NITROGEN CONCENTRATION IN GRAIN SIZE FRACTIONS OF SOILS OF CONTRASTING LAND UNITS IN THE HUMID RAINFOREST, SOUTHEASTERN NIGERIA

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ABSTRACT: *Nitrogen is critical for ecosystem functioning and environmental health. Its concentration in grain size fraction provides useful information about the activities in soils. Nitrogen (total, organic, nitrate and ammonium) contents in grain size fraction of soils of contrasting units (back swamp, levee and upland) in Egbema, southeastern, Nigeria were evaluated. Also nitrogen contents were correlated with selected soil properties (sand, silt, clay, bd, pH, available P, OC and ECEC). Equally bulk soil N contents were related with were the grain size fractions using regression analysis. Mean total, organic, nitrate and ammonium N contents ranged between 0.60-0.65, 0.82-0.84, 0.77-0.87 and 0.78-1.35 g kg^{-1}, 0.57-0.66, 0.84-1.56, 0.50-1.08 and 0.77-0.84 g kg^{-1}, 5.96-6.91, 4.50-7.00, 5.04-7.20 and 6.90-8.30 mg kg^{-1}and 0.23-1.33, 0.84-1.56, 0.50-1.08 and 0.80-1.52 mg kg^{-1} in bulk soil, sand, silt and clay grain size fractions respectively. Also averaged over land units, mean total, organic, nitrate and ammonium nitrogen in top and sub soils varied as 0.65 and 0.62, 0.86 and 0.79, 0.86 and 0.78 and 1.21and 0.77 g kg^{-1} , 0.64 and 0.61, 1.13 and 1.43, 0.50 and 1.24 and 1.20 and 0.76 g kg^{-1}, 6.71 and 6.28, 5.27 and 6.27, 6.33 and 6.49 and 8.71 and 6.53 mg kg^{-1} and 0.94 and 0.92, 1.13 and 1.43, 0.50 and 1.24 and 1.39 and 1.12 mg kg^{-1} in bulk soil, sand, silt and clay fractions respectively. Bulk soil N forms were higher in levee except being nitrate in upland while those in particle size fractions varied amongst land units. Concentrations of all N forms in bulk and grain size fractions were were better in top than sub soils. Total, organic, nitrate and ammonium N enrichment of sand, silt and clay grain size fractions varied with soil depth and land units with clay fraction more enriched than other size fractions. Nitrogen contents correlated with selected soil properties, with the magnitude varying. Furthermore, N content of bulk soil was related with concentrations of the grain size fraction. In general, N content of grain size fractions will seriously influence N activity in soils of different land units.*

KEYWORDS: Nitrogen, Grain Size, Land Unit, Humid, Rainforest and Southeastern Nigeria

INTRODUCTION

Nitrogen plays important role in the nutrition of many biological organisms including animals, plants and microbes and also in environmental sustainability (Fan et al., 2010; Jha et al., 2010; Hirel et al., 2011). Its activities and chemistry varies depending on the dominant chemical forms in the soil. Two forms of soil N include organic and inorganic, with organic N associated with nucleic acids, amino acids, proteins and amino sugars and accounting for about 90- 98% of total soil nitrogen (Havelin et al., 2012; Mubyana- John and Musamba, 2014). Through a two stage process of ammonification and nitrification, organic N could be transformed into inorganic forms. Ammonification refers to a continuous decomposition process in which high molecular weight organic nitrogenous compounds are sequentially hydrolyzed into simpler compounds by extracellular enzyme activities, followed by the breakdown of the dissolved amino compounds and the release of ammonium nitrogen (Ma et al., 2008). Nitrification is the conversion of ammonium nitrogen into nitrate nitrogen (Rochette et al., 2006; Havlin et al.,

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2012). Thus ammonium and nitrate nitrogen constitute the two main inorganic N forms that are usually taken up by plants and microbes or lost through leaching (Zhijing et al., 2013). Ammonium nitrogen is often associated with soil cation exchange complex and easily retained or fixed in soils high in clay (Havlin et al., 2012). Nitrate nitrogen readily combines with soil exchangeable cations and becomes soluble, mobile and easily lost through leaching or erosion from plant root zone (Hirel et al. 2011; Uzoho et al., 2014)

Concentration of soil nitrogen forms varies with the landscape and influenced by several factors especially land use, topography, soil type and climate. Effect of landuse on soil N status has been widely studied (Zhijing et al., 2013; Uzoho et al., 2014). For instance, it has been indicated that changes in land use can cause changes in land coverage and associated carbon and nitrogen stock (Bolin and Sukumah, 2000; Sun et al., 2005; Zhijing et al., 2013) and that past land use practices are associated with modifications of decomposition dynamics through the alteration of soil aeration, water dynamics and aggregation and the biochemistry and quantity of crop residues (Drinkwater and Snapp, 2006). Also, research has shown that the conversion of forest into agricultural land use depressed total soil N and organic matter due to reduction in plant litter, high rate of soil disturbance, breakdown in soil aggregation and reduction in soil cohesion (Khreast et al., 2008; Zhang et al., 2011; Gebrelibanos and Assen, 2013). Topography influences runoff, erosion, drainage and soil temperature causing differences in soil formation and nitrogen concentration and thus patterns of plant production, litter production and decomposition (Brubaker et al. 1993, 1994). Impact of climate and soil type on nitrogen forms is related to the differences in mineralization patterns (Jonathan 2006; Wei and Shao, 2007). It has been reported that nitrogen mineralization and transformation is affected by soil moisture and agronomic practices (Tilman et al., 1996; Burke et al., 1997) and that whereas nitrate concentration is high in well drained soils the reverse is the case for ammonium nitrate (Ma et al., 2008).

Within a given landscape, concentration of nitrogen forms may vary with soil grain size fractions. For instance, low total N has been reported in the sand fraction due to increased drainage and leaching but with concentrations better in silt and clay fractions due to increased ammonium nitrate fixation (Burke et al, 1989). Also in studies of carbohydrate distribution in soil particle size fractions, concentrations of water soluble carbohydrate was higher in the sand fractions while those of other fractions were in the silt and clay fractions (Spaccini et al., 2001; Uzoho and Igbojionu, 2014). Equally, reports of K forms in particle size fractions of soils indicated high concentration in clay size fraction of soils developed over talc and talc overburden soils of Ejiba, Kogi state (Ajibade and Ogunwale, 2008; 2012), silt fraction of floodplain soils in southeastern, Nigeria (Igwe et al., 2008) and sand fraction of some Atlantic Coastal Plain sands and arid Iranian soils (Parker et al., 1989; Najafi-Ghiri and Abtahi, 2013). Differences in concentrations with particle size fractions have been attributed to variation in soil mineralogical composition and surface areas (Spaccini et al., 2001; Najafi-Ghiri and Abtahi, 2013). Though nitrogen forms of southeastern Nigerian soils have been extensively studied (Onweremadu et al., 2011; Uzoho et al., 2014), information concerning N forms in grain size fractions of the soils is limited. The objectives of the present study were to evaluate the N forms in grain size fractions of soils of contrasting land units in the humid rainforest, southeastern, Nigeria, correlate the N forms with selected soil properties and evaluate the relationship between N forms in grain size fractions and the bulk soils of different land units.

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MATERIALS AND METHODS

Study Location and Sites

The study location was Egbema lying between Latitudes 5^0 20^1 and 5^0 40^1 N and Longitudes 6^o 40^1 and 6^o 47^1E. It has a mean annual rainfall range of 2450-2500 mm, daily temperature range of 26.5-27.5^o C, daily relative humidity range of 65-75%, evapo-transipiration range of 1445-1450 mm/yr and an altitude of 45-70 m.a.s.l (IPEDC, 2006). Geology of the area has been classified as quarternary, alluvium, meander belt, wooded back swamp, fresh water swamps and the Sombreiro-Warri Deltaic plains with deposits of petroleum and natural gas (Orajiaka, 1975). The study sites consisted of three land units; upland, backswamp and levee with the soil types already classified in another study (Uzoho and Okechukwu, 2014). Climax vegetation consisted of cassava (Manihot esculentum) and oil palm (Elaeis guineensis, Jacq) in the upland, raffia palm (Raphia farinifera) and riparian forest in the Levee and cassava (Manihot esculentum) and bamboo (Bambusa vulgaris) in the backswamp. Major economic activities of Egbema consisted of farming, fishing, trading and crude oil exploitation.

Sample Collection and Preparation

Three profile pits each from each of the three land units (upland, levee and back swamp) were sunk and five soil samples collected from each horizon using natural horizonization and giving a total of fifty samples. The samples were air dried and replicate samples from each depth of a land unit were bulked to obtain a composite. The samples were then sieved using a 2 mm diameter mesh and the fine earth soil fractions stored for laboratory analysis. Subsamples from the first and second horizons of each land unit were taken as top and sub soils respectively and used for determination of N forms.

Soil Particle Size Fractionation

Soil samples were fractionated into three grain size particles (<0.002 mm, 0.002-0.02 mm and 0.02-2.0mm) according to the method described by Sequaris and Lewandowski, 2003). The procedure involved a three stage process as follows:
Stage 1.

One hundred gram (100g) soil sample was weighed into a 1000 ml glass bottle containing 200 ml distilled water and shaken on a horizontal shaker for 6 hrs at a revolution of 15 x 1000 g. Then 600 ml of distilled water was added, agitated by hand for 1 minute, left undisturbed for sedimentation for 6 mins after which about 700 ml of the supernatant was transferred into another glass bottle. The sediments left in the first glass bottle were then dried at 40^o C to obtain the 0.02-2.0 mm fraction.

Stage 2:

The 700 ml supernatant from step 1 was shaken for 2 mins and then left undisturbed for 12 hrs after which 600 ml was removed. The sediments left were dried at 40 ^{o} C to obtain the 0.002-0.02 mm fraction.

Stage 3:

The 600 ml supernatant from stage 2 were transfer into 250 ml centrifuge tubes and centrifuged for 90 mins at 12000 g and 20 ^{o} C. The sediment remaining after the supernatant was discarded was dried at 40 ^{o} C to obtain the < 0.002 mm fraction.

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Laboratory Analysis

Subsamples of the fine earth fractions were subjected to routine analysis using standard methods. Texture (Gee and Or, 2002), bulk density (Blake and Hartage, 1986), OM (Nelson, 1996), ECEC (Thomas, 1996), available P (Olson and Sommers, 1982), pH (Thomas, 1996). Total N and N forms in the soils were determined using the following procedure:

Total N was determined calorimetrically using the following procedure; finely ground soil sample (0.2 g) was weighed into a digestion flask and 1 g of copper catalyst plus 4mls of Conc. H2SO4 were added and digested on a digestion block till frothing stopped. The tube was cooled and about 20 ml de-ionized water added before filtration into a 100 ml flask and subsequent dilution to mark using de-ionized water. A 10 ml aliquot of the clear supernatant was pipetted into a 20 ml volumetric flask and 6 ml of potassium sodium tartarate, 2 ml alkaline sodium phenate and 2 ml sodium hypochlorite solutions added before mixing and making-up to mark with deionized water. The N in the solution was then determined at a wavelength of 630 nm using a Spectrophotometer. Total N in the sample was calculated using the relation:

Sample N (g kg^{-1}) = Solution N x dilution factor x volume of solution Wt of sample x total volume of extract

Colorimetric determination of nitrate nitrogen was conducted as follows: A 10g soil sample was weighed into polythene bottle and 0.5 g activated carbon plus 40 ml Morgan solution added and shaken for 45-60 mins before filtration. Furthermore, 10 ml of the filtrate was pipetted into a 25 ml volumetric flask and 2 ml of brucine reagent and 10ml Conc. H_2SO_4 rapidly added, thoroughly mixed and allowed to cool for 20 mins before finally making up to mark with de-ionized water. The brucine treated sample was read on a Spectrophotometer at a wavelength of 470 nm.

Concentration of NO_3-N (mg kg^{-1}) = AC conc. (mg l-1) x D.F x EV (L) colour Vol. of extract in (L) x wt of soil Ammonium-Nitrogen was determined using the following procedures; Ten gram (10g) soil sample was weighed into a polythene bottle and 0.5g activated carbon plus 40 ml Morgan extracting reagent added and shaken for 45-60 mins before filtration using whatman no. 2 filter paper. Also 10ml of the filterate, 6ml of potassium sodium tartarate and 2ml of alkaline sodium phenate solution were added into a 25ml volumetric flask and shook thoroughly before the flask was made up to mark using de-ionized water. The NH_4-N in the solution was determined in a spectrophotometer at a wavelength of 630 nm and the concentration in the sample calculated as:

Concentration of NH4-N in the sample (mg kg^{-1}) = AC conc. (mg l-1) x D.F x EV (L) vol. of extract (L) x Wt of soil

Where AC = Concentration (mg l-1), D.F = Dilution factor, EV = Final volume and Wt = Weight of soil.

STATISTICAL ANALYSIS

Data generated for N forms in the soils were subjected to analysis of variance (ANOVA) and means separated using Fischer's Least Significant Difference at 5% probability level (F-LSD 0.05). Also correlation between soil properties and N forms was determined using correlation

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analysis while regression analysis was used to estimate the relationship between bulk soil N and those of the particle size fractions. All analyses were conducted using Genstat statistical package (Buyse et al., 2004).

RESULTS

Soil Characterization

Mean sand, silt and clay ranged between 645.20-822.70, 47.20-97.20 and 82.60-257.60 g kg^{-1} respectively with sand greater than others and decreased with depth in each land unit while clay increased with depth (Table 1). Distribution of the silt fraction was irregular with depth exception being upland where it was uniform. Texture of the soils was dominantly sandy with variations of sand, sandy clay loam and loamy sand amongst horizons of the various land units. Mean moisture content and total porosity were better in the upland (23.43 and 48.35% respectively) than others and decreased with depth in all land units. Mean WSA increased in the

Table 1. Selected Physical Properties of Soils of various Land units Studied

Land Units	Depth	Sand	Silt	Clay	MC	TP	WSA	MWD	Bd	TC
			g kg^{-1}		%			mm	g cm^{-3}	
Upland	0-12	935.20	47.20	17.60	37.50	50.80	62.00	0.24	1.26	S
	12-45	895.20	47.20	57.60	30.90	48.80	61.00	1.38	1.31	S
	45-70	835.20	47.20	117.60	11.80	46.10	42.20	0.17	1.38	LS
	70-120	815.20	47.20	137.60	13.50	47.70	44.70	0.18	1.34	LS
	Mean	870.20	47.20	82.60	23.43	48.35	52.48	0.49	1.32	S
Levee	0-7	855.20	27.20	117.60	14.90	40.63	37.10	0.20	1.52	LS
	7-30	435.20	167.20	397.60	12.40	30.10	61.80	0.26	1.79	SCL
	Mean	645.20	97.20	257.60	13.65	35.37	49.45	0.23	1.66	SCL
Back swamp	0-10	825.20	47.20	97.60	20.00	43.40	36.09	0.08	1.45	S
	10-40	815.20	47.20	137.60	19.50	53.50	67.50	0.40	1.19	S
	40-45	855.20	67.20	77.60	20.00	11.30	96.40	0.42	1.27	S
	45-100	795.20	47.20	157.60	20.60	46.90	59.10	0.26	1.36	LS
	Mean	822.70	52.20	117.60	20.03	38.78	64.77	0.29	1.32	LS

MC = Moisture content, TP = Total porosity, WSA = Water stable aggregate, MWD = Mean weight diameter, Bd = Bulk density, TC = Textural class, S = Sand, LS = Loamy sand and SCL = Sandy clay loam

order levee < upland < back swamp and varied with depth in all land units. Upland (0.49 mm) soil had the best mean MWD followed by back swamp (0.29 mm) and then levee (0.23 mm) with distribution down the depth irregular. Mean bulk density was higher in the levee than the others, with distribution down the depth irregular for the land units.

Mean soil pH varied as 5.50, 5.58 and 5.62 for the back swamp, upland and levee respectively (Table 2). Mean soil OC ranged between 4.94-9.38g kg^{-1} being better in the levee than others

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and decreased with depth in all land units. Mean concentrations of all soil nutrients (TN, P, Ca, Mg, K and ECEC) followed the same trend as soil OC.

Soil Nitrogen

Total nitrogen, organic nitrogen and inorganic or mineral N forms especially ammonium and nitrate nitrogen of the soils varied.

Total Nitrogen

Mean total N averaged over soil horizons was significantly ($LSD_{0.05}$) higher in the bulk soil of the levee, sand fraction of the back swamp and silt and clay size fractions of upland land units (Table 3). Averaged over land units, topsoil had better mean concentration than subsoil in both the bulk soil and the particle size (sand, silt and clay) fractions. Within each land unit, concentrations were seriously ($LSD_{0.05}$) better in the top than subsoil's of bulk soil, sand, silt and clay particle size fractions exception being sand fraction of the back swamp land unit. In general, mean concentrations in the bulk soil was lower than the particle size fractions of most land units. Averaged over soil horizons, total N was more distinctly ($LSD_{0.05}$) enriched in the upland than the other land units while averaged over land units topsoil was seriously ($LSD_{0.05}$) better than subsoil. Within each land unit, total N enrichment was significantly higher in the top than the sub soils exception being in sand and silt fractions of the back swamp. Amongst particle size fractions, clay size fraction was more enriched than the sand and silt particle size fractions of most land units.

Organic Nitrogen

Mean organic N content of the bulk soil, sand, silt and clay particle size fractions varied as 0.59, 1.44, 1.03 and 0.84, 0.66, 0.84, 0.50 and 1.34 and 0.64, 1.56, 1.08 and 0.77 g kg^{-1} in the upland, levee and back swamp land units respectively, with concentrations significantly ($LSD_{0.05}$) higher in the bulk soil and the clay particle size fraction of the levee and the sand and silt particle size fractions of the back swamp (Table 4). Averaged over land units, mean concentrations were better in the top than subsoil of the bulk soil and clay particle size fractions and in sub than topsoil of the sand and silt particle size fractions. Mean organic N concentrations were generally better in particle size fractions (sand, silt and clay) than the bulk soil of all the three land units. Within land units, clay sized fractions were better enriched in the upland and levee while silt was in the back swamp land unit. Also whereas, sand and clay fractions were better enriched in the topsoil, silt was in the subsoil. Amongst land units and soil depths, sand fractions were better enriched in the top soil of upland and levee and subsoil of back swamp, silt

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Table 2. Selected Chemical Properties of Soils of various Land units Studied

Land Units	Depth	pH H_2O	OC $g\ kg^{-1}$	TN	P mg kg^{-1}	Ca Cmol (+) kg^{-1}	Mg	K	Na	ECEC
Upland	0-12	5.60	5.59	0.47	18.20	0.30	0.33	0.10	0.34	1.89
	12-45	5.70	4.79	0.49	11.20	0.20	0.33	0.09	0.30	2.32
	45-70	5.62	4.60	0.41	15.40	0.10	0.17	0.07	0.16	2.5
	70-120	5.38	4.79	0.43	9.10	0.10	0.08	0.10	0.40	2.93
	Mean	5.58	4.94	0.45	13.48	0.18	0.23	0.09	0.30	2.32
Levee	0-7	5.57	9.98	0.77	9.10	4.52	1.17	0.21	0.38	6.54
	7-30	5.67	8.78	0.86	29.40	4.70	1.00	0.14	0.40	8.11
	Mean	5.62	9.38	0.82	19.25	4.61	1.09	0.17	0.39	7.33
Back swamp	0-10	5.57	10.18	0.90	11.20	1.30	1.33	0.17	0.19	4.05
	10-45	5.27	9.38	0.71	21.70	1.10	1.33	0.13	0.40	4.17
	40-45	5.75	8.18	0.82	12.60	0.50	1.00	0.07	0.32	2.91
	45-100	5.40	3.59	0.32	11.90	0.20	0.83	0.10	0.31	4.00
	Mean	5.50	7.83	0.69	14.35	0.78	1.12	0.12	0.30	3.78

Table 3. Total Nitrogen (g kg^{-1}) in bulk and Particle Size fractions of Soils of the various Land units

Land units	Horizon	Bulk soil	Particle Size Fractions			Enrichment Factors		
			Sand	Silt	Clay	Sand	Silt	Clay
Upland	Topsoil	0.61	0.90	0.92	0.92	1.48	1.51	1.51
Upland	Subsoil	0.58	0.76	0.81	0.78	1.31	1.28	1.35
Upland	Mean	0.60	0.83	0.87	0.85	1.40	1.40	1.43
Levee	Topsoil	0.68	0.92	0.90	1.92	1.36	1.20	2.82
Levee	Subsoil	0.66	0.72	0.77	0.77	1.09	1.17	1.17
Levee	Mean	0.67	0.82	0.84	1.35	1.23	1.19	2.00
Back swamp	Topsoil	0.66	0.77	0.77	0.80	1.17	1.17	1.21
Back swamp	Subsoil	0.63	0.90	0.77	0.75	1.43	1.22	1.20
Back swamp	Mean	0.65	0.84	0.77	0.78	1.30	1.20	1.21
LSD 0.05	Land unit (A)	0.011	0.054	0.06	0.055	0.011	0.069	0.054
	Horizon (B)	0.009	0.044	0.046	0.045	0.01	0.056	0.044
	Fact (A x B)	0.016	0.076	0.079	0.078	0.015	0.097	0.076

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Table 4. Organic Nitrogen (g kg^{-1}) in bulk and Particle Size fractions of Soils of the various Land units

Land units	Horizon	Bulk soil	Particle Size Fractions			Enrichment Factors		
			Sand	Silt	Clay	Sand	Silt	Clay
Upland	Topsoil	0.60	1.44	0.50	0.91	1.48	0.35	1.51
Upland	Subsoil	0.57	1.44	1.56	0.77	1.32	1.49	1.35
Upland	Mean	0.59	1.44	1.03	0.84	1.40	0.92	1.43
Levee	Topsoil	0.67	0.40	0.40	1.91	1.36	0.33	2.84
Levee	Subsoil	0.65	1.28	0.60	0.77	1.09	0.88	1.18
Levee	Mean	0.66	0.84	0.50	1.34	1.23	0.61	2.01
Back swamp	Topsoil	0.65	1.56	0.60	0.79	1.17	7.44	1.21
Back swamp	Subsoil	0.62	1.56	1.56	0.74	1.43	6.25	1.19
Back swamp	Mean	0.64	1.56	1.08	0.77	1.30	6.85	1.20
LSD 0.05	Land unit(A)	0.057	0.056	0.103	0.011	0.011	0.013	0.011
	Horizon (B)	0.046	0.046	0.084	0.009	0.009	0.011	0.009
	fact (A x B)	0.080	0.079	0.146	0.015	0.015	0.019	0.019

fraction of subsoil of the upland and levee and topsoil of back swamp and clay particle size fractions in the topsoil of all land units.

Nitrate Nitrogen

Mean nitrate N averaged over soil depths in bulk soil, sand, silt and clay particle size fractions varied as 6.91, 5.80, 7.00 and 6.90, 6.61, 4.50, 5.04 and 8.30 and 5.96, 7.00, 7.20 and 7.67 mg kg^{-1} in upland, levee and back swamp land units respectively with bulk soil distinctly (LSD $_{0.05}$) better in the upland, clay sized fraction in the levee and silt and sand grain size fractions in the back swamp land units (Table 5). Averaged over land units, variations included 6.71 and 6.28, 5.27 and 6.27, 6.33 and 6.49 and 8.71 and 6.53 mg kg^{-1} in the top and sub soils of bulk soil, sand, silt and clay fractions respectively, with concentrations better in the topsoil of bulk soil and clay particle size fraction and the subsoil of sand and silt fractions. Within each land unit, concentrations of the bulk soil were better in the topsoil of the levee and back swamp and the subsoil of upland land units, sand and silt particle size fractions in sub soils of upland and levee and topsoil of the back swamp and clay particle size fractions in the top soil of upland and levee and subsoil of back swamp land units. Also concentrations were better in particle size fractions (sand, silt and clay) than the bulk soil in most horizons of the various land units. Mean enrichment factors averaged over horizons varied as 1.21, 1.22and 1.35in sand, silt and clay particle size fractions respectively and better in the back swamp than other land units while between particle size fractions and land units, upland land unit was more enriched in the silt while levee and back swamp were in the clay particle size fractions.

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Ammonium Nitrogen

Mean ammonium nitrogen concentrations averaged over soil depths increased in the order back swamp < upland < levee for bulk soil, levee < upland < back swamp for sand and silt fractions and levee < back swamp < upland for clay fraction (Table 6). Averaged over land units topsoil (0.93) was greater than subsoil (0.92) in the bulk soil while subsoil (1.43, 1.24 and 1.39) was better than topsoil (1.13, 0.50 and 1.12) in the sand, silt and clay fractions respectively. In each land unit, concentrations of bulk soil were better in topsoil of the upland and subsoil of levee and back swamp. Sand fractions were better in top soil of the upland and back swamp and subsoil of the levee, silt fraction in the subsoil of all land units while clay fraction had no distinct sequence amongst soil depths of the land units. Also, clay fraction was more enriched in the upland (1.27) and levee (0.64) while sand was in the back swamp (6.85) land unit. Amongst land units, back swamp were more enriched in all size fractions with subsoil better in sand and silt fractions in the upland and levee land units while the reverse was the case for the back swamp. Subsoil was more enriched in clay fraction of upland and back swamp and topsoil of levee land units.

Relationship between Soil Properties and N Forms of the Bulk Soil and Particle Size Fractions

Correlations between soil properties and N forms of bulk soil and grain size fractions of

Table 5. Nitrate Nitrogen (mg kg^{-1}) in bulk and Particle Size fractions of Soils of the various Land units

Land units	Horizon	Bulk soil	Particle Size Fractions			Enrichment Factors		
			Sand	Silt	Clay	Sand	Silt	Clay
Upland	Topsoil	6.21	4.60	6.80	7.40	0.80	1.10	1.19
Upland	Subsoil	7.61	7.00	7.20	6.40	0.92	0.95	0.84
Upland	Mean	6.91	5.80	7.00	6.90	0.86	1.03	1.02
Levee	Topsoil	6.81	4.00	3.80	11.40	0.59	0.56	1.67
Levee	Subsoil	6.41	5.00	6.27	5.20	0.78	0.98	0.81
Levee	Mean	6.61	4.50	5.04	8.30	0.69	0.77	1.24
Back swamp	Topsoil	7.10	7.20	8.40	7.33	1.01	1.18	1.03
Back swamp	Subsoil	4.81	6.80	6.00	8.00	1.41	1.25	1.66
Back swamp	Mean	5.96	7.00	7.20	7.67	1.21	1.22	1.35
LSD 0.05	Land unit(A)	0.055	0.688	0.48	0.539	0.050	0.047	0.011
	Horizon (B)	0.045	0.561	0.396	0.440	0.041	0.039	0.009
	Fact (A x B)	0.078	0.972	0.685	0.762	0.071	0.067	0.015

ISSN 2056-7537(print), ISSN 2056-7545(online)

Table 6. Ammonium Nitrogen (mg kg^{-1}) in bulk and Particle Size fractions of Soils of the various Land units

Land units	Horizon	Bulk soil	Particle Size Fractions			Enrichment Factors		
			Sand	Silt	Clay	Sand	Silt	Clay
Upland	Topsoil	1.41	1.44	0.50	1.44	1.02	0.35	1.02
Upland	Subsoil	1.05	1.44	1.56	1.60	1.37	1.49	1.52
Upland	Mean	1.23	1.44	1.03	1.52	1.20	0.92	1.27
Levee	Topsoil	1.21	0.40	0.40	1.28	0.33	0.33	1.00
Levee	Subsoil	1.45	1.28	0.60	0.32	0.88	0.41	0.22
Levee	Mean	1.33	0.84	0.50	0.80	0.61	0.37	0.64
Back swamp	Topsoil	0.21	1.56	0.60	1.44	7.44	2.86	6.87
Back swamp	Subsoil	0.25	1.56	1.56	1.44	6.25	6.25	5.77
Back swamp	Mean	0.23	1.56	1.08	1.44	6.85	4.56	6.32
LSD 0.05	Land unit (A)	0.014	0.056	0.10	0.058	0.011	0.013	0.053
	Horizon (B)	0.012	0.046	0.084	0.047	0.009	0.011	0.043
	Fact (A x B)	0.019	0.079	0.146	0.082	0.015	0.019	0.075

the soils studied are presented in Table 7. Sand content correlated significantly ($P \leq 0.05$) with ammonium nitrogen (r = 0.75) in bulk soil, total N in sand (r = 0.53) and silt fractions (r = 0.51) but none with N forms in soil clay fractions. Also Silt content correlated significantly ($P \leq 0.05$) with ammonium nitrogen (r = -0.69) in the bulk soil, organic (r = 0.41), ammonium (r = 0.41) and nitrate nitrogen (r = 0.56) in the sand fraction, total N (r = 0.46) and nitrate nitrogen (r= 0.46) in the silt fraction and not with N forms in the clay size fractions. Equally, besides ammonium N in the bulk soil (r = 0.70), nitrate nitrogen in the sand fraction and total nitrogen in the silt fraction that correlated seriously ($P \leq 0.05$) with clay content, there was no distinct relationship ($P \leq 0.05$) between clay content and N forms in the bulk soil and grain size fractions. Furthermore, there was serious ($P \leq 0.05$) relationship between soil bulk density and ammonium nitrogen (r = 0.77) in the bulk soil, nitrate nitrogen (r = 0.53) in the sand fraction (r = 0.53) and total nitrogen (r = 0.57) in the silt grain size fraction. There was also distinct ($P \leq 0.05$) relationship between soil pH and total N (r = 0.65) and organic N (r = -0.65) in the bulk soil, total N (r = 0.55), organic N (r = 0.84), nitrate-N (r = 0.71) and ammonium-N (r = 0.84) in the sand fraction, total N (r = -0.45), organic N (r = 0.55), nitrate-N (r = 0.84) and ammonium nitrogen (r= 0.55) in the silt fraction and total N (r = 0.86), organic N (r =-0.86) and nitrate nitrogen (r = 0.78) in the clay fraction of the soils. Except total nitrogen (r = 0.52) in silt grain size fraction, total N (r = 0.40), organic N (r = 0.40), nitrate-N (r = 0.50) and ammonium-N (r = 0.68) in the bulk soil there was no serious relationship between organic carbon and all other N forms in the sand, silt and clay grain size fractions. In addition, available P was significantly ($P \leq 0.05$) correlated with nitrate nitrogen (r = -0.51) of the bulk soil, organic N (r = 0.57), nitrate-N (r = 0.47) and ammonium –N (r = 0.57) in the sand fraction, nitrate nitrogen (r = 0.66) in the silt fraction and total nitrogen (r= 0.47) and organic nitrogen (r = -0.48) forms in the clay fraction of the soils. Finally, total nitrogen (r = 0.41), organic nitrogen (r= 0.41) and ammonium nitrogen (r = -0.68) in the bulk soil and total N in the silt grain size fraction but not

ISSN 2056-7537(print), ISSN 2056-7545(online)

other N forms in bulk soil and grain size fractions correlated seriously (P ≤ 0.05) with soil ECEC. A predictive equation explained the relationship between N forms of the bulk soil and those of the grain size fractions (Table 8). Total N in the sand, silt and clay fractions accounted for about 45% of total N of the bulk soil, with concentrations of the silt size fraction (0.42) better than sand (0.01) and clay (0.09) size fractions. Also organic nitrogen content in grain size fractions (sand, silt and clay) of the soil contributed less than 20% of the organic N of the bulk bulk with the order of magnitude being a decreasing sequence of silt > sand > clay. More than 90% of bulk soil nitrate nitrogen content was due to concentrations of the particle size fractions with the magnitude being a decreasing sequence of clay (0.08) < sand (0.31) < silt (0.40). Finally, ammonium content of soil particle size fractions contributed more than 50% of that in the bulk soil with decree being a decreasing order of sand (0.45), clay (0.37) and silt (0.15).

DISCUSSION

Dominance of sand in the particle size fractions could be ascribable to the nature of the parent material which ranges from Coastal Plain Sands (upland) and alluvium (levee and back swamp) (Uzoho and Okechukwu, 2014). Increased clay content with soil depth of various land

Table 7. Simple Correlation between Selected Soil Properties and N Forms in bulk Soil and Particle Size Fractions

Soil Properties	Bulk Soil				Sand				Silt				Clay			
	Nitrogen Forms															
	TN	Org. N	Nit. N	Amm. N	TN	Org. N	Nit. N	Amm. N	TN	Org. N	Nit. N	Amm. N	TN	Org. N	Nit. N	Amm. N
Sand	-0.31	-0.31	0.11	0.75	0.08	-0.27	-0.53	-0.27	0.51	-0.05	-0.37	-0.05	0.17	0.18	-0.09	-0.22
Silt	0.13	0.14	-0.05	-0.69	-0.14	0.41	0.57	0.41	-0.46	0.06	0.53	0.06	-0.31	-0.31	-0.05	0.28
Clay	0.35	0.35	-0.11	-0.70	-0.06	0.19	0.47	0.19	-0.48	0.03	0.28	0.03	-0.10	-0.1	0.14	0.18
Bd	0.34	0.34	-0.26	-0.77	-0.06	0.27	0.53	0.27	-0.57	0.12	0.30	0.12	-0.2	-0.2	0.08	0.14
pH	-0.65	-0.65	0.13	-0.28	-0.55	0.84	0.71	0.84	-0.45	0.55	0.84	0.55	0.86	-0.86	-0.78	0.27
OC	0.40	0.40	-0.5	-0.68	0.11	0.22	0.38	0.23	-0.52	0.1	0.12	0.1	-0.15	-0.16	0.12	0.03
Avail P	-0.07	-0.07	-0.09	-0.51	-0.12	0.57	0.47	0.57	-0.28	-0.01	0.66	-0.01	-0.47	-0.48	-0.25	0.28
ECEC	0.41	0.41	-0.32	-0.68	0.02	0.14	0.39	0.14	-0.51	0.07	0.13	0.07	-0.08	-0.08	0.16	0.05

TN - Total nitrogen, Org. N = Organic nitrogen, Nit. N = Nitrate nitrogen and Amm. N = Ammonium nitrogen

Table 8. Multiple Regression Equation and Coefficient of Determination of the Relationship between Bulk Soil N and Particle Size N Forms

Parameters	Equation	R^2
Bulk soil vs. sand, silt and clay TN	Y (bs TN) = 0.89 + 0.01 sand TN + 0.09 clay TN - 0.42 silt TN	0.45
Bulk soil vs. sand, silt and clay Org.N	Y (bs Org. N) = 0.72 - 0.04 sand Org. N - 0.04 silt Org. N - 0.01 clay Org.N	0.18
Bulk soil vs. sand, silt and clay Nit. N	Y (bs Nit. N) = 5.09 + 0.40 silt Nit. N + 0.08 clay Nit. N - 0.31 sand Nit. N	0.94
Bulk soil vs. sand, silt and clay Amm. N	Y (bs Amm. N) = 2.10 - 0.45 sand Amm.N - 0.15 silt Amm. N - 0.37 clay Amm. N	0.54

Bs = bulk soil, TN = Total nitrogen, Org. N = Organic nitrogen, Nit N = Nitrate nitrogen and Amm. N = Ammonium nitrogen

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units could be attributed to clay illuviation resulting from leaching (Essoka and Esu, 2005). Moisture content and aggregate stability were better in the top than sub soil of most land units probably due to the high organic matter content of the top soil. It has been reported that organic matter improves soil physical, chemical and biological properties especially water holding capacity, structural stability, tilt etc (Hargreaves et al., 2008; Uzoho et al., 2012). Acidic pH of the soils could be ascribable to intense leaching of bases by the high tropical rainfall.

High total N content in bulk soil of the levee relative to other land units could be ascribed to increased N mineralization and decomposition of the large stock of organic matter in the land unit. It has be noted that increased total N content of soils varying land uses was due to increasedorganic matter decomposition and N mineralization (Mubyana-Musamba, 2014). Also, the high total N content of the levee could be due to deposition of N transported by runoff or erosion (Zhijing et al, 2013). High total N content in sand fraction of back swamp and silt and clay fractions of upland land unit than others could be associated with the presence of greater surfaces for N retention than grain size fractions of other land units. Equally, better total N content in bulk and grain size fractions of the topsoil could be due to the high organic matter content of the topsoil. It has been reported that N is mineralized from soil organic matter and the higher the organic matter content, the higher the soil total N content (Chu and Grogan, 2010); Zhijing et al., 2013). The high organic matter content of the topsoil could be from deposition of N and organic materials by runoff or accumulation from plant litter. Equally, the high content in particle size fractions than bulk soil could be due to the ease in pulling out the N from soil separates than the aggregates. Also due to its large surface and ability to retain N, clay fraction contained more N than the other grain size fractions. It has been reported that the finer the grain size fraction, the higher the surface area and capacity to retain nutrients (Spaccini et al., 2001).

Organic N constituted about 95% of total N in the soils as has been reported by other workers (Meysner et al., 2006; Sabiene et al., 2010; Havlin et al., 2012). High concentrations in bulk soil and particle fractions of levee and back swamp and in the topsoil of all land units could probably be due to deposition of organic matter by runoff or accumulation of plant litter in the topsoil. It could also be due to poor oxidation of organic material as a result of the reducing condition in the levee than other land units. As in total N, high content of the grain size fractions than bulk soil could be due to ease of the removal of materials in soil separates than soil aggregates.

High nitrate concentration in bulk soil of upland land unit could be due to increased nitrification of ammonium nitrogen resulting from good soil drained in the land unit than others. It has been reported that nitrification is rapid in soils with no limiting environmental conditions such as good aeration and adequate moisture (Rochette et al., 2006; Ma et al., 2008). Variation in consideration of the particle size fractions could be associated with differences in surface area.

Poor nitrification due to poor aeration could be responsible for the high ammonium nitrogen content of bulk soils of the levee land unit. Variation in soil ammonium nitrogen concentration and the enrichment of soil particle size fractions of the various land units could be related to availability of active surfaces for their retention.

Relationship between N forms and soil properties have been reported (Onweremadu et al., 2011; Moges et al., 2013; Gebrallibanos and Assen, 2013; Uzoho et al., 2014). Significant relationship has been reported between total N and soil organic matter ascribable to high organic matter accumulation (Moges et al., 2013; Gebrallibanos and Assen, 2013). Negative

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relation due to increased drainage and leaching losses has been reported between sand fraction and total while positive correlation with silt and clay has been arrogated to increased NH4-N fixation in the soil fractions (Burke et al., 1989; Onweremadu, 2011). Total, Organic, ammonium and nitrate nitrogen have been distinctly correlated with soil pH attributable to high organic matter decomposition and N mineralization (Zhijing et al., 2013). In a study of N status of soils of selected land uses of two cropping systems in the humid tropical rainforest, southeastern Nigeria, varying relationship between soil properties (ECEC,pH, OM, clay, silt and P) and N forms (total, organic, ammonium and nitrate nitrogen) have been reported (Uzoho et al., 2014).

CONCLUSION

Soil N contents (total, organic, nitrate and ammonium) varied in bulk soil and grain size fractions of soils of the various land units. Mean total, organic, nitrate and ammonium nitrogen content in bulk soils of various land units increased in the order upland < back swamp < levee, upland < levee < back swamp, back swamp < levee < upland and back swamp < upland < levee respectively, variation in sand grain fraction increased as levee < upland < back swamp, levee < upland < back swamp, levee < upland < back swamp and levee < upland < back swamp for total, organic, nitrate and ammonium nitrogen respectively, that for silt fraction increased as back swamp < levee < upland, levee < upland < back swamp, levee < upland < back swamp and levee < upland < back swamp for total, organic, nitrate and ammonium nitrogen respectively while that for clay size fraction varied as back swamp < upland < levee for total and organic nitrogen, upland < back swamp < levee and levee < back swamp < upland for total for nitrate and ammonium nitrogen respectively. Whereas total and organic N contents of bulk soil and grain size fractions were higher in top than subsoil, the reverse was the case for nitrate and ammonium nitrogen in most land units. In most land units, N (total, organic, nitrate and ammonium) contents in grain size particle fractions were better than concentrations of the bulk soil.

Total N enrichment in the sand and silt grain sized fractions increased in the order levee < back swamp < upland and in clay size fraction as back swamp < upland < levee. Also sand and silt grain sized fractions were more enriched in total N for top soils of upland and levee and subsoil of back swamp, with clay fraction better amongst grain sized fractions of the land units. Enrichment of organic N in the sand fraction increased in the order levee < back swamp < upland, silt as levee < upland < back swamp and clay as back swamp < upland < levee. Sand and silt fraction enrichment of the topsoil with organic N was better in upland and levee and subsoil in the back swamp land units while that for clay fraction was in top soil of all land units. Clay fraction was more enriched in organic N than other grain sized fractions in the land units. Nitrate enrichment of sand and silt fractions increased in the sequence levee < upland < back swamp and clay fraction as upland < levee < back swamp. Whereas subsoils were more enriched in sand fractions of back swamp, levee and upland, silt fraction of levee and back swamp and clay fraction of back swamp, topsoil was for the other grain size fractions of the land units. Enrichment of ammonium N in the sand, silt and clay grain sized fractions increased in the order levee < upland < back swamp with sub soils better in sand, silt and clay fractions of upland, sand and silt fractions of levee and silt fraction of back swamp.

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Soil properties especially sand, silt, clay, Bd, pH, OC, available P and ECEC influenced N (total, organic, nitrate and ammonium) contents in bulk soil and soil grain size fractions. Nitrogen content of the bulk soils was affected by concentrations of the grain size fractions.

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