




Depth-wise Variation of Cationic Micronutrients in Lateritic Soil under Rice, Non-rice and Fallow Land Ecology

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ABSTRACT

The study was conducted from May, 2022 to February, 2023 in Birbhum district of West Bengal, India to examine variations of DTPA extractable Zn, Cu, Fe, and Mn content and their correlations with soil physico-chemical properties in lateritic soil across different depths (0–15 cm, 15–30 cm, and 30–45 cm) and agricultural ecologies (rice, non-rice, and fallow lands). Ninety soil samples (10 locations×3 ecosystems×3 depths) were collected and analysed. Soils varied from strong to moderate acidity, low salinity; surface soil had lower pH, while sub-surface was higher. Organic carbon content was low to moderate. Overall, the Zn, Cu, Fe, and Mn contents and soil physico-chemical properties varied across soil ecologies and depths. Irrespective of soil ecologies, their mean values were highest at 0–15 cm and lowest in 30–45 cm soil depth, indicating decreasing trend with increased depth. Irrespective of depths, fallow land exhibited the highest levels of the Zn, Cu, Fe, and Mn. However, the lowest Zn content was recorded in rice soil ecologies, and that of the lowest Cu, Fe, and Mn were recorded in non-rice ecologies. DTPA extractable Zn correlated positively with pH, EC, OC, CEC, and negatively with available N. DTPA extractable Fe negatively correlated with K₂O, while Mn correlated positively with OC, CEC, and available N, negatively with clay. DTPA extractable Cu correlated negatively with clay. The results suggested enhancing integrated land management and micronutrient fertilization to improve soil fertility and agricultural productivity lateritic soils of West Bengal, India.

KEYWORDS: Land uses, soil depth, cationic micronutrients, lateritic soil

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1. INTRODUCTION

The soil is a natural body created by interaction between physical, chemical and biological processes, which is arranged on the horizon that varies in texture, mineralogy, nutrients and biological activity, and affects its ability to grow plants. Macronutrients and micronutrients are required to maintain crop productivity, but research indicates that micronutrient deficiency affects soil, crops, and human health. Micronutrients such as iron, manganese, zinc, copper, boron, molybdenum and chlorine are essential for enzymatic reactions, redox processes, and various metabolic functions. Even a decrease in one of these micronutrients can hamper physiological functions and cause complete crop failure in extreme cases. Their significance is important for cereals and pulses being sources of micronutrients to humans; thus, poor soil management exacerbates "hidden hunger" impacting around two billion people globally (Hafeez et al., 2021). Intensive agriculture faces worsening problems, including reduced crop growth periods, poor organic matter recycling, and dependence on NPK fertilizers, neglecting essential micronutrients (Rattan et al., 1999; Meena et al., 2022). Long-term experiments indicate neglecting balanced nutrient management depletes soil micronutrients, limiting sustainable productivity despite recommended NPK application levels (Gabhane et al., 2014). Contrarily, integrated nutrient management enhances soil fertility and micronutrient solubility, protecting crops like rice–wheat through the combination of organic and inorganic inputs. (Meena et al., 2022; Nayyar and Chhibba, 2000). In Eastern India, red as well as lateritic soils cover large areas—around 2.8 m hain West Bengal—mainly in Birbhum, Bankura, Purulia, Jhargram, West Burdwan, and West Midnapur (Panda et al., 1991). These soils are primarily composed of kaolinite clays and sporadic gibbsite, show high base saturation but poor nutrient retention due to light texture and low cation exchange capacity. Intensive agriculture and limited organic recycling worsen micronutrient deficiencies, starting with Zn, then Fe and Mn. Thus, lateritic soils show susceptibility to nutrient stress requiring careful observation. Micronutrient availability in soils is controlled by a number of factors, which include pH, organic carbon, texture, and redox status. Micronutrient solubility is usually higher in slightly acidic to neutral soils (Elbordiny and Camilia, 2008). Surface horizons contain higher micronutrient levels than subsurface layers due to organic matter, root growth, and residue addition (Khan et al., 2002; Wei et al., 2006). Redox variations increase the solubility of Fe and Mn, with alternating wetting and drying cycles affecting oxidation states and depth distribution (Maisch et al., 2019; Wang et al., 2022). Micronutrient cycling is influenced by management practices as well. Application

of NPK fertilizers increases availability of Zn, Cu, Fe, and Mn, whereas joint N and P applications particularly enhance Zn and Fe status (Zhang et al., 2004; Setia and Sharma, 2004). Tillage regimes also influence stratification of micronutrients between soil fractions (Shuman and Hargrove, 1985). Lu et al. (2004) documented lowered surface Mn but elevated subsurface accumulation in rice–wheat rotations. With such dynamics, knowledge of micronutrient depth-wise variations is essential. Root structures tend to penetrate subsurface horizons, and uptake by crops during the critical growth phase relies on nutrient availability beyond topsoil. Further, ecological differences—rice (flooded), non-rice (upland), fallow systems—result in unique environments for cycling of micronutrients (Peng et al., 2023). Though important, systematic studies focusing on vertical distribution of DTPA-extractable Zn, Cu, Fe, and Mn in Birbhum's lateritic soils are scanty. The study was aimed to measure depth-wise trends of DTPA-extractable Zn, Cu, Fe, and Mn in rice, non-rice, and fallow ecologies of Birbhum's lateritic soils and their associations with soil properties to indicate sustainable nutrient management practices.

2. MATERIALS AND METHODS

2.1. Location, climate, and description of study area

The study was conducted during May, 2022–February, 2023 in Birbhum district, West Bengal. The Birbhum district was triangular, spanning around 4,545 km², situated between 23°32'30" to 24°35' 0" north latitude and 87°525" to 88° 1 40" east longitude. Its northern tip points up, with the Ajay river forming its southern boundary and separating it from Bardhaman. The district shared its western and northern borders with Jharkhand and its eastern boundary with Murshidabad. The eastern climate was milder than the drier western climate, with summer temperatures exceeding 40°C and winter temperatures dropping to around 10°C. Rainfall varies, with Rajnagar and Nanoor receiving 1,212 mm and 1,405 mm annually, mainly during monsoons.

2.2. Physiography and soil

This region features the Chota Nagpur Plateau merging with the Ganges alluvial plains at its northeastern edge. Mama Bhagne Pahar was the only hilly natural rock formation near Dubrajpur. Historically known as Vajjabhumi, the district's western side was an arid upland, while the eastern part, more fertile and part of the northern Rarh region, was called Sumha, differentiating it from Vajjabhumi. Red and laterite soil was light, porous, gravel-based, and low in organic content, with phosphorus and bases. The Eastern, South-Eastern, North-Eastern, and Southern districts feature old and new alluvium soils, primarily loamy and rich in organic matter, with a pH of 5.0 to 6.5, supporting agriculture in

this mixed terrain of plateaus and alluvial plains.

2.3. Collection and processing of soil samples

Soil samples were collected from ten sites—Kendra Dangal, Bisnubati, Srichandrapur, Sattor, Binuria, Bahadurpur, Ruppur, Khoai, Mahidpur, and PSB agriculture farm—showcasing different soil types (rice, non-rice, and fallow land) within the lateritic soils of Birbhum. Sampling methods employed a tube auger, spade, or khurpi for moist soil and a screw-type auger for dry soil. Composite samples were gathered from three depths: 0–15 cm, 15–30 cm, and 30–45 cm, while steering clear of recently fertilized and non-representative zones. A total of 90 samples (10 locations×3 ecosystems×3 depths) were gathered, in addition to individual samples for bulk density assessment using a core sampler. Soil samples were dried in the shade, ground with a wooden pestle, sifted through a 2 mm mesh, and kept in labelled polythene bags.

2.4. Methods of soil analysis

Particle size analysis was conducted according to Bouyoucos (1927) with the use of a hydrometer and sodium hexametaphosphate. Soil texture was assessed using a textural diagram that considered the proportions of sand, silt, and clay. Soil samples were dried at 105°C, and the bulk density was measured using the undisturbed core sampling technique (Blake and Hartge, 1986). Soil pH was measured by immersing the combination electrode of a digital pH metre in a suspension of 1:2.5 soil to water (Jackson, 1958). Electrical conductivity of soil samples was measured in 1:2.5 soil to water extract using a conductivity bridge (Jackson, 1958). The wet oxidation method quantifies easily oxidizable organic carbon in soil by converting it to carbon dioxide. A 0.5 g sample was treated with excess potassium dichromate and concentrated sulfuric acid, then the unreacted dichromate was back titrated with standard ferrous ammonium sulphate using ferroin indicator (Walkley and Black, 1934). The amount of available nitrogen was calculated using the method by Subbiah and Asija (1956). 5 g of soil and 20 ml of distilled water were added to a Kjeldahl flask, along with 25 ml of a 2.5% NaOH and 0.32% KMnO_4 solution. After assembling the Kjeldahl apparatus, 10 ml of 0.02 N H_2SO_4 absorbed the evolved NH_3 , resulting in a distillate of about 30 ml. Titration with 0.02 N NaOH showed a color change from pink to yellow. Available phosphorus in acid soil was determined using 0.03 N NH_4F and 0.025 N HCl extractants (Bray and Kurtz, 1945). The Olsen method with 0.5M NaHCO_3 was used for neutral/alkaline soil analysis. Neutral ammonium acetate extracted potassium from soil (1:5 w v⁻¹), and K_2O amount was measured with a flame photometer (Jackson, 1958). The Cation Exchange Capacity (CEC) of soil was measured by using Ammonium Acetate (pH 7) (Chapman, 1965). Soil

samples were analyzed for DTPA extractable Zn, Cu, Fe, and Mn using the Lindsay and Norvell (1978) method with a 0.005 M DTPA extraction solution (pH 7.3) prepared from 1.965 g DTPA, 1.470 g CaCl_2 , and 13.29 mg TEA. The pH was adjusted using dilute HCL or NH_4OH . 10 g of sieved soil was mixed with 20 ml of DTPA, agitated for 2 h, filtered through Whatman No. 42 paper, and the filtrate was analyzed via atomic absorption spectrophotometer.

2.5. Statistical analysis

The range, mean, and standard deviation of all the studied physico-chemical properties of soil, along with DTPA extractable micronutrients content, were calculated using standard formulas in Excel. Data on DTPA extractable micronutrient content in soil was analyzed using Duncan's multiple-range test (DMRT) to study their significant depth-wise and cropping system-wise variations. Moreover, simple correlation analysis was carried out to determine the relationship of DTPA extractable micronutrients with selected soil physico-chemical properties using SPSS statistical software version 20.0.

3. RESULTS AND DISCUSSION

3.1. Effects of different soil ecologies and soil depths on DTPA extractable cationic micro-nutrients (Zn, Cu, Fe and Mn) in soils

3.1.1. Effect on DTPA extractable Zn content

The DTPA extractable Zn content in rice ecology in 0–15 cm soil depth ranged from 0.51–1.10 mg kg⁻¹ (mean 0.78 mg kg⁻¹) (Table 1). At 15–30 cm, it varied from 0.44–1.01 mg kg⁻¹ (mean 0.71 mg kg⁻¹). At 30–45 cm, values ranged from 0.38–0.94 mg kg⁻¹, with a mean of 0.65 mg kg⁻¹. Its content in non-rice ecology showed variations across soil depths: 0–15 cm ranged from 0.54–1.37 mg kg⁻¹ (mean 0.96 mg kg⁻¹), 15–30 cm from 0.42–1.25 mg kg⁻¹ (mean 0.85 mg kg⁻¹), and 30–45 cm from 0.31–1.18 mg kg⁻¹ (mean 0.73 mg kg⁻¹). Again, its content in fallow land varied across soil depths: 0–15 cm ranged from 0.53–1.59 mg kg⁻¹ (mean 1.08 mg kg⁻¹), 15–30 cm from 0.47–1.41 mg kg⁻¹ (mean 0.96 mg kg⁻¹), and 30–45 cm from 0.42–1.34 mg kg⁻¹ (mean 0.88 mg kg⁻¹). Results indicated no significant depth-wise variation in DTPA extractable average Zn content across different soil ecologies (rice, non-rice, and fallow land). The highest mean DTPA extractable Zn was found at 0–15 cm depth, statistically comparable to 15–30 cm and 30–45 cm depths. Conversely, the lowest mean Zn content was at 30–45 cm depth, also statistically similar to both 15–30 cm and 0–15 cm depths in all studied soil ecologies. Irrespective of soil ecologies, the mean DTPA extractable Zn content was highest at 0–15 cm (0.94 mg kg⁻¹), similar to 15–30 cm, and lowest at 30–45 cm (0.76 mg kg⁻¹), also comparable to 15–30 cm. Overall, DTPA extractable Zn decreased with

increasing soil depth.

While comparing Zn content of various soil ecologies along various depths, it was noted that in the 0–15 cm depth, fallow land exhibited the highest mean Zn content (1.08 mg kg^{-1}), comparable to non-rice soil, while rice soil showed the lowest (0.78 mg kg^{-1}), also statistically similar to non-rice ecologies (Table 1). In both 15–30 cm and 30–45 cm soil depths, there were no significant variations in the mean DTPA extractable Zn content of all the studied soil ecologies. However, irrespective of soil depths, the mean DTPA extractable Zn was highest in fallow land (0.98 mg

kg^{-1}), comparable to non-rice soils, while rice soil had the lowest level (0.71 mg kg^{-1}), similar to non-rice soils.

Enrichment of organic carbon in topsoil layers significantly increases the availability of zinc. Lindsay and Norvell (1978) demonstrated that consistent additions of plant residues increased organic matter in the topsoil, which subsequently relates to elevated DTPA-extractable zinc levels. Their study also showed that the amount of available zinc usually decreases significantly with depth, often reaching low-to-medium levels in subsoil layers. In line with this, Katyal and Sharma (1991) found that organic matter significantly

Table 1: Variations in DTPA extractable Zn content at different soil depths under different soil ecologies

Soil Ecologies	Criteria	DTPA Extractable Zn content (mg kg ⁻¹)			Overall mean (irrespective of depth)
		Soil depth (cm)			
		0–15	15–30	30–45	
Rice Ecology	Range	0.51–1.10	0.44–1.01	0.38–0.94	0.71 ^b
	Mean	0.78 ^{Ab}	0.71 ^{Aa}	0.65 ^{Aa}	
	SD	0.21	0.20	0.21	
Non-Rice Ecology	Range	0.54–1.37	0.42–1.25	0.31–1.18	0.85 ^{ab}
	Mean	0.96 ^{Aab}	0.85 ^{Aa}	0.73 ^{Aa}	
	SD	0.30	0.30	0.30	
Fallow Land Ecology	Range	0.53–1.59	0.47–1.41	0.42–1.34	0.98 ^a
	Mean	1.08 ^{Aa}	0.96 ^{Aa}	0.88 ^{Aa}	
	SD	0.39	0.34	0.33	
Overall mean (irrespective of soil ecologies)		0.94 ^A	0.84 ^{AB}	0.76 ^B	

Different small letters superscripted in mean values between columns and capital letters superscripted in mean values between rows indicate significant differences ($p < 0.05$) according to DMRT for separation of means

influenced extractable zinc levels in Indian soils, with deeper profiles consistently showing reduced extractable Zn because of fixation processes and decreased biological activity. Sidhu and Sharma (2010) reported that available micronutrient concentrations tended to increase with an increase in soil organic carbon content and decrease with increasing pH and sand content. Consequently, the deduced decrease of zinc present in deeper layers noted could be justifiably attributed to minimal organic carbon contribution, rapid binding within organo-clay complexes, and limited mobility, elements strongly supported by prior studies on soil zinc behaviour.

3.1.2. Effect on DTPA extractable Cu content

In rice ecology, DTPA extractable Cu in 0–15 cm soil depth ranged from 0.72 – 1.41 mg kg^{-1} (mean: 1.17 mg kg^{-1}) (Table 2). In 15–30 cm, it ranged from 0.68 – 1.38 mg kg^{-1} (mean: 1.14 mg kg^{-1}); in 30–45 cm, from 0.63 – 1.33 mg kg^{-1} (mean: 1.09 mg kg^{-1}). In non-rice ecology, its content at 0–15 cm depth ranged from 0.74 – 1.38 mg kg^{-1} (mean: 1.13 mg kg^{-1}), at 15–30 cm from 0.71 – 1.32 mg kg^{-1} (mean:

1.08 mg kg^{-1}), and at 30–45 cm from 0.68 – 1.32 mg kg^{-1} (mean: 1.06 mg kg^{-1}). However, its content in fallow land ecology at different soil depths varied as follows: 0–15 cm ranged from 0.90 – 1.68 mg kg^{-1} (mean 1.37 mg kg^{-1}), 15–30 cm from 0.80 – 1.49 mg kg^{-1} (mean 1.22 mg kg^{-1}), and 30–45 cm from 0.77 – 1.49 mg kg^{-1} (mean 1.20 mg kg^{-1}). Results indicated no significant depth-wise variation in DTPA extractable Cu across different soil ecologies (rice, non-rice, fallow). Irrespective of soil ecologies, there was no statistically significant depth-wise variation of DTPA extractable Cu content, although its content was highest at 0–15 cm (1.22 mg kg^{-1}) and lowest at 30–45 cm (1.12 mg kg^{-1}), decreasing with soil depth.

Soil ecology variations showed significant differences in DTPA extractable Cu content at 0–15 cm depths (Table 2). Fallow land had the highest mean Cu content (1.37 mg kg^{-1}), while non-rice soil had the lowest (1.13 mg kg^{-1}), comparable to rice soil ecology. In soil depths of 15–30 cm and 30–45 cm, mean DTPA extractable Cu showed no significant variation across rice, non-rice, and fallow land

Table 2: Variations in DTPA extractable Cu content at different soil depths under different soil ecologies

Soil ecologies	Criteria	DTPA Extractable Cu content (mg kg ⁻¹)			
		Soil depth (cm)			Overall mean (Irrespective of depth)
		0–15	15–30	30–45	
Rice ecology	Range	0.72 – 1.41	0.68–1.38	0.63–1.33	1.13 ^b
	Mean	1.17 ^{Ab}	1.14 ^{Aa}	1.09 ^{Aa}	
	SD	0.21	0.21	0.21	
Non-rice ecology	Range	0.74–1.38	0.71–1.32	0.68–1.32	1.09 ^b
	Mean	1.13 ^{Ab}	1.08 ^{Aa}	1.06 ^{Aa}	
	SD	0.20	0.18	0.20	
Fallow land ecology	Range	0.90–1.68	0.80–1.49	0.77–1.49	1.26 ^a
	Mean	1.37 ^{Aa}	1.22 ^{Aa}	1.20 ^{Aa}	
	SD	0.23	0.21	0.22	
Overall mean (irrespective of soil ecologies)		1.22 ^A	1.14 ^A	1.12 ^A	

Different small letters superscripted in mean values between columns and capital letters superscripted in mean values between rows indicate significant differences ($p < 0.05$) according to DMRT for separation of means

ecologies. However, irrespective of soil depths, the fallow land had the highest mean Cu content (1.26 mg kg⁻¹), while non-rice had the lowest (1.09 mg kg⁻¹), which was again statistically equal to rice ecology.

The availability of copper (Cu) was significantly influenced by pedogenic factors such as organic matter, pH, and soil depth. The current results showed that DTPA-extractable Cu decreased with increasing soil depth, which was consistent with the findings of previous studies. The limited mobility of these metals in the soil column and the surface build-up of organic matter and biological activity that promoted micronutrient availability have been cited as explanations for this type of vertical gradient (Alloway, 2008). Alloway (2008) pointed out that Cu was more readily available in upper horizons because of frequent contributions of organic matter and microbial degradation, whereas lower levels would generally exhibit Cu deficiency as a result of immobilization or precipitation as insoluble hydroxides. Dhaliwal et al. (2022) found a notable reduction in available micronutrients in subsoil horizons of dominant soil orders of Punjab and blamed it on low organic carbon and high pH values that decreased the solubility of micronutrients. The role of organic matter in boosting micronutrient availability has been emphasized in a number of studies. Dissolving organic matter could result in the formation of Cu soluble complexes, enhancing their mobility and making them more accessible to plant roots (Alloway, 2008). Based on these results, soil depth, pH, and organic carbon significantly affect micronutrient dynamics, aligning with previous studies that demonstrated the importance of managing surface soil for sustaining crop nutrition.

3.1.3. Effect on DTPA extractable Fe content

DTPA extractable Fe content in rice ecology in 0–15 cm soil depth ranged from 37.01–44.60 mg kg⁻¹ (mean 41.47 mg kg⁻¹) (Table 3). In 15–30 cm depth, it ranged from 35.15–38.81 mg kg⁻¹ (mean 36.64 mg kg⁻¹) and in 30–45 cm depth, from 32.49–38.89 mg kg⁻¹ (mean 36.64 mg kg⁻¹). In non-rice ecology, its content showed variations with depth: 0–15 cm ranged from 37.74–41.96 mg kg⁻¹ (mean 40.39 mg kg⁻¹), 15–30 cm from 35.54–39.10 mg kg⁻¹ (mean 37.75 mg kg⁻¹), and 30–45 cm from 32.89–37.71 mg kg⁻¹ (mean 35.44 mg kg⁻¹). In fallow land ecology, its content at 0–15 cm depth ranged from 45.21–9.47 mg kg⁻¹, mean 48.02 mg kg⁻¹. At 15–30 cm, it varied from 40.08–44.10 mg kg⁻¹, mean 42.58 mg kg⁻¹; and 30–45 cm, from 37.10–42.53 mg kg⁻¹, mean 39.97 mg kg⁻¹. Significant depth-wise variation of DTPA extractable Fe was found across different soil ecologies (rice, non-rice, and fallow). The highest mean DTPA extractable Fe content occurred at 0–15 cm, while the lowest was at 30–45 cm across all soil types studied. Irrespective of soil ecologies, the mean DTPA extractable Fe content was highest at 0–15 cm depth (43.29 mg kg⁻¹) and lowest at 30–45 cm depth (37.35 mg kg⁻¹), decreasing with increased soil depth.

Soil ecology significantly influenced DTPA extractable Fe across depths. In 0–15 cm soil depth, its content was highest in fallow land (48.02 mg kg⁻¹), while non-rice soil ecology had the lowest (40.39 mg kg⁻¹), which was again statistically at par with rice soil ecology (Table 3). In 15–30 cm soil depth, fallow land ecology showed the highest DTPA extractable Fe content (42.58 mg kg⁻¹), while non-rice soil had the lowest (37.75 mg kg⁻¹), statistically equal to rice soil.

Table 3: Variations in DTPA extractable Fe content at different soil depths under different soil ecologies

Soil Ecologies	Criteria	DTPA extractable Fe content (mg kg ⁻¹)			Overall mean (irrespective of depth)
		Soil depth (cm)			
		0–15	15–30	30–45	
Rice Ecology	Range	37.01–44.60	35.15–41.39	32.49–38.89	38.97 ^b
	Mean	41.47 ^{Ab}	38.81 ^{Bb}	36.64 ^{Bb}	
	SD	2.84	2.23	2.22	
Non-Rice Ecology	Range	37.74–41.96	35.54–39.10	32.89–37.71	37.86 ^c
	Mean	40.39 ^{Ab}	37.75 ^{Bb}	35.44 ^{Cb}	
	SD	1.49	1.29	1.47	
Fallow Land Ecology	Range	45.21–49.74	40.08–44.10	37.10–42.53	43.52 ^a
	Mean	48.02 ^{Aa}	42.58 ^{Ba}	39.97 ^{Ca}	
	SD	1.64	1.45	1.66	
Overall mean (irrespective of soil ecologies)		43.29 ^A	39.71 ^B	37.35 ^C	

Different small letters superscripted in mean values between columns and capital letters superscripted in mean values between rows indicate significant differences ($p < 0.05$) according to DMRT for separation of means

In 30–45 cm soil depth, fallow land had the highest mean DTPA extractable Fe at 39.97 mg kg⁻¹, while non-rice soil had the lowest at 35.44 mg kg⁻¹, statistically equal to rice soil. However, irrespective of soil depths, the mean DTPA extractable Fe was highest in fallow land (43.52 mg kg⁻¹) and lowest in non-rice soil (37.86 mg kg⁻¹).

The existing findings indicated that DTPA-extractable Fe was higher in surface soil horizons and decreased with depth increase. The trend corroborates Lindsay and Norvell (1978), who demonstrated that DTPA-Fe contents would be lower where the soil was deeper, primarily due to lower organic matter contents in deeper horizons. Organic matter played a vital role in ensuring Fe availability by creating stable chelates that hindered iron oxidation and precipitation (Lindsay and Norvell, 1978). Soil pH also had a significant impact on iron solubility. With rising pH, Fe²⁺ was converted to Fe³⁺, which easily formed insoluble Fe(OH)₃ precipitate, thus lowering its availability to plants. This accounted for the noted reduced DTPA-Fe levels in deeper and more alkaline layers. The topsoil typically had higher levels of organic matter and exhibited greater microbial activity, both of which aided in keeping iron in forms accessible to plants. Sharma et al. (1992) in Punjab found a strong positive relationship between organic carbon and DTPA-extractable iron (Fe), which declined linearly as depth increased. Dhaliwal et al. (2022) found that elements affecting soil development, such as the addition of organic matter and redox states, govern the accessibility of Fe in agricultural soils. Thus, the vertical distribution of DTPA-extractable Fe mirrors the organic carbon gradient of the soil profile. Greater surface feasibility was correlated with greater accumulation of organic matter and greater

microbial activity, while lower subsoil concentrations were due to fewer organic chelators as well as greater fixation in the form of precipitation in alkaline environments (Dhaliwal et al., 2022).

3.1.4. Effect on DTPA extractable Mn content

DTPA extractable Mn content in rice ecology ranged from 16.61–26.61 mg kg⁻¹ (mean: 20.36 mg kg⁻¹) at 0–15 cm, 12.42–23.37 mg kg⁻¹ (mean: 16.91 mg kg⁻¹) at 15–30 cm, and 10.34–19.97 mg kg⁻¹ (mean: 14.62 mg kg⁻¹) at 30–45 cm soil depths) (Table 4). In non-rice ecology, its content at 0–15 cm depth ranged from 14.46 to 24.46 mg kg⁻¹ (mean: 18.65 mg kg⁻¹), at 15–30 cm from 12.86 to 20.86 mg kg⁻¹ (mean: 15.82 mg kg⁻¹), and at 30–45 cm from 10.49 to 17.79 mg kg⁻¹ (mean: 13.13 mg kg⁻¹). In fallow land ecology, its content at different soil depths showed 20.12–32.64 mg kg⁻¹ (mean 24.75 mg kg⁻¹) for 0–15 cm, 17.84–28.94 mg kg⁻¹ (mean 21.95 mg kg⁻¹) for 15–30 cm, and 14.55–24.68 mg kg⁻¹ (mean 18.21 mg kg⁻¹) for 30–45 cm. Significant depth-wise variation in DTPA extractable Mn content was observed across different soil ecologies (rice, non-rice, and fallow land). The highest mean Mn content was found at 0–15 cm soil depth, while the lowest mean Mn content occurred at 30–45 cm depth in all studied soil ecologies. Irrespective of soil ecologies, the mean DTPA extractable Mn content was highest at 0–15 cm (21.25 mg kg⁻¹) and lowest at 30–45 cm (15.32 mg kg⁻¹), decreasing with increased soil depth.

DTPA extractable Mn content varied significantly across soil depths. In the 0–15 cm depth, fallow land ecology had the highest mean Mn content (24.75 mg kg⁻¹), while non-rice soil ecology had the lowest (18.65 mg kg⁻¹), statistically

Table 4: Variations in DTPA extractable Mn content at different soil depths under different soil ecologies

Soil Ecologies	Criteria	DTPA extractable Mn content (mg kg ⁻¹)			Overall mean (Irrespective of depth)
		Soil depth (cm)			
		0–15	15–30	30–45	
Rice Ecology	Range	16.61–26.61	12.42–23.37	10.34–19.97	17.29 ^b
	Mean	20.36 ^{Ab}	16.91 ^{Bb}	14.62 ^{Bb}	
	SD	2.75	2.87	2.51	
Non-Rice Ecology	Range	14.46–24.46	12.86–20.86	10.49–17.79	15.86 ^b
	Mean	18.65 ^{Ab}	15.82 ^{Bb}	13.13 ^{Cb}	
	SD	3.01	2.63	2.50	
Fallow Land Ecology	Range	20.12–32.64	17.84–28.94	14.55–24.68	21.64 ^a
	Mean	24.75 ^{Aa}	21.95 ^{Aa}	18.21 ^{Ba}	
	SD	4.11	3.64	3.47	
Overall mean (irrespective of soil ecologies)		21.25 ^A	18.22 ^B	15.32 ^C	

Different small letters superscripted in mean values between columns and capital letters superscripted in mean values between rows indicate significant differences ($p < 0.05$) according to DMRT for separation of means

equal to rice soil (Table 4). In 15–30 cm soil depth, fallow land had the highest DTPA extractable Mn content (21.95 mg kg⁻¹), while non-rice soil had the lowest (15.82 mg kg⁻¹), statistically equal to rice soil. In 30–45 cm soil depth, fallow land had the highest DTPA extractable Mn content (18.21 mg kg⁻¹), while non-rice soil recorded the lowest (13.13 mg kg⁻¹), statistically equal to rice soil. However, irrespective of soil depths, the mean DTPA extractable Mn was highest in fallow land (21.64 mg kg⁻¹) and lowest in non-rice soil (15.86 mg kg⁻¹), which was, however, statistically equal with rice ecology.

As the depth increased in soil, the DTPA-extractable manganese (Mn) content decreased. High microbial activity and organic matter in the near-surface soil were the main reasons behind such a gradient, which enhanced the reduction of insoluble Mn oxides and retained Mn in soluble, plant-available Mn²⁺ form. Sharma et al. (1992) reported that Mn levels were typically higher in the topsoil and diminish with depth, attributed to decreasing organic carbon and lower aeration in deeper layers, which restricted the conversion of Mn³⁺/Mn⁴⁺ oxides into Mn²⁺. Soil pH had a significant impact on the availability of Mn. In acidic conditions, Mn²⁺ was dominant and had greater solubility; however, with rising soil pH, Mn²⁺ oxidized into the less soluble forms of Mn³⁺ or Mn⁴⁺ oxides, which reduced the concentrations of DTPA-extractable Mn in deeper and more alkaline layers (Alloway, 2008). Dhaliwal et al. (2022) emphasized that pedogenic factors-like clay buildup, redox gradients, and organic carbon distribution-were essential in influencing Mn mobility. Differences in Mn availability throughout the soil profile were often due to varying mineral weathering and leaching processes affecting Mn-containing

minerals. Collectively, these validated results highlighted the significance of surface soil properties—especially organic carbon and pH—in influencing Mn availability. Ensuring organic amendments and regulating soil reaction in surface layers were crucial for preserving Mn bioavailability in agricultural soils.

3.2. Soil physico-chemical properties of different soil ecologies

Irrespective of cropping systems and soil depths studied, the clay content of soil samples varied from 20.80–33.65% with a mean of 27.40. pH varied from 4.51–5.99, averaging 5.39. Electrical Conductivity (EC) ranged from 0.16–0.24 with a mean of 0.20. Organic Carbon content fluctuated between 0.15–0.56%, with a mean of 0.36%. Bulk Density (BD) varied from 1.20–1.36 Mg m⁻³, averaging 1.29. Cation Exchange Capacity (CEC) ranged from 20.80–33.65 cmol (P+) kg⁻¹, with a mean of 9.90 cmol (P+) kg⁻¹. Available Nitrogen content was from 190.17–299.94 kg ha⁻¹, averaging 247.39 kg ha⁻¹. Available Phosphorus content varied from 7.65–22.88 kg ha⁻¹, with a mean of 13.12 kg ha⁻¹. Available Potassium content ranged from 97.79–148.82 kg ha⁻¹, averaging 122.64 kg ha⁻¹. All results were consistent across various cropping systems and soil depths (Table 5).

3.3. Co-Relationship of DTPA extractable cationic micronutrient contents and soil properties

3.3.1. Co-relationship of DTPA extractable Zn with studied soil properties

The DTPA extractable Zn content was positively correlated with pH ($r = 0.332$, $p \leq 0.01$), EC ($r = 0.359$, $p \leq 0.01$), OC ($r = 0.636$, $p \leq 0.01$), and CEC ($r = 0.658$, $p \leq 0.01$) while negatively correlated with available N ($r = -0.379$, $p \leq 0.01$) (Table 6). No significant correlation was found with bulk

Table 5: Range, mean and standard deviation of some soil properties of the studied soil ecologies

	Clay (%)	BD (Mg m ⁻³)	pH	EC (dS m ⁻¹)	OC (%)	CEC [cmol (p+) kg ⁻¹]	Av. N (kg ha ⁻¹)	Av. P ₂ O ₅ (kg ha ⁻¹)	Av. K ₂ O (kg ha ⁻¹)
Range	20.80– 33.65	1.20–1.36	4.51– 5.99	0.16– 0.24	0.15– 0.56	6.85–13.30	190.17– 299.94	7.65–22.88	97.79– 148.82
Mean	27.40	1.29	5.39	0.20	0.36	9.90	247.39	13.12	122.64
SD	3.39	0.04	0.37	0.01	0.09	1.37	26.75	3.80	10.27

density, clay content, available P₂O₅, or K₂O. Available zinc showed a significant and positive correlation with soil organic carbon which could be explained by considering the fact that organic matter reacted with zinc and formed soluble organo-zinc complexes, which were readily plant available. The significant and positive correlation between DTPA-extractable Zn and OC, along with Zn and CEC, states the important role of organic matter in enhancing the solubility as well as retention of Zn in soil (Katyal and Sharma, 1991; Bassirani et al., 2011). Athokpam et al. (2013) reported significant and positive correlation between available zinc and soil organic carbon ($r=0.708$, $p\leq 0.01$) in the soils of Senapati district, Manipur. The high relationship established between OC and CEC demonstrated that organic matter promotes the development of soluble organo-zinc complexes, while improved CEC leads to enhanced zinc retention, thus enhancing its availability for plant absorption. The poor positive correlation with pH might well be due to a limited range of pH or a buffering capacity of organic matter, as suggested by previous studies in the context of DTPA extractable Zn distribution in Indian soils (Katyal and Sharma, 1991). The inverse connection with accessible nitrogen might suggest heightened Zn uptake when N availability was elevated, a trend observed in micronutrient behaviour studies in similar soil conditions (Bassirani et al., 2011). The lack of significant associations with bulk density, clay content, P₂O₅, or K₂O suggested that these factors exerted a minor influence on Zn availability in the soils studied. Similar observations were reported by Sharma et al. (2006); Yadav and Meena (2009), Chitdeshwari and Krishnaswamy (1997).

3.2. Co-relationship of DTPA extractable Cu with studied soil properties

The correlation coefficient analysis confirmed that the concentration of DTPA-extractable copper (Cu) in soils of the various ecologies studied had strong negative correlation with clay content ($r=-0.528$, $p\leq 0.01$), indicating that a high percentage of clay could result in low Cu availability (Table 6). Conversely, Cu availability was not observed to have any significant correlation with bulk density, pH, electrical conductivity (EC), organic carbon (OC), cation exchange capacity (CEC), or major nutrients such as available nitrogen (N), phosphorus (P₂O₅), and potassium

(K₂O). This signified that among the soil properties tested, clay content was a key factor in deciding Cu bioavailability, likely due to Cu fixation in finer fractions of the soils and lower desorption in the soils with higher clay content. Nagendran and Angayarkanni, (2010) also reported a statistically significant negative relationship between available copper and soil pH ($r=-0.33$, $p\leq 0.05$) in the soils of Cumbum Valley, Tamil Nadu. However, a significant positive relationship between Cu and organic carbon ($r=0.44$, $p\leq 0.01$) was reported by them, which indicated that organic matter played a role in improving Cu solubility and retention. Conversely, Yadav and Meena (2009) identified a minor negative correlation only between pH and Cu, indicating that the effect of pH on Cu availability might vary based on soil type and regional influences. The weak correlations observed between Cu and other factors such as pH, EC, and organic carbon in this study might result from the ecological and mineralogical variances in the analyzed soils. However, the significant correlation with clay content challenges the accepted notion that soil texture influenced micronutrient mobility, as demonstrated by prior studies by Katyal and Sharma (1991), which emphasized the role of physical soil properties in impacting copper dynamics.

3.3. Co-relationship of DTPA extractable Fe with studied soil properties

DTPA-extractable iron (Fe) in the soils studied showed a statistically significant negative correlation with available potassium (K₂O) ($r=-0.275$, $p\leq 0.01$). No significant correlations were found between DTPA-Fe and clay content, organic carbon (OC), cation exchange capacity (CEC), bulk density, pH, electrical conductivity (EC), available nitrogen, or available phosphorus (P₂O₅) (Table 6).

The significant negative correlation between DTPA-extractable Fe and available K₂O suggested possible antagonistic interactions, where higher exchangeable K might suppress Fe availability through competitive adsorption or ion competition mechanisms. In contrast, earlier studies in alluvial soils from western Uttar Pradesh and Gujarat have underscored strong correlations of Fe with pH, OC, and EC. For instance, Singh and Kumar (2022) reported a strong negative correlation between available Fe and soil pH ($r=-0.674$, $p\leq 0.01$), and positive correlations with OC ($r=0.734$, $p\leq 0.01$) and EC ($r=0.628$, $p\leq 0.01$) in

Table 6: Pearson's correlation matrix for linear relationship of DTPA extractable cationic micronutrients with various soil properties

	Clay	BD	pH	EC	OC	CEC	Av. N	Av. P ₂ O ₅	Av. K ₂ O
Zn	0.094	-0.144	0.332**	0.359**	0.636**	0.658**	-0.379**	-0.096	0.199
Fe	0.057	-0.075	-0.197	-0.179	0.140	0.024	0.021	-0.024	-0.275**
Mn	-0.280**	-0.145	-0.004	0.033	0.370**	0.309**	0.211*	0.009	-0.035
Cu	-0.528**	0.052	0.132	0.141	0.005	0.047	-0.100	0.025	-0.132

** : Correlation is significant at the $p=0.01$ level (2-tailed); * : Correlation is significant at the $p=0.05$ level (2-tailed)

Muzaffarnagar district soils. Similarly, in Mehsana district of Gujarat, Fe was found to be significantly negatively correlated with pH ($r=-0.218$, $p\leq 0.01$) and positively associated with OC ($r=0.193$, $p\leq 0.01$). The absence of such correlations in our study might stem from limited variation in soil pH, OC, and EC across our sampling locations, which reduced statistical detectability. Alternatively, the differences could be due to site-specific soil mineralogy or management regimes that emphasized K₂O as a more controlling factor for Fe availability in these soils.

3.4. Co-relationship of DTPA extractable Mn with studied soil properties

The correlation analysis indicated that DTPA-extractable Mn content in soils of various ecologies had significant correlations with certain soil properties. There was a high positive correlation with organic carbon (OC) ($r=0.370$, $p\leq 0.01$), cation exchange capacity (CEC) ($r=0.309$, $p\leq 0.01$), and available nitrogen (N) ($r=0.211$, $p\leq 0.05$), but a significant negative correlation with clay content ($r=-0.280$, $p\leq 0.01$). No high correlation was observed for DTPA-extractable Mn with pH, EC, bulk density, available P₂O₅, or available K₂O (Table 6).

The positive relationship with organic carbon was due to the function of organic matter to increase Mn availability. Organic matter chelates with Mn, thus keeping it more soluble and plant-accessible and inhibiting its oxidation into less accessible forms (Alloway, 2008). Also, increased CEC allowed for Mn to be retained in exchangeable forms, increasing its plant availability (Lindsay and Norvell, 1978).

The adverse correlation with clay content could result from manganese fixation or adsorption on mineral surfaces, making it less available in finer-textured soils (Kabata-Pendias, 2010). Though Mn tends to be more available in acidic environments, the absence of noteworthy correlation with soil pH in this study could indicate that fluctuations in pH within the soils under investigation were not sufficient to affect Mn solubility significantly.

Taken together, these results emphasized the need to retain sufficient organic matter and control CEC in order to ensure manganese availability in soils. They aligned with the more general literature indicating that Mn dynamics

were highly sensitive to biological and chemical reactions in the rhizosphere (Alloway, 2008; Lindsay and Norvell, 1978; Kabata-Pendias, 2010).

4. CONCLUSION

DTPA-extractable Zn, Cu, Fe, Mn declined with soil depth in various ecologies. Fallow land had the highest micronutrients; rice soils had the least Zn, while non-rice soils had the lowest Cu, Fe, and Mn. DTPA-extractable Zn positively correlated with pH, EC, OC, CEC; negatively with nitrogen. Negative correlations were observed between DTPA-Fe and K₂O. Additionally, DTPA-Mn and Cu showed significant relationships with OC, CEC, and clay. These results highlighted the significance of sustainable soil management for maintaining nutrient equilibrium.

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