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Dithionite and oxalate extraction of iron and manganese in some basement complex soils of southwestern Nigeria

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Abstract

In soil, the presence of free iron oxide serve as important parameters in understanding its development and they are known to influence soil properties. Their influence gives rise to different soil management problems which may inhibit the level of agricultural production. Iron and Manganese were extracted from the basement complex soils of Egbedi area in Osun State, Southwestern-Nigeria. Both Dithionite citrate bicarbonate method and acid ammonium oxalate method were used for the extraction. Dithionite citrate bicarbonate extractant removed both the crystalline and non-crystalline iron and manganese oxides from the soil while the Acid ammonium oxide method removed the non-crystalline or amorphous iron and manganese oxides from the soil.

Representative samples were obtained from six (6) well described profile pits. These samples were subjected to analysis for both their physical and chemical properties. Results indicated that soil texture was generally sandy at the surface with increasing proportion of clay with depth. Percentage gravel content showed an irregular trend which indicates the nature of the parent material. The pH values of the soil ranged from 4.7 - 6.4 indicating strong acidity to slight acidity. Magnetite was also dissolved by the Acid ammonium oxalate extractant and this was reflected in the active Fe ratio. Horizons with an active Fe ratio greater than one served as an indicator to the presence of magnetite in such horizons hence values ranging between 1.19 and 4.32 were recorded as active iron ratio in respective horizons. Thus the extraction of iron oxides with Acid ammonium oxalate alongside Dithionite citrate bicarbonate is essential in the differentiation and identification of horizons with magnetite.

Keywords: Dithionite, oxalate extraction, basement complex, horizons, crystalline and amorphous

INTRODUCTION

Forms of free iron oxides in soils are important parameters for the proper understanding of soil development. Majority of total irons found in soils exist as oxides. These oxides are found as iron concretions as well as coatings on the soil minerals or bind the different soil particles. Particle size with free iron oxides has been exclusively studied at both small and large scales [1]. Their distribution and amount in the soil are known to influence some soil properties such as anion adsorption, surface charges, specific surface area, nutrient transformation, swelling and aggregate formation and pollutant retention in soils [2]. Percentages of free iron have long been used as aids in distinguishing soil types, differentiating soil horizons and determination of soil age or degree of soil development.. According to Walker (1983), the origin of free iron oxides in soils is due to free iron release during weathering of rocks. They are precipitated as poorly crystalline and crystalline iron oxide. These free iron oxides are removed from soils for the following reasons: Free iron oxides in soils serve as some of the cementing agents that bind soil particles together so to get our sand, silt and clay fractions, it is necessary in mineral studies to remove free iron oxides. The removal of free oxides enhances the sensitivity of incident x-ray radiation on clay mineral slides. This leads to production of sharper peaks or better diffracted peaks in x-ray diffactograms. The removal of free iron oxides results in concentration of silicate minerals. The effect of this on x-ray diffraction is that it enhances the degree of parallel orientation of the silicate clays as shown by increase in basal diffraction or intensity of x-ray peaks. Differential thermal analysis, infrared, electron microscopy etc examination of silicate clays minerals also produce sharper peaks and shapes of minerals which help in their identification. Free iron removal from silt and sand sized fraction enhances their identification by means of depolarizing microscope. Several methods have been proposed for the removal of free iron oxides. The methods currently in use are the acid ammonium oxalate method and the sodium dithionate method. The former method was modified by Walker and he identified two commonly used methods for estimating percentage of free iron in the soil. They are: The dithionate-citrate-bicarbonate (Fe_d) and the acid ammonium oxalate method (Fe_o). The dithionate method extracts organic matter iron oxide plus the non-crystalline oxides and finely crystalline oxides. Ammonium oxalate extractant removes the organic matter iron oxides and the non-crystalline iron oxides in the soil. From the above statement, the amount of (Fe_d) extracted should be equal to or greater than the amount of (Fe_o). The differences between the values obtained by the two methods represent the amount of iron present in definite crystalline forms. This trend is reflected on the ratio of (Fe_o) to (Fe_d) i.e. Active Fe ratio).

A good understanding of the percentage of free iron oxide determination using both methods is necessary for easy

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management of soil as well as enhancement in agricultural production. For example, phosphate management problems in weathered tropical soils are mostly associated with the abundance of free iron oxides. Parent material is one of the five soil-forming factors and depending on the influence of other soil forming factors, the nature of the parent material may strongly influence soil development and consequently, the nature and properties of the resulting soil. In the Piedmont province of Southeastern, U.S.A., parent material strongly influences soil development. In most parts of the tropics, information on the underlying geology/parent material is not readily available to farmers and if present is of limited significance to them. Farmers in Southwestern Nigeria are more familiar with topographic differences and have exploited it with respect to decision making on land suitability for a particular crop or crop combinations as well as their management. Topography is both an internal and external factor in pedogenesis as it influences or is a consequence of soil formation [3]. Different geochemical conditions are experience on different landscape positions (upper slope, middle slope, foot slope), depending upon the influence of topography on the drainage and the hydrology of the soil cover. Soil landscape relationships could often be hidden by parent material. Banded gneiss and quartzite schist are some of the major soil parent materials n Southwestern Nigeria. Information on how these parent materials influence soil properties in an undulating landscape that characterize south western Nigeria is limited. [4] reported on the variability of soil properties on these parent materials. His investigations were limited to comparing the variability of soil properties between the two parent materials and establishing a method of delineating a highly variable landscape into homogeneous units for effective management. As such, it is common to find different crops (or crop combinations) on different topographic positions on which different levels of management are imposed. The distribution of available micro nutrients within soil profiles has been considered useful for a better understanding of soil capacity to sustain an adequate supply of these nutrients to plants and their downward movement in soil. Micronutrients are metallic chemical elements necessary for plant growth in only extremely small amounts. Although required in minute quantities however, micronutrients have the same agronomic importance as macronutrients and play vital roles in the growth of plants [5]. These metallic chemical elements includes zinc (Zn), iron (Fe), copper (Cu) and manganese (Mn). The origin and sources of micronutrients in soils are as diverse as they are variant. However, the major sources include: parent materials, sewage sludge, town refuse, farm yard manure and organic matter. In Nigeria, micronutrient deficiencies were quiet rare, owing in part to the extensive system of agriculture practices that permitted the recuperation of soils over a fairly long period of fallow.. Most tropical soils are highly in iron oxides. They occur as concretions, lateritic crusts and in fine earth. Free iron oxides are high in clay fraction whenever they are absent as concretions. Their occurrence exert important effect on soil physical properties thus, a positive correlation exists between free iron oxides and the degree of clay and silt particles. Clay reacts rapidly with phosphates forming series of difficulty soluble hydroxyl phosphate. Fe and Mn concretions have been found in many soils especially the soils with restrictive internal drainage. The quantity, chemical composition and size of concretions in soils are site specific depending on the action of weathering process for that location. Many researchers define concretions as mixtures of soil materials cemented together. The cementing agents for Fe-Mn concretions are Fe and Mn oxides. Therefore the concretionary material is characterized by a greater concentration of Fe and Mn oxide than the surrounding soil matrix. It also differs from the surrounding soil matrix by containing less SiO_2. [6] found that Fe and Mn are not evenly distributed in all concretions found within a given soil horizon or within a given concretion. Manganese content is usually related to concretion size with larger concretions containing more Mn and lower Fe/Mn ratios. Also dark colored concretions are generally higher in Mn content than lighter coloured concretions but colour shape and hardness may differ among many soils. The effect of concretion accumulation on soil chemical properties could be similar at high concentrations depending on the chemistry and mineralogy of the oxide components. Fe oxides are present in all forms and are responsible for laterite hardening. This is due to the presence of magnetite in such soils. Many soils in south western Nigeria contain free iron oxides in varying proportions. Soils of south western Nigeria are dominantly on basement complex and sedimentary toposequences. The basement complex has undulating topograghy leading to free iron dynamics. [7-8] reported that with a long annual wet period, dithionate Fe extractable clay consecration occurred in the topsoil. This phenomenon was attributed to lateral removal of iron in solution. The objective of this study therefore, is to test the effectiveness of the acid ammonium oxalate extractable iron and manganese in comparison with dithionate-citrate-bicarbonate extractable iron and manganese for differentiating horizons with concentration of magnetite in basement complex soils in South Western Nigeria

MATERIALS AND METHODS

Location of the study area

The study area was located at Egbedi town, Osun State, Nigeria. The site was about 102.22 ha land enclosed with latitudes 07^{0}47'and 07^{0}49'N and longitude 4^{0}26' and 4^{0}28'E. It was situated about 1.5km North-East of Ede and West of Osogbo off Egbedi-Erin, Osun Ilobu road in Egbedore Local Government Area, Osun State. It was about 5km and 7km South-West of Erin Osun and Ilobu respectively. Osogbo, the state capital is only about 10km East of the site. The site was polygonal in shape, bounded in the East by the seasonal Awon stream.

Climate

The area like most parts of Nigeria is influenced by two wind currents. One from the North-East which is cold and dry while the other is from the South-East and it is warm and very moist. The North-East current rises over the South-West one so that at the surface, there is a zone of demarcation known as intertropical discontinuity (ITD), which runs approximately East-West. The climate can be very classified as humid tropical or semi-humid tropical.

Rainfall

The mean monthly rainfall over two periods of twenty-one years i.e. (1939-1960) and (1979-2000) gave an annual mean monthly rainfall of 115mm and 109mm and a total of 1,378mm and 1,308mm respectively per annum. The rainy season is interrupted by a minor dry season typically lasting from late July to early or mid-August but varying from year to year in its incidence. This short break is usually referred to as 'August break'.

Table 1: Physical Characteristics of the Study Area

Horizon Designation	Depth (cm)	Sand (g/kg)	Clay (g/kg)	Silt (g/kg)	Gravel (g/kg)	Soil Textural Class
EGP1 = Ikire Series (Ferralic Fluvisol/Tropaquent)						
A1	0-28	692	94	214	12.0	Sandy loam
AB	28-67	692	154	154	27.8	Sandy loam
B1	67-97	692	154	154	17.6	Sandy loam
B2	97-140	672	194	134	11.3	Sandy loam
BC	140-175	712	194	94	23.2	Sandy loam
EGP2 = Ibadan Series (Ferric Lixisol/Typic Kanhaplustalf						
Ap	0-30	812	154	34	49.0	Sandy loam
AB	30-70	752	134	114	88.2	Gravelly Sandy loam
Bt1	70-110	572	274	154	85.2	Gravelly Sandy clay loam
EGP3 = Iwo Series (Pilinthic Lixisol/Plinthic Kanhaplustalf)						
Ap	0-24	812	54	134	46.9	Loamy sand
Bt1	24-36	592	194	214	47.3	Sandy loam
Bt2	30-36	552	94	354	70.7	Gravelly Sandy loam
Bt3	50-75	652	234	114	64.7	Gravelly Sandy clay loam
EGP4 = Iregun Series (Haplic Lixisol/Typic Haplustalf)						
Ap	0-32	812	74	114	23.3	Loamy sand
Bt1	32-51	712	194	94	34.3	Sandy loam
Bt2	51-78	512	414	74	20.3	Sandy clay
BC	78-150	452	374	174	71.0	Clay loam
EGP5 = Iwo Series (Haplic Lixisol/Typic Kanhaplustalf)						
Ap	0-25	832	74	94	55.8	Loamy sand
AB	25-37	752	114	134	16.3	Sandy loam
Bt1	37-48	552	294	154	53.5	Slightly gravelly Sandy clay loam
Bt2	48-90	512	314	134	31.7	Sandy clay loam
Bt3	90-117	532	294	174	7.7	Sandy clay loam
BC	117-190	512	294	194	8.7	Sandy clay loam
EGP6 = Egbeda Series (Rhodic Ferrasol/Kanhaplic Rhodustalf)						
Ap	0-34	672	134	194	58.5	Sandy loam
AB	34-62	612	174	214	70.9	Gravelly Sandy loam
Bt1	62-88	412	414	174	69.7	Gravelly clay
Bt2	88-142	372	432	194	41.7	Clay
Bt3	142-170	352	454	194	44.1	Clay

Temperature

The mean daily maximum and minimum temperatures in the area range from 37-34.5^{0}C and 17-22.8^{0}C respectively and 18.7-22.8^{0}Cand 27.7-34.5^{0}C respectively. A hot dry season is experienced from November to March and cooler rainy season April to October. In late December and January, the dry air mass carrying dust particles from the North predominates, giving rise to harmattan season with short periods of hazy weather.

Land use

The vegetation or land use of the site was agrarian. Six major land use types were identified in the study area. They include Arable/Fallow mosaic, Derived Savannah vegetation, Open ploughed land, Cashew plantation, Riparian Forest and Grass land depression.

Soil

The entire area overlies ancient metamorphic crystalline basement complex formations which are considerably more acidic than basic. The soils in the area are primarily of Iwo Association according to Smyth and Montgomery classification. They are derived from coarse-grained granites and pegmatites, weathered into clayed soils whenever they occur. Other soil associations identified in this area are Egbeda and Jago Association but on the whole, six (6) major soil types (series) were encountered (Figure 2). They include: Ikire (EGP1), Ibadan (EGP2), Iwo (Concretionary variation) (EGP3), Iregun (EGP4), Iwo (Normal variation) (EGP5), and Egbeda Series (EGP6). The soils are generally sandy except Egbeda series (EGP6) which is clayed at the subsoil. Their colour ranges from grayish brown to brownish red in most of the profiles.

Table 2: Chemical properties of the study area

HD	DEPTH (cm)	pH (H_2O)	pH (KCL)	O.C	N	P	EA	Ca	Mg	K	Na	ECEC	BS	Fe	Mn	Cu	Zn
				g/kg	mg/kg			cmol/kg					(%)	mg/kg			
EGP1 = Ikire Series (Ferralic Fluvisol/Tropaquent)																	
A1	0-28	4.7	3.8	25.9	1.64	2.10	1.3	1.39	2.38	0.15	0.31	5.53	76.49	218	6.9	1.13	3.88
AB	28-67	5.0	4.2	17.5	1.51	0.83	0.9	0.70	1.73	0.07	0.28	3.68	75.54	107	7.7	1.32	3.38
B1	67-97	5.8	4.3	7.6	0.66	1.02	0.6	0.56	1.62	0.08	0.28	3.14	80.69	79.8	11.6	0.92	3.23
B2	97-140	5.9	4.2	5.2	0.44	1.46	0.7	0.34	1.77	0.06	0.31	3.18	77.99	88.7	15.5	0.67	3.28
Bc	140-175	5.6	4.1	2.5	0.22	1.10	0.7	0.25	2.17	0.08	0.35	3.55	80.28	154	10.0	1.10	3.58
EGP2 = Ibadan Series (Ferric Lixisol/Typic Kanhaplustalf)																	
Ap	0-30	5.8	4.7	16	1.38	4.08	0.4	1.15	1.37	0.14	0.26	3.32	87.95	110	140	1.04	4.116
AB	30-70	5.4	4.0	9.9	0.85	1.89	0.9	0.13	0.77	0.12	0.28	2.20	59.09	76.8	79.1	1.46	3.94
Bt1	70-110	5.3	4.1	6.7	0.58	0.89	0.7	0.38	2.21	0.26	0.27	3.82	81.68	95.8	92.8	0.75	2.95
EGP3 = Iwo Series (Pilinthic Lixisol/Plinthic Kanhaplustalf)																	
Ap	0-24	6.4	5.4	9.0	0.78	2.10	0.4	1.58	1.87	0.49	0.29	4.63	91.36	144	271	1.61	5.17
Bt1	24-36	6	4.3	8.3	0.72	0.37	0.4	1.10	1.04	0.90	0.30	2.74	85.40	133	148	3.08	3.41
Bt2	30-36	5.8	4.1	7.0	0.06	1.02	0.9	0.05	0.54	1.26	0.29	3.04	70.39	136	156	2.1i	3.40
Bt3	50-75	5.8	5.1	4.1	0.35	0.40	0.5	0.12	0.87	1.38	0.32	3.19	84.33	114	219	1,24	3.83

Experimental soil

The primary information on which this study was based was acquired by [9] who studied the physical and chemical properties of the soil in Egbedi town, Osun-State, Nigeria. Twenty-seven (27) samples were collected from already described soil profiles and these samples were used for this study.

The samples were sieved through a 2mm mesh and also through a 0.5mm mesh. Extractable Fe and Mn was done using the citrate-bicarbonate extractant procedure.

Laboratory analysis

The extraction solution was prepared. Four grams (4g) of 0.5mm sieved soil was weighed into 120ml plastic bottles with 1 blank. Forty-five milliliters (45mls) of citrate-bicarbonate-dithionate solution was added to each of the weighed samples and the mixture was heated to 80^{0}C in a water bath. Three grams (3g) of $Na_2S_2O_4$ was added to flocculate the sample and centrifuging was carried out at 2000rpm for 5 minutes. The clear supernatant liquid was decanted and the solution was read using an AAS.

Acid ammonium oxalate extraction of Fe and Mn was determined using McKeague and Day procedure. The extraction solution was prepared. One gram (1g) of 0.5mm sieved soil was weighed into 102ml plastic bottles. One blank was prepared. Forty millilitres (40mls) of acid oxalate solution was added to the sample and was placed in a mechanical shaker to shake for 4hours. Centrifuge was carried out at 2400rpm for 10minutes. The clear supernatant liquid was decanted and read using the AAS.

RESULTS

The first profile (EGP1) was generally sandy (Table 1). It had a sandy loam texture from the top soil to the subsoil. The gravel percentage was less than 80% and there was quite an appreciable amount of quartz grains at depth. The second profile (EGP2) was sandy at the upper horizon becoming more gravelly and clayed with depth. It occupied about 40% of the site. Its gravelly nature made it very difficult to dig especially in the dry season. The third profile (EGP3) occupied about 19% of the land mass. The soil texture was loamy sand at the top soil and became clayed with depth. Evidence of plinthic indurated layer was encountered at 75cm depth of the profile and this serves as a characteristic considered in naming the soil.

The fourth profile (EGP4) occupied 6% of the site at the upper middle slope of the land scape. The texture was loamy sand at the surface and became clayey with depth. The fifth profile (EGP5) and sixth profile (EGP6) occupied 25% and 4% of the land mass respectively. The fifth profile was generally sandy with its third horizon being slightly gravelly. The sixth profile was clay at depth with gravel percentages of 70.9 and 69.7 at the second and third horizons respectively.

DISCUSSION

The pH was generally acidic ranging from 4.7-6.4 which shows a range of slight acidity to medium acidity for all six profiles (Table 2). The organic carbon decreased with depth through the profiles. The based saturation for the first (EGP1) and second profiles (EGP2) were higher than 50% while the effective cation exchange capacity was low. In the third profile (EGP3), the organic carbon was highest at the top horizon (9 g/kg) and decreased with depth (4.1 g/kg).

The critical range for phosphorus in soils of south western Nigeria is 10-15 mg/kg [10]. Based on this range, it can be inferred that the phosphorus in the soil is low through all the profiles and it could be as a result of fixation by the free iron oxides [11]. The critical range for nitrogen is 2.0 g/kg and it is observed from the results that the nitrogen level is also low for all six profiles. Iron and manganese were higher than their critical range which is both 5 mg/kg. This indicates abundance of free iron oxides in the soil.

The percentages of the Fe and Mn extracted through the dithionite citrate bicarbonate and the acid ammonium oxalate methods are reflected in the Table 3. The percentages of Mn extracted by the dithionite citrate bicarbonate method was more than the percentage of Mn extracted by the acid ammonium oxalate method and this observation agrees with [12] that higher percentages of free iron oxides should be extracted by the dithionite citrate bicarbonate method.

In the case of Fe, acid ammonium oxalate method extracted more Fe than the dithionite citrate bicarbonate method at different horizons within the second to the sixth profile. This increased the value of the active iron ratio which should be less than one according to [13]. The increase in the active iron ratio to a value more than one (1) was an indication of the presence of magnetite in the respective horizons where such increase was observed.

CONCLUSION

The distribution of soil properties in south western Nigeria is a function of parent materials. However, topography has an influence on the soil properties. From the research, the following conclusions can be deduced: Oxalate and Dithionite-extractable Fe and Mn values aid in distinguishing horizons. The horizons which have an active iron ratio that is more than one (1) have magnetite present in them. The oxalate Fe values indicate the degree of accumulation of amorphous products while Dithionite Fe values indicates combined presence of amorphous iron and crystalline iron oxides. The presence of iron oxides causes fixation in nutrients especially phosphorus which is required by crops during agricultural production.

REFERENCES

[1] Agbenin, J.O, 2003. Extractable iron and aluminum effects on phosphate sorption in savannah alfisol. *Soil Science Society of America Journal*. 67: 589-593.

[2] Enya, O.O, Omueti, J.A.I, Akinbola, G.E., 2011. Particle size and free iron oxide distribution along two toposequence in South Western Nigeria. Wilolud Journals; *Continental. J. Agromony*. 5(2):22-31

[3] Esu, I.E, 1999. Fundamentals of Pedology. Stirling Horden Publishers (Nig) Ltd; Ibadan. Pg.139

[4] Igwe, C.A., Zarei, M. Stahr, K., 2005. Mineral and elemental distribution in soils formed on the River Niger floodplains Eastern Nigeria. *Australian Journal of Soil Research.* 43: 147-158

[5] Lucas, Y. and Chauvel, A., 1992. Soil formation in tropically weathering terrains. In Regolith exploration. Geochemistry in Tropical and Subtropical terrains. Butt CFM, Zeegers H (ed) Handbook Exploration Geochemistry. Volume 4, Goveth GJS (ed.) Elservier.

[6] McDaniel, P. A, Bathke, G.R, Buol, S.W, Cassel, D.K, Falen, A.L., 1992. Secondary manganese/iron ratios as pedochemicals in indicators of scale through flow water movement. *Soil Science Society of America J.* 56: 1211-1217.

[7] Mustapha, S. Mamman, H.K and Abdulhamid, N.A., 2010. Status and distribution of extractable nutrients in haplustults in Yamaltu-Deba Local Government Area, Gombe Area, Nigeria. *Journal of Soil Science and Environmental Management*. 8: 200-204

[8] Mustapha, S. Voncir, N. Umar, S and Abdulhamid, N.A., 2011. Status and distribution of some available micronutrients in the haplic userts of Akko Local Government Area, Gombe Area,Nigeria. *International Journal of Soil Science*. 6: 267-274.

[9] Obi, J.C., Akinbola, G.E., and Anozie, H.I., 2009. Distribution of dithionite and oxalate extractable iron oxides of a catena in the basement complex soils of South-West Nigeria. *Nigerian Journal of Soil Science.* 19(1): 100-109.

[10] Ogunkunle, A.O., 1993. Variation of some soil properties along two toposequence on quartzite schist and banded gneiss in South Western Nigeria. *An International Journal of Physical Social and Economic Geography and Application in Environmental Planning and Ecology.* 30.(4): 397-402.

[11] Ogunsola, O.A. and Omueti, J.A.I., 1990. The physical, chemical and mineraological characteristics of soils overlying limestone areas in South Nigeria. *Nigeria Journal of Science.* 24:110-118.

[12] Oluwatosin, G.A., Ojo-Atere, J.O., Osiname, O and Adediran, J.A., 2001. Influence of topograph position on crop response to different rates of fertilizer in South-Western Nigeria. *Moor Journal of Agricultural Research*. 2:1-7.

[13] Temogoua, E. Tchapnga, H.D, Tanawa, E., and Pfeifer, H., 2005. Ground water fluctuations and footslope ferricrete soils in the humid tropical zone of Southern Cameroon. *Hydrol. Process*. 19: 3097-3111