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STATUS OF AVAILABLE MICRONUTRIENTS IN SOIL PROFILES OF DIFFERENT PARENT MATERIALS IN IMO STATE, SOUTHEASTERN, NIGERIA

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ABSTRACT
The status of available Zn, Cu, Ni and Fe was studied in four representative soil profiles of different parent materials (Coastal Plain Sands, Alluvium, Falsebedded Sandstones and Imo Clay Shale) in Imo State, Southeastern Nigeria. Sample collection was guided by horizon differentiation. Available Zn, Cu, Ni and Fe were evaluated using double acid extraction method. Variation in distribution of available micronutrients studied was evaluated using coefficient of variation while the relationship between available Zn, Cu, Fe and Ni and selected soil properties was estimated using correlation and regression analyses. The results showed that in soil profile derived from Coastal Plain Sands, available Zn, Cu, Fe and Ni were low (mean=0.45 mg/kg), moderate (mean = 0.76 mg/kg), low (mean=0.65 mg/kg) and moderate (mean=2.89 mg/kg), respectively. In soil profile derived from Alluvium available Zn, Cu, Fe and Ni were low (mean = 0.75 mg/kg), moderate (mean=0.70 mg/kg), low (mean=1.15 mg/kg) and moderate (mean=3.34mg/kg), respectively. In soil profile derived from Falsebedded Sandstones, available Zn, Cu, Fe and Ni were low (mean=0.46 mg/kg), moderate (mean=1.46 mg/kg), low (mean=1.03 mg/kg) and moderate (mean=3.99mg/kg), respectively while in soil profile derived from Imo Clay Shale, available Zn, Cu, Fe and Ni were low (mean= 0.74 mg/kg), moderate (mean=0.92 mg/kg), low (mean=1.25 mg/kg) and moderate (mean=4.56 mg/kg), respectively. The results further revealed high variation, moderate to high variation, low to high variation and moderate to high variation in the distribution of available Zn, Cu, Fe and Ni, respectively in soil profiles studied. Available zinc (r=0.46) correlated significantly with OM while available iron (r=0.45) and nickel (r=0.47) had significant positive correlation with clay. Multiple regression analysis showed that the combined effect of available P, Ca, clay, ECEC, OM and pH on available Zn, Cu, Fe and Ni was not significant at 34.9 %,18.4 %, 38.9 % and 21.5 % respectively. Application of Iron and Zinc Chelates to all the soils of different parent materials studied and Nickel containing fertilizer is recommended particularly to soils of Imo Clay Shale.
Keywords: Available Micronutrients, Parent Materials, Soil Profile, Soil Properties

INTRODUCTION

Micronutrients are chemical elements that are required for plant growth in extremely small amounts (Mustapha *et al.,* 2011). They include elements such as Zinc (Zn), Iron (Fe), Nickel (Ni) and copper (Cu) amongst others and they perform complex roles in plant nutrition (Havlin *et al.*, 2012). Though their specific roles in plant nutrition vary but they are usually important in the activation of various enzymatic processes in plants (Food and Fertilizer Technology Center, 2001). For instance, while Zinc and Copper activate peptidase and oxidase enzymes respectively (Brady and Weil, 2010), iron on the other hand is a structural component of porphyrin molecules that involve in oxidation-reduction reactions that take place in plants during respiration and photosynthesis (Das, 2011); whereas Nickel is a constituent of seven enzymes, among which urease is extremely important for nitrogen metabolism in plants (Liu, 2001).

Distributions of micronutrient forms vary with parent materials and profile depths (Verma *et al.,* 2005). Brady and Weil (2010) reported that the deficiency and toxicity of trace elements are often related to level of these elements in the parent material from which the soils form. It has been reported that most soils derived from marine sediments are reported to be rich in boron. Also, soils derived from shale are richer in zinc than soils derived from Sandstone (Havlin *et al.,* 2012).

The concentration of micronutrients varies with soil depths. Mustapha *et al.* (2011) found higher concentrations of zinc and copper in the topsoil than in subsoil whereas the concentrations of iron and manganese were higher in subsoil than in topsoil, while it has been found that the concentration of nickel decreases with soil depth (Ideriah *et al.,* 2013).

Total micronutrient content of soils is useful for many geochemical applications but often the bioavailability of these micronutrients is more of an interest agriculturally in terms of what is biologically extractable (Ashraf *et al.,* 2012).

Several soil properties are known to affect the concentration of bioavailable micronutrients in soils. According to Brady and Weil (2010), soil pH especially in well aerated soils, has a decided influence on the availability of all the micronutrients except chlorine. Under acid conditions, molybdenum is rendered unavailable, while most trace element cations are freely available, sometimes at toxic level. Except iron, increasing organic matter (OM) content in soils, decreases availability of metallic micronutrients (Havlin *et al.,* 2012). In a study conducted by Oyinlola and Chude (2010), available copper, zinc, manganese and iron had significant positive correlation with clay.

In Nigeria and indeed Imo State, Southeastern Nigeria, limited information exists on the distribution of available micronutrients in soil profiles of different parent materials. The major objective of this study was therefore to evaluate the status of available micronutrients (Zn, Cu, Ni and Fe) in soil profiles of different parent materials in Imo State, Southeastern Nigeria.

MATERIALS AND METHODS

Study Area

The study was conducted in four different locations which include Ihiagwa (Owerri) located between latitude 5^0 21^1 and 5^0 27^1 N and longitude 7^0 02^1 and 7^0 15^1 E, Egwe (Oguta) located between latitude 5^0 42^1 and 5^0 46^1 N and longitude 6^0 $47^1$and 6^0 49^1 E, Amauro (Okigwe) located between latitude 5^0 $48^1$and 5^0 53^1 N and longitude 7^0 20^1 and 7^0 25^1 E and Mbato (Okigwe) located between latitude 5^0 55^1 and 5^0 58^1 N and longitude 7^0 02^1 and 7^0 08^1. The four study locations are in Imo State, Southeastern Nigeria which lies between latitude 4^0 $40^1$and 8^0 15^1 N and longitude 6^0 40^1 and 8^0 15^1 E (Department of Agricultural Land Resources, 1985). Imo State lies within the humid tropics. Temperatures are high and change slightly during the year (mean daily temperature about 27^0C). The average annual rainfall is about 2400 mm and there is a distinct dry season of about 3 months dryness. Imo State has rainforest vegetation characterized by multiple tree species (Onweremadu *et al.*, 2007). Agriculture is a major socio-economic activity in the study area. Agricultural crops mostly cultivated in the study area include yam (*Dioscorea spp*) cassava (*Manihot* spp), oil palm (*Elaeis guineensis*) and maize (*Zea mays*).

The four study locations namely; Ihiagwa, Egwe, Amauro, and Mbato are underlain by Coastal Plain Sands, Alluvium, Imo Clay Shale and falsebedded Sandstones parent materials, respectively (Orajaka, 1975).

Sample Collection and Routine Analyses

One profile pit was dug at each of the various sampling sites, and a total of four profile pits were used for the study and soil samples were collected based on horizon differentiation. Soil samples collected were air-dried, crushed, sieved through 2 mm size sieve and subjected to laboratory analyses. Routine analyses were conducted for particle size (Gee and Or, 2002) and pH in 1: 2.5 solute/suspension ratio using glass electrode of a pH meter (Thomas, 1996). Exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) were extracted with NH_4OAc buffered at pH 7.0 (Thomas, 1982). Exchangeable K^{+} and Na^{+} contents of extracts were read on flame photometer while exchangeable Ca^{2+} and Mg^{2+} were determined using Atomic Absorption Spectrometer. Exchangeable acidity (Al^{3+} and H^{+}) was extracted with 1 N KCl (Thomas,1982) and determined by titrating with 0.5N NaOH using phenolphthalein indicator. Effective Cation Exchange Capacity was obtained by summation of basic and acidic cations, Organic Matter was determined using wet oxidation method (Nelson and Sommers, 1982), Total Nitrogen (Bremner, 1996) and Available Phosphorus (Olson and Sommers, 1982).

Determination of Available Micronutrients

Available Zn, Cu, Fe and Ni were extracted by the double acid extraction method as described by Udo *et al.* (2009). This was done by extracting 5g of soil with 25ml of 0.05M HCl in 0.125M H_2SO_4 for 15 minutes. After extraction, available Zn, Cu, Fe and Ni were determined using ICE 3300 Atomic Absorption Spectrophotometer at 324.8 nm, 213.9nm, 248.3nm and 232nm wavelengths for Cu, Zn, Fe and Ni, respectively.

Fertility Rating of Micronutrients

For the purpose of fertility ratings, the plant available form of Zn, Cu and Fe were rated according to the limits given by Esu (1991), while available form of Ni was rated according to the limits given by Nikoli and Matsi (2014). For Zn, values <0.8, 0.8-2.0 and >2.0 mg/kg were rated 'low', 'medium' and 'high' respectively while for Cu, the respective fertility rating limits were <0.2, 0.21-2.0 and >2.0 mg/kg for 'low', 'medium' and 'high'. Fe was regarded as 'low' if <2.5, 'medium' if 2.51-5.0 and 'high' if >5.0mg/kg while for Ni, it was regarded as 'low' if <2.0, 'medium' if 2-5.0 and 'high' if >5.0 mg/kg.

Statistical Analyses

Coefficient of variation (CV) was used to estimate variation in distribution of available micronutrients in the profiles studied and data ranked according to the ratings of Wilding *et al.* (1994) where CV ≤15% (low variation); CV > 15% ; CV>35% ≤100% (high variation). Also, correlation and regression analyses were used to determine existing relationships between available micronutrients and selected soil properties. All the statistical analyses were conducted using Genstat statistical package (Buysse *et al.,* 2004).

RESULTS AND DISCUSSION

Physico-chemical properties of the soils of different parent materials studied.

Soils of Coastal Plain Sands and Alluvium were dominantly sandy loam and sandy, respectively (table 1); that of soils derived from Falsebedded Sandstones and Imo Clay Shale were dominated by sandy clay loam and clay, respectively. Generally, clay fraction increased with depth and could be due to illuviation pedogenic process that may have taken place in the location.

Soil pH measured in 1NKCl was lower than the pH measured in distilled water in all the soils studied, resulting to negative ⌂pH (pHKCL-pHwater), which indicates the dominance of silicate clay instead of sesquioxides in the soils studied as well as negative charges on the adsorption complex of the soils of the study area (Woods *et al.,* 2008). Generally, pH of the soils studied were low and varied from extremely (<4.5) acidic to moderately (5.6-6.5) acidic (FAO, 2004). The low pH of the soils could be due to high amount of rainfall in the study area, resulting to leaching of basic cations which has made the exchange complex of the soils to be dominated by acidic cations. Similar pH results have been reported by Eshett *et al.* (1990) in soils of Southeastern Nigeria.

Effective cation exchange capacity in all the soils studied were less than 6 cmol/kg critical level recommended by Esu (1991), hence it was considered low. Higher ECEC values were recorded mostly in the surface horizon (Ap) and

Table 1: Physico-Chemical Properties of the Soils Studied

Horizon	Soil Depth (cm)	Sand ←	Silt	Clay g kg^{-1}	Total N	OM →	Ca Cmol/kg	pH (H_2O)	pH (KCl)	Avail. P mg kg^{-1}	ECEC Cmol (+) kg^{-1}	TC
						Coastal plain sands						
Ap	0-17	900	40	60	0.73	13.99	1.22	4.28	3.61	0.86	4.14	S
AB	17-36	880	40	80	0.06	1.28	1.61	4.89	3.55	0.66	4.70	S
Bt1	36-53	860	20	120	0.06	1.28	1.22	5.63	4.12	0.73	3.75	LS
Bt2	53-91	840	40	120	0.33	6.41	2.03	4.91	3.57	0.47	5.11	LS
Bt3	91-150	800	40	160	0.08	1.56	1.81	5.26	4.12	0.56	5.09	SL
Mean		**856**	**36**	**108**	**0.25**	**4.90**	**1.59**	**4.99**	**3.79**	**0.66**	**4.56**	
						Alluvium						
Ap	0-4	940	20	40	0.11	2.27	1.22	5.36	4.05	2.19	4.03	S
BC	4-84	960	0	40	0.11	1.91	1.61	5.62	4.15	1.44	3.81	S
C	84-100	940	20	40	0.11	1.91	2.01	5.32	4.12	2.56	4.67	S
Mean		**946.67**	**13.33**	**40**	**0.11**	**2.03**	**1.61**	**5.43**	**4.11**	**2.06**	**4.17**	
						False Bedded Sandstones						
Ap	0-9	680	140	80	1.91	38.51	3.41	5.41	4.01	0.92	6.47	SL
AB	9-28	500	200	300	0.23	5.72	1.40	5.41	3.77	0.76	4.14	SCL
Bt1	28-49	520	180	300	0.60	13.63	1.83	5.21	3.86	0.36	4.69	SCL
Bt2	49-73	520	160	320	0.11	2.24	1.61	5.12	3.83	0.27	4.88	SCL
Bt3	73-170	490	190	320	0.11	1.91	1.61	5.31	3.68	0.23	5.14	SCL
Mean		542	174	284	0.59	12.40	1.97	5.29	3.83	0.51	5.06	
						Imo Clay Shale						
Ap	0-11	440	280	280	0.94	48.87	2.04	5.56	4.35	3.36	5.37	CL
AB	11-19	300	260	440	0.11	47.95	1.02	5.56	4.17	0.39	2.89	C
Bt1	19-36	260	240	500	2.32	47.78	3.23	5.55	4.35	0.23	6.59	C
Bt2	36-55	280	120	600	0.40	43.28	2.00	5.98	4.27	0.96	4.79	C
Bt3	55-83	420	260	320	2.32	46.03	2.61	5.85	4.84	1.56	6.78	CL
Mean		340	232	428	1.22	46.78	2.18	5.70	4.40	1.30	5.28	

could be due to higher organic matter content of the horizons. Onweremadu *et al.* (2011) also obtained low ECEC in soils derived from Coastal Plain Sands, Alluvium and Falsebedded Sandstones in Southeastern Nigeria and attributed parent material, climate and land use interactions to result to low ECEC.

Organic matter content of all the soils studied were low (FAO, 2004) and that could be attributed to high temperature and rainfall in the study area, resulting to rapid mineralization, erosion and leaching of organic matter. Generally, OM decreased with soil depth.

Total N varied from low to high (Esu, 1999). Most of the high values of nitrogen were found in the upper horizons than the lower horizons and could be due to higher organic litter content of surface soil (Yang *et al.,* 2004). Decrease in total nitrogen content with soil depth has been reported (Zhijing *et al.*, 2013).

Except in soils derived from Imo Clay Shale where exchangeable calcium was moderate (FAO, 2004), other soils had low exchangeable calcium. Onweremadu *et al.* (2011) also reported low exchangeable calcium in soils derived from Coastal Plain Sands and Alluvium in Southeastern Nigeria and attributed the low results to the sandiness of the soils which encouraged leaching of calcium. Available Phosphorus (Av. P) was below the critical limit of 10 mg/kg given by Esu (1999), hence considered low. The low values of available P in all the soils studied could be attributed to the acidic nature of the soils which resulted to fixation of P by sesquioxides in the soils making P less available (Havlin *et al.,* 2012).

Status of Available Micronutrients in Profile Derived from Coastal Plain Sands

The status of available Zn, Cu, Fe and Ni in soils of Coastal Plain Sands is presented in Table 2. Available Zn was low (Esu 1991) and ranged from 0.283-0.913 mg/kg with mean value of 0.241mg/kg. Eteng *et al.* (2014) also obtained low available form of zinc in soils derived from Coastal Plain Sands in Southeastern, Nigeria. The low available zinc could be due to sandiness of the soils and excessive rainfall in the area coupled with the acidic nature of the soils which encouraged leaching losses of zinc. According to Alloway (2008), sandy soils and acid highly leached soils with low total and plant-available zinc concentrations are highly prone to zinc deficiency. Lower concentrations were found in the lower horizons and could be due to increasing pH with depth. Havlin *et al.* (2012) noted that zinc availability decreases with increase in soil pH. Furthermore, its distribution in the profile studied followed high variation (CV=58.4 %), indicating lack of homogeneity in distribution of available zinc in the profile studied.

Available copper ranged from 0.250-1.342 mg/kg with mean value of 0.764 mg/kg (Table 2). Using the fertility rating of available copper given by Esu (1991), the mean value falls within the 'medium' category; hence plants growing in the area will not suffer copper deficiency. Adiele *et al.* (2015) also reported medium level of available copper (0.8 mg/kg) in soils derived from coastal plain sands in National Root Crop Research Institute farm, Abia State, Southeastern Nigeria. The results further revealed decreasing available copper with soil depth and could be due to increasing pH of the soils with depth. Its distribution in the profile studied followed high variation (CV= 64.4%), an indication of uneven distribution.

Available iron was low (Esu, 1991) and ranged from 0.296 - 1.109 mg/kg with mean value of 0.654 mg/kg. The low available iron in the soils studied could be due to sandiness of the soils as well as low ECEC of the soils coupled with excessive rainfall in the area which encouraged leaching losses of iron. Highest concentration was found in the Ap horizon and could be due to higher organic matter content of the horizon (Table 2). According to Spectrum Analytic Inc (2013), in addition to being a source of Fe, OM compounds are able to form Fe chelates that improve iron availability. The results further revealed that available iron distribution followed high variation (CV=60.04%) hence it was not homogenously distributed in the profile studied.

Available nickel in soils of coastal plain sands studied ranged from 2.379-3.697mg/kg with mean value of 2.885 mg/kg. Using the fertility rating of available nickel by Nikoli and Matsi (2014), the available nickel concentrations fall within the 'moderate' limit (2-5 mg/kg), hence the available nickel concentration is sufficient for crop production. Its concentration in the profile studied neither increased nor decreased with soil depth and also moderate variation in distribution was found (CV=22.2%) hence it was uniformly distributed in the profile studied.

Table 2: Status of Available Micronutrients in Soil Profiles of Different Parent Materials Studied

Horizon	Depth (cm)	Zn	Cu	Fe	Ni
		←	mg/kg		→
		Coastal Plain Sands			
Ap	0-17	0.913	1.342	1.06	3.464
AB	17-36	0.400	0.882	0.406	2.399
Bt1	36-53	0.315	0.25	0.402	2.488
Bt2	53-91	0.283	0.306	0.296	3.694
Bt3	91-150	0.336	1.036	1.109	2.379
Mean		**0.449**	**0.764**	**0.654**	**2.885**
%CV		58.4	64.4	60.4	22.2
		Alluvium			
Ap	0-4	0.629	1.198	1.158	1.66
BC	4—84	1.319	0.281	1.022	4.557
C	84-100	0.310	0.620	1.277	3.793
Mean		**0.753**	**0.700**	**1.152**	**3.336**
%CV		68.5	66.3	11.3	111.3
		Falsebedded Sandstones			
Ap	0-9	0.291	1.028	0.469	6.165
AB	9—28	0.894	0.922	1.004	3.976
Bt1	28-49	0.381	3.202	1.241	3.339
Bt2	49-73	0.395	1.236	0.773	2.505
Bt3	73-170	0.361	0.891	1.669	4.557
Mean		**0.464**	**1.456**	**1.031**	**4.108**
%CV		52.4	67.7	44.3	33.6
		Imo Clay Shale			
Ap	0-11	0.242	0.867	1.033	2.335
AB	11-19	0.216	0.736	1.115	1.819
Bt1	19-36	0.969	0.844	1.092	0.993
Bt2	36-55	1.089	1.060	1.560	1.369
Bt3	55-83	1.188	1.079	1.440	0.925
Mean		**0.741**	**0.917**	**1.248**	**1.488**
%CV		63.9	16.1	18.9	39.8

Status of Available Micronutrients in Profile Derived from Alluvium

Table 1 shows the distribution of available Zn, Cu, Fe and Ni in soil profile derived from alluvium. Zn ranged from 0.310 -1.319 mg/kg with mean value of 0.753 mg/kg, placing it in the low limits as the values were below the critical value of 0.80 mg/kg as reported by Esu (1991).The low available zinc in the soil could be due to sandiness of the soils as well acid condition of the soils. According to Alloway (2008), sandy soils and acid highly leached soils with low total and plant-available zinc concentrations are highly prone to zinc deficiency. The results further showed that available zinc distribution in the profile studied did not follow a definite pattern and high variation (CV=68.5%) in distribution was also found. The high variation showed it was not homogeneously distributed in the profile studied.

Available copper was moderate (Esu 1991) and ranged from 0.281 mg/kg to 1.198 mg/kg with mean value of 1.456 mg/kg. Ukaegbu *et al*. (2015), also obtained moderate level of available copper in soils derived from Alluvium (0.4-1.2 mg/kg) in Imo State, Southeastern Nigeria. Highest concentration was found in the surface horizon and could be due to higher organic matter content as well as lower pH of the horizon. According to Food and Fertilizer Technology Center (2001), concentrations of micronutrients tend to be higher in the surface horizons of uncultivated soils, much of them presumably in the organic matter. Furthermore, its distribution in profile studied followed high variation (CV=66.3 %) hence it was not homogeneously distributed in the profile.

Available iron ranged from 1.022 - 1.277 mg/kg with mean value of 1.152 mg/kg. The concentration increased down the profile which is in line with the findings of Mustapha *et al.* (2011). Comparing the values of available iron with critical value of 2.5 mg/kg as reported by Esu (1991), the available iron falls within the 'low' limit and could be due to sandiness of the soils. Singh (2011), stated that fine textured soils have higher iron availability. Mengel and Gurtzen (1986), reported that iron deficiency is very unlikely in acid soils; as it is known to be soluble under relatively acid and reducing soil conditions (Chesworth, 1991). Therefore, the low concentration of available iron in the soils studied even though the soils were acidic suggests that the soils could be low in total iron. Available iron was uniformly distributed in the profile studied as low variation (CV=11.1%) was obtained.

Table 2 indicated that available nickel ranged from 1.660 - 4.557 mg/kg with mean value of 3.336 mg/kg, placing it in the 'moderate' category when matched with the ratings given by Nikoli and Matsi (2014). Its concentration was higher in the lower horizons and could be due to decreasing organic matter content with soil depth. According to Chauhan *et al.* (2008), nickel availability decreases with increasing organic matter levels in soils. Its distribution followed high variation (CV=111.3), hence it was not homogeneously distributed in the profile studied.

Status of Available Micronutrients in Profile Derived from False Bedded Sandstones

In soils of Falsebedded Sandstones studied, available Zn decreased with soil depth (Table 2). It ranged from 0.283 - 0.913 mg/kg with mean value of 0.449 mg/kg. Using the fertility rating of Esu (1991), the mean value falls within the 'low' limit hence the soils are considered deficient in available zinc. Highest concentration was found in the surface horizon and could be attributed to higher ECEC of the horizon as increasing ECEC has been found to favour Zinc availability. Its variation in the profile studied was high (CV = 52.4 %), meaning it was not uniformly distributed in the profile studied.

Available copper was higher in lower horizons (Table 2). It ranged from 0.891-3.202 mg/kg with mean value of 1.736 mg/kg placing it in the moderate category (Esu, 1991). Available copper in the soils of Falsebedded Sandstones studied was higher than 0.18mg/kg mean value of available copper found by Mustapha *et al.* (2011) in soils of Akko, Bauchi State, Nigeria derived from Sandstones and could be attributed to the low soil pH of the soils studied which favoured solubility of copper. The higher values of available found in the lower horizons could be attributed to decreasing organic matter content of the soils with depth. Havlin *et al.* (2012), noted that copper is more strongly bound to OM than any other micronutrient hence increasing organic matter in soils decreases copper availability. The higher available copper with depth could also be due to increasing clay content down the profile as increase in clay increases copper availability (Oyinlola and Chude, 2010). Furthermore, available copper was not uniformly distributed in the profile studied since it followed high variation (CV = 39.8 %).

Available iron ranged from 0.469-1.669 mg/kg with mean value of 1.031 mg/kg. The results revealed increase in available iron down the profile which could be attributed to higher clay content of the soils in the lower horizons. Hardy and Cornu (2006) stated concisely that micronutrient contents increases as clay decreases. However, the available iron was below the critical limit of 2.5 m/kg as reported by Esu (1991). This shows that plants growing in the area are in need of iron fertilizer. Also, its distribution followed high variation (CV= 44.3 %) indicating that it was not evenly distributed in the profile studied.

In the profile studied, available nickel was reached moderate level (Nikoli and Matsi, 2014). It ranged from 2.505 - 6.165 m/kg with mean value of 4.108 mg/kg. The distribution in the profile studied did not follow a definite pattern, but highest concentration was found in the surface horizon (Ap) and could be attributed to the agricultural activities in the area. Ayodele and Mohammed (2011), noted that nickel is generally distributed uniformly through the soil profile but typically accumulates at the surface from deposition by industrial and agricultural activities. This also justifies the moderate variation (CV=33.6 %) obtained in the distribution of available nickel in the profile studied.

Status of Available Micronutrients in Profile Derived from Imo Clay Shale

Available zinc followed similar distribution trend with other soils of different parent materials studied as it was below the critical limit of Esu (1991) and was not evenly distributed in the profile studied since high variation was found (CV= 63.9 %). The findings showed that available zinc ranged from 0.216-1.188 mg/kg with mean value of 0.741 mg/kg (Table 2). The results further revealed that its concentration increased with soil depth and could be attributed to increasing clay content of the soils down the profile.

Available copper ranged from 0.736-1.079 mg/kg with mean value of 0.917 mg/kg, placing it in the ‘moderate’ limit (Esu, 1991). Its concentration was higher in lower horizons and could be due to increasing clay content with depth. The results were higher than the findings of Ahukaemere *et al.* (2014) who reported available copper in the range of 0.05-0.25 mg/kg in organic matter rich paddy soils of Abia State, Southeastern Nigeria derived from Shale parent material. This could be due to lower organic matter content of the soils studied as decrease in organic matter increases copper availability due to reduced adsorption and vice versa (Havlin *et al*., 2012). Moderate variation (CV=16.1 %) was observed in distribution of available copper in the soil profile studied.

The concentration of available iron was low (Esu, 1991) and ranged from 1.092-1.560 mg/kg with mean value of 1.248 mg/kg (Table 2). The results were lower than the findings of Ahukaemere *et al.* (2014) in organic matter rich paddy soils derived from Shale in Southeastern Nigeria and could be attributed to the lower level of organic matter in the soils studied as increasing organic matter in soils increases iron availability (Singh, 2011). It was higher in lower horizons and could be due to illuviation pedogenic process that has taken place, resulting to accumulation of iron in lower horizons. The variation in distribution of available iron in the profile studied was moderate (CV=18.9 %).

The results (Table 2) indicate that available nickel decreased with soil depth. Average value of 1.488 mg/kg available nickel was recorded. Higher content of available nickel observed in surface soils could be attributed to the chelating of organic compounds released during decomposing of organic matter after harvesting of crop. The soils were considered low in available nickel since the mean available nickel was below the critical level of 2.0 mg/kg as recommended by Nikoli and Matsi (2014). The results further showed uneven distribution of available nickel in the profile studied since high variation was found (CV=39.8 %).

Correlation between Available Micronutrients studied and Selected Soil Properties

The correlations between available micronutrients (Zn, Cu, Fe and Ni) studied and selected soil properties (pH, clay, OM, ECEC and available P) are presented in table 3.The correlation analysis showed that available zinc significantly and positively correlated with OM (r=0.46*). This indicates that increasing organic matter in the soils studied will significantly result to increase in concentration of available zinc due to increasing chelation of zinc by complexing agents generated by organic matter. pH (r=-0.19), clay (r=0.19), OM (r=0.12n), ECEC (r=0.11) and available P (r=-0.18) had no serious association with available copper as no significant correlation between copper and aforementioned soil properties was observed (Table 3). The implication of the findings is that increase or decrease in any of the soil properties will not result to significant increase or decrease in the concentration of available copper in the soils studied. However, Oyinlola and Chude (2010) reported significant positive correlation between copper and clay. Clay had serious relationship with available iron of soils studied as supported by significant and positive correlation

Table 3: Correlation between Selected Soil Properties and Available Micronutrients

	pH	Clay	Om	ECEC	Avail. P
Zn	0.27	0.18	0.46*	0.13	0.02
Cu	-0.19	0.19	0.12	0.11	-0.18
Fe	0.35	0.45*	0.24	0.06	0.17
Ni	0.35	0.47*	0.24	0.40	0.17

*indicates significance at 5% level

Table 4: Linear Regression Equations Showing Combined effect Selected Soil Properties on Available Micronutrients Studied

Equation	R^2
1 $Y_{Avail.Zn}$ = -0.040+0.149(pH)+0.005(OM)- 0.174(ECEC)+0.009 (AvP)+0.000(clay)	0.349^{ns}
2$Y_{Avail.Cu}$=4.143-0.707(pH)-0.003(OM) -0.012(ECEC) +0.006 (AvP) +0.002(Clay)	0.184^{ns}
3 $Y_{Avail.Fe}$ =0.354+0.310(pH)-0.014(OM)+0.030(ECEC)+0.012 (AvP)+0.001(clay)	0.389^{ns}
4 $Y_{Avail.Ni}$=3.955-0.432(pH)+0.007(OM)+0.505(ECEC)-0.043(AvP)-0.002(Clay)	0.215^{ns}

Keys: *=significance at 5% level. $Y_{Avail.Zn=}$ Available Zn, $Y_{Avail.Cu=}$ Available Cu,
$Y_{Avail.Fe=}$ Available Fe and $Y_{Avail.Ni=}$ Available Ni

found (r=0.45*).

This is in agreement with research conducted by Sharma *et al.* (2003). Available nickel also correlated significantly and positively with clay (r=0.47*). Hence increasing clay content will significantly result to increase in available nickel in the soils studied (Table 3).

Combined Effect of Selected Soil Properties on Available Micronutrients

The combined effect of pH, clay, OM, ECEC and available using multiple regression analysis is presented in table 4. The results indicate that the combined effect of the soil properties studied on available Zn (R2=0.349), Cu (R2 = 0.184), Fe (R2=0.389) and Ni (R2=0.215) was not significant (p> 0.05). Going by the findings, about 34.9 %, 18.4 %, 38.9 % and 21.5 % variations in available Zn, Cu, Fe and Ni respectively was due to the combined effect of the properties studied. It is evident from the regression equations (Table 4) that a regression model can predict about 34.9 %, 18.4 %, 38.9 % and 21.5 % of combined effect of soil properties studied on available Zn, Cu, Fe and Ni respectively.

CONCLUSION

The study indicated that the soils of the different parent materials studied had sufficient available copper for crop production. Except in soil profile derived Imo clay shale, other soil profile had their available nickel above the critical level, hence considered sufficient for crop production. All studied soils were low in available Zn and Iron. Therefore, application of Iron and Zinc chelates to all the soils of different parent materials studied and Nickel containing fertilizer particularly to soils of Imo Clay Shale is recommended.

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