# **Total and Extractable Iron and Manganese in Soils Developed on Charnockite in Ekiti State, Nigeria**

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#### **ABSTARCT**

*The profile distribution of Iron (Fe) and Manganese (Mn) was surveyed in six locations of Ekiti State where charnockite parent rocks occur. The perchloric-hydrochloric acid digestion method was used for the determination of total Fe and Mn. Extractable Fe and Mn were determined using two extractants: 0.1M HCl at 1:10 soil: solution ratio. The study revealed that Ap horizon contained the highest total Fe and lower values in the immediate Bt1 horizon followed by increases with depth while extractable Fe decreased down the profile. Total Mn range was 34-340mg.kg-1 with mean of 101.17mg.kg-1 while mean 0.1MHCl- and DTPAextractable Mn was 22.53 and 7.37mg.kg-1 with ranges of 3.14- 95.08 and 0.33-23.70mg.kg-1 respectively. Total Mn and extractable Mn decreased down the profile in all locations. The high extractable Fe and Mn in the top-soils is an indication that prospects of deficiency are little under the predominant lowintensity farming practices. The significant correlations of extractable Fe and Mn with pH suggest that this soil property is relevant to availability of the nutrients while the correlations with organic matter mean that soil management practices which raise and maintain soil organic matter should be emphasized. Keywords: Charnockite, profile distribution, total iron, total manganese, extraction methods*

# **INTRODUCTION**

Deficiencies of iron (Fe) and manganese (Mn) in West Africa were first recorded in Cote d'Ivoire and Gambia, especially on crops grown in the arid zone with calcareous or alkaline soils. The dominant acid soils In Nigeria contain normal to excessive levels and so are adequately supplied with Fe and Mn such that deficiency problems are unlikely and will be of little economic importance in the immediate future (Sillampaa, 1982; Lombin, 1983). There is a strong relationship between micronutrient status and the nature of parent materials even though climate and processes of soil formation have modifying effects (FMANR, 1990). Yield reduction was most pronounced when Mn was omitted from fertilizers applied to maize in an Ultisol derived from Coastal Plain Sands (Okoye, 1973) that contained low total amounts (20-90 mg.kg-1) and a high degree of deficiency. On the other hand, upland soils formed on basement complex rocks contain high values of Fe and Mn (Cottenie et al., 1981) which imply that deficiencies are more of local problems.

Burning of fallow residues on farmlands raises soil pH that renders Fe less available due to fixation to insoluble forms and causes Fe-chlorosis in upland rice (Kang, Abifarin and Sajjapongse, 1976). The micronutrients are more available under reducing conditions, as in wet poorly-drained soils, than in well-drained, aerated dry soils in which they are fixed in insoluble forms. The soluble lower-valent state compounds give the soils blue to grey colours which change to red, brown and yellow high-valent state compounds when dry (Agbede, 2009). Nigeria has embraced intensive crop cultivation practices which emphasize the use of improved high nutrient-demanding varieties and high-analysis chemical fertilizers that no longer contain micronutrients, even as impurities. Thus, nutrient mining and rapid nutrient depletion have led to common incidences of micronutrient deficiencies (Katyal and Shuman, 1991).

Charnockite is an igneous rock that contains quartz, feldspars and pyroxene whose main constituent is hypersthene [(Mg.Fe) $2Si_2O_6$ ]. It is one of the dimension stones found abundant in five local government areas (Ado Ekiti, Ekiti East, Gbonyin, Ikere and Ikole) of Ekiti State in Nigeria. Thus, it provided most of the parent materials from which most of the agricultural soils formed in the forest zone to the south (Ikere, Ado Ekiti, Gbonyin) and derived savannah- southern guinea savannah to the north-east (Ikole, Ekiti East).

There is general information that indicates the sufficiency of Fe and Mn in soils developed on basement complex rocks (igneous and metamorphic) but which is lacking on soils developed on charnockite. The large extent of these soils in agrarian Ekiti State requires that the nutrient status be documented for proper agricultural land use planning especially as slash-and-burn bush clearing employed in the predominant smallholder traditional farming operations can affect Fe and Mn availability. This paper reports the study of the profile distribution of total and extractable Fe and Mn as part of the efforts to provide nutrient management information for crop development on soils formed on charnockite in Ekiti State of Nigeria.

# MATERIALS AND METHOD

Six profile pits were dug to represent the five local government areas of Ekiti State in which charnockite rocks occur in abundance, and the main vegetation types: dry forest (Ado, Ijan, Ikere) and derived savannah (Ijesa-Isu, Ire, Osin-Itapa) (Fig. 1). The profiles were described to obtain information of morphological properties using the criteria of Soil Survey Manual (Soil Survey Staff, 2003) and guidelines for soil profile description (FAO, 1990). Soil samples were taken from each pedogenic horizon, bulked and sub-sampled for the composite used for laboratory studies. The soil samples were air-dried, gently crushed in a porcelain mortar with pestle and screened through a 2mm sieve. The soils were analyzed for some physical and chemical properties using the procedures described in Udo and Ogunwale (1986). Particle size distribution was determined by the hydrometer method, soil pH in 1:2 soil water mixture using a digital pH meter and organic carbon by dichromate wet oxidation.

The perchloric-hydrochloric acid digestion method was used for the determination of total Fe and Mn. Extractable Fe and Mn were determined using two extractants: 0.1M HCl at 1: 10 soil: solution ratio and 30 minutes time (Osiname, Kang, and Corey, 1973) and diethylene triamine penta-acetic acid (DTPA) combined with triethanolamine (TEA) and Calcium Chloride  $(CaCl<sub>2</sub>)$  buffered to pH 7.3 (Lindsay and Norvel, 1978) at 1:2 soil to solution ratio and 2 hour extraction time. Fe and Mn in the extracts were determined with atomic absorption spectrophotometry. Simple regression analysis was run between the forms of Fe and Mn and with some soil properties to obtain correlation coefficients and their significance at 5% level of probability.

# RESULTS AND DISCUSSION

Table 1 shows the means and ranges of values of the major soil physical and chemical characteristics in the profiles. Mean sand, silt and clay across the sites, at 77.2, 6.2 and 16.6% respectively show that the soils were coarse-textured. The textural class ranged from sand to sandy loam with the high sand content largely a reflection of the nature of parent materials and the preferential removal of clay and silt by erosion (Greenland, 1981). Coarse-textured soils are characterized by high infiltration rate, rapid internal drainage and low water holding capacity. The soil pH varied from moderately acid to slightly alkaline (pH 5.60-7.50) with a mean value of 6.40.

The high pH (average 7.10 and 7.38) observed for soil profiles at Ijan and Osin-Itapa might be due to the liming effect of bush burning prevalent in land clearing for traditional crop farming. Lower pH values at Ire, Ado, Ikere and Ijesa-Isu might be due to the effects of cultivation, erosion and leaching of basic nutrients. The pH values decreased with depth probably because of nutrient biocycling which is more in the surface layer of soils (Ogunwale et al., 1982). Soil organic carbon varied between 0.99 and 3.39% with the highest values in the top layers of soils. The values in profiles located in the savannah may be due to faster rate of mineralization from intense cultivation, prevalent slash-and-burn bush clearing and seasonal burning (Brady and Weil, 2005).

**Iron:** Total Fe content ranged from 6.75 to 8.50; 6.50 to 8.50; 6.50 to 7.50; 6.82 to 8.50 and 6.75 to 8.60% at Ado, Ikere, Ijan, Osin-Itapa, Ijesa-Isu and Ire respectively. Total Fe was irregularly distributed within the profiles suggesting that it was not tied to any single soil property or a particular pedogenic process. HCl-extractable Fe ranged from 1.54-33.19, 1.10- 19.12, 1.98-14.29, 3.74-58.24, 11.20-40.60 and 0,88-26.60mg/kg in the profiles at Ado, Ikere, Ijan, Osin-Itapa, Ijesa-Isu and Ire respectively. The values were highest in Apt horizon and decreased in the immediate underlying Bt horizon and increased thereafter, giving a bimodal maxima distribution pattern suggesting that the HCl-extractable Fe held by inorganic colloids in the sub-soil is eluviated from the upper part but that held by organic colloids in the Ap horizon is largely in the form of water-soluble complexes (Kparmwang et al., 1995). DTPA-extractable Fe ranged from 1.10-26.70, 3.70-23.70,4.30-18.80,2.07-2.81,1.30-26.70 and 2.30-6.90mg/kg in Ado,

Ikere, Ijan, Osin-Itapa, Ijesa-Isu and Ire respectively. The higher levels in the Ap horizon are similar to results obtained by Mosugu (1989) in soils developed on older granites in Nigeria. The decrease with depth was, in most cases, rather sharp and seems to follow the trend in organic matter distribution. Kparmwang et al, (1995) had noted that DTPA-extractable Fe is largely associated with organic matter such that values in the Ap horizons are higher than the critical level of 3.0-4.5mg/kg suggested by Sillampaa (1987) and Kparmwang et al., (1995). Thus, the soils were sufficient in available Fe.

**Manganese:** Total Mn ranged from 110-310, 50-140, 220-340, 34-90, 50-140 and 48-81mg/kg in the profiles at Ado, Ikere, Ijan, Osin-Itapa, Ijesa-Isu and Ire with mean values of 206, 85, 278, 54.5, 93.5 and 62.3mg/ kg respectively. Total Mn is much lower than total Fe because of the initial content in the granitic rocks and parent materials. The initial ratio of Mn/Fe in the igneous rock is about 1:60 but since Mn is more easily lost in soil than Fe (Krauskopf, 1972), the large disparity is understandable and the ratio is expected to widen as a result of susceptibility to weathering.

The means and ranges of 0.1MHCl and DTPA- extractable Mn are shown in Table 2. Values at Ado and Osin-itapa were higher than in other sites and at each site HCl-extractable Mn decreased gradually with depth which suggests retention in organic than inorganic colloids and a greater susceptibility to leaching losses. The values fall within the range of 6.0-105.0mg/kg obtained for soils of Michigan and Indiana (Salcedo, Linday W.L. and Sabey, 1978) and range of 8.2-94.0mg/kg reported by McNeal, Stevenson and Gough (1985). DTPA-extractable decreased with depth, but rather sharply and so appears to be largely associated with organic matter in soils (Katyal and Shuman, 1981). The values in the Ap horizon exceed the critical level of 3.0-5.0mg/kg suggested by Sillanpaa (1987) and also within the range of 3.7-15.0mg/kg reported by and McNeal, Stevenson and Gough (1985).

**Relationship of Fe and Mn with soil properties:** Soil pH correlated significantly with total Fe and Mn but the correlations were negative for the extractable forms suggesting that pH exerts control on the availability of these micronutrient cations. This finding contradicts the irregular correlation of available Fe forms with pH and suggested that availability of Mn and Fe are controlled by more factors than pH (Kparmwang, Chude and Esu, 1995). The implication is that liming practices and the expected local influence on soil pH caused by addition of ash from slash-and-burn bush clearing should be given consideration in the management of Fe and Mn nutrition for crops. Extractable Mn and Fe have significant correlations with organic matter but not with clay content (Table 3). This suggests that availability of these nutrients will be affected by farming practices which cause rapid depletion of soil organic matter.

**Relationships among Fe and Mn forms:** The 0.1MHCl and DTPAextractable Mn correlated significantly with each other and total Mn. These suggest that the sources of Mn forms are probably similar and would be readily replenished from unavailable forms which constitute the greater portion of total Mn. The extractable forms of Fe were also significantly correlated but not with total Fe which is mostly not labile. There were no significant correlations between DTPA and 0.1MHCl-extractable Mn with DTPAextractable Fe and total Fe with total Mn. The latter may be due to differences in geochemistry of the Fe and Mn compounds in the soil which include greater electropositivity and solubility of Mn compounds than the Fe compounds (Kraukopf, 1972).

# **CONCLUSION**

There are no reports on the micronutrient cation content of soils developed on charnockite. The geology of Ekiti State in Nigeria is dominated by granitic parent rocks, with large areas containing varietal minerals such as charnockite, and from which soils in the agricultural lands have developed. This study shows that the soils contain high amounts of total Fe and Mn which increased or decreased steadily with depth. Also, the 0.1MHCl and DTPA-extractable Fe and Mn were at high levels of sufficiency in the surface (0-15cm) layer, based on established critical levels, but constitute negligible proportions of the total forms. The higher values of Fe and Mn determined with 0.1MHCl than DTPA is due to the strong nature (pH) of the extractant but the significant correlations between the forms show that the methods are probably extracting the nutrients from the same sources and so would indicate, in similar fashion, the cases of deficiency or sufficiency in soils. The significant correlations of extractable Fe and Mn with pH suggest that this soil property is relevant to availability of the nutrients while the correlations with organic matter mean that soil management practices which raise and maintain soil organic matter should be emphasized.





Horizons	Depth (cm)	Manganese mgkg-1			Iron mgkg-1		
Ado		$0.1$ MHCl	<b>DTPA</b>	Total		0.1MHCl DTPA	Total
$\mathbf{A}_{_{\rm p}}$	$0 - 11$	95.08	10.20	120	33.19	26.70	7.50x104
$B_t$ <sub>1</sub>	$12 - 21$	48.02	8.50	110	24.62	11.90	6.75x104
$Bt_2$	$22 - 62$	18.17	8.20	240	21.76	4.60	8.40x104
$Bt_{3}$	62-118	8.61	6.30	250	7.09	1.60	8.50x104
$\mathsf{C}$	119-150	6.69	5.10	310	1.54	1.10	7.50x104
Mean		35.31	7.60	206	17.64	9.18	7.65x104
Ikere							
$\mathbf{A}_{\rm p}$	$0 - 23$	48.22	6.40	140	19.12	17.70	7.50x104
$B_t$	$24 - 64$	44.26	4.80	90	12.75	13.80	6.50x104
Bt,	65-92	24.04	2.60	60	5.71	23.70	8.25x104
$\mathbf C$	$93 - 140$	3.28	3.00	50	1.10	3.70	8.50x104
Mean		29.95	4.20	85	9.67	14.73	7.69x104
Ijan							
	$0 - 20$	28.28	13.90	250	14.29	18.80	9.56x104
$A_p$ <sub>p</sub> $Bt_1$	$21 - 35$	17'16	13.50	340	3.30	6.30	8.92x104
$Bt_2$	$36 - 60$	9.06	10.70	220	3.52	4.40	9.75x104
	61-90	15.16	7.80	250	1.98	4.30	9.75x104
$Bt_3$ C	91-120	3.14	3.00	330	3.30	10.90	9.28x104
Mean		14.68	9.78	278	5.28	8.92	9.45x104
Osin-Itapa							
$\mathbf{A}_{_{\rm p}}$	$0 - 23$	43.99	10.20	60	58.24	2.48	7.5X104
$B_t$	$24 - 50$	80.19	6.00	34	5.05	2.81	6.74x104
Bt,	$51 - 80$	12.12	5.10	64	3.74	2.07	6.50x104
$\mathsf{C}$	81-130	7.51	18.70	90	5.05	2.32	7.00x104
Mean		28.76	10.00	62.25	18.02	2.42	6.94x104
Ijesa-Isu							
$\mathbf{A}_{_{\rm p}}$	$0 - 20$	8.74	2.60	140	40.60	26.70	7.92x104
$\dot{\mathbf{B}}$ t <sub>1</sub>	$21 - 30$	24.32	1.20	90	14.29	11.90	6.82x104
$Bt_2$	$33 - 110$	6.15	0.60	94	11.20	1.80	8.20x104
$\mathsf{C}$	111-150	4.64	0.30	50	23.69	1.30	8.50x104
Mean		11.01	1.18	93.5	22.42	10.43	8.36x104
Ire							
Ap	$0 - 20$	39.34	23.70	81	26.60	6.90	7.58x104
Bt1	$21 - 43$	9.70	6.00	58	21.54	6.30	8.60x104
Bt2	44-70	3.42	5.30	48	1.32	5.10	6.75x104
$\mathsf{C}$	$71 - 120$	9.29	10.90	62	0.88	2.30	8.00x104
${\bf Mean}$			15.44	11.48	62.25	12.59	5.15
8.23x104							
Source: Shittu, 2008.							

**Table 2:** Profile distribution of extractable and total Mn and Fe in the soils

# **Table 3:** Relationship Between Some Forms of Iron and Manganese with Some Soil Properties in Charnockitic Soils



\*\*\* Significant at  $p < 0.05$  and  $p < 0.01$  respectively.

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