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Impact of Long-Term Fertilization and Manuring on Cation Bridging in Clay-Humus Complex under Four Soil Orders

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ABSTRACT: A study examined clay-humus complexes (COMF) in tropical soils (Inceptisol, Alfisol, Vertisol, Mollisol). High temperatures and leaching in these conditions challenge soil organic matter. Stabilization involves physical, chemical, and microbial mechanisms. Sustainable practices like no-till farming and organic matter additions can help. The study aimed to identify bridging cations (Ca^{2+}, Mg^{2+}, Fe$^{3+/2+}$, Al^{3+}) in COMF. The treatments comprised of control (no fertilization), 100% NPK (100% of recommended N, P and K through fertilizer), 50% NPK + 50% of recommended N supplied through either farm yard manure (FYM) or cereal residue (CR) or green manure (GM). Bridging cations like Ca^{2+}, Mg^{2+}, Fe$^{3+/2+}$, Al^{3+} were extracted with 0.1 N citrate, 0.1 EDTA, and 0.1 ammonium oxalate at pH 7. Ca^{2+} is dominant in the Inceptisol clay–humus extract. In Alfisol sample apart from monovalent cations, bonding is mainly through Al^{3+}. The extract from Vertisol sample contains little Fe$^{3+/2+}$ or Al^{3+} and major bonding is through Ca^{2+} in Mollisol Ca^{2+}, Mg^{2+} and Fe$^{3+/2+}$ are all involved in bonding. Irrespective of all the soil types EDTA showed better extraction of Ca^{2+} and Mg^{2+} compared to citrate and ammonium oxalate whereas ammonium oxalate showed better extraction of Al^{3+}. In Inceptisol and Alfisol Al^{3+} content was the highest under NPK + CR and lowest under control. Application of NPK + GM or NPK + FYM or NPK+CR showed better bridging cations over control in COMF.

Keywords: Clay-humus complex, Cation Bridging, Organic Manure, FYM, EDTA, Ammonium oxalate, Citric acid.

INTRODUCTION

Soil fertility is a crucial aspect of agriculture, as it determines the productivity and sustainability of crops (Nair, 2019). Nutrient availability in soil governed by its organic matter content. Organic matter (OM) in soil is mainly associated with minerals in the form of organo-mineral complexes of varying stability. One area of particular interest is the impact of long-term fertilization and manuring on cation bridging in clay-humus complexes. Long-term fertilization and manuring can alter the cation bridging process in various ways (Bhandari *et al.*, 2018; Ahmed *et al.*, 2002). SOM interacts with the reactive mineral surfaces by hydrogen (H)-bonding, van der Waals attraction, hydrophobic interactions, polyvalent cation bridging, and ligand exchange. The study of cation bridging in clay-humus complexes has gained significant attention in recent years due to its impact on structure, aggregate formation and different soil functions. Cation bridging refers to the formation of bonds between soil particles through different cations, which can affect the stability and aggregation of soil particles. Cation bridging is influenced by various factors, including soil type, soil management practices, and climatic conditions. Naveed *et al.* (2019) found that the application of manures and fertilizers can increase the concentration of cations in the soil, leading to increased cation bridging and improved soil structure. Contrarily, the type of fertilizers and manures used can affect the cation bridging process differently, with some fertilizers leading to increased cation bridging while others had no effect or even decreased cation bridging (Sharma *et al.*, 2016).

The effect of soil order on cation bridging in clay-humus complexes has not been extensively studied to address these gaps in knowledge, the present study aims to investigate the impact of long-term fertilization and manuring on cation bridging in clay-humus complexes across four different soil orders: Inceptisols, Alfisols, Mollisols, and Ultisols which represent a range of soil characteristics, including clay content, nutrient availability, pH and different nutrient supply options. This study aims to provide valuable insights for improving soil fertility and sustainability in agriculture.

METHODS AND MATERIALS

A. Experimental sites

Four on-going long-term experiments (LTEs) continuing since 1983-84 under the aegis of All India Coordinated Research Project on Integrated Farming Systems (AICRP-IFS) of Indian Council of Agricultural

Research (ICAR), located at Ludhiana (Inceptisol), Jabalpur (Vertisol), Pantnagar (Mollisol) and Ranchi (Alfisol) of India were chosen for the present study. Locations, elevations, climatic variables, soil types and existing cropping systems of the four sites are given in Table 1. Important physio-chemical properties of surface (0–15 cm) soils of those sites at the beginning of the experiments are briefed in Table 2.

Table 1: Site details of the long-term experiments (LTEs) selected for the study.

Experimental site	Latitude	Longitude	Mean annual temperature (°C)		Mean annual rainfall (mm)	Agro-climatic region	Cropping system	Soil taxonomy
			Min.	Max.				
Ludhiana	30° 56′ N	75° 52′ E	5.7	40.6	500	Trans-Gangetic Plains region	Rice-wheat	Typic Haplustept
Jabalpur	23° 10′ N	79° 57′ E	22.8	31.9	1386	Central Plateau and Hills region	Rice-wheat	Typic Haplustert
Pantnagar	29° 08′ N	79° 05′ E	7.3	37.4	1383	Western Himalayan region	Rice-wheat	Aquic Hapludoll
Ranchi	23° 17′ N	85° 19′ E	16.7	31	1450	Eastern Plateau and Hills region	Maize-wheat	Typic Haplusalf

Table 2: Important physico-chemical properties of surface (0–15 cm) soil of the four LTE sites at the beginning of the experiments.

Soil property	Inceptisol (Ludhiana)	Vertisol (Jabalpur)	Mollisol (Pantnagar)	Alfisol (Ranchi)
Sand (%)	54	28	32	55
Silt (%)	28	19	39	22
Clay (%)	18	53	29	23
Texture	Sandy loam	Clay	Silty clay loam	Sandy clay loam
pH (1:2.5)	8.15	7.54	7.3	6.5
EC (1:2.5) (dS m^{-1})	0.32	0.48	0.35	0.10
Organic C (g kg^{-1})	3.1	6.0	14.2	4.2
Available N (kg ha^{-1})	143	238	280	255
Available P (kg ha^{-1})	11.0	8.6	14.5	14.2
Available K (kg ha^{-1})	101	287	120	195

B. Details of the field experiments and treatments

Rice-wheat sequence was followed every year in Ludhiana, Jabalpur and Pantnagar whereas, maize-wheat sequence was followed in Ranchi since the initiation of the experiments. Rice and maize were grown in monsoon season (July–October) without any irrigation and wheat was grown in rabi (winter) season (November–April) with 4–5 irrigations each of 6 cm depth. All the LTEs have 12 treatments laid out in completely randomized block design, from which 5 treatments (each with 3 replications), *viz*., control, 100% NPK, NPK + FYM, NPK + CR, and NPK + GM were chosen for the study. Treatment details for monsoon and winter seasons are provided in Tables 3 and 4.

In the NPK + CR treatment, wheat straw was applied in Ludhiana, Jabalpur, Pantnagar, and paddy straw in Ranchi. In the NPK + GM treatment, the applied green manure was sesbania (*Sesbania aculeata*) at Ludhiana, sunhemp (*Crotalaria juncea*) at Jabalpur, green-gram (*Vigna radiata*) at Pantnagar, and pongamia (*Pongamia pinnata*) at Ranchi. All these treatments were applied in monsoon, while in winter season only N, P and K fertilizers were applied. The C and N content of different organic sources are presented in Table 5.

Table 3: Treatment details of the LTEs.

Treatment	Monsoon (Rice/Maize)	Winter (Wheat)
Control (T1)	No fertilizer or manure	No fertilizer or manure
100% NPK (T2)	100% of recommended rate of NPK through fertilizers	100% of recommended rate of NPK through fertilizers
NPK + FYM (T3)	50% of recommended rate of NPK through fertilizers +50% N through FYM	100% of recommended rate of NPK through fertilizers
NPK + CR (T4)	50% of recommended rate of NPK through fertilizers +50% N through wheat straw	100% of recommended rate of NPK through fertilizers
NPK + GM (T5)	50% of recommended rate of NPK through fertilizers +50% N through green manure	100% of recommended rate of NPK through fertilizers

Table 4: Recommended fertilizer dose of different crops in LTEs.

Location/soil type	Cropping system	100% recommended fertilizer dose (kg ha^{-1})		
		N	P	K
Ludhiana (Inceptisol)	Rice (*Oryza sativa* L.), cv. PR-116 (Monsoon season)	120	30	30
	Wheat (*Triticum aestivum* L.), cv. PBW-343 (Winter season)	120	60	30
Jabalpur (Vertisol)	Rice (*Oryza sativa* L.), cv. MR-219 (Monsoon season)	120	60	40
	Wheat (*Triticum aestivum* L.), cv. GW-273 (Winter season)	120	60	40
Pantnagar (Mollisol)	Rice (*Oryza sativa* L.), cv. PR-113 (Monsoon season)	120	40	–
	Wheat (*Triticum aestivum* L.), cv.PBW-343 (Winter season)	120	40	–
Ranchi (Alfisol)	Maize (*Zea mays* L.), cv. M-9000 (Monsoon season)	100	22	21
	Wheat (*Triticum aestivum* L.), cv. DWR-162 (Winter season)	100	22	21

Table 5: Total N and C content (% on dry weight basis) in organic sources used in those LTEs.

Organic source	C (%)	N (%)
FYM	27.3 ± 7.1*	0.75 ± 0.21
Crop residue Rice straw	38.9 ± 8.2	0.50 ± 0.11
Wheat straw	40.8 ± 5.1	0.64 ± 0.15
Green manure Dhaincha	49.8 ± 9.2	3.10 ± 0.42
Green-gram	43.3 ± 9.6	2.12 ± 0.11
Sunhemp	42.3 ± 4.1	2.24 ± 0.21
Karanj	48.1 ± 6.1	2.36 ± 1.15

* Mean ± standard error of mean (SEM). Source Das *et al.* (2019)

C. Collection and analyses of soil samples

Collection of soil (0–15 cm) samples were done after the harvest of wheat crop, from five randomly chosen spots in each replicated plot with a core sampler. Five sub-samples from each plot were pooled together to represent a replication of a particular treatment. Soil samples were dried in air, ground by wooden pestle and mortar, and passed through a 2-mm sieved and analysed in 2019-2020.

D. Colloidal organo-mineral fraction (COMF)

Separation of COMF from bulk soil was done following the method of Datta *et al.* (2015). Briefly, 20 g soil along with 200 mL distilled water were taken in a stainless-steel beaker and the mixture was stirred for15 min with a mechanical stirrer. The suspension was then subjected to ultrasonic vibration for 5 min to further disperse the microaggregates. The dispersed suspension was entirely transferred to a 2.5-L bottle and distilled water was added up to the neck. The suspension in the bottle was kept undisturbed for 8 h, after which upper10 cm portion, containing COMF having diameter b 2 μm as per Stokes' law (Jackson, 1985), was siphoned out. Again, distilled water was added to the suspension in the bottle up to the neck, and the same procedure, as mentioned above, was repeated until the upper 10 cm the suspension became clear after 8 hours of settling time. The extracted suspensions containing COMF (b2 μm) were pooled together, and concentrated by repeated centrifugation and decantation. After centrifugation the concentrated suspension was freeze dried in a lyophilizer (Kaiser and Guggenberger 2003) and stored for further analysis.

E. Cations Analysis

Clay-humus complex was treated with ligands 0.1 N citrate, 0.1 N EDTA and 0.1 N oxalate. The ligands were prepared by weighing exactly 3.5 g of citric acid (AR BDH), 4.65 g of EDTA (disodium salt, GR E. Merck), and 3.55 g of ammonium oxalate (GR E. Merck) and dissolving in 400 ml water. The pH of the extracting solution was adjusted to pH 7 with dilute (1:1) ammonia solution. Finally, the volume of the solution was made up to 500 ml to give 0.1 N solutions of the respective reactants.

Then to estimate cations, exactly 100 mg of clay-humus complexes was weighed and put into clean dry 50 ml centrifuge tubes. After weighing, 10 ml of pH 7extracting ligand solution was added into each set. The centrifuge tubes were shaken for 2 hrs and then left for 48 hrs. The suspension was then centrifuged at 5000 rpm for 30 minutes and supernatant was decanted into 50ml beaker. Thereby, Al^{3+}, $Fe^{3+}/^{2+}$, Ca^{2+} and Mg^{2+} metal was immediately estimated from the supernatant using Atomic Absorption Spectrophotometer (AAS). A standard solution of respective ligands was prepared. One should take caution that ligands do not interfere during the AAS reading.

F. Statistical Analysis

Analysis of statistical significance of long-term fertilization and manuring on cation bridging in clay-humus complex was performed using one-way analysis of variance (ANOVA) to compare cation bridging among the treatments.

RESULT

The results revealed significant variations in cation extraction across different soil orders and treatment conditions.

Extraction of cations by EDTA from clay humus complexes: In Fig. 1 data shows that the Mollisol soil order, the highest average concentrations of Fe (3.80 g kg^{-1}), Mg (2.00 g kg^{-1}), and Ca (14.85 g kg^{-1}) were observed in the NPK + FYM treatment. The highest concentration of Al (0.34 g kg^{-1}) was found in NPK+GM treatment. The control treatment exhibited the lowest concentrations for all cations.

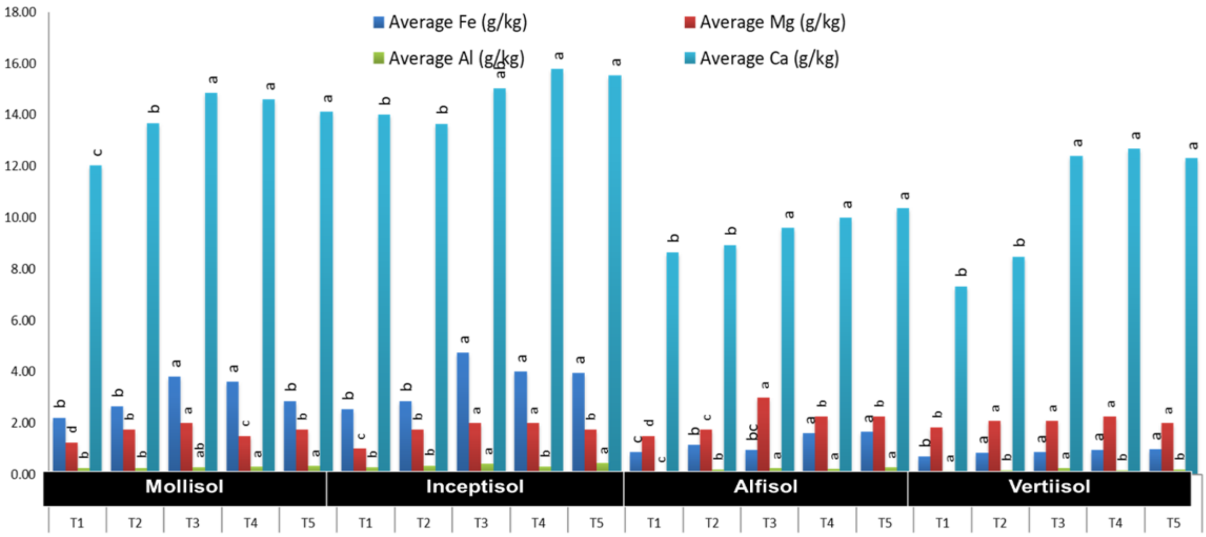

Fig. 1. Extraction of cations by EDTA from clay humus complexes.

For the Inceptisol soil order, the highest average concentrations of Fe (4.75 g kg^{-1}) and Mg (2.00 g kg^{-1}) were recorded in the NPK + FYM treatment. While the highest concentrations of Al (0.45 g kg^{-1}) were observed in NPK+GM treatment and highest Ca was found in NPK+CR treatment. The 100% NPK treatment also resulted in relatively higher cation concentrations compared to the control.

In the Alfisol soil order, the highest average concentrations of Fe (1.68 g kg^{-1}), Al (0.27 g kg^{-1}), and Ca (10.4 g kg^{-1}) were observed in the NPK + GM treatment. The highest concentration of Mg (3.00 g kg^{-1}) was found in NPK+FYM treatment. The control treatment exhibited the lowest concentrations for Fe, Mg, Ca and Al.

In the Vertisol soil order, the NPK + GM treatment yielded the highest average concentrations of Fe (0.98 g kg^{-1}), while the highest concentration of Mg (2.25 g kg^{-1}) and Ca (12.7 g kg^{-1}) was found in NPK+CR treatment. The highest concentration of Al (0.24 g kg^{-1}) was found in NPK+FYM treatment. The control treatment showed the lowest concentrations for all the cations.

Extraction of cations by Ammonium Oxalate from clay humus complexes: Fig. 2 shows that in Mollisol soil order, the NPK + CR treatment exhibited the highest average concentrations of Fe (0.57 g kg^{-1}), while the NPK + FYM treatment showed the significantly highest average Mg (1.99 g kg^{-1}) concentration. Highest Al (0.05 g kg^{-1}) concentration was found in NPK+GM treatment The control treatment yielded the lowest concentrations for all three cations.

In the Inceptisol soil order, the NPK + FYM treatment resulted in the highest (0.58 g kg^{-1}) average concentrations of Fe and NPK+CR showed highest (0.07 g kg^{-1}) Al and Mg (1.56 g kg^{-1}) concentration. Once again, the control treatment had the lowest concentrations for all three cations.

In the Alfisol soil order, the NPK + CR treatment displayed the highest average concentrations of Fe (0.40 g kg^{-1}), Mg (1.34 g kg^{-1}) and Al (0.48 g kg^{-1}). The control treatment consistently exhibited the lowest concentrations for all three cations.

In the Vertisol soil order, the NPK + GM treatment demonstrated the highest average concentration of Fe (1.10 g kg^{-1}) and Al (0.34 g kg^{-1}). The NPK + CR treatment resulted in the highest average concentrations of Mg (1.78 g kg^{-1}). The control treatment displayed the lowest concentrations for all three cations.

Extraction of cations by Citric Acid from clay humus complexes: Data shown in Fig. 3 for the Mollisol soil order, the NPK + FYM treatment displayed the highest average concentrations of Fe (2.09 g kg^{-1}) and Mg (1.69 g kg^{-1}). The NPK + CR treatment showed the highest average concentration of Al (0.22 g kg^{-1}). The control treatment exhibited the lowest concentrations for all three cations.

In the Inceptisol soil order, the NPK + FYM treatment exhibited the highest average concentrations of Fe (4.37 g kg^{-1}) and Mg (1.48 g kg^{-1}). The highest concentration of Al (0.46 g/kg) was found in NPK+GM treatment. The control treatment yielded the lowest concentrations for all three cations.

In the Alfisol soil order, the NPK + GM treatment demonstrated the highest average concentrations of Fe (2.65 g kg^{-1}), and Mg (1.13 g kg^{-1}). The control treatment displayed the lowest concentrations for Fe and Mg, while the highest Al (0.75 g kg^{-1}) concentration was observed in the 100% NPK treatment.

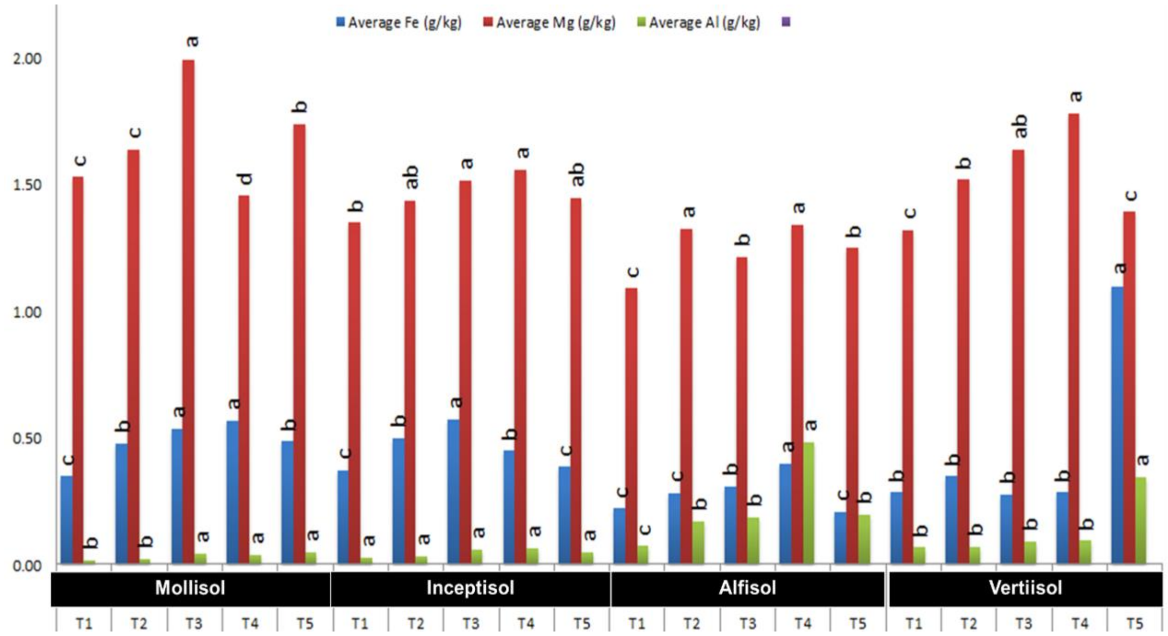

Fig. 2. Extraction of cations by ammonium oxalate from clay humus complexes.

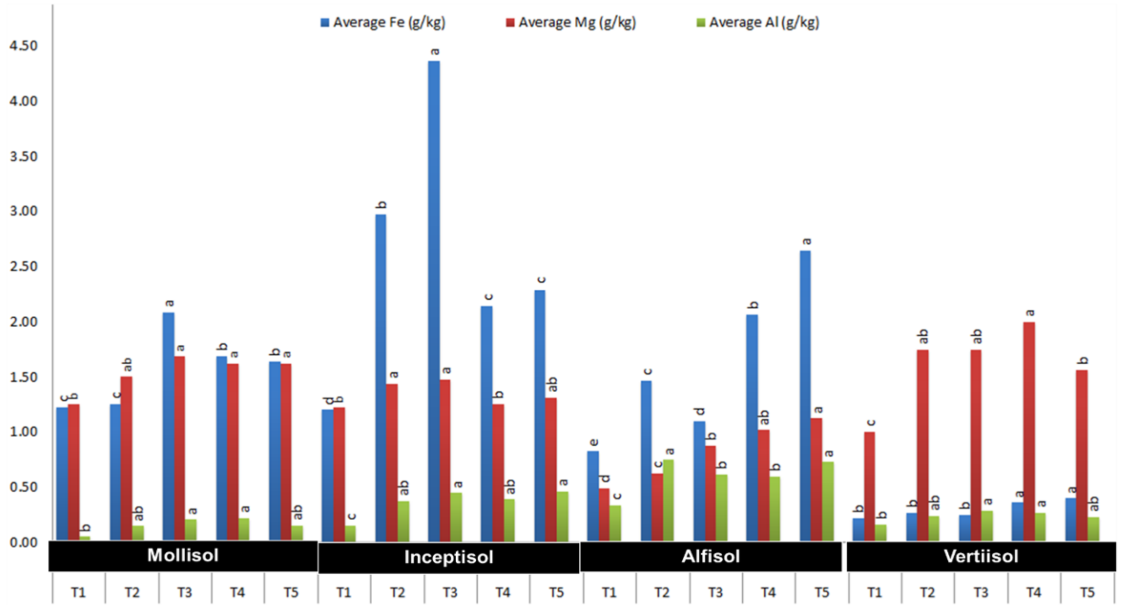

Fig. 3. Extraction of cations by citrate from clay humus complexes.

In the Vertisol soil order, the NPK + GM treatment resulted in the highest average concentrations of Fe (0.40 g kg^{-1}). The NPK + CR treatment showed the highest average concentration of Mg (2.00 g kg^{-1}). The highest concentration of Al (0.29 g kg^{-1}) was found in NPK+FYM treatment. The control treatment consistently exhibited the lowest concentrations for all three cations.

DISCUSSION

The significance of divalent and trivalent cations (bridging cations) on humus retention in clay mineral was assessed using EDTA, citric acid, and ammonium oxalate extractants. These extractants play a role in breaking the bonds between cations and humus in the clay humus complexes, allowing the cations to be extracted (Yang *et al.* 2016). In this study, we have investigated the effects of different combination of nutrient sources (organic and inorganic) on the concentrations of bridging cations in different soil orders. EDTA being a chelating agent, forms stable complexes with bridging cations and breaks the clay-metal -HA linkages, allowing the cations to be released. EDTA has a high affinity for a wide range of cations, including Ca^{2+}, Mg^{2+}, Fe^{3+}/Fe^{2+}, and Al^{3+}. Among the extractants, EDTA showed higher extraction of Fe from clay humus complexes which is similar to study by Tandy *et al.* (2003), which implies that EDTA is an effective extracting agent, from clay humus complexes. It was also observed that the NPK + CR treatment consistently resulted in the highest average concentrations of Fe^{3+}/Fe^{2+}, and Al^{3+} across the soil orders. This suggests that incorporating crop residues into the soil can significantly increase the concentration of these cations. Interestingly, the NPK + FYM treatment displayed the highest Mg concentration in both the Inceptisol and Mollisol soil order which might be attributed to the beneficial effect of FYM (Li *et al.*, 2018). Furthermore, the control treatment consistently exhibited the lowest concentrations of Fe, Al, and Mg in all soil orders, indicating that bridging cations may be limited in soil. One possible explanation for the higher concentrations of Fe and Al in the NPK + CR treatment can be attributed to the decomposition of crop residues. As these residues break down, they release organic acids that can chelate with Fe and Al ions in the soil, making them more soluble and thus improving the bonding between clay humus and cations. This is supported by previous research that has shown an increase (Das *et al.*, 2019) in soluble Fe and Al concentrations following the addition of crop residues. Additionally, the higher concentrations of Mg observed in the NPK + FYM treatment can be attributed to the role of farmyard manure in providing Mg to the soil. It was presumed that humus being inherently recalcitrant (Schneider *et al.*, 2010), having stronger linkage (via bridging cations) with clay minerals (Mikutta *et al.*, 2005) also could impart higher C stability. Among three extractants EDTA showed higher extraction of bridging cations in all the soil orders followed by citrate and ammonium oxalate.

CONCLUSIONS

Long-term application of inorganic and organic sources like FYM, crop residue and green manure significantly increased the bridging cations in clay humus which might lead to higher carbon stability in these treatments. Among the cations Fe and Ca concentrations was higher and they might play key role in clay humus bridging. Knowledge of the binding bridging cations and clay mineral contributes to our understanding of the sequestration process of SOM and clay humus stability.

FUTURE SCOPE

1. Investigate the influence of soil microorganisms and enzymes on cation bridging in clay-humus complexes, enhancing our understanding of microbial contributions to soil structure and organic matter stability.
2. Assess how the observed cation bridging affects the effectiveness of integrated soil management practices and develop decision support tools for optimizing soil management based on specific soil orders and conditions.

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