



Influence of Land Use Practices on Soil Extractable Iron and Manganese

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Abstract: Land use changes may influence the availability of iron (Fe) and manganese (Mn) in soil. Therefore, the present study was undertaken to assess the influence of land use changes on the extractability of Fe and Mn by different chemical reagents. Four land use practices such as rice-rice, rice-fallow, rice-green gram and uncultivated fallow were chosen for the study. Soil samples were collected from these land use practices and the Fe and Mn contents were extracted with different extractants (DTPA, AB-DTPA, Mehlich-3 and HCl). The land use practices highly influenced the extractability of soil Fe and Mn. Mehlich-3 extracted higher amount of Fe and Mn compared to other extractants across the land use practices. The HCl and Mehlich-3 extractants extracted on average 1.9 and 3.8 and 1.9 and 2.5 times more Fe and Mn than those extracted with DTPA extractant, respectively. Across the land use practices, AB-DTPA and DTPA extractants extracted similar magnitude of Fe and Mn. Among the four land use practices, the rice-green gram system always had the highest amount of extractable Fe and Mn compared to others. Significant positive correlations were observed among the extractants which is a testament to the fact that these extractants could extract Fe and Mn from similar pools. Pearson correlations showed significant positive correlations between organic carbon and extractable Fe and Mn. The inclusion of soil properties in the regression equation resulted improved predictability of extractable soil Fe and Mn.

Keywords: Land use practices, DTPA, AB-DTPA, Mehlich-3, HCl, Extractable Fe and Mn

Iron (Fe) and manganese (Mn) are the essential micronutrients required for the growth and development of plants (Alejandro et al., 2020, Rai et al., 2021, Li et al., 2023). Iron plays important role in nucleic acid metabolism (Ciosek et al., 2023), synthesis and maintenance of chlorophyll in plants (Ning et al., 2023), activates large number of enzymes etc (Ciosek et al., 2023). Manganese participates in the photosynthesis (water splitting enzymes associated with P.S-II) (Alejandro et al., 2020) and detoxification of superoxide free radicals by synthesizing superoxide dismutase (Li et al., 2017) besides playing important role in tricarboxylic acid cycle in oxidative and non-oxidative decarboxylation reaction. Due to these immense roles in plant metabolism, the deficiency of Fe and Mn affects chlorophyll formation, plant growth and grain yield (Moreira et al., 2018). About 19.2 and 17.4% of Indian soils are deficient in Fe and Mn respectively (Shukla et al., 2021). Iron and manganese exist in different chemical pools in soils and their bioavailability for plant nutrition is influenced by the soil properties (Mogta and Sharma, 2018). Soil properties such as pH, redox potential, organic matter content, and mineralogy strongly influence the bioavailability of Fe and Mn for plant nutrition. Further, the bioavailability of these micronutrients may vary with the land use practices. The rice-wheat land use system represents alternate flooding (reduced state) and upland (oxidised state) which may affect the transformation of Fe and Mn in soils

influencing their bioavailability. The management practices could alter the distribution of Fe and Mn in soil. Assessing the concentration of micronutrients is highly essential since high levels of Fe and Mn in soils may contribute to secondary contamination of groundwater (Xu and Li, 2024).

Several extractants have been tested for their extraction efficiency and capturing the changes in concentration of Fe and Mn in soils due to management practices. Extractants containing weak acids and weak chelating agents with weak replacement of ions in salts primarily used for predicting plant available forms of micronutrients (Pradhan et al., 2018). Rao et al (2008) reported that extractants used for measuring plant available forms of Fe and Mn vary with mode of action and strength of extraction. Multi-nutrient extractants such as Mehlich-3 and AB-DTPA have also widely been validated in different soil types. However, information on the availability of Fe and Mn under different land use practices is lacking. Hence, the present study was undertaken to assess the extractable Fe and Mn in soils under different land use practices.

MATERIAL AND METHODS

Surface soil samples (0-15cm) were collected from farmers' fields in Bargarh district (21°33'N and 83°62'E) of Odisha under four different land uses practices viz., rice-rice, rice-fallow, rice-green gram, and uncultivated fallow. In total, 20 geo-referenced soil samples were collected after the

harvest of rice using a simple random technique. The site falls under the Western Central table land zone of Odisha and is characterized by a hot and moist sub-humid climate. It receives an annual rainfall of ~1,400mm, and more than 90% of the rainfall occurs from June to September. In winter, the minimum temperature goes down to 12°C, while in summer, the maximum temperature goes up to 40°C. Recommended doses of fertilizers were applied for rice while no fertilizer was applied for green gram. The collected soil samples were air-dried, ground, sieved with a 2.0mm sieve, and stored in moisture-proof bags for further analysis of soil properties. Different soil properties and extractable Fe and Mn were analysed following standard protocols (Table 1 and 2).

RESULTS AND DISCUSSION

Soil properties: Soil properties were influenced by the land use practices (Table 3). Soil pH was lowest in rice-green gram (6.48) while the highest in rice-rice (6.78) which was at par with fallow system (6.72). Soil organic carbon content (g kg^{-1}) varied between 6.10 and 7.10 across different land use practices. Compared with the rice-rice system, the fallow, rice-fallow and rice-green gram systems showed an increase in SOC content by 3.3, 6.6, and 16.4%, respectively. Calcium

carbonate content (g kg^{-1}) was lowest in rice-green gram system while the highest amount noticed in rice-rice system. Interestingly, there was an increasing trend of CaCO_3 content with rising soil pH, while oxides of Fe and Al decreased with increasing pH. The iron oxide content (g kg^{-1}) ranged from 0.807 (rice-rice) to 1.102 (rice-green gram). Similarly, the Al_{ox} content (g kg^{-1}) was found to be in the range of 0.533 to 0.604. The microbial biomass carbon (MBC) which serves as one of the sensitive indicators for change in land use practices varied from $168.4 \mu\text{g g}^{-1}$ in rice-rice system to $190.3 \mu\text{g g}^{-1}$ in rice-green gram system accounting 2.76 and 2.68% of SOC respectively. The low pH in the rice-green gram system could be due to the higher content of amorphous Fe_{ox} and Al_{ox} . Higher SOC content in the rice-green gram system may be due to the higher rhizodeposition.

Extractable iron and manganese: Land use practices significantly influenced the extractability of all four extractants (Table 4). The DTPA extractable Fe ranged from 22.4 mg kg^{-1} in the rice-rice system to 28.3 mg kg^{-1} in the rice-green gram system. Irrespective of the extractants tested for extraction of Fe, the lowest amount of extractable Fe was observed in the rice-rice system, while the highest amount was observed in the rice-green gram system. Interestingly,

Table 1. Methods used for analysis of soil properties.

Soil properties	Abbreviation	Unit	References
pH	-	-	Jackson (1972)
Soil organic carbon	SOC	g kg^{-1}	Walkley and Black (1934)
Aluminium oxide	Al_{ox}	g kg^{-1}	McKeague and Day (1966)
Iron oxide	Fe_{ox}	g kg^{-1}	McKeague and Day (1966)
Calcium carbonate	CaCO_3	g kg^{-1}	Page et al (1982)
Microbial biomass carbon	MBC	$\mu\text{g g}^{-1}$	Vance et al (1987)

Table 2. Extractants used for estimation of extractable Fe and Mn in soils under different land use practices

Extractants used	Extractants composition	Soil: extractant ratio	Shaking time	References
DTPA	0.005M DTPA+ 0.01M CaCl_2 + 0.1M TEA	1:2	2 hrs	Lindsay and Norvell (1978)
AB-DTPA	1.0M NH_4HCO_3 + 0.5M DTPA (pH 7.6)	1:2	15 min	Soltanpour and Schwab (1977)
Mehlich-3	0.2 MHOAc+0.25M NH_4NO_3 +0.015M NH_4F +0.013M HNO_3 + 0.001M EDTA (pH 2.5±0.1)	1:10	5 min	Mehlich (1984)
HCl	0.1N HCl	1:5	30 min	Osiname et al (1973)

Table 3. Soil properties under different land use practices

Land use practices	pH	SOC	Al_{ox}	Fe_{ox}	CaCO_3	MBC
Rice-rice	6.78 ^a	6.10 ^a	0.533 ^c	0.807 ^d	2.08 ^a	168.4 ^d
Rice-fallow	6.63 ^b	6.50 ^b	0.596 ^a	0.918 ^b	1.96 ^b	184.2 ^b
Rice-green gram	6.48 ^c	7.10 ^a	0.604 ^a	1.102 ^a	1.87 ^c	190.3 ^a
Uncultivated fallow	6.72 ^{ab}	6.30 ^c	0.576 ^b	0.878 ^c	2.03 ^a	173.1 ^c

Different letters (a–d) in each column indicate significant differences between the land use practices according to Duncan's multiple range test ($p < 0.05$). SOC: Soil organic carbon; Al_{ox} : Aluminium oxide; Fe_{ox} : Iron oxide; CaCO_3 : Calcium carbonate; MBC: Microbial biomass carbon

the HCl and Mehlich-3 extractants obtained on average 1.9 and 3.8 times more Fe than those extracted with DTPA extractant, respectively. Across all land use practices, the order of extractability was: Mehlich-3 > HCl > AB-DTPA > DTPA. In case of Mn, the DTPA extractant extracted lowest amount while Mehlich-3 extracted higher amount followed by HCl and AB-DTPA respectively across the land use practices.

The highest amount of Mehlich-3 extractable Fe and Mn across land use practices compared to other extractants could be due to the presence of acid reagents and chelating agent such as EDTA. Moreover, the presence of NH_4^+ ion in Mehlich-3 could displace the exchangeable cations (Pradhan et al., 2018). Higher amount of extractable Fe and Mn by Mehlich-3 was also reported from several studies

Table 4. Extractable iron and manganese (mg kg^{-1}) in soils under different land use practices

Land use practices	Iron				Manganese			
	DTPA	AB-DTPA	Mehlich-3	HCl	DTPA	AB-DTPA	Mehlich-3	HCl
Rice-rice	22.4 ^c	23.1 ^c	84.2 ^d	42.2 ^d	10.8 ^d	11.6 ^c	26.4 ^c	20.8 ^d
Rice-fallow	24.8 ^b	25.6 ^b	96.1 ^b	47.5 ^b	11.6 ^b	12.4 ^b	28.2 ^b	22.6 ^b
Rice-green gram	28.3 ^a	30.2 ^a	104.2 ^a	53.2 ^a	14.2 ^a	15.8 ^a	36.5 ^a	24.6 ^a
Uncultivated fallow	24.1 ^b	25.4 ^b	92.8 ^c	45.3 ^c	11.2 ^c	11.4 ^c	27.5 ^b	21.6 ^c

Different letters (a–d) in each column indicate significant differences between the land use practices according to Duncan's multiple range test ($p < 0.05$)

Table 5. Pearson correlation between extractable Fe and soil properties.

	pH	SOC	Al_{ox}	Fe_{ox}	CaCO_3	MBC	DTPA_Fe	AB-DTPA_Fe	Mehlich-3_Fe	HCl_Fe
pH	1									
SOC	-0.849**	1								
Al_{ox}	-0.722**	0.774**	1							
Fe_{ox}	-0.825**	0.946**	0.755**	1						
CaCO_3	0.829**	-0.935**	-0.841**	-0.882**	1					
MBC	-0.823**	0.895**	0.830**	0.891**	-0.930**	1				
DTPA_Fe	-0.801**	0.951**	0.756**	0.955**	-0.882**	0.903**	1			
AB-DTPA_Fe	-0.825**	0.944**	0.761**	0.970**	-0.893**	0.872**	0.956**	1		
Mehlich-3_Fe	-0.846**	0.913**	0.879**	0.906**	-0.899**	0.923**	0.941**	0.924**	1	
HCl_Fe	-0.821**	0.963**	0.812**	0.946**	-0.924**	0.923**	0.971**	0.955**	0.943**	1

* $p < 0.05$, ** $p < 0.01$

SOC: Soil organic carbon; Al_{ox} : Aluminium oxide; Fe_{ox} : Iron oxide; CaCO_3 : Calcium carbonate; MBC: Microbial biomass carbon; DTPA_Fe: Diethylene triamine penta acetic acid extractable Fe; AB-DTPA_Fe: Ammonium bicarbonate-diethylene triamine penta acetic acid extractable Fe; Mehlich-3_Fe: Mehlich-3 extractable Fe; HCl_Fe: Hydrochloric acid extractable Fe

Table 6. Pearson correlation between extractable Mn and soil properties

	pH	SOC	Al_{ox}	Fe_{ox}	CaCO_3	MBC	DTPA_Mn	AB-DTPA_Mn	Mehlich-3_Mn	HCl_Mn
pH	1									
SOC	-0.849**	1								
Al_{ox}	-0.722**	0.774**	1							
Fe_{ox}	-0.825**	0.946**	0.755**	1						
CaCO_3	0.829**	-0.935**	-0.841**	-0.882**	1					
MBC	-0.823**	0.895**	0.830**	0.891**	-0.930**	1				
DTPA_Mn	-0.807**	0.955**	0.672**	0.969**	-0.877**	0.860**	1			
AB-DTPA_Mn	-0.801**	0.922**	0.615*	0.924**	-0.831**	0.845**	0.976**	1		
Mehlich-3_Mn	-0.819**	0.947**	0.635**	0.955**	-0.846**	0.821**	0.990**	0.969**	1	
HCl_Mn	-0.853**	0.948**	0.780**	0.958**	-0.913**	0.926**	0.947**	0.914**	0.928**	1

* $p < 0.05$, ** $p < 0.01$

SOC: Soil organic carbon; Al_{ox} : Aluminium oxide; Fe_{ox} : Iron oxide; CaCO_3 : Calcium carbonate; MBC: Microbial biomass carbon; DTPA_Mn: Diethylene triamine penta acetic acid extractable Mn; AB-DTPA_Mn: Ammonium bicarbonate-diethylene triamine penta acetic acid extractable Mn; Mehlich-3_Mn: Mehlich-3 extractable Mn; HCl_Mn: Hydrochloric acid extractable Mn

Table 7. Multiple linear regression equation showing the relationship between extractable Fe and Mn and soil properties

Extractable Fe	Regression equation	R ²
DTPA	114.12-(13.4)pH ⁺	0.642
	-13.7+ (0.39)pH+ (5.53)SOC ⁺	0.905
	-16.3+ (0.61)pH+ (5.35)SOC ⁺ + (4.14)Al _{ox}	0.906
	-12.0+(1.19)pH + (2.27)SOC+(2.29)Al _{ox} + (10.4) Fe _{ox}	0.935
	-18.3+ (1.10)pH+ (3.10)SOC+ (3.92)Al _{ox} + (10.3)Fe _{ox} + (1.98)CaCO ₃	0.935
	-44.9 + (1.58) pH + (3.52) SOC + (0.89) Al _{ox} + (7.77) Fe _{ox} + (7.18) CaCO ₃ + (0.08) MBC	0.946
AB-DTPA	135.6-(16.4)pH ⁺	0.680
	-1.35-(0.16)pH+ (5.93)SOC ⁺	0.892
	-5.13-(1.36)pH+ (5.67)SOC ⁺ + (5.95)Al _{ox}	0.894
	1.84-(0.42)pH+ (1.47)SOC+ (2.93)Al _{ox} + (17.0) Fe _{ox}	0.947
	11.4-(0.29)pH+ (0.97)SOC+ (0.44)Al _{ox} + (17.3) Fe _{ox} -(3.02)CaCO ₃	0.948
	26.4-(0.56)pH+ (0.73)SOC+ (2.15)Al _{ox} + (18.7)Fe _{ox} -(5.96)CaCO ₃ - (0.45)MBC	0.950
Mehlich-3	409.3- (47.3)pH ⁺	0.716
	102.7-(14.2)pH+ (13.2)SOC ⁺	0.851
	38.3- (0.89)pH+ (8.81)SOC+ (101.2)Al _{ox}	0.914
	46.3-(7.92)pH+ (4.04)SOC+ (97.8)Al _{ox} + (19.3)Fe _{ox}	0.923
	33.9- (8.09)pH+ (4.69)SOC+ (101.0)Al _{ox} + (19.0)Fe _{ox} + (3.92)CaCO ₃	0.923
	-55.6-(6.47)pH+ (6.09)SOC+ (90.8)Al _{ox} + (10.5)Fe _{ox} + (21.4)CaCO ₃ + (0.27)MBC	0.934
HCl	219.0 – (25.8) pH [*]	0.675
	-16.5 – (0.40) pH + (10.1) SOC ^{**}	0.927
	-31.9 + (0.84) pH + (9.13) SOC ^{**} + (24.1)Al _{ox}	0.938
	-27.1 + (1.47) pH + (6.29) SOC [*] + (22.1)Al _{ox} + (11.5) Fe _{ox}	0.948
	-13.4+ (1.66) pH + (5.58) SOC + (18.5)Al _{ox} + (11.8) Fe _{ox} – (4.33) CaCO ₃	0.949
	-50.3 + (2.33) pH + (6.15) SOC + (14.3)Al _{ox} + (8.38) Fe _{ox} + (2.89) CaCO ₃ + (0.11) MBC	0.955
Extractable Mn		
DTPA	66.8-(8.24)pH ⁺	0.651
	-10.9+ (0.14)pH+ (3.36)SOC ⁺	0.912
	-5.97- (0.25)pH+ (3.70)SOC ⁺ - (7.77)Al _{ox}	0.923
	-2.64+ (0.19)pH+ (1.70)SOC ⁻ -(9.21)Al _{ox} + (8.15)Fe _{ox}	0.969
	3.45+ (0.27)pH+ (1.38)SOC- (10.7)Al _{ox} + (8.31) Fe _{ox} - (1.92)CaCO ₃	0.971
	4.31+ (0.26)pH+ (1.37)SOC- (10.6)Al _{ox} + (8.40) Fe _{ox} - (2.09)CaCO ₃ -(0.003)MBC	0.971
AB-DTPA	85.2- (10.8)pH ⁺	0.642
	-7.36- (0.88)pH+ (4.01)SOC ⁺	0.852
	2.91- (1.72)pH+ (4.72)SOC ⁻ - (16.1)Al _{ox}	0.879
	6.47- (1.24)pH+ (2.58)SOC- (17.7)Al _{ox} + (8.68) Fe _{ox}	0.909
	7.71- (1.23)pH+ (2.52)SOC- (18.0)Al _{ox} + (8.71)Fe _{ox} -(0.39)CaCO ₃	0.909
	-11.7- (0.87)pH+ (2.82)SOC- (20.2)Al _{ox} + (6.86)Fe _{ox} + (3.42)CaCO ₃ + (0.05)MBC	0.917
Mehlich-3	197.1- (25.1)pH ⁺	0.670
	-21.0-(1.61)pH+(9.44)SOC ⁺	0.897
	1.86- (3.47)pH+ (11.0)SOC ⁻ - (36.0)Al _{ox}	0.923
	11.0- (2.24)pH+ (5.51)SOC ⁻ -(39.9)Al _{ox} + (22.1)Fe _{ox} + (2.78)CaCO ₃	0.962
	2.20- (2.36)pH+ (5.97)SOC- (37.6)Al _{ox} + (22.1)Fe _{ox} + (2.78)CaCO ₃	0.962
	24.2- (2.76)pH+ (5.63)SOC- (35.1)Al _{ox} + (24.2)Fe _{ox} - (1.52)CaCO ₃ -(0.06)MBC	0.964
HCl	85.4- (9.47)pH ⁺	0.727
	15.4- (1.91)pH+ (3.03)SOC	0.906
	12.5- (1.67)pH+ (2.83)SOC+ (4.56)Al _{ox}	0.909
	15.4- (1.27)pH+ (1.04)SOC+ (3.27)Al _{ox} + (7.27)Fe _{ox}	0.941
	25.8- (1.13)pH+ (0.50)SOC+ (0.59)Al _{ox} + (7.54)Fe _{ox} - (3.27)CaCO ₃	0.944
	11.2- (0.86)pH+ (0.73)SOC- (1.07)Al _{ox} + (6.15)Fe _{ox} -(0.41)CaCO ₃ + (0.04)MBC	0.951

* p < 0.05, ** p < 0.01; SOC: Soil organic carbon; Al_{ox}: Aluminium oxide; Fe_{ox}: Iron oxide; CaCO₃: Calcium carbonate; MBC: Microbial biomass carbon

(Rodrigues et al., 2001, Pradhan et al., 2018). Dilute acid (0.1N HCl) may only capable of solubilizing soil Fe and Mn partially (Pradhan et al., 2018). Among the four land use practices, the rice-green gram system always had the highest amount of extractable Fe and Mn compared to others. Moreover, the influence of the rice-green gram system over the rice-rice system was more pronounced when Fe was extracted with AB-DTPA (30.7%), followed by DTPA (26.3%), HCl (26.1%) and Mehlich-3 (23.8%) (whereas in Mn the extractability followed the order of Mehlich-3 (38.3%) followed by AB-DTPA (36.2%), DTPA (31.5%) and HCl (18.3%) respectively (Fig. 1 and 2). High organic C content in the rice-green gram system (Table 3) might be the reason for increase in the availability of Fe and Mn in soils which was captured by the extractants used in the present study. Increase in organic C content in soils could increase the availability of Fe and Mn in soils (Annepu et al., 2017, Siva Prasad et al., 2023).

Pearson correlation matrix was constructed between the extractable Fe and Mn and soil properties to establish their relationships. The extractable Fe and Mn showed significant positive correlations with SOC and MBC while significant

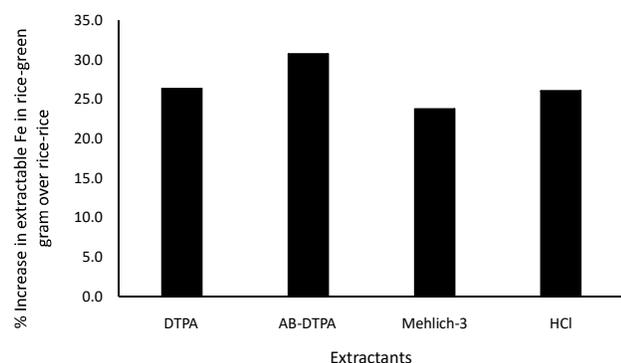


Fig 1. Relative increase in extractable Fe in rice-green gram over rice-rice land use system

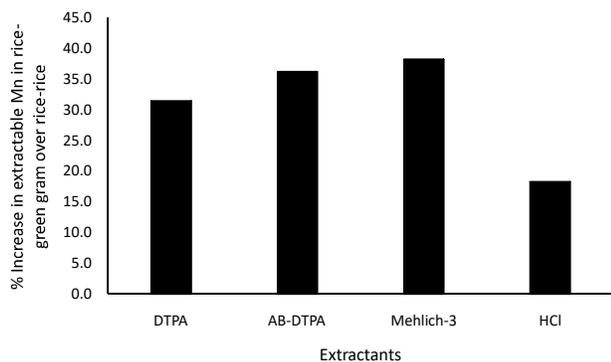


Fig 2. Relative increase in extractable Mn in rice-green gram over rice-rice land use system

negative correlations with soil pH and CaCO₃ content (Table 5, 6). DTPA extractable Fe showed significant positive correlation with AB-DTPA ($r = 0.956^{**}$), Mehlich-3 ($r = 0.941^{**}$) and HCl ($r = 0.971^{**}$). Similar correlations were obtained among the extractable Mn. Such dynamic relationships among the extractable Fe and Mn suggested that the extractants could extract Fe and Mn from similar pools. The extractability of different extractants is influenced by soil properties (Table 8). In the case of DTPA extractable Fe, soil pH alone caused a variation of 60.2%, which was improved to 94.6% with the inclusion of other soil properties such as SOC, Al_{ox}, Fe_{ox}, CaCO₃ and MBC. Similarly, the variation in Mehlich-3 extractable Fe caused by soil pH alone was 71.6%, and it was improved to 85.1 and 91.4% with the inclusion of SOC and Al_{ox} respectively. Both soil pH and SOC could explain 91.2% of the variability in DTPA extractable Mn. In general, with the inclusion of different soil properties in the regression equation, the prediction of extractable Fe and Mn improved.

CONCLUSION

Land use practices significantly influenced the extractability of Fe and Mn by different chemical extractants. Mehlich-3 extracted higher amount of Fe and Mn while DTPA extracted the lowest amount. Across the land use practices, the order of extractability for Fe and Mn was Mehlich-3 > HCl > AB-DTPA > DTPA. Similarly, among the land use practices rice-rice system had lowest amount of extractable Fe and Mn while rice-green gram system showed highest amount of extractable Fe and Mn.

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