg Zn + 5t FYM/ha)	-1.82	0.167	-3.05	0.055	-1.35	0.269
6	10 kg Zn/ha – 10t FYM/ha	3.23	0.048	-3.34	0.044	-1.22	0.309
7	10 kg Zn/ha – (10 kg Zn + 10t FYM/ha)	-1.88	0.157	-3.23	0.048	-1.95	0.146
8	(10 kg Zn + 5t FYM/ha) – 10t FYM/ha	0.33	0.060	0.05	0.966	1.80	0.169
9	(10 kg Zn + 5t FYM/ha) – (10 kg Zn + 10t FYM/ha)	-1.52	0.226	-3.06	0.055	-0.37	0.739
10	10t FYM/ha – (10 kg Zn + 10t FYM/ha)	-6.10	0.009	-1.73	0.181	-1.13	0.341
	Rice-Mustard-Moong (RMM)						
1	Control – 10 kg Zn/ha	-5.17	0.014	-0.94	0.418	-2.98	0.059
2	Control – (10 kg Zn + 5t FYM/ha)	-7.30	0.005	-3.37	0.043	-5.57	0.011
3	Control – 10t FYM/ha	-2.78	0.069	-17.29	0.000	-5.81	0.010
4	Control – (10 kg Zn + 10t FYM/ha)	-4.30	0.023	-3.40	0.042	-3.96	0.029
5	10 kg Zn/ha – (10 kg Zn + 5t FYM/ha)	-2.05	0.133	-3.03	0.056	-1.49	0.233
6	10 kg Zn/ha – 10t FYM/ha	3.46	0.041	-3.45	0.041	-1.33	0.276
7	10 kg Zn/ha – (10 kg Zn + 10t FYM/ha)	-1.91	0.152	-3.35	0.044	-1.12	0.343
8	(10 kg Zn + 5t FYM/ha) – 10t FYM/ha	6.22	0.072	0.42	0.704	-0.12	0.910
9	(10 kg Zn + 5t FYM/ha) – (10 kg Zn + 10t FYM/ha)	-1.27	0.293	-3.16	0.051	-0.65	0.561
10	10t FYM/ha – (10 kg Zn + 10t FYM/ha)	-5.81	0.010	-2.07	0.131	-0.71	0.527

Table 4a: Paired t-test statistics for the effect of long-term application of Zinc, FYM and their combination on Soil N, P, K and S, under R-W-S and R-M-M cropping system

Sl. No.	Pair Member	N		P		K		S	
		t-value	Sig.	t-value	Sig.	t-value	Sig.	t-value	Sig.
Rice-Wheat-Sorghum (RWS)									
1	Control – 10 kg Zn/ha	-16.60	0.000	-3.97	0.029	-0.33	0.761	-13.09	0.001
2	Control – (10 kg Zn + 5t FYM/ha)	-20.90	0.000	-6.97	0.006	-6.26	0.008	-12.15	0.001
3	Control – 10t FYM/ha	-17.08	0.000	-4.97	0.016	-0.97	0.402	-17.63	0.000
4	Control – (10 kg Zn + 10t FYM/ha)	-39.14	0.000	-6.94	0.006	-4.18	0.025	-42.28	0.000
5	10 kg Zn/ha – (10 kg Zn + 5t FYM/ha)	-3.26	0.047	-2.44	0.092	-3.72	0.034	-3.35	0.044
6	10 kg Zn/ha – 10t FYM/ha	-4.67	0.019	-2.53	0.086	-0.73	0.518	-5.13	0.014
7	10 kg Zn/ha – (10 kg Zn + 10t FYM/ha)	-6.59	0.007	-2.45	0.091	-3.54	0.038	-9.92	0.002
8	(10 kg Zn + 5t FYM/ha) – 10t FYM/ha	1.73	0.182	1.26	0.298	0.00	1.000	1.27	0.295
9	(10 kg Zn + 5t FYM/ha) – (10 kg Zn + 10t FYM/ha)	-0.48	0.664	-2.30	0.105	-3.22	0.049	-0.30	0.783
10	10t FYM/ha – (10 kg Zn + 10t FYM/ha)	-4.93	0.016	-1.87	0.158	-5.46	0.012	-3.76	0.033
Rice-Mustard-Moong (RMM)									
1	Control – 10 kg Zn/ha	-7.02	0.006	-3.68	0.035	-1.48	0.235	-8.67	0.003
2	Control – (10 kg Zn + 5t FYM/ha)	-9.50	0.002	-6.59	0.007	-3.37	0.043	-9.65	0.002
3	Control – 10t FYM/ha	-10.19	0.002	-4.59	0.019	-1.67	0.194	-22.29	0.000
4	Control – (10 kg Zn + 10t FYM/ha)	-25.71	0.000	-8.03	0.004	-6.20	0.008	-33.81	0.000
5	10 kg Zn/ha – (10 kg Zn + 5t FYM/ha)	-19.35	0.000	-2.72	0.073	-11.95	0.001	-3.78	0.032
6	10 kg Zn/ha – 10t FYM/ha	-4.54	0.020	-2.53	0.086	-0.76	0.505	-5.08	0.015
7	10 kg Zn/ha – (10 kg Zn + 10t FYM/ha)	-4.65	0.019	-3.09	0.054	-5.48	0.012	-7.12	0.006
8	(10 kg Zn + 5t FYM/ha) – 10t FYM/ha	2.20	0.115	1.41	0.253	0.28	0.797	1.30	0.284
9	(10 kg Zn + 5t FYM/ha) – (10 kg Zn + 10t FYM/ha)	-1.11	0.350	-2.94	0.061	-3.57	0.038	-0.78	0.494
10	10t FYM/ha – (10 kg Zn + 10t FYM/ha)	-3.23	0.048	-2.32	0.103	-8.35	0.004	-5.04	0.015

Table 5a: Paired t-test statistics for the effect of long-term application of Zinc, FYM and their combination on Soil Zn, Cu, Fe, Mn & B, under R-W-S and R-M-M cropping system

Sl. No.	Pair Member	Zn		Cu		Fe		Mn		B	
		t-value	Sig.	t-value	Sig.	t-value	Sig.	t-value	Sig.	t-value	Sig.
Rice-Wheat-Sorghum (RWS)											
1	Control – 10 kg Zn/ha	-4.88	0.016	-0.91	0.432	-0.17	0.879	-1.31	0.283	-2.05	0.073
2	Control – (10 kg Zn + 5t FYM/ha)	-6.64	0.007	-3.39	0.043	-3.65	0.035	-4.29	0.023	-10.18	0.002
3	Control – 10t FYM/ha	-2.62	0.079	-21.06	0.000	-3.58	0.037	-3.37	0.043	-31.84	0.002
4	Control – (10 kg Zn + 10t FYM/ha)	-4.33	0.023	-3.33	0.045	-6.64	0.007	-5.73	0.011	-16.19	0.003
5	10 kg Zn/ha – (10 kg Zn + 5t FYM/ha)	-1.82	0.167	-3.05	0.055	-1.35	0.269	-2.15	0.121	-19.80	0.011
6	10 kg Zn/ha – 10t FYM/ha	3.23	0.048	-3.34	0.044	-1.22	0.309	-2.38	0.097	-13.18	0.041
7	10 kg Zn/ha – (10 kg Zn + 10t FYM/ha)	-1.88	0.157	-3.23	0.048	-1.95	0.146	-2.81	0.067	-55.00	0.003
8	(10 kg Zn + 5t FYM/ha) – 10t FYM/ha	0.33	0.060	0.05	0.966	1.80	0.169	1.67	0.193	1.78	0.051
9	(10 kg Zn + 5t FYM/ha) – (10 kg Zn + 10t FYM/ha)	-1.52	0.226	-3.06	0.055	-0.37	0.739	-1.85	0.161	0.40	0.789
10	10t FYM/ha – (10 kg Zn + 10t FYM/ha)	-6.10	0.009	-1.73	0.181	-1.13	0.341	-2.95	0.060	-2.40	0.069
Rice-Mustard-Moong (RMM)											
1	Control – 10 kg Zn/ha	-5.17	0.014	-0.94	0.418	-2.98	0.059	-1.42	0.252	-2.71	0.076
2	Control – (10 kg Zn + 5t FYM/ha)	-7.30	0.005	-3.37	0.043	-5.57	0.011	-4.15	0.025	-9.92	0.026
3	Control – 10t FYM/ha	-2.78	0.069	-17.29	0.000	-5.81	0.010	-3.39	0.043	-10.18	0.011
4	Control – (10 kg Zn + 10t FYM/ha)	-4.30	0.023	-3.40	0.042	-3.96	0.029	-5.68	0.011	-8.74	0.018
5	10 kg Zn/ha – (10 kg Zn + 5t FYM/ha)	-2.05	0.133	-3.03	0.056	-1.49	0.233	-1.93	0.149	-5.57	0.032
6	10 kg Zn/ha – 10t FYM/ha	3.46	0.041	-3.45	0.041	-1.33	0.276	-2.29	0.106	-3.43	0.006
7	10 kg Zn/ha – (10 kg Zn + 10t FYM/ha)	-1.91	0.152	-3.35	0.044	-1.12	0.343	-2.78	0.069	-8.66	0.029
8	(10 kg Zn + 5t FYM/ha) – 10t FYM/ha	6.22	0.072	0.42	0.704	-0.12	0.910	1.46	0.240	3.15	0.808
9	(10 kg Zn + 5t FYM/ha) – (10 kg Zn + 10t FYM/ha)	-1.27	0.293	-3.16	0.051	-0.65	0.561	-2.18	0.118	-0.29	0.036
10	10t FYM/ha – (10 kg Zn + 10t FYM/ha)	-5.81	0.010	-2.07	0.131	-0.71	0.527	-2.93	0.061	-2.78	0.056

and farmyard manure (FYM) did not significantly affect electrical conductivity (EC) and bulk density (BD), maintaining values below 0.8 dS m^{-1}, which is ideal for crop growth (Brar *et al.* 2015). However, increasing levels of crop residues notably decreased soil pH. Studies in saline-sodic soils have shown that integrating FYM with chemical fertilizers can reduce soil pH and increase EC (Jagtap *et al.* 2007).

Differences in soil organic carbon (OC) were more pronounced in the rice-wheat-sorghum (R-W-S) rotation compared to rice-mustard-moong (R-M-M), reflecting variations in root biomass production among different crop types (Mathew *et al.* 2017). Manure applications maintained soil pH and enhanced soil organic carbon across all depths, whereas inorganic fertilizers tended to lower pH compared to manure (Ozlu *et al.* 2018; Jadhao *et al.* 2019; Ram *et al.* 2016). Enhanced OC levels with increased fertility and various superimposed treatments were observed, driven by increased carbon inputs from roots, crop residues, and improved humification rates (Kundu *et al.* 2007). Studies have shown that combining 100% NPK fertilizers with FYM significantly increases soil organic carbon compared to other treatments (Desai *et al.* 2009; Padre *et al.* 2007; Singh, Singh, and Singh, 2013).

Soil available Nitrogen, Phosphorous and potassium (N, P_2O_5, K_2O and S)

Over 36 years of studying a rice-based cropping system on calcareous soil, we observed consistent increases in available nitrogen (N), phosphorus (P_2O_5), potassium (K_2O), and sulfur (S) contents in both the R-W-S and R-M-M cropping sequences. This rise can be attributed to the regular application of NPK-based fertilizers at recommended doses (Bhatt *et al.* 2019; Das *et al.* 2021; Jadhao *et al.* 2019; Ashworth *et al.* 2020). Specifically, the R-W-S rotation showed higher accumulations of N, P_2O_5, and K_2O compared to R-M-M, reflecting the greater biomass accumulation in soils under R-W-S due to its crop rotation dynamics (Ashworth *et al.* 2020; Mathew *et al.* 2017). Combined applications of 10 kg Zn/ha + 10 t FYM/ha or 10 kg Zn/ha + 5 t FYM/ha proved more effective than using 10 kg Zn/ha alone, highlighting the beneficial role of FYM in enhancing soil nutrient availability, particularly nitrogen (Ram *et al.* 2016; Nayak *et al.* 2017).

The paired comparisons among these treatments generally showed similar outcomes, suggesting flexibility in choosing treatments based on economic and logistical factors (Yadhuvanshi *et al.* 2013; Keram *et al.* 2013; Katkar *et al.* 2012). Organic manure applications have also been shown to increase available nitrogen content through organic matter decomposition (Narwal and Antil, 2005), while phosphate fertilizers have similarly enhanced available phosphorus in soils (Yang *et al.* 2011). Studies highlight that integrated nutrient management (INM), such as combining 100% RDF NPK with organic amendments like FYM, consistently improves soil organic carbon (SOC) and the availability of N, P, and K (Ram *et al.* 2016; Rout *et al.* 2004; Yaduvanshi *et al.* 2015). Additionally, integrated applications of fertilizers and organic matter have been noted for their positive impacts on total nitrogen and available phosphorus levels (Sarma *et al.* 2015; Hemalatha *et al.* 2013; Singh *et al.* 2006), demonstrating effective strategies for sustainable soil fertility management.

Available Micronutrients cations (Zn, Cu, Fe &Mn) and Boron

In our examination of long-term rice-based cropping systems on calcareous soil, we observed minimal variation in the availability of micronutrient cations (DTPA-extractable Zn, Cu, Fe, Mn) and boron between the R-W-S and R-M-M crop rotations. The higher organic carbon (OC) content associated with increased fertility levels likely contributed to the production of organic acids at microsites, thereby lowering pH and enhancing the availability of Zn in the soil (Brar *et al.* 2015; Jadhao *et al.* 2019). Notably, the combined application of zinc and farmyard manure (FYM) yielded superior results compared to their individual applications. This enhancement in DTPA-Zn content in FYM-treated plots can be attributed to both direct zinc application and the mineralization of organically bound zinc within FYM (Shambhavi *et al.* 2018; Sharma & Bali, 2001).

Similarly, studies have highlighted significant increases in DTPA-extractable Cu content due to FYM amendments in both R-W-S and R-M-M rotations, underscoring the chelating action of organic compounds released during FYM decomposition (Sarkar *et al.* 2002; Sidhu and Sharma, 2010). The availability of Cu was further enhanced by combined applications of chemical fertilizers and FYM, surpassing levels seen in sole chemical fertilizer treatments (Gawde *et al.* 2017). For iron (Fe), while standalone zinc treatments did not notably increase availability, their combined applications with FYM significantly boosted DTPA-extractable Fe in both cropping sequences, aligning with previous findings (Rutkawska *et al.* 2018; Rao *et al.* 2018). Similarly, increased Mn availability was observed with the combined use of chemical fertilizers and FYM, reflecting prolonged mineralization of organic manure and its contribution to labile pool Mn (Selvi *et al.* 1997; Saha *et al.* 2020).

Moreover, micronutrient enhancements (Zn, Cu, Mn, Fe) were positively correlated with OC levels and inversely related to sand content and pH, further highlighting the role of FYM in micronutrient enrichment by lowering pH and forming chelates (Sidhu *et al.* 2010a,b; Nayak *et al.* 2017). Additionally, FYM treatments significantly increased boron content, attributed to enhanced root biomass and organic matter breakdown, which improves boron solubility and availability (Niaz *et al.* 2013; Yermiyahu *et al.* 2001). The integrated application of NPK with FYM proved effective in enhancing soil fertility and micronutrient availability, particularly with higher rates of FYM, which contributed more significantly to boron availability compared to zinc alone (Majhi *et al.* 2021). Overall, these findings underscore the efficacy of integrated nutrient management strategies in optimizing soil health and micronutrient dynamics in long-term agricultural systems.

CONCLUSION

In this long-term study, the combined application of 10 kg Zn/ha with 10 t FYM/ha in alternate years emerged as the optimal strategy for enhancing soil quality parameters in rice-based cropping systems. Significant improvements were observed in organic carbon (OC) percent and the availability of key nutrients (N, P, K, S, Zn, Cu, Fe, Mn, and B). However, these treatments did not significantly affect soil pH and electrical conductivity (EC). The integration of NPK fertilizers with FYM proved beneficial, emphasizing balanced nutrient management for sustaining soil health and crop productivity over the long term. Notably, while FYM alone did not significantly enhance soil Zn content due to calcareous soil conditions and frequent NPK use, the application of 10 kg Zn/ha provided a viable solution for addressing zinc deficiencies.

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