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Evaluation of Universal Extractants for Determination of Selected Micronutrients on Soils Developed over Charnockite in Ekiti State

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Abstract

Twenty six pedogenic soils developed on charnockite were used to evaluate the suitability of extractants for bioavailability of manganese, copper, zinc and iron in the soils to plants. These micronutrients cation were extracted from the soils using five different extractants, namely, Neutral Normal NH_4OAc, NH_4OAc buffered with glacial acetic acid to pH 4.8, 0.1 M HCl, 0.05 M HCl + 0.025 M H_2SO_4, 0.05 M EDTA + 0.1 M $(NH_4)_2CO_3$. The contents of extractable Mn, Cu and Fe ranged were 0.04-1.50, 0.39-9.01 and 14.10-639.90 mg kg^{-1} respectively with $Mehlich_1$ having the highest mean values of 0.83, 5.45 and 341.46 mg kg^{-1} across the locations. EDTA was more efficient in the extraction of the available Zn having a mean value of 0.11 mg kg^{-1} and varied from 0.01-0.22 mg kg^{-1} in all the soils. The 0.1 M HCl was moderately efficient in the micronutrients cation assessment, but the NH_4OAc extractants were generally less effective in assessing the micronutrients cation even though the buffered solution gave a better extractability over the neutral normal solution. All the extractants were significantly correlated ($p < 0.05$ and $p < 0.01$) with one another for available Mn and Fe in the soils except the $Mehlich_1$ and neutral normal NH_4OAc in the extraction of Mn. Whereas, only 0.1 M HCl correlated significantly with NH_4OAc pH 4.8 in determining the extractable Zn. Likewise, $Mehlich_1$ vs. NH_4OAc pH 4.8 and 0.1 M HCl vs. NH_4OAc pH 7.0 had moderate significant correlations ($p < 0.05$) for extractable Cu. It shows that the extractants were generally extracting the available forms of these micronutrients cation from the same source in charnockitic soils irrespective of the likely chemical, physical and mineralogical variations across the locations. The order of extractability of the extractants were: 0.05 M HCl + 0.025 M H_2SO_4 > 0.05 M EDTA + 0.1 M $(NH_4)_2CO_3$ > 0.1M HCl > NH_4OAc pH 4.8 > NH_4OAc pH 7.0.

Keywords: Charnockite, Correlation, Extractants, Micronutrients

1. Introduction

Soil micronutrients are elements that are essential to plant growth, but are utilized in minimum quantities. The term does not imply that these elements occurs in meager quantities in rocks and soils. The copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) made up the micronutrients cation. While micronutrients are required in small amount by plants, they may be harmful when added to the soils in high quantities. The developing of several methods for determining plant available nutrients in soil has begun for over 150 years across the world. A chemical reagent with an ability to extract more than one class of elements and/or ions from a soil is known as universal soil extractant, the concentration of which is used as a measure for determining soil fertility status or level of soil toxicity. The advantages of universal extractants in soil testing methods include increasing the reliability of soil test, increasing accuracy and precision of the tests and it saves time and increase the efficiency of the methods in routine soil analysis (Ayodele *et al.* 2013).

Soil testing is the most widely used chemical analysis performed in agriculture, and is very cost effective (van Raij 1998). Several extraction procedures suitable for removing the soil micronutrients cation, Mn, Cu, Zn and Fe in their ionic forms have been used on many soils (Aduloju & Abdulmumini 2013; Korzeniowska & Stanislawska-Glubiak 2013; Da Fonseca *et al.* 2010; Shittu *et. al.*, 2010) over the years in order to predict the crop production capacity of a given soil. However, the reliability of the analytical results can be affected by the lack of standardized extraction methods, since the success of soil testing is associated with the choice of an extractant suited for the specific agricultural conditions in the region under investigation. The soil test for the selected micronutrients currently used include dilute acids, chelate based extractants such as Ethylenediaminetetraacceticacid (EDTA), Mehlich III and Diethylenetriamineentaaceticacid (DTPA), and acetate based soil extractants buffered to pH 7.0 and 4.8 by several laboratories. In most cases, these extraction techniques were based on the nature of the soil reactions rather than the micronutrients cation resulting in these contradictory reports that calls for more additional studies around the world, to abreast agronomists in predicting soil micronutrients availability and plant response. Moreover, little information is available on the suitability of these extractants to estimate the extractable micronutrients cation in Nigeria soils particularly those developed on charnockite.

Charnockitic soils are developed on charnockite rocks. Nicollet (2004) defines charnockite rock as a rock with granitic composition containing orthopyroxene, the pyroxene present is hypersthene, [$(Mg, Fe)_2 Si_2O_6$] which is either or not associated with biotite, sometimes with amphibole or garnet, opaque minerals (metallic oxides) to which are added leucocratic minerals of the granite, quartz, plagioclase, and potassic feldspar. Pichamuthu (2003), also reported the mineral constitution of charnockite rocks to include quartz, perthitic alkaline feldspar, plagioclase feldspars, very weakly pleochroic orthopyroxene, microcline, olivine, hornblende, biotite and accessory zircon, apatite and Fe oxide. Charnockites are found in every continent, but are limited to deep, high grade terraces making them unfamiliar in many regions. But, Africa has about sixty-three citations, which include Ekiti State, Nigeria (Ekiti Investor Handbook 2002).

The replenishment of micronutrients through fertilizer is still in its infancy in Nigeria. Fertilizer applications in Nigeria involves only the macronutrients even though cropping (and harvesting), erosion and leaching deplete soil of micronutrients which should be replenished by the return of organic materials such as crop residues, farm yard manure and compost. Therefore, it is important to know the original micronutrients in the soils and add only as much of the micronutrients as is beneficial to plants and foraging animals.

The aim of this study was to compare the suitability of five extractants; 0.05 M HCl + 0.025 M H_2SO_4 (Mehlich$_1$), 0.05 M EDTA + 0.1 M $(NH_4)_2CO_3$ (EDTA), 0.1M HCl (HCl), NH_4OAc pH 4.8 (AAc$_{4.8}$) and NH_4OAc pH 7.0 (AAc$_{7.0}$) for the assessment of extractable micronutrients cation in charnockitic soils.

2. Materials and Methods

Twenty six pedogenic soils were collected from six profiles dug at Ado, Ikere, Ijan, Ijesa-Isu, Ire and Osin-Itapa in Ekiti State where charnockite are found in South Western Nigeria. The soil samples were taken from a derived savanna region (Ire, Ijesa-Isu and Osin-Itapa) and a dry forest region (Ado, Ijan and Ikere), both with a mean annual total rainfall and temperature of 1367 mm and 25^{o}c respectively and crop production is the major land use. The soils were air dried, gently crushed and sieved through 2mm plastic sieve and kept in plastic bags ahead chemical analysis.

The extractable Cu, Mn, Fe and Zn in the soil samples were extracted by 5 different extractants: Neutral Normal NH_4OAc, NH_4OAc pH 4.8, 0.1 M HCl, 0.05 M HCl + 0.025 M H_2SO_4 and 0.05 M EDTA + 0.1 M $(NH_4)_2CO_3$. 5g of each prepared soil samples were weighed into four 50ml and a 100ml extraction vessels. 25 ml of each extractants were added to the 50 ml extraction vessels except the 0.05 M EDTA + 0.1M $(NH_4)_2CO_3$ extractant which 50ml of it was added to each of the six 100 ml extraction vessels. The vessels were shaken for 5-minutes on a rotary shaker at a minimum of 180 oscillations per minute except for soils treated with 0.1 M HCl which were shaken for 30-minutes at the same oscillation. In all extracts, Cu, Mn, Fe, and Zn were determined by atomic absorption spectrophotometry with flame atomization.

Additionally, the distribution of particle sizes in soils was determined by hydrometer method, soil pH measured in water at 1:1 soil/water ratio using glass electrode pH meter and organic carbon by potassium dichromate method. Cation exchange capacity (CEC) was obtained by the summation of the exchangeable bases extracted from the soils using neutral normal ammonium acetate and determine using the appropriate instruments. The extractable micronutrients cation contents were subjected to analysis of variance using generalized linear model and means separated by Duncan's multiple range test. Relationship among the extractants were determined by Pearson correlation and simple linear regression model.

3. Results and Discussion

3.1 Physical and Chemical Characteristics of the Charnockitic Soil

The means and ranges of values of some of the important physical and chemical properties of the investigated soils are given in Table 1.

The percentage mean values of sand, silt and clay across the locations are 77.42, 5.93, and 16.65% respectively, indicates that the soils were generally coarse-textured. Such soils are characterized by high infiltration rate, rapid internal drainage and low water holding capacity. The soils were Sandy loam in texture except Ado and Ijan that were Sandy clay loam and Loamy sand respectively. The predominance of sand in the soils signifies the influence of the parent materials and preferential removal of clay and silt by surface erosion (Mustapha *et al.* 2011; Shittu 2008; Greenland 1981). The pH ranged from 5.6 to 7.5 with a mean value of 6.5, showed the soils reactions varied from moderately acid to slightly alkaline reactions. The slightly above neutral pH (> 7.0) observed on soils of Ijan, and Itapa-Osin pedons with mean values of 7.1 and 7.4 respectively might be due to the liming effect of the rampant bush burning for hunting and land clearing. For profiles of Ado, Ijesa-Isu, Ikere and Ire, the lower pH might be due to the effect of intense cultivation, erosion and leaching of nutrients down the profile. The pH of most of the soils decreased irregularly with depth. These decrease pH values with profile depth could be due to the effect of nutrient biocycling (Ogunwale *et al.* 2002). The pH values indicated that charnockitic soils would give an optimum yield for nearly all crops if all other environmental conditions are favorable. All the soils followed the general trend of having the highest organic carbon content in the Ap-horizons although low, and decreases down the profile ranging from 0.99 to 3.91%. The high surface values is an indication of continuous deposition of organic materials from previous cultivations. The generally low organic carbon content could be as a result of high rate of mineralization due to the humid climate, intense cultivation and seasonal burning that characterized the derived Savanna belt (Brady & Weil 2005).

3.2 Mean Values of the Extractable Micronutrients

The range and means of the extractable micronutrients cation were presented on Table 2.

The extractable Mn-EDTA, Mn-Mehlich$_1$, Mn-HCl, Mn-AAc$_{7.0}$ and Mn-AAC$_{4.8}$ values ranged from 0.03-0.90, 0.15-1.50, 0.14-1.12, 0.04-0.44 and 0.09-0.66 mg kg^{-1} with mean values of 0.43, 0.83, 0.65, 0.24 and 0.35 mg kg^{-1}. The Mehlich$_1$ extracted more extractable Mn from the soils than any other extractants though their mean values were not significantly different from one another. This could be due to the double acid effect and strong nature (pH) of the extractant. Abreu *et al.* (2004) and Da Fonseca *et al.* (2010) also observed in Brazil kaolinitic soils that Mehlich I solution extracted more Mn than Mehlich III solution, 0.1 M HCl solution and DTPA-TEA solution. HCl ranked second in the extraction of Mn, but Shittu *et al.* (2010) found it to be better but not significantly different from DTPA. Pereira *et al.* (2001), also reported that the Mn extraction capacity of 0.1 M HCl was greater than that of DTPA and Mehlich I. The other extractants ranked as follows: EDTA > AAc$_{4.8}$ > AAc$_{7.0}$.

Table 1. Physical and chemical properties of soils developed on charnockite

		Ado	Ijesa-Isu	Ijan	Ire	Ikere	Osin-Itapa
pH	Range	5.7-6.3	6.0-6.3	7.3-7.5	5.6-5.7	6.1-7.0	6.9-7.3
	Mean	5.9	6.1	7.4	5.6	6.6	7.1
% Org. Carbon	Range	0.99-3.75	1.15-2.59	1.63-2.31	1.66-3.39	1.15-2.91	1.83-3.91
	Mean	2.17	2.05	1.95	2.51	1.73	2.53
CEC	Range	3.4-10.2	2.6-6.2	3.3-7.6	4.0-7.0	4.0-8.4	8.4-13.4
	Mean	5.8	5.1	5.3	5.5	6.5	10.1
% Sand	Range	62.24-83.24	74.24-87.24	78.24-89.24	72.24-81.24	71.24-83.24	72.24-86.24
	Mean	70.04	80.24	83.04	76.49	76.74	77.99
% Silt	Range	4.00-9.00	4.00-5.00	3.00-5.00	6.00-9.00	6.00-10.00	5.00-7.00
	Mean	6.00	4.50	3.80	7.25	8.25	5.76
% Clay	Range	7.76-33.76	7.76-21.76	5.76-18.76	9.76-21.76	6.76-22.76	8.76-21.76
	Mean	23.96	15.26	13.16	16.26	15.01	16.26
Textural Class		Sandy clay loam	Sandy loam	Loamy sand	Sandy loam	Sandy loam	Sandy loam

The order of the Cu extraction, based on the mean capacity and range of the various extractants: Mehlich$_1$ > EDTA > HCl > AAc$_{7.0}$ > AAc$_{4.8}$. EDTA and Mehlich$_1$ were not significantly different from each other, although Mehlich$_1$ gave the highest extractable mean value of 5.45 mg kg^{-1}for Cu but were both significantly different from the mean values of other extractants which could be due to their strong and more aggressive chelation ability than chelation occurring under natural circumstances (Meers *et al.* 2007; Labanowski *et al.* 2008). Conversely, Shittu (2008) reported that EDTA gave the highest mean values for extractable Cu in charnockitic soils in nearly all the locations studied in Ekiti State, Nigeria and was significantly different from other extractants used but not with Mehlich I and Mehlich III. Muraoka *et al.* (1983) also observed superiority of EDTA and DTPA over 0.1 M HCl in soils of Sao Paulo, Brazil. Brennan (2002) reported that EDTA extracted on minimum average 30% more available Cu from limestone and sandstone shale soils than Mehlich III. The mean extractable Cu value obtained with HCl extractant was significantly different from those obtained with AAc$_{4.8}$ and AAc$_{7.0}$ which are in turn not significantly different from each other.

In the charnockitic soils studied, EDTA, Mehlich$_1$, HCl, AAc$_{7.0}$ and AAc$_{4.8}$ extractants have the mean values of extractable Zn which were not significantly different from each other although EDTA has the highest mean value of 0.11 mg kg^{-1} followed by HCl and AAc$_{4.8}$ then Mehlich$_1$ and AAc$_{7.0}$ both having 0.08 and 0.05 mg kg^{-1} mean values respectively. This can be interpreted as a direct effect of the high chelation capacity of EDTA and the liming effect of the rampant bush burning for hunting and land clearing in the studied area.

Table 2. Range and means of extractable micronutrients cation in charnockitic soils (n = 26)

Extractant	Ado	Ijan	Ijesa-Isu	Ikere	Ire	Osin-Itapa	Range	Mean
				Mn (mg kg^{-1})				
EDTA	0.76	0.90	0.12	0.28	0.03	0.49	0.03-0.90	0.43a
$\mathrm{Mehlich_1}$	1.50	1.50	0.15	0.31	0.73	0.76	0.15-1.50	0.83a
HCl	0.95	1.12	0.14	0.30	0.70	0.66	0.14-1.12	0.65a
$\mathrm{AAc_{7.0}}$	0.44	0.34	0.12	0.08	0.42	0.04	0.04-0.44	0.24a
$\mathrm{AAc_{4.8}}$	0.66	0.63	0.10	0.09	0.49	0.14	0.09-0.66	0.35a
				Cu (mg kg^{-1})				
EDTA	4.86	4.74	3.74	5.73	5.31	6.28	3.74-6.28	5.11a
$\mathrm{Mehlich_1}$	4.45	3.69	9.01	6.01	4.25	5.28	3.69-9.01	5.45a
HCl	2.16	2.75	4.80	5.36	1.87	3.24	1.87-5.36	3.36b
$\mathrm{AAc_{7.0}}$	1.08	0.66	1.08	0.39	1.01	0.71	0.39-1.08	0.82c
$\mathrm{AAc_{4.8}}$	1.71	1.45	0.00	0.80	1.60	1.94	0.00-1.94	1.25c
				Zn (mg kg^{-1})				
EDTA	0.05	0.12	0.04	0.22	0.07	0.13	0.04-0.22	0.11a
$\mathrm{Mehlich_1}$	0.04	0.01	0.04	0.07	0.04	0.11	0.01-0.11	0.05a
HCl	0.04	0.07	0.17	0.00	0.13	0.05	0.00-0.17	0.08a
$\mathrm{AAc_{7.0}}$	0.04	0.01	0.05	0.11	0.08	0.03	0.01-0.11	0.05a
$\mathrm{AAc_{4.8}}$	0.02	0.08	0.15	0.02	0.12	0.05	0.02-0.15	0.08a
				Fe (mg kg^{-1})				
EDTA	345.23	403.60	47.48	132.63	298.05	206.58	47.48-403.60	238.93ab
$\mathrm{Mehlich_1}$	415.64	691.10	61.53	182.73	358.05	339.68	61.53-691.10	341.46a
HCl	395.72	639.90	28.43	133.45	291.80	170.93	28.43-639.90	294.34ab
$\mathrm{AAc_{7.0}}$	189.32	134.60	43.83	14.10	170.93	22.88	14.10-189.32	95.94b
$\mathrm{AAc_{4.8}}$	294.60	264.50	19.63	19.55	195.95	39.08	19.55-294.60	138.89ab

† Means with the same letter are not significantly different down the column.
$\mathrm{Mehlich_1}$ – 0.05 M HCl + 0.025 M H_2SO_4, EDTA - 0.05 M EDTA + 0.1 M $(NH_4)_2CO_3$,
HCl – 0.1 M HCl, $\mathrm{AAc_{4.8}}$ – NH_4OAc pH 4.8 and $\mathrm{AAc_{7.0}}$ - NH_4OAc pH 7.0

Acid extractants have normally not been efficient to detect slight changes in extractable Zn as a consequence of liming, becoming a hard task to select an adequate extractant for this micronutrient (Abreu *et al.* 2007). However, 0.1M HCl and NH_4OAc at pH 4.8 extractants were reported to give the highest mean values of extractable Zn in the similar charnockitic soils (Shittu 2008). Study of Brazilian soils by Araújo & Nascimento (2005), Ortiz *et al.* (2007) and Silva *et al.* (2009), also shown that the highest extractable Zn from the soils occurred using HCl and $\mathrm{Mehlich_1}$ which may be attributed to solubilization of Zn forms in the soils.

$\mathrm{Mehlich_1}$ gave the highest and significantly different mean value of 341.46 mg kg^{-1} and ranged from 61.53–691.10 mg kg^{-1} for the extractable Fe in the studied charnockitic soils. It was expected since the extractant is a combination of dilute acids. This is in line with the findings of Alva (1992) and Walworth *et al.* (1992). This is also similar to the findings of Shittu (2008), who reported that $\mathrm{Mehlich_1}$ extractant gave greater quantity of extractable Fe than all other extractants employed. The extractable Fe-HCl, Fe-EDTA and Fe-$\mathrm{AAc_{4.8}}$ followed the Fe-$\mathrm{Mehlich_1}$ as listed in the sequence with mean values of 294.34, 238.93 and 138.89 mg kg^{-1} respectively and were not significantly different from one another but from the Fe-$\mathrm{AAc_{7.0}}$ which gave the lowest mean value of 95.94 mg kg^{-1}.

3.3 Relationships among the Extractants in Charnockitic Soils

Figure 1-4 illustrated the relationships among the micronutrients cation extractants assessed in charnockitic soils. Figure 1 showed that the extractable Fe extracted from the soil by $\mathrm{Mehlich_1}$ has high and significant correlation ($p < 0.01$) with the contents extracted by EDTA, HCl, $\mathrm{AAc_{4.8}}$, and $\mathrm{AAc_{7.0}}$. These results indicate that regardless of the nature of the extractant, acid, chelate or acetate based, the extraction capacity of all methods studied is similar for estimating Fe contents in charnockitic soils, which are highly changeable in chemical, physical and mineralogical properties.

All the extractants were not significantly correlated with one another for the extractable Zn with the exception of HCl extractant which had a moderate significant correlation with the $\mathrm{AAc_{4.8}}$ at $p < 0.01$ having coefficient of 0.56 (Figure 2). This may be attributed to the acid nature (pH) of both extractants which makes them to have similar extraction ability for Zn. However, Bataglia & Raij (1994) obtained a high degree of association ($r = 0.99$; $p < 0.01$) between the Zn contents extracted by HCl and Mehlich_1 in soils from the state of São Paulo.

Figure 3 revealed that the extractable Cu-Mehlich_1 and Cu- $\text{AAc}_{4.8}$ shown moderate correlation (0.39). Likewise, the extractable Cu-HCl and Cu-$\text{AAc}_{7.0}$ have a moderate correlation (0.41). Both relationships were significantly correlated at $p < 0.01$. Whereas, there were no significant correlations among other extractants. Pereira *et al.* (2001) compared Mehlich_1 and HCl extractants for in soil samples from Brazil and found a correlation coefficient of 0.75 ($p < 0.05$) and the Cu contents extracted by HCl were approximately 25 % lower than determined with Mehlich_1.

The correlation for the extractable Mn contents in the soils by the extractants were shown in Figure 4. Mehlich_1 and other extractants were significantly correlated except with $\text{AAc}_{7.0}$ extractant. The highest correlation was with HCl having coefficient of 0.66 ($p < 0.01$). The significant correlation between the Mehlich_1 and HCl extractants for the extracted Mn contents may be explained by the fact that the chemical extraction principle of these procedures is the same. Shittu *et al.* (2010), reported a significant correlation between 0.1 M HCl and DPTA for extractable Mn in charnockitic soils and suggested that the sources of the Mn forms are probably similar. Alva (1992) also found that Mehlich III extracted more Mn than did 1 M NH_4Oac, but the two extractants were poorly correlated, $R^2 = 0.46$.

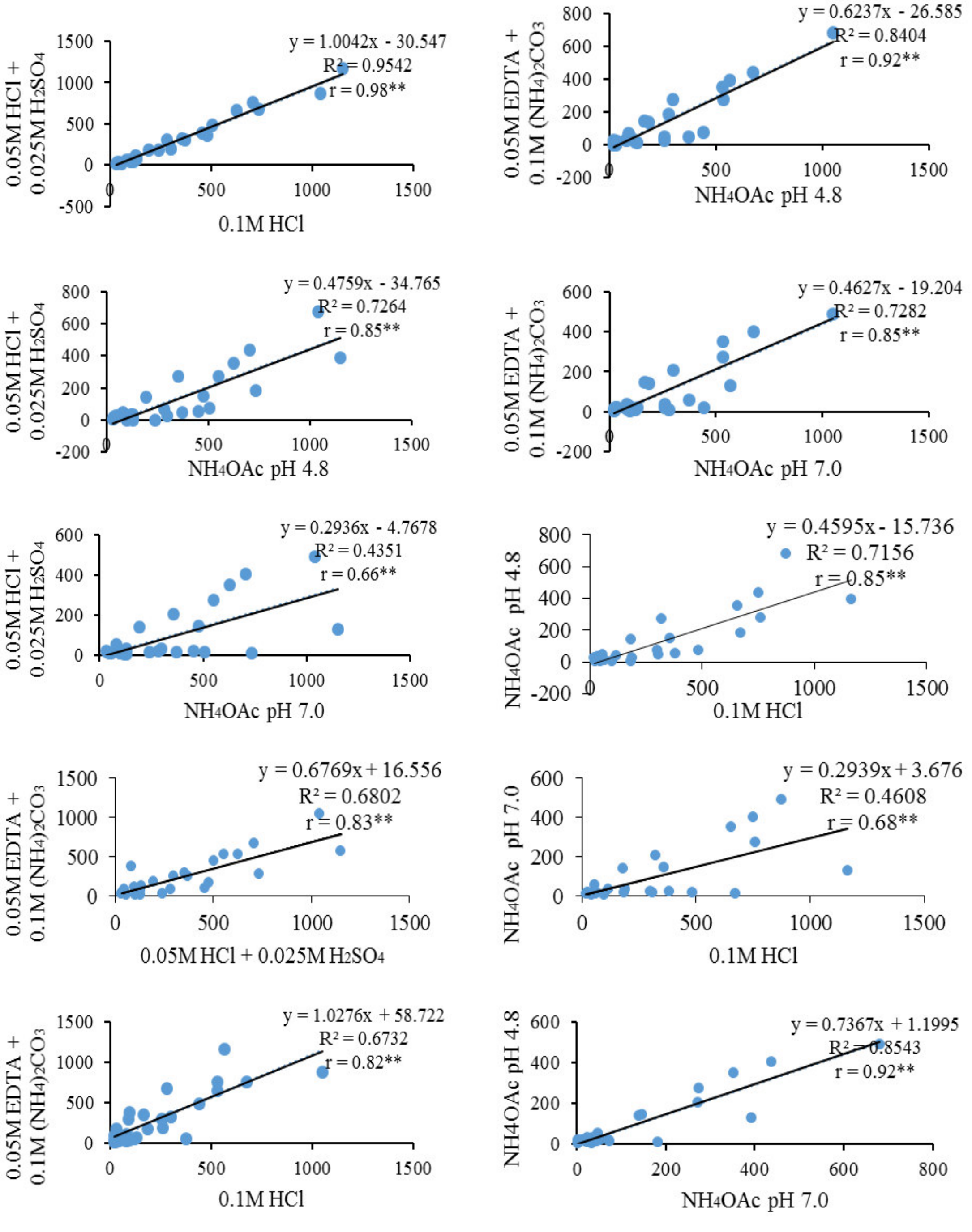

Figure1. Relationships among the extractants in extracting iron (Fe) cation in charnockitic soils. $^{*}p < 0.05$ and $^{**}p < 0.01$.

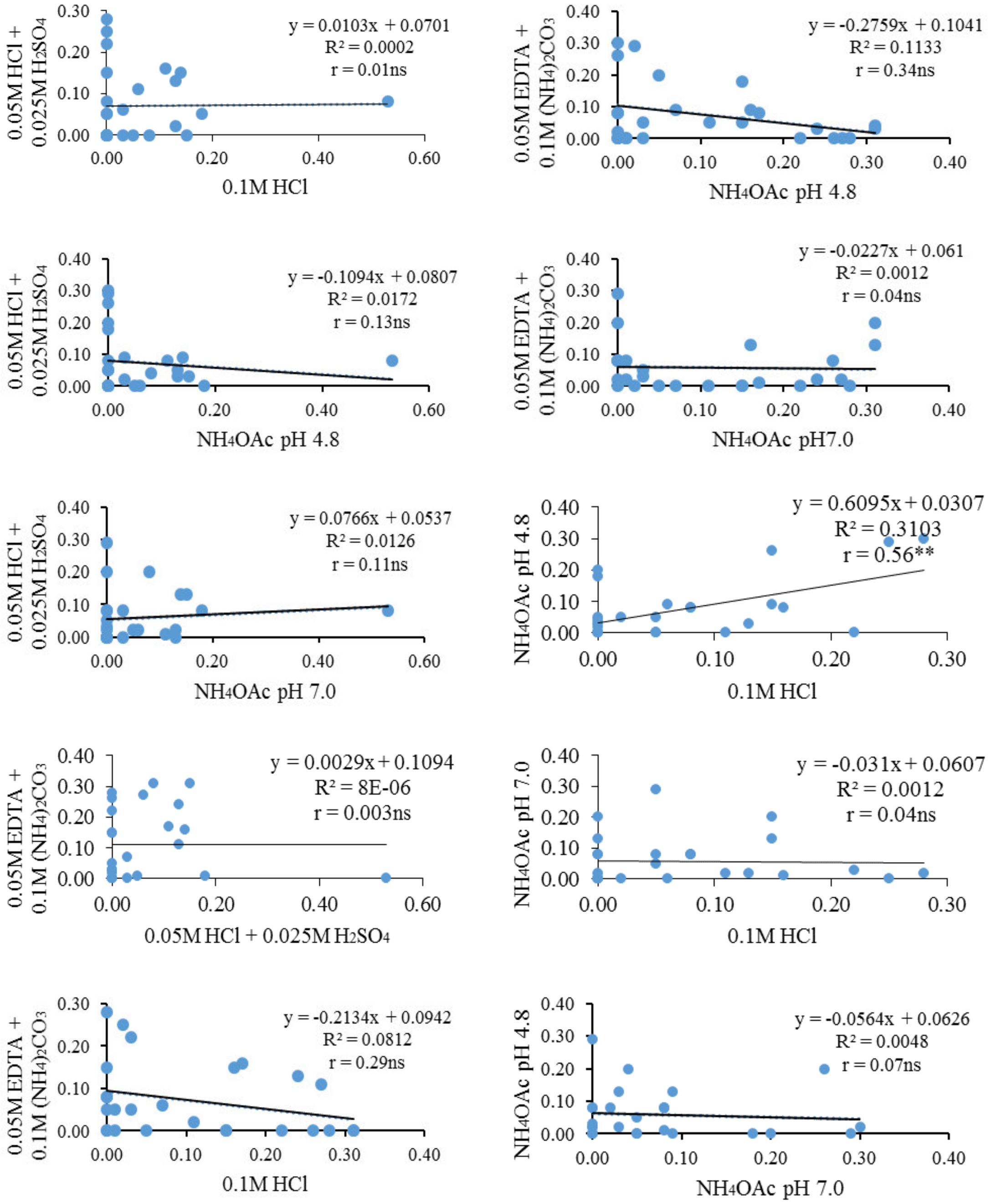

Figure 2. Relationships among the extractants in extracting zinc (Zn) cation in charnockitic soils.
*p < 0.05, **p < 0.01 and ns: not significant.

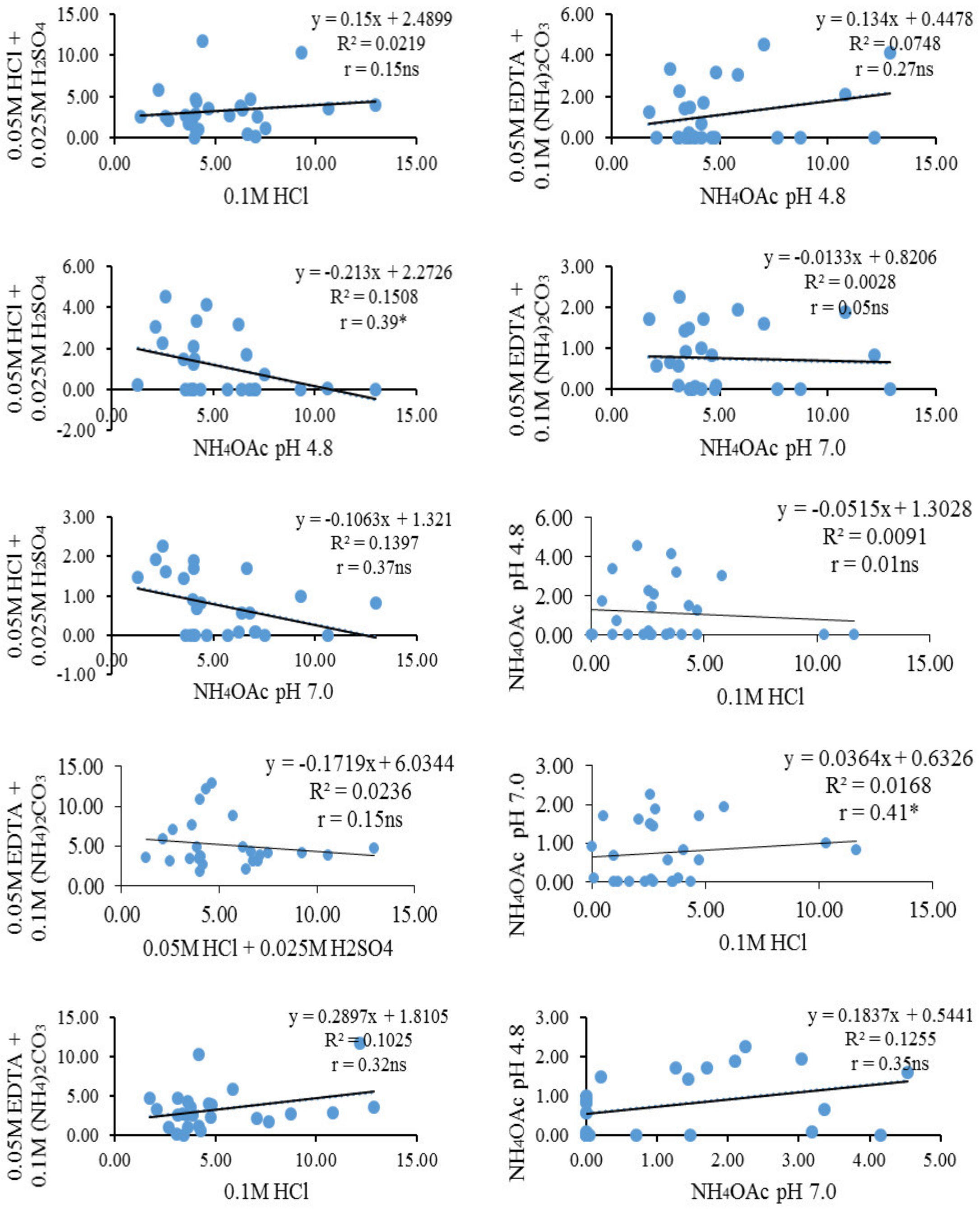

Figure 3. Relationships among the extractants in extracting copper (Cu) cation in charnockitic soils. $^*p < 0.05$, $^{**}p < 0.01$ and ns: not significant.

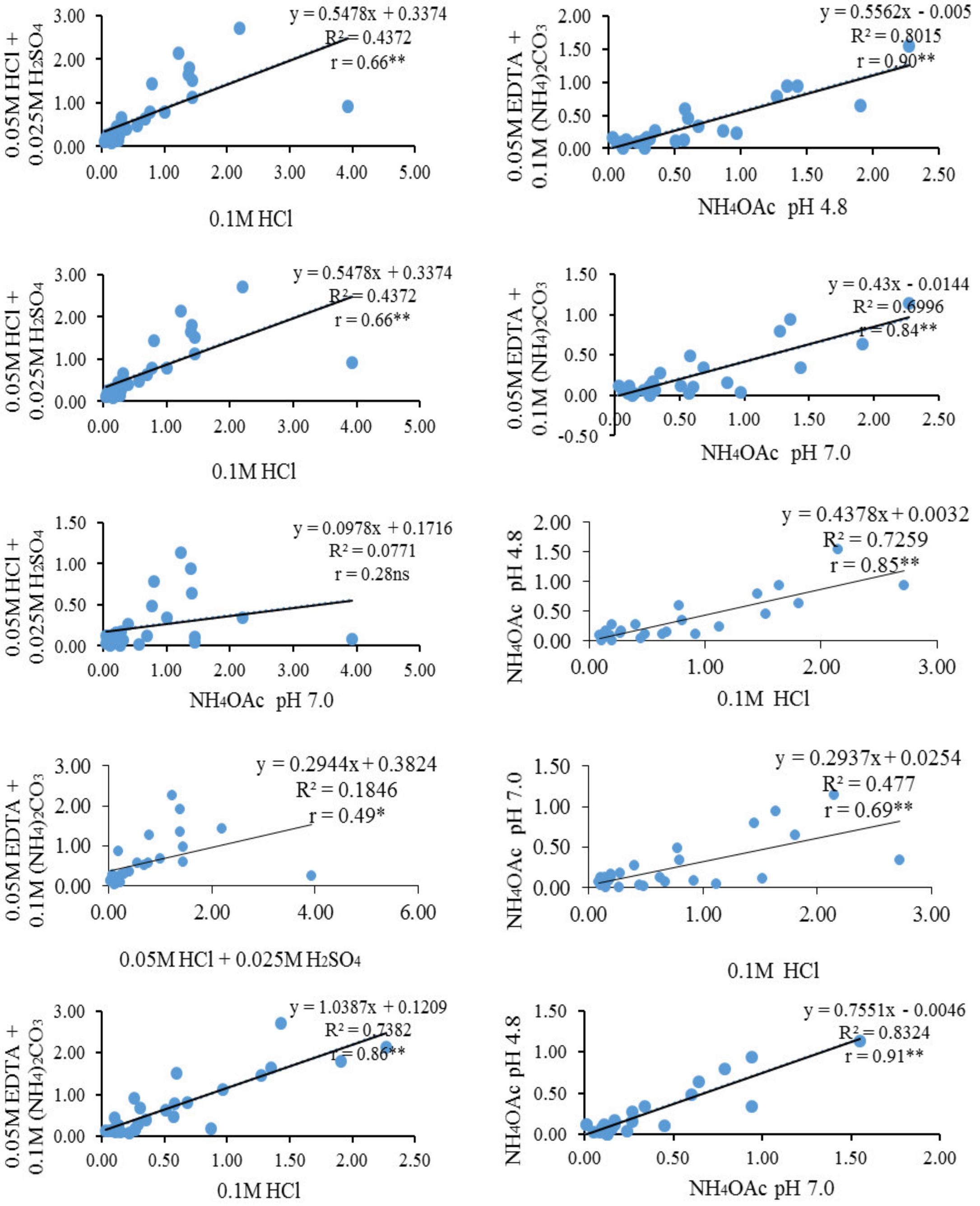

Figure 4. Relationships among the extractants in extracting manganese (Mn) cation in charnockitic soils. $^*p < 0.05$, $^{**}p < 0.01$ and ns: not significant.

4. Conclusion

1. Mehlich$_1$ extractant shown to have better efficiency for the estimation of extractable Mn, Cu and Fe than all other extractants compared.
2. EDTA extractant showed higher efficiency than every other extractants for the determination of the available Zn in the charnockitic soils.
3. HCl extractant has a moderate efficiency for all the selected micronutrients cation in the charnockitic soils.
4. The NH_4OAc extractant both at pH 4.8 and 7.0 were shown to be less efficient for determining the micronutrients cation in the charnockitic soils though it's more efficient at pH 4.8.

5. The order of extractability of the extractants were: 0.05 M HCl + 0.025 M H_2SO_4 > 0.05 M EDTA + 0.1 M $(NH_4)_2CO_3$ > 0.1M HCl > NH_4OAc pH 4.8 > NH_4OAc pH 7.0

The extractants compared are micronutrient specific with $Mehlich_1$ been the most suitable for estimating micronutrients cation in the charnockitic soils as it extracted over 50% of the available micronutrients and would be more indicative and cost effective since this method also allows P and K determination. Thus, due to the greater ease of operation in laboratories for routine soil testing, $Mehlich_1$ is the most indicated extractant for combined extractions of the studied micronutrients. Further research should be conducted to investigate plant uptake in relation to these extraction methods.

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