



Residual Influence of Organic Acid-loaded Nano Clay Polymer Composites of Rock Phosphate on Performance of Succeeding Cowpea [*Vigna unguiculata* (L.)] in a Maize-Cowpea Cropping System

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ABSTRACT

Background: Phosphorus (P) deficiency is a major constraint in Indian soils, limiting crop yields. Low-grade rock phosphate (RP) is a potential source of P but has poor solubility. Organic acids such as oxalic and citric acid improve RP solubilization through chelation, yet their rapid microbial degradation limits persistence. Encapsulation of these acids in nano clay polymer composites (NCPC) ensures controlled, sustained P release. As part of a maize-cowpea sequence, residual P from these treatments can be effectively utilized by cowpea (*Vigna unguiculata*), a legume with efficient P uptake and N-fixation ability. This study evaluated the residual effect of organic acid-loaded NCPC of RP on cowpea performance in a maize-cowpea cropping system.

Methods: A field experiment was conducted for two consecutive summer seasons (2023 and 2024) at Machanahalli village, Chikkaballapura district, Karnataka, to evaluate the residual effect of organic acid-loaded NCPC of RP on cowpea [*Vigna unguiculata* (L.)] grown after maize. Cowpea was cultivated as a test crop to assess the residual effect of organic acid-loaded NCPC of rock phosphate after maize, while simultaneously contributing to soil fertility as a legume. The trial included 12 treatments arranged in RCBD with three replications. Cowpea received the recommended N and K, while P was supplied only through residual sources from maize.

Result: Residual application of NCPC significantly improved cowpea growth, yield attributes, yield and nutrient uptake compared to conventional sources. Among treatments, oxalic acid-loaded NCPC of nano RP (T₁₁) recorded the highest grain yield (1649.24 kg ha⁻¹) and haulm yield (2034.23 kg ha⁻¹), reflecting 111.5% and 81.9% increases over the control, respectively, followed by citric acid-loaded NCPC of nano RP (T₁₂). These treatments also maximized NPK uptake.

Key words: Citric acid, Nutrient uptake, Oxalic acid, Plant height, Rock phosphate.

INTRODUCTION

Phosphorus (P) deficiency is one of the most widespread constraints in Indian agriculture, with about 61% of soils classified as low in available P (Singh *et al.*, 2023). In Karnataka's Eastern Dry Zone, encompassing Bangalore Rural, Kolar and Chikkaballapura soil P availability often ranges between 10-65 kg P₂O₅ ha⁻¹ (Chandrakala *et al.*, 2017). India's dependence on costly imported P fertilizers further limits their application by farmers, accelerating soil P depletion (Sharma *et al.*, 2003). Hence, use of indigenous low-grade rock phosphate (RP) represents a sustainable alternative. However, RP has poor solubility in neutral soils, resulting in low plant availability (Sarkar *et al.*, 2018).

To enhance RP reactivity, organic acids such as oxalic and citric acid have been studied. These acids chelate Ca and other ions, releasing plant-available P (Ali *et al.*, 2014). However, their rapid microbial degradation reduces persistence in soil. Encapsulation of organic acids in nano clay polymer composites (NCPC) has emerged as a promising strategy to overcome this limitation. The clay-polymer matrix protects acids from microbial breakdown, enabling their slow release and sustained RP solubilization (Kumar *et al.*, 2018; Verma *et al.*, 2017). NCPC also minimizes fixation and leaching losses, thereby improving nutrient-use efficiency.

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Despite these advantages, not all applied P from NCPC-treated RP is utilized in the first crop and a considerable

portion remains as residual P (Roy *et al.*, 2018). Efficient utilization of this residual P is critical for system productivity. Growing a legume such as cowpea (*Vigna unguiculata*) after maize is strategic, as legumes possess extensive root systems and efficient P-acquisition mechanisms (Tiware and Shivhare, 2016). Cowpea also fixes atmospheric nitrogen, improving soil fertility and reducing the need for synthetic inputs (Birla and Patel, 2022). Thus, evaluating the residual impact of NCPC-treated RP in a maize-cowpea sequence can provide insights into sustainable P management.

The present study aims to evaluate the residual impact of organic acid loaded NCPC of rock phosphate on cowpea growth, yield and nutrient uptake as a subsequent crop after maize. The research focus is on assessing P availability, growth and yield performance of cowpea, thereby providing insights into the efficacy of NCPCs in sustaining long term phosphorus supply in cropping systems.

MATERIALS AND METHODS

Experimental site and soil characteristics

Field experiments were conducted during the summer seasons of 2023 and 2024 at Machanahalli village, Chikkaballapura district, Karnataka, under a maize-cowpea sequence. The soil was sandy loam with bulk density 1.42 Mg m^{-3} , maximum water-holding capacity 57.46%, pH 7.18, EC 0.16 dS m^{-1} , organic carbon 5.7 g kg^{-1} and available N, P and K 280.87, 34.67 and $279.22 \text{ kg ha}^{-1}$ respectively. Exchangeable Ca and Mg were 4.81 and $3.46 \text{ C mol (pZ)} \text{ kg}^{-1}$ and DTPA-extractable Fe, Cu, Mn and Zn were 11.83, 0.74, 7.82 and 0.67 mg kg^{-1} , respectively.

Synthesis of nano rock phosphate

Nano rock phosphate was synthesized in 2022–2023 at Department of Soil Science and Agricultural Chemistry, College of Agriculture, GKV, UAS, Bangalore, according to Adhikari *et al.* (2014). Rock phosphate was sieved (2 mm) and ground to $\leq 74 \mu\text{m}$ in a high-speed vibrating sample mill at 1500 rpm for 5 min, five times repeated. The material was ball-milled in a mixer mill at 1500 rpm for 10 min with 2-minutes breaks.

Loading of organic acids on rock phosphate nano clay polymer composites

The commercially available nano clay polymer composite (NCPC) was loaded separately with two organic acids, citric acid and oxalic acid, at 2% (w/w). For this, 2% (w/v) aqueous solutions of ammonium citrate and ammonium oxalate were prepared using distilled water. To achieve 2% (w/w) loading, 10 mL of the respective solution (containing 0.2 g citrate or oxalate) was added to 9.8 g of NCPC and mixed thoroughly. The acid-loaded NCPC was then dried in a hot air oven at 80°C until constant weight was attained, followed by gentle grinding. The oxalic acid-loaded (OA-NCPC) and citric acid-loaded (CA-NCPC) composites thus obtained were subsequently mixed with rock phosphate (RP) or nano rock phosphate (nano RP) at a rate of 40 mg kg^{-1} soil for use in the experiment (equivalent to $\sim 75 \text{ kg P ha}^{-1}$

supplied through 763 kg RP or 552 kg nano RP, along with $90 \text{ kg NCPC ha}^{-1}$ for acid loading) (Roy *et al.*, 2015).

Since the experimental soil had a neutral pH (7.18), the direct dissolution of RP was limited. To overcome this, citric and oxalic acids were externally applied and loaded into NCPC to enhance their persistence and create localized acidic conditions, thereby facilitating RP solubilization and improving phosphorus availability.

Experimental design and treatments

The experiment was laid out in randomized block design (RCBD) with three replications and twelve treatments: T_1 : absolute control, T_2 : 100% ($75 \text{ P}_2\text{O}_5 \text{ kg ha}^{-1}$) phosphorus through single superphosphate (SSP), T_3 : 100% phosphorus through RP, T_4 : 100% phosphorus through nano RP, T_5 : 100% phosphorus through oxalic acid-loaded RP (OA-RP), T_6 : 100% phosphorus through citric acid-loaded RP (CA-RP), T_7 : 100% phosphorus through oxalic acid-loaded nano RP (OA-nano RP), T_8 : 100% phosphorus through citric acid-loaded RP (CA-nano RP), T_9 : 100% phosphorus from oxalic acid-loaded NCPC of RP (OA-NCPC-RP), T_{10} : 100% phosphorus from citric acid-loaded NCPC of RP (CA-NCPC-RP), T_{11} : 100% phosphorus from oxalic acid-loaded NCPC of nano RP (OA-NCPC-nano RP) and T_{12} : 100% phosphorus from citric acid-loaded NCPC of nano RP (CA-NCPC-nano RP).

In all treatments except the control, $25:25 \text{ kg ha}^{-1}$ of N and K were applied at sowing. No additional P was given and cowpea utilized the residual P from maize. Seeds were sown at 25 kg ha^{-1} and the crop was raised as a bulk stand to assess yield and residual effects of the P treatments.

Collection of growth and yield parameters

Five plants per treatment in each replication were tagged for recording growth and yield attributes at 30, 60 DAS and harvest. Plant height, leaf number, pod length, seeds per pod and 100-seed weight were measured using standard procedure.

Plant analysis

Cowpea seeds and plants were collected at the time of harvest and analyzed for total N by micro-Kjeldahl method, total P by Vanadomolybdate yellow colour method and total K by flame photometer (Piper, 1966).

Statistical analyses

Data were analyzed using analysis of variance (ANOVA) as per Gomez and Gomez (1984). Treatment means were compared using the critical difference (CD) test at 5% probability. Standard error of mean (SEm) and CD values are presented with tables.

RESULTS AND DISCUSSION

Growth parameters

The residual effect of organic acid-loaded NCPC of rock phosphate significantly influenced cowpea growth parameters, including plant height (Table 1), number of

Table 1: Residual effect of organic acid loaded NCPC of rock phosphate on plant height (cm) of cowpea at differ rent growth stages.

Treatment	30 DAS			60 DAS			At harvest		
	2023	2024	Pooled	2023	2024	Pooled	2023	2024	Pooled
T ₁ : Absolute control	23.61	23.95	23.78	27.29	27.84	27.57	29.52	30.02	29.77
T ₂ : RDF (100% P through SSP)	28.98	29.43	29.21	37.67	38.28	37.98	40.43	41.11	40.77
T ₃ : RDF (100% P through RP)	30.17	30.89	30.53	40.18	40.94	40.56	42.69	43.09	42.89
T ₄ : RDF (100% P through nano RP)	30.86	31.54	31.20	41.55	42.03	41.79	43.72	44.57	44.15
T ₅ : 100% P through OA-RP	32.84	33.12	32.98	42.81	43.25	43.03	45.78	46.73	46.26
T ₆ : 100% P through CA-RP	32.28	32.79	32.54	42.06	42.91	42.49	45.07	46.32	45.70
T ₇ : 100% P through OA- nano RP	33.80	34.45	34.13	44.41	45.19	44.80	46.61	47.77	47.19
T ₈ : 100% P through CA- nano RP	32.96	33.58	33.27	43.78	44.67	44.23	46.13	46.98	46.56
T ₉ : 100% P through OA-NCPC- RP	34.72	35.23	34.98	45.22	46.06	45.64	47.86	48.65	48.26
T ₁₀ : 100% P through CA-NCPC- RP	34.15	34.96	34.56	44.67	45.53	45.10	47.24	48.14	47.69
T ₁₁ : 100% P through OA-NCPC- nano RP	35.24	36.27	35.76	46.76	47.48	47.12	49.01	50.34	49.68
T ₁₂ : 100% P through CA-NCPC- nano RP	34.83	35.41	35.12	45.81	46.44	46.13	48.45	49.76	49.11
S.E.m±	1.36	1.49	1.47	1.90	1.99	1.97	1.93	2.05	2.03
CD@5%	3.99	4.37	4.32	5.56	5.74	5.89	5.66	6.01	5.95

SEm-Standard error of Mean; CD-Critical difference.

leaves per plant (Table 2) and dry weight (Table 3) at different growth stages.

Among the treatments, T₁₁ consistently recorded the highest values for plant height, leaf number and dry weight at 30 DAS (35.76 cm, 15.11 and 7.75 g plant⁻¹, respectively), 60 DAS (47.12 cm, 20.58 and 11.86 g plant⁻¹) and at harvest (49.68 cm, 17.15 and 13.24 g plant⁻¹). However, these values were statistically on par with other NCPC-based treatments, including T₁₂, T₉ and T₁₀. This treatment significant with T₂ (100% P through SSP) and rest of treatments with conventional phosphorus sources. The absolute control (T₁) had the lowest values at all growth stages.

Although SSP (T₂) supplies fully water-soluble P, its residual effect was lower, attributed to rapid precipitation of Ca-P complexes in neutral soil (Ali *et al.*, 2014). In contrast, organic acid-loaded NCPC formulations provided a more gradual and sustained release of P. The citric and oxalic acids chelated Ca and other ions, minimized fixation and enhanced P solubilization, while the modified clay matrix of NCPC allowed slow and controlled nutrient release (Roy *et al.*, 2018). This mechanism ensured that P remained available throughout the growth stages of cowpea, supporting better biomass production (Kantwa *et al.*, 2024). The nano-particle size and altered clay matrix in NCPC also allowed for slow release of nutrients, resulting in enhanced growth and biomass production (Singaram and Kothandaraman, 1991; Jones and Darrah, 1994; Clarholm *et al.*, 2015; Roy, 2015).

Yield parameters and yield of cowpea

The residual effect of phosphorus sources significantly influenced cowpea yield components (Table 4). The absolute control (T₁) recorded the lowest pod length (13.37 cm), number of pods per plant (6.5), seeds per pod (6.8) and test weight (7.2 g). Among treatments, T₁₁ recorded the highest values: pod length 20.2 cm (51.1% increase), pods per plant 13.0 (100.0% increase), seeds per pod 11.0 (61.8% increase) and test weight 10.2 g (41.7% increase) over the control. T₁₂ followed closely with pod length 19.8 cm (48.1%), pods per plant 12.8 (96.9%), seeds per pod 10.8 (58.8%) and test weight 10.0 g (38.9%). Conventional sources- T₂, T₃ and T₄ showed moderate increases in pod length (24.1-33.7%), pods per plant (30.8-46.2%), seeds per pod (20.6-29.4%) and test weight (18.1-23.6%), with no significant differences among them.

The residual effect of phosphorus sources also significantly influenced cowpea yield (Table 5). The control (T₁) recorded the lowest grain (779.58 kg ha⁻¹) and haulm yield (1118.15 kg ha⁻¹). T₁₁ (OA-NCPC-nano RP) produced the highest grain (1649.24 kg ha⁻¹; 111.5% increase) and haulm yield (2034.23 kg ha⁻¹; 81.9% increase), followed by T₁₂ (CA-NCPC-nano RP; 1633.31 kg ha⁻¹ grain, 109.6% and 2016.52 kg ha⁻¹ haulm, 80.3%), T₉ (1516.44 kg ha⁻¹ grain, 94.5%; 1957.88 kg ha⁻¹ haulm, 75.0%) and T₁₀ (1485.90 kg ha⁻¹ grain, 90.5%; 1903.62 kg ha⁻¹ haulm, 70.3%) over the control. Conventional sources-T₂ (SSP), T₃ (RP) and T₄ (nano RP)-showed moderate increases in

Table 2: Residual effect of organic acid loaded NCPC of rock phosphate on number of leaves per plant of cowpea at different growth stages.

Treatment	30 DAS				60 DAS				At harvest	
	2023	2024	Pooled		2023	2024	Pooled		2023	2024
T ₁ : Absolute control	4.53	4.61	4.57		10.08	10.24	10.16		7.46	7.67
T ₂ : RDF (100% P through SSP)	9.89	10.08	9.99		15.12	15.45	15.29		11.39	11.73
T ₃ : RDF (100% P through RP)	10.76	10.92	10.84		16.37	16.73	16.55		12.44	12.79
T ₄ : RDF (100% P through nano RP)	11.08	11.40	11.24		17.11	17.37	17.24		12.98	13.32
T ₅ : 100% P through OA-RP	11.39	11.64	11.52		17.86	18.19	18.03		13.81	14.25
T ₆ : 100% P through CA-RP	11.12	11.31	11.22		17.39	17.69	17.54		13.27	13.77
T ₇ : 100% P through OA- nano RP	12.48	12.69	12.59		18.32	18.54	18.43		14.73	15.50
T ₈ : 100% P through CA- nano RP	11.77	12.00	11.89		17.91	18.33	18.12		13.95	14.35
T ₉ : 100% P through OA-NCPC- RP	13.86	14.10	13.98		19.27	19.80	19.53		15.65	16.00
T ₁₀ : 100% P through CA-NCPC- RP	13.11	13.62	13.37		18.43	19.00	18.72		15.18	15.74
T ₁₁ : 100% P through OA-NCPC- nano RP	14.97	15.25	15.11		20.27	20.90	20.58		16.84	17.46
T ₁₂ : 100% P through CA-NCPC- nano RP	14.15	14.50	14.33		19.67	20.03	19.85		16.25	16.94
S.E.m±	0.54	0.55	0.55		0.79	0.81	0.80		0.63	0.65
CD@5%	1.58	1.62	1.60		2.31	2.36	2.34		1.85	1.91

Sem-Standard error of mean; CD-Critical difference.

Table 3: Residual effect of organic acid loaded NCPC of rock phosphate on dry weight (g plant⁻¹) of cowpea at different growth stages.

Treatment	30 DAS				60 DAS				At harvest	
	2023	2024	Pooled		2023	2024	Pooled		2023	2024
T ₁ : Absolute control	3.28	3.32	3.30		5.57	5.65	5.61		6.47	6.51
T ₂ : RDF (100% P through SSP)	4.52	4.64	4.58		8.39	8.47	8.43		10.36	10.41
T ₃ : RDF (100% P through RP)	4.98	5.06	5.02		8.94	9.09	9.02		10.56	10.64
T ₄ : RDF (100% P through nano RP)	5.33	5.45	5.39		9.16	9.24	9.20		11.06	11.16
T ₅ : 100% P through OA-RP	5.97	6.11	6.04		9.93	10.06	10.00		11.38	11.47
T ₆ : 100% P through CA-RP	5.46	5.58	5.52		9.52	9.63	9.58		11.19	11.23
T ₇ : 100% P through OA- nano RP	6.42	6.53	6.48		10.54	10.68	10.61		11.79	11.87
T ₈ : 100% P through CA- nano RP	6.17	6.29	6.23		10.07	10.13	10.10		11.42	11.56
T ₉ : 100% P through OA-NCPC- RP	7.16	7.22	7.19		11.26	11.41	11.34		12.57	12.69
T ₁₀ : 100% P through CA-NCPC- RP	6.84	6.97	6.91		10.88	10.99	10.94		12.26	12.38
T ₁₁ : 100% P through OA-NCPC- nano RP	7.68	7.81	7.75		11.75	11.97	11.86		13.19	13.28
T ₁₂ : 100% P through CA-NCPC- nano RP	7.25	7.39	7.32		11.37	11.52	11.45		12.84	12.96
S.E.m±	0.28	0.28	0.28		0.45	0.46	0.45		0.51	0.52
CD@5%	0.82	0.83	0.82		1.32	1.34	1.33		1.50	1.52

Sem- Standard error of mean; CD- Critical difference.

Table 4: Yield parameters of cowpea as influenced by residual effect organic acid loaded NCPC of rock phosphate.

Treatment	Pod length (cm)			Number of pods plant ⁻¹			Number of seeds pod ⁻¹			Test weight		
	2023	2024	Pooled	2023	2024	Pooled	2023	2024	Pooled	2023	2024	Pooled
T ₁ : Absolute control	13.31	13.43	13.37	9.49	9.51	9.53	10.34	10.41	10.38	10.16	10.22	10.19
T ₂ : RDF (100% P through SSP)	18.24	18.39	18.32	11.74	12.05	11.90	12.87	12.93	12.90	13.01	13.18	13.10
T ₃ : RDF (100% P through RP)	20.73	20.84	20.79	11.91	12.12	12.02	13.03	13.18	13.11	13.37	13.46	13.42
T ₄ : RDF (100% P through nano RP)	22.76	22.91	22.84	12.04	12.65	12.35	13.56	13.67	13.62	13.88	13.97	13.93
T ₅ : 100% P through OA-RP	24.17	24.29	24.23	12.62	12.89	12.76	14.08	14.23	14.16	14.46	14.54	14.50
T ₆ : 100% P through CA-RP	23.43	23.52	23.48	12.23	12.76	12.50	13.71	13.88	13.80	14.12	14.23	14.18
T ₇ : 100% P through OA- nano RP	24.88	24.97	24.93	13.54	14.16	13.85	14.63	14.85	14.74	15.05	15.18	15.12
T ₈ : 100% P through CA- nano RP	24.27	24.43	24.35	13.17	13.87	13.52	14.35	14.51	14.43	14.87	14.96	14.92
T ₉ : 100% P through OA-NCPC- RP	25.82	26.02	25.92	14.13	14.57	14.35	15.27	15.49	15.38	15.75	15.86	15.81
T ₁₀ : 100% P through CA-NCPC- RP	25.39	25.57	25.48	13.96	14.28	14.12	14.89	14.96	14.93	15.22	15.37	15.30
T ₁₁ : 100% P through OA-NCPC- nano RP	26.58	26.79	26.69	14.87	14.98	14.93	15.92	16.21	16.07	16.48	16.61	16.55
T ₁₂ : 100% P through CA-NCPC- nano RP	25.96	26.18	26.07	14.35	14.64	14.50	15.48	15.67	15.58	16.06	16.25	16.16
S.E.m±	0.83	0.65	1.05	0.60	0.61	0.59	0.64	0.55	0.65	0.47	0.46	0.66
CD@5%	2.44	1.95	3.07	1.77	1.79	1.73	1.88	1.62	1.89	1.38	1.35	1.94

Sem- Standard error of mean; CD- Critical difference.

Table 5: Kernel and haulm yield (kg ha⁻¹) as influenced by residual effect of organic acid loaded NCPC of rock phosphate in neutral soil.

Treatment	Grain yield (kg ha ⁻¹)			Haulm yield (kg ha ⁻¹)		
	2023	2024	Pooled	2023	2024	Pooled
T ₁ : Absolute control	775.34	783.82	779.58	1050.37	1185.93	1118.15
T ₂ : RDF (100% P through SSP)	1025.90	1136.27	1081.08	1272.48	1382.36	1327.42
T ₃ : RDF (100% P through RP)	1035.01	1168.45	1101.73	1365.55	1463.67	1414.61
T ₄ : RDF (100% P through nano RP)	1061.67	1196.56	1129.12	1471.74	1587.54	1529.64
T ₅ : 100% P through OA-RP	1197.23	1282.49	1239.86	1665.93	1782.16	1724.05
T ₆ : 100% P through CA-RP	1175.01	1276.61	1225.81	1643.67	1763.73	1703.70
T ₇ : 100% P through OA- nano RP	1280.57	1392.92	1336.74	1808.21	1946.46	1877.34
T ₈ : 100% P through CA- nano RP	1213.90	1366.85	1290.37	1777.93	1868.54	1823.24
T ₉ : 100% P through OA-NCPC- RP	1458.34	1574.53	1516.44	1906.86	2008.89	1957.88
T ₁₀ : 100% P through CA-NCPC- RP	1419.45	1552.34	1485.90	1849.65	1957.58	1903.62
T ₁₁ : 100% P through OA-NCPC- nano RP	1581.68	1716.81	1649.24	1963.72	2104.73	2034.23
T ₁₂ : 100% P through CA-NCPC- nano RP	1563.90	1702.72	1633.31	1934.88	2098.15	2016.52
S.E.m±	51.89	69.45	56.26	55.13	52.09	50.76
CD @ 5%	152.21	203.71	165.00	161.69	152.80	148.89

Sem- Standard error of mean; CD- Critical difference.

grain (38.5-44.8%) and haulm yield (18.7-36.7%) with no significant differences among them. Intermediate increases were observed for OA-RP, CA-RP, OA-nano RP and CA-nano RP (T_5 - T_8).

The superior performance of NCPCs is attributed to the controlled release of P and prolonged availability through organic acid chelation, which reduced Ca-P precipitation in neutral soils. Nano-scale carriers further enhanced surface area and gradual release, ensuring continuous nutrient supply for pod initiation, seed setting and grain filling (Biswas and Narayanasamy, 1998; Roy *et al.*, 2018). Nano-sized particles enhance surface area, promoting gradual P adsorption and release, which supports continuous P availability during critical growth stages,

resulting in improved pod formation, seed setting, grain and haulm yield (Panhwar *et al.*, 2013). Conversely, conventional sources released P rapidly, followed by fixation and limited residual availability, explaining their poorer performance (Jones and Darrah, 1994; Sarkar and Datta, 2014; Monika *et al.*, 2023). The intermediate response of OA/CA-treated RP without NCPC indicates that although organic acids enhance solubilization, their rapid microbial degradation limits sustained effect.

Nutrient uptake by cowpea grain and haulm

The residual effect of phosphorus sources significantly influenced nutrient uptake by cowpea at harvest under neutral soil conditions (Fig 1, 2 and 3). Uptake of N, P and

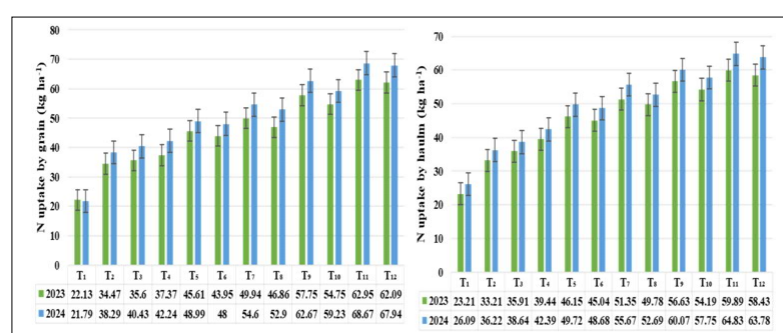


Fig 1: Residual effect of organic acid loaded NCPC of rock phosphate on nitrogen uptake by cowpea grain and haulm (kg ha^{-1}) at harvest.

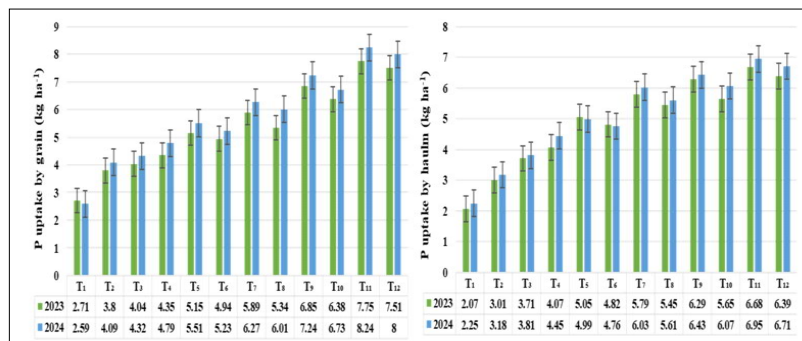


Fig 2: Residual effect of organic acid loaded NCPC of rock phosphate on phosphorus uptake by cowpea grain and haulm (kg ha^{-1}) at harvest.

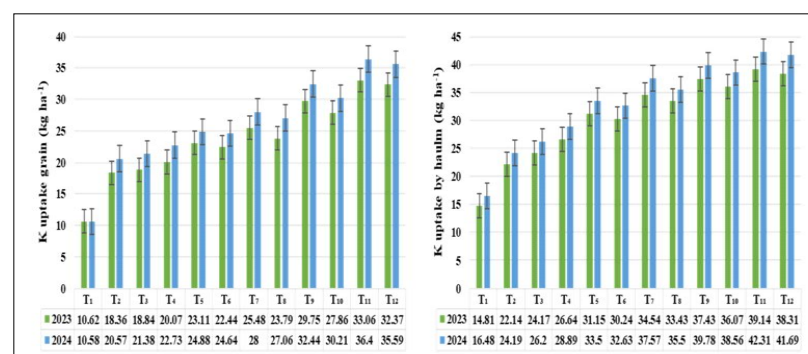


Fig 3: Residual effect of organic acid loaded NCPC of rock phosphate on potassium uptake by cowpea grain and haulm (kg ha^{-1}) at harvest.

K was highest in T₁₁ (128.17, 14.81 and 75.45 kg ha⁻¹, respectively) followed by T₁₂ (126.12, 14.30 and 73.69 kg ha⁻¹). T₉ and T₁₀ also showed marked improvements (112.96-118.56 kg N, 12.41-13.41 kg P and 69.70-72.12 kg K ha⁻¹) compared to T₂ (71.10, 7.04 and 42.63 kg ha⁻¹), T₃ (76.35, 7.61 and 45.29 kg ha⁻¹) and T₄ (80.72, 7.48 and 44.71 kg ha⁻¹). The absolute control (T₁) had the lowest nutrition uptake values for all nutrients measured.

Overall, the NCPC treatments consistently outperformed conventional sources across all nutrients. The superior performance of T₁₁ and T₁₂ was due to the combined effect of organic acid chelation and nano-scale controlled release, which improved nutrient solubilization, minimized fixation and sustained nutrient availability throughout the crop growth period (Biswas and Narayanasamy, 1998; Bansiwala *et al.*, 2006). Organic acids improved nutrient availability by chelating metal ions, while rock phosphate contributed additional Ca, Mg, S and micronutrients essential for plant growth (Biswas and Narayanasamy, 2006). The NCPC also promoted microbial activity, enhancing nutrient mobilization in the rhizosphere (Liu and Lal, 2014). In contrast, phosphorus fixation in SSP-treated soil reduced the nutrient uptake (Meena and Biswas, 2013). Thus, the synergistic action of organic acids and nano clay polymers in NCPC treatments resulted in superior nutrient acquisition by cowpea.

CONCLUSION

The residual effect of organic acid loaded NCPC of rock phosphate significantly enhanced cowpea growth, yield and residual nutrient uptake, in maize-cowpea cropping system. The slow-release mechanism of NCPC, combined with organic acid mediated chelation, minimized phosphorus fixation and ensured sustained availability for plant uptake. Treatments with NCPC nano RP consistently outperformed conventional SSP and RP, demonstrating greater fertilizer use efficiency and the value of low grade rock phosphate. This technology thus represents a sustainable strategy to optimize phosphorus utilization, reduce reliance on imported fertilizers and maintain long term soil fertility in legume based cropping system.

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Conflict of interest

All authors declare that they have no conflicts of interest.

REFERENCES

- Adhikari, T., Kundu, S., Meena, V. and Rao, A.S. (2014). Utilization of nano rock phosphate by maize (*Zea mays* L.) crop in a Vertisol of central India. *J. Agric. Sci. Technol.* **4**: 384-394.
- Ali, A., Sharif, M., Wahid, F., Zhang, Z., Shah, S.N.M., Rafiullah, Zaheer, S., Khan, F. and Rehman, F. (2014). Effect of composted rock phosphate with organic materials on yield and phosphorus uptake of berseem and maize. *Am. J. Plant Sci.* **5**: 975-984.
- Bansiwala, A.K., Rayalu, S.S., Labhasetwar, N.K. and Devotta, S. (2006). Surfactant-modified zeolite as a slow release fertilizer for phosphorus. *J. Agric. Food Chem.* **54**: 4773-4779.
- Birla, J. and Patel, B.M. (2022). Effect of organic sources of nitrogen on soil fertility of cowpea [*Vigna unguiculata* (L.) walp]. *Bhartiya Krishi Anusandhan Patrika.* **37(4)**: 391-394. doi: 10.18805/BKAP547.
- Biswas, D.R. and Narayanasamy, G. (1998). Direct and residual effectiveness of partially acidulated phosphate rocks as P fertilizer in a cowpea-wheat cropping sequence. *J. Indian Soc. Soil Sci.* **46**: 406-412.
- Biswas, D.R. and Narayanasamy, G. (2006). Rock phosphate enriched compost: An approach to improve low-grade Indian rock phosphate. *Bioresource Technol.* **97**: 2243-2251.
- Chandrakala, M., Srinivasamurthy, C.A., Kumar, S., Bhaskar, S., Parama, V.R.R. and Naveen, D.V. (2017). Phosphorus status in soils of Eastern Dry Zone, Karnataka, India. *Int. J. Curr. Microbiol. App. Sci.* **6(11)**: 310-324. doi: <https://doi.org/10.20546/ijcmas.2017.611.035>.
- Clarholm, M., Skjellberg, U. and Rosling, A. (2015). Organic acid induced release of nutrients from metal-stabilized soil organic matter - The unbutton model. *Soil Biology and Biochemistry.* **84**: 168-176.
- Gomez, K.A. and Gomez, A.A. (1984). Statistical Procedures for Agricultural Research. 2nd Ed. John Wiley Sons, New York.
- Jones, D.L. and Darrah, P.R. (1994). Role of root derived organic-acids in the mobilization of nutrients from the rhizosphere. *Plant Soil.* **166**: 247-257.
- Kantwa, C.R., Vyas, K.G., Patel, S.A. and Patel, B.J. (2024). Residual effect of wheat varieties and integrated nutrient management on productivity and profitability of green gram under north gujarat agro-climatic condition. *Legume Research.* **47(7)**: 1120-1127. doi: 10.18805/LR-4629.
- Kumar, S., Meena, R.S. and De, N. (2018). Interactive effect of nanoclay polymer composites and fertility levels on dry matter accumulation of linseed (*Linum usitatissimum* L.) under different irrigation frequency. *Int. J. Chem. Stud.* **6(6)**: 385-388.
- Liu, R. and Lal, R. (2014). Synthetic apatite nanoparticles as a phosphorus fertilizer for soybean (*Glycine max*). *Scientific Reports.* **4**: 5686.
- Meena, M.D. and Biswas D.R. (2013). Residual effect of rock phosphate and waste mica enriched compost on yield and nutrient uptake by soybean. *Legume Research.* **36(5)**: 406-413.
- Monika, B., Sharma B.C., Nandan B., Kumar R. (2023). Effect of differential substitution of nutrients through organics on growth, quality, nutrient uptake and economics of green gram (*Vigna radiata*) in Shiwalik foothill region. *Legume Research.* **46(7)**: 862-868. doi: 10.18805/LR-4257.
- Panhwar, Q.A., Jusop, S., Naher, U.A., Othman, R. and Razi, M.I. (2013). Application of potential phosphate-solubilizing bacteria and organic acids on phosphate solubilization from phosphate rock in aerobic rice. *Sci. World J.* doi.org/10.1155/2013/272409.

- Piper, C.S. (1966). Soil and Plant Analysis, Interscience Publ. Inc., New York. pp. 1- 368.
- Roy, T., Biswas, D.R., Datta, S.C., Dwivedi, B.S., Lata, Bandyopadhyay, K.K., Sarkar, A., Agarwal, B.K. and Shahi, D.K. (2015). Solubilization of Purulia rock phosphate through organic acid loaded nanoclay polymer composite and phosphate solubilizing bacteria and its effectiveness as p-fertilizer to wheat. *J. Indian Soc. Soil Sci.* **63(3)**: 327-338.
- Roy, T., Biswas, D.R., Datta, S.C., Sarkar, A. and Biswas, S.S. (2018). Citric acid loaded nano clay polymer composite for solubilization of Indian rock phosphates: A step towards sustainable and phosphorus secure future. *Arch. Agron. Soil Sci.* **23**: 1476-3567.
- Sarkar, A., Biswas, D.R., Datta, S.C., Roy, T., Moharana, P.C., Biswas, S.S. and Ghosh, A. (2018). Polymer coated novel controlled release rock phosphate formulations for improving phosphorus use efficiency by wheat in an *Inceptisol*. *Soil and Tillage Res.* **180**: 48-62.
- Sarkar, S. and Datta, S.C. (2014). Influence of fertilizer loaded nanoclay superabsorbent polymer composite (NCPG) on dynamics of P and N availability and their uptake by pearl millet (*Pennisetum glaucum*) in an *Inceptisols*. *Int. J. Bio-resour. Stress Manag.* **5(2)**: 221-227.
- Sharma, S.N. and Prasad, R. (2003). Yield and P uptake by rice and wheat grown in a sequence as influenced by phosphate fertilization with di-ammonium phosphate and Mussoorie rock phosphate with or without crop residues and phosphate solubilizing bacteria. *J. Agric. Sci.* **141**: 359-369.
- Singaram, P. and Kothandaraman, G.V. (1991). Direct, residual and cumulative effects of phosphatic fertilizers as yield attribute on yield of finger millet, maize and black gram grown in cropping sequence. *Fert. News.* **36(8)**: 21- 27.
- Singh, A., Choudhary, S., Prasad M., R. and Das, A. (2023). Nutrient supplying potential of crop residues in indian agriculture. agricultural waste - New Insights. IntechOpen. <http://dx.doi.org/10.5772/intechopen.108970>.
- Tiwari, A.K. and Shivhare, A.K. (2016). Pulses in India: Retrospect and prospects. Directorate of Pulses Development, Vindhya Bhavan, Bhopal, Ministry of Agriculture and Farmers Welfare (DAC and FW), Government of India, Publication No.: DPD/Pub.1 Vol.2.
- Verma, M.K., Pandey, P. and De, N. (2017). Characterization of water retention and release capacity of innovative nano clay polymer composite superabsorbent. *J. Pharmacog. Phytochem.* **63(3)**: 42-48.