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Ammonium Sorption Characteristics of Soils of Coastal Plain Sand in Owerri West Imo State

[1]Osisi A.F., [2]Azu, D. E. O., [3]Agim, L.C. and [4]Chukwu, E.D

[1,3&4]Department of Soil Science and Technology, Federal University of Technology, Owerri, Imo State

[2]Department of Horticulture and Landscape Technology, AkanuIbiam Federal Polytechnic, Unwana, Ebonyi State

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Corresponding Author's E-mail Address:

donblessed01@gmail.com +234038663924

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ABSTRACT

Information on the ammonium sorption capacity of soils is very crucial in the development of sound ammonium fertilization and management. This study was therefore carried out to determine the ammonium sorption characteristics of soils of coastal plain sand formation in Owerri West LGA of Imo State. Samples were collected from three locations (FUTO, Ihiagwa and Umuokanne), at three depths (0-15, 15-30, 30-45 cm), giving a total of nine observational units. The experimental design was a 3 x 1 factorial in Randomized Complete Block Design (RCBD), the parent material and soil depth was the factors under consideration. Statistical analysis did not show significant (P>0.05) variation in soil physical and chemical properties with location. However, most of the properties increased with depth. Data obtained from the analysis were statistically analyzed using Analysis of Variance (ANOVA) and means separated using Lsd(0.05). Correlations between soil routine properties and ammonium sorption parameters were done using SPSS (Version 16.0). Soil Ammonium sorption properties of the soils showed variability with location and depth. FUTO had the highest capacity to absorb ammonium (445mg/kg). For all locations, maximum adsorption capacity increased with depth. However, the affinity coefficient was greatest in soil of Ihiagwa (3.25mg/kg) and this increased with depth for all soils. The adsorption maximum and affinity coefficient correlated positively with clay and negatively with sand and organic matter. Langmuir and Freundlich isotherms were applied to test the sorption data. Comparing the fitness of the ammonium sorption models using the R2 values, it was evident that Freundlich Model better described and predicated the ammonium sorption parameters and is therefore recommended for the study of soils of these locations.

1.0 Introduction

Ammonium in soil serves not only as a major source of Nitrogen for plant growth, but also as an important product or reactant in the Nitrogen transformation processes in soil (Brady and Weil, 2008). Ammonium is also the main form in which fertilizer Nitrogen is applied in agriculture. The composition of nitrogen fertilizers is dominated by ammonium nitrate, which provides half of the nitrogen in the ammonium form and half in the nitrate form *(Zanget al.,* 2011). Ammonium is a prevalent Nitrogen subsurface pollutant, which emerges from different sources, such as landfill sites, industrial polluted areas, sewage systems, wastewater, and fertilizers (Ranjbar and Jalali,2013). The concentrations of ammonium might exceed the standard limits of disposal to water bodies (Zhu *et al.,* 2011), with high concentrations hindering the decomposition of organic matter via microorganisms (Ranjbar and Jalali, 2013). The three major routes of NH_4^+removal in the ecosystems are mainly nitrification, assimilation into microbial cells, and adsorption onto substrate media (Sun *et al.,* 2005*;* Tyrrel *et al.,* 2002).

Ammonium adsorption or sorption involves the attraction or adhesion of ammonium to soil colloidal particle thereby preventing its release to crops (Brady and Weil, 2008). With the increased use of ammonium fertilizers, a study of the absorption, retention and release of NH_4^+ by soil is gaining considerable importance (Sutton *et al.,* 2011a). Adequate understanding of the ammonium sorption characteristics of soils provides useful index for soil ammonium nitrogen management as this will promote efficient ammonium nitrogen utilization by crops to maximize yield. However, this information is lacking in the coastal plain sand of Owerri. In order to bridge this information gap, this study was embarked upon.

Materials and Method

2.1 Study Area

This study was carried out in three locations of Owerri West LGA, Imo State (lhiagwa, Umuokanne and FUTO Campus). Ihiagwa lies between Latitude 5'40' N and Longitude 7'12 E, Umuokanne lies between 5'25' N and Longitude 6'58' E and FUTO lies between Latitude 5'29' N and Longitude 7'02' E. The rainfall of the area ranged from 1950mm to 2250m per annum with average mean annual temperature of 27^{o}C -29^{o}C. (NIMET 2008). The dominated soil type is ultisols derived from Coastal plain sand and characterized by low Cation exchange Capacity, low organic matter, low pH and are highly weathered soils (Onweremmadu and Ufot, 2011).

2.2. Soil Sample Collection

Soil samples were collected from the identified locations (lhiagwa, Umuokanne and FUTO Campus) at three depths (0-15cm and 15-30 and 30 -45cm) using soil auger. The samples were analyzed in the laboratory for routine analysis according to standard methods: Particle size distribution using hydrometer method according to the procedure of Gee and Or (2002),Bulk density (BD), according to Grossman and Reinsch (2002),soil pH was determined in soil to water and soil to $CaCl_2$ at a ratio 1:2 soil water and soil $CaCl_2$ respectively using glass electrode pH meter (Udo*et al*; 2009).Organic carbon was determined by the wet oxidation method according to Pansu and Gautheyrous (2006) and converted to organic matter by multiplying by 1.792. The total nitrogen determination was done by the macro Kjeidahl digestion method (Simmone*et al.,* 1994). Available P was determined using the Bray II method of Bray as described by Udo*et al*; (2009). Exchangeable acidity was determined by the nikel extraction procedure as described by Udo*et al*., (2009). Exchangeable basic cations (K^+, Ca^{2+}, Mg^{2+}, Na^+) were determined by the ammonium acetate method (Carter and Gregorich, 2008). Ca and Mg in the extract were determined using the atomic absorption spectrophotometer, while K and Na were determined using the flame photometer. Effective cation exchange capacity **(**ECEC) was obtained by summation of all the exchangeable cations and exchangeable acidity as described by Udo, *et al*; (2009). The base saturation was obtained mathematically with

$$BS (\%) = \frac{\text{Total cation}}{\text{ECEC}} \times \frac{100}{1}$$

2.3 Ammonium Sorption Studies

Ammonium sorption study was conducted using Batch studies as described by to Fox and Kamprath (1970). This briefly involves weighing 5g fine earth soil particle into a centrifuge tube and adding 25m/s of NH_4^+ ppm solution containing graded concentrations of 0, 10, 20, 30, 40, and 50gkg^{-1} of NH_4^+ ppm . The tube was shaken on a rotary shaker GFL 3040 with a speed of 14 minutes at 200apm for 1 hr. After the equilibration time, the tube and its ronterts was centrifuged at 3500 x g for 30 mins and the clear supernatant decanted into the 50ml glass. Aliquots of the superset were taken and color developed using a Nessler reagent.

The percent contribution of ammonium absorbed (%R) and ammonium adsorption capacity (q) was calculated using the following expression:

$$\%R = \frac{C_o - C_e}{CO} \quad 1000\ \% \ldots\ldots\ldots(1)$$

$$qv = \frac{(C_o - C_e)}{m} / m \ldots\ldots\ldots(2)$$

Where C_o - initial concentration of ammonium in the solution (Mg/L)

C_e- final ammonium concentration in the solution (Mg/L)

V - volume of the solution (mL)

M - amount of sorbention the dry basis (g)

2.4 Statistical Analysis

Generated data was analyzed using analysis of variance (ANOVA). Significant means were separated using least significant difference (LSD) at 5% probability level. Correlation between soil properties and ammonium sorption parameters were determined using SPSS (16.0 version).

3.0 Results and Discussion

3.1 Physical and chemical properties of the soils used for the study

The physical and chemical properties of the soils used for the study is presented in tables 1 and 2. According to table 1, there is obvious variability in the textural properties of the soils among the different locations. FUTO had a textural class of loamy sand with sand occurring at above 75% and clay ranging from 6.96 to 8.96%. While sand decreased with depth, clay was found to be proportional to depth. According to Azu*et al.,*(2018), direct proportionality exists between clay content and soil depth in most weathered tropical soils of southeastern Nigeria. Ihiagwa and Umuokanne had similar textural class of sandy loam.

Bulk density and moisture content were low, while the total porosity was high. Sandy particle with their large pore spaces are prone high water drainage and low water and nutrient retention abilities (Brady and Weil, 2008). The clay component of the soil is very important in the determination of soil fertility properties, especially with regards to the potential of soils to retain or adsorb nutrients Azu *et al*., (2018).

The chemical properties of the different soils did not show significant variation among soils of contracting locations, (Table 2). All of the different soil samples were slightly acidicforalldepthswiththepHgenerallyabove6. However, soil depth did not cause obvious variability on pH. Organic matter was very high for all locations and sampling depths. Ihiagwa had the highest value of organic matter (9.31%), while FUTO had the least value (8.56%). For all locations, organic matter decreased with depth. Farming systems involving the addition of organic manure, planting of cover crops may have influenced this result. Onyegbule *et al.,* (2019), in their study of organic matter distribution reported decrease in organic matter concentration of soils down the soil profile.

Total nitrogen was high in all location and also showed a depth wise decline. Surface accumulation of organic mat-

Table 1: Physical properties of the Soil

Land Use	Sand %	Silt %	Clay %	S/C Ratio	Textural Class	Bd g/cm3	Tp %	Mc %
	Futo							
0-15	85.76	7.28	6.96	1.05	LS	1.05	42.00	17.54
15-30	83.76	8.28	7.96	1.04	LS	1.54	60.40	23.31
30-45	79.76	11.28	8.96	1.26	LS	1.42	46.40	15.32
Mean	83.09	8.94	7.96	1.12		1.34	49.6	18.7
CV	11.22	144.7	12.96	1.25		2.99	186.1	90.91
CV Ranking	*	***	*	*		*	***	**
	Ihiagwa							
0-15	79.76	9.28	10.96	0.85	SL	1.54	41.90	13.31
15-30	67.76	19.28	12.96	1.49	SL	1.05	42.00	19.06
30-45	69.76	15.28	14.96	1.02	SL	1.54	41.90	13.30
Mean	72.43	14.61	12.94	1.12		1.38	41.93	15.22
CV	57.29	173.3	30.91	10.27		5.79	0.01	72.47
CV Ranking	**	***	**	*		*	*	**
	Umuokanne							
0-15	77.76	11.28	10.96	1.01	SL	1.05	42.00	17.50
15-30	79.76	12.28	7.96	1.53	LS	1.54	60.40	23.29
30-45	65.76	22.28	11.96	1.86	SL	1.42	46.40	14.32
Mean	74.43	15.28	10.13	1.47		1.34	49.6	18.37
CV	77.02	242.2	43.04	13.05		4.72	186.1	112.6
CV Ranking	*	***	*	*		*	**	**

ter, artificial application of nitrogen could be considered important factors for this observation. Osodeke and Ubah, (2005) and Azu*et al*., (2018), have earlier reported declining trend of soil total nitrogen with depth in all locations

Available phosphorus was high in all locations and beyond the critical concentration of 15mg/kg proposed by Osodeke (2005) for tropical crops. The high values of phosphorus observed in this study contradicts earlier literatures for acid tropical soils of southeastern Nigeria (Osodeke and Ubah, 2005, Azu*et al*., 2017), who consistently reported low phosphorus availability in most soils of southeastern Nigeria.

The total exchangeable bases were low for all locations and the effective cation exchange capacity were low. This is in line with reports of Onwuka *et al*., (2007) for sandy soils of southeastern Nigeria. According to Osodeke, (1996), leaching of exchangeable bases was caused by the heavy tropical rainfall.

In general, even where there were no significant variation of soil chemical and physical properties of the studied soils, soils from Ihiagwa consistently proved to be better than others.

Table 1: Study locations and coordinates

LAND USE	$pH(H_2O)$	Oc%	OM%	TN %	Av. P (PPM)	Ca2+	Mg2+	Na+	K+	Al3++H	Al3+	TEA	TEB	%BS	ECEC cmol/kg
SITE1							FUTO								
0-15	6.98	5.79	9.98	0.32	20.44	1.37	0 .01	0.006	0.008	0.334	-	0.334	1.39	80.67	1.73
15-30	7.01	4.65	8.02	0.15	9.52	0.11	0.11	0.017	0.007	1.336	-	1.244	0.24	15.24	1.58
30-45	6.98	4.45	7.67	0.116	18.62	0.27	0.15	0.006	0.005	1.503	-	0.431	0.43	22.29	1.93
Mean	6.99	4.96	8.56		16.19	0.58	0.12	0.009	0.007	1.06		0.67	0.69	39.4	1.75
CV	0.005	10.56	18.11		211.4	81.03	9.17	0.46	0.04	37.74		37.31	56.52	3273.9	1.89
CV Ranking	*	*	*		**	*	*	*	*	*		*	*	***	*
LSD															
SITE2	**Ihiagwa**														
0-15	6.42	5.79	9.98	0.355	19.11	0.93	0.13	0.008	0.007	0.501	-	1.075	1.08	68.21	1.58
15-30	6.22	5.29	9.12	0.256	22.61	0.19	0.43	0.027	0.015	0.668	0.48	0.662	0.66	36.57	1.81
30-45	6.13	5.13	8.84	0.197	16.17	0.25	0.07	0.01	0.009	0.083	-	0.319	0.32	79.35	0.4
Mean	6.26	5.4	9.31		29.29	0.46	0.21	0.015	0.01	0.42		0.69	0.69	61.38	1.26
CV	0.46	2.41	3.87		53.76	36.96	17.62	0.73	0.18	21.59		20.72	20.72	802.5	45.24
CV Ranking	*	*	*		**	**	*	*	*	*		*	*	***	**
LSD															
SITE3	**Umuokanne**														
0-15	6.06	5.25	9.05	0.216	19.6	0.51	0.19	0.01	0.014	1.67	-	0.724	0.72	30.24	2.39
15-30	6.31	4.73	8.15	0.149	25.48	0.13	0.33	0.008	0.006	1.336	-	0.474	0.47	26.18	1.81
30-45	6.57	4 .99	8 .60	0.132	20.72	0.07	0.08	0.009	0.016	0.668	-	0.175	0.18	20.76	0.84
Mean	6.31	4.99	8.6		21.93	0.24	0.2	0.009	0.012	1.22		0.46	1.37	25.73	1.68
CV	1.11	1.6	3.63		44.41	25	7.85	0.01	0.38	21.31		16.74	96.64	87.91	36.31
CV Ranking	*	*	*		**	**	*	*	*	**		*	***	***	**
LSD															

3.2 Ammonium Sorption Parameters using Langmuir and Freundlich Models

The ammonium sorption characteristics of the soils using Freundlich and Langmuirs equations are shown in table 3.

According to this Table, the ammonium sorption maximum was highest in soils of Ihiagwa for Langmuir model

Table. 3.. Ammonium sorption characteristics of the soil profiles using Langmuir and Freundlich equations at different locations and soil depth

Location	Depth	Langmuir				Freundlich			
		b	k	MBC	R^2	a	n	MBC	R^2
	(cm)	(mg/kf)				(mg/kg)			
FUTO	0 - 15	112	7.4	829	0.185	250	1.4	350	0.849
	15 - 30	170	5.9	1003	0.180	252	1.4	353	0.873
	30 - 45	278	1.8	500	0.505	220	0.08	176	0.800
Mean		**187**	**5.03**	**777.3**	**0.290**	**240.7**	**1.2**	**293**	**0.591**
	0 - 15	196	2.7	529	0.400	230	0.9	207	0.744
	15 - 30	667	0.53	354	0.315	280	2.5	700	0.794
	30 - 45	110	5.05	556	0.509	250	1.2	300	0.692
Mean		324	2.74	479.7	0.408	253	1.5	402	0.74
Umuokanne	0 - 15	105	5.01	526	0.461	240	1.3	312	0.910
	15 - 30	417	0.60	250	0.080	250	1.5	375	0.868
	30 - 45	435	1.28	557	0.575	270	2.6	702	0.560
Mean		319	2.30	444	0.372	253	1.8	463	0.779

b= Maximum adsorption, k=Affinity coefficient, MBC=Maximum buffering capacity, R^2=Correlation coefficient, a=NH_4^+-sorption capacity, n= NH_4^+--sorption energy

(324mg/kg) and it increased with soil depth. Generally, the energy coefficient (k and n) increased with the adsorption maximum. This agrees with the earlier report by Wissen and Mongi (2015), who reported direct relationship between ammonium sorption maximum and energy coefficient. The correlation between ammonium sorption maximum, energy coefficients and some soil properties (Table 4) indicated that adsorption maxima and energy coefficients correlated negatively and significantly with clay content and pH. The clay fraction of the soil is dominated by varying types of minerals especially 2:1 clay minerals which have high affinity for cations such as ammonium (Brady and Weil, 2008). Thus, the higher the clay constituent of a given soil, the more it's potential to adsorb nutrient elements such as ammonium. This agrees with the report of Wang *et al.,* (2000), who observed that ammonium sorption increases with clay content.

The energy coefficients (k and n), describes the ability and the tenacity to which ammonium ions are adsorbed to clay mineral surfaces of the soils (Brady and Weil, 2008). The more the energy coefficients, the more the tenacity of ammonium adsorption and the less likely ammonium will be available in soil solution (Wang *et al*., 2000). For Langmuir model, the k values increased with depth. This agrees with the earlier report by Wissen and Mongi (2015), who reported direct relationship between ammonium sorption maximum and energy coefficient. The higher the depthof the soil, the more the occurrence of mineral reactive surfaces thus the greater the affinity coefficient for ammonium adsorption. FUTO had the greatest affinity for ammonium. The implication may be advantageous owing to the fact; leaching ammonium nitrogen may be reduced due to sorption. However, to ensure adequate ammonium nitrogen utilization by plants in this location, large and continuous ammonium fertilizer should be applied to compensate for the adsorbed fraction. Ihiagwa and Umuokanne that had lesser energy coefficients may be presented with more leaching of nitrogen. Sand and organic matter correlated neg-

Table 4. Correlation between Langmuir and Freundlich constants and some soil properties

	Sand	Clay	pH	Organic Matter
b	-0.89	0.844	-1.000**	-0.567
k	0.944	0.728	-0.976	-0.401
a	-0.984**	0.827**	-0.998**	-0.540
n	-0.764	0.435	-0.834	-0.047

atively with the affinity coefficients, while clay correlated positively with the energy coefficients (Table 4).

Considering the values of the R^2 for both Langmuir and Freundlich equations, it can be deduced that the Freundlich equation described the sorption parameters than the Langmuir equation. Comparing the two equations, it can be established that the Fruendlich model showed a better fit to the data than the Langmuir model The Freundlich isotherm provided the information about the surface heterogeneity and the exponential distribution of the active sites, their energies, and predicted the saturation of the surface of the sorbent by the sorbate. This result however contracted the report of Wissen and Mongi (2015), who posited that Langmuir better fitted the sorption parameters of ammonium. The Langmuir poorly fitted the ammonium sorption data because of the heterogeneity the energy of the absorbent surfaces.

4.0 Conclusion

This study evaluated the ammonium sorption characteristics of soils from three locations (FUTO, Ihiagwa andUmuokanne) in Owerri west at three sampling depths (0-15cm, 15-30cm and 30-45cm). There was no significant variability on the soil physical and chemical properties of the soils with respect to location. However, soils from Ihiagwa consistently showed better fertility status compared with the other soils. The role of depth as it affects soil properties was significant. While soil pH did not follow a particular occurring trend, other nutrients generally decreased with depth.

Results of ammonium sorption study showed variability of ammonium sorption characteristics of the soils from different locations. The maximum sorption capacity of ammonium was obtained from soil of Ihiagwa (Mean =324mg/kg), while the highest value of energy coefficient (5.03mg/kg) was obtained in soils of FUTO.

Generally, both the adsorption maxima and energy coefficients increased with soil depth. Results also indicated that soil properties, including pH, organic matter, amounts of sand and clay, significantly influenced the sorption of NH_4^+ by soils. Langmuir and Freundlich equations were applied to test the equilibrium data. Freundlich equation better described the sorption data, thus indicating the heterogeneity in the ammonium sorption characteristics of the different soil sampled.

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