Seasonal changes in physico-chemical properties of River sediments in Agbabu areas, Nigeria: Insight from principal component analysis

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Abstract: The paper assesses the seasonal changes in the physico-chemical properties and the textural characteristic of the sediments for the duration of 2008 to 2009. The study appraises variations of physico-chemical parameters such as P, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, pH, EC, TN, TOC and CEC during the dry and rainy seasons. Texturally, the sediment composed mostly of sand size particles with small aggregates of silt and clay particles. The silt and clay fractions of sediments were enriched during dry season but depleted during the rainy season. The pore water pH is slightly acidic with values varying between 4.42 – 6.74 and 4.36 – 6.20 during the dry and rainy seasons respectively. The mean pH values of 5.58 and 5.44 for the periods of dry and rainy seasons respectively fall below the World Health Organisation (WHO) threshold standards of 6.5 - 8.5. A significant increase in TOC, CEC, TN, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} during the dry season is attributed to the increase in the percentage of fine materials (i.e. clay and silt) and organic matter constituents in the sediments. Principal component analysis (PCA) performed identified three extracted components namely comp. 1, comp. 2 and comp. 3. The Fe oxide, Mn oxide, TOC and the clay components of sediments are controlling the variation in the physico-chemical characteristics. The cluster analysis results corroborated the observed pattern in the principal component analysis.

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1. Introduction

In the study areas, the problem of river water and sediment contamination has been of great concern to the rural dwellers. This is due to extent of deterioration of the environment and water bodies by human activities, mainly from on-loading and off-loading of petroleum products at the southern part of the study area. The indiscriminate discharge of sewages and solid wastes into the surroundings which eventually enter the natural water bodies could adversely affect the aquatic ecosystem. The supply ways of the metals entering the natural waters are governed by a dynamic set of physico-chemical influences while their solubility are mostly controlled by pH, concentration, nature of metal species, organic ligands, the oxidation condition of mineral components and the redox state of the aquatic system (Lala et al., 2008; Koffi et al., 2014). Metals were adsorbed onto both inorganic and organic particulates and are thus incorporated into sediment which led to elevated concentration of heavy metals in bottom sediments (Ochieng et al., 2007; Liu et al., 2009). Physico-chemical properties play an essential role in the evaluation of water quality. The accretion of metals from the water body to the sediment depends on a number of external environmental factors such as pH, - (DO), - (EC) and the available surface area for adsorption due to the changes in grain size distribution (Davies et al., 2006). Nonetheless, metals are not continually fixed by sediments. Metals incorporated in the sediments may be re-activated and released back to waters. This takes pace through the changes of environmental conditions such as acidification, redox potential, and the organic ligand levels which adversely affect the living organisms (Liu et al., 2009). This research was carried out to illustrate the seasonal changes in the physico-chemical properties of bottom sediments using multivariate statistical analytical techniques. This will in turn reveal the principal factors responsible for seasonal variations in the physico-chemical properties of the studied bottom sediments.

2. Material and Methods

2.1 Particle-size distribution

Size distribution analysis was carried out using Bouyoucous hydrometer methods as modified by Day (1965). Sediment samples were deflocculated with sodium haxametaphosphate solution (Calgon 44g/L) and sodium carbonate (8g/L). The pH of the solutions were adjusted to about 8.3. The particle size distribution was determined using the textural triangular diagram.

2.2 Determination of pore water pH

The pH of the pore water in the sediments was determined by using 1:2.5 ratio of sediment to deionised water to form slurry. The measurement of pH was carried out using Corning pH meter Model 7 according to Jackson (1964).

2.3 Determination of total organic carbon

The total organic carbon in the sediments was determined by the wet combustion method of Walkey and Black (1934) as modified by Jackson (1964).

2.4 Exchangeable cations

Exchangeable Na^+, K^+, Ca^{2+}, and Mg^{2+} were determined at neutral pH (i.e. pH 7) with ammonium acetate ($C_2H_3O_2NH_4$) extraction method proposed by Thomas (1992). The filtrate was analysed for Na^+ and K^+ by photoelectric flame photometer, but Ca^{2+} and Mg^{2+} were determined by ethylene diamine tetra acetic (EDTA) titration method.

2.5 Available phosphorus

The available phosphorus in the sediment was measured using Bray and Kurt No. 1 methods as modified by Jackson (1964).

2.6 Total nitrogen

Total nitrogen in the sediment samples were determined using macro Kjadah's methods as described by Bremner (1965).

2.7 Statistical analyses

Descriptive statistical parameters such as mean, standard deviation were calculated along with Pearson's correlation coefficient. Multivariate statistics in term of dendogram hierarchy cluster analysis (DHCA) and principal component analysis (PCA) were also carried out. PCA is an unverified configuration method with Varimax rotation and Kaiser Normalisation. This is commonly used for dimension reduction of data and extraction of a small number of principal components. This was used for discovering the possible comparable pattern in the behaviour of metals and analyzing relationships among the observed various variables (Loska and Wiechuła, 2003). Principal component analysis is consequently used to analyze relationships among the observed physico-chemical parameters and identify possible underlying factors for seasonal changes. This was carried out using the SPSS V17.0 for Windows. Dendogram hierarchy cluster analysis (DHCA) combines all physico-chemical parameters together and could be used to ascertain similarities and differences between them. This could provide details to further verify the results of the PCA analysis. Dendogram groups the elements as clustering variable using Euclidian distance and Ward procedure (Laursen et al., 2014).

3. Results and discussion

3.1 Sediment texture analyses

Textural constituents of sediments varied among the five sampling points in the study areas (Table 1). The studied sediment composed mainly of sand with an admixture of silt and clay. Sand components range between 5.50 – 90.50% followed by clay fraction (6.18 – 59.25%) and silt constituents (3.23 – 46.10%). Sand fraction is higher in most of the studied samples ~~in~~ during the rainy season but higher in silt and clay in the dry season. Nonetheless, OLWS4 has higher constituents of silt during rainy season. Different combinations of sediments texture observed are due to the transport of sediments from one place to another which are always associated with tidal currents (Satheeshkumar and Khan, 2009). Correlation matrix revealed significant positive correlation of silt and clay components with all considered physico-chemical parameters during dry season but with the exception of pH during rainy season (Table 3).

3.2 Physico-chemical parameters of sediments

3.2.1 Pore water pH

Statistical evaluation of the physico-chemical properties of the sediments revealed that the average pH varied between 4.42 – 6.74 during the dry season and 4.36 – 6.20 during the rainy season. Average pH of sediment for dry and rainy seasons were 5.58 and 5.44 respectively, with average pH of 5.51. This is slightly acidic but below WHO threshold standards of 6.5 - 8.5. Slight difference was recorded in pH levels during dry and rainy seasons (Fig. 1 & Table 2). The pH values were lower during the rainy season months than during the dry season. This is similar to research data available in literature (Jamabon, 2011; Daka and Moslen, 2013; Nwadinigwe et al., 2014). Commonly, the pH of bioleaching process of contaminated sediments is dependent on the buffering capacity, which determines metals to be released from sediments (Chen and Kin, 2001; Bartoli et al., 2012). Usually, variations in pH values during different seasons could be attributed to factors like removal of CO_2 by photosynthesis through bicarbonate degradation, temperature and organic matter decay.

3.2.2 Total organic carbon (TOC)

Average values of TOC ranged from 1.05 to 4.15% during the dry season and 0.07 to 2.24% during the rainy season (Fig. 1). The distribution of TOC closely followed the particle size distribution of the sediment. The sediment with low clay content also have low TOC and as the clay content increased, the TOC content also increased (Saravanakumar et al., 2008 and reference therein). In the present study, lower value of TOC was obtained during rainy season than during dry season for samples code-named AGM2, OLSW3 and OLSW4. Average TOC of sediment for dry and rainy seasons were 2.84 and 1.20

respectively, with average TOC of 2.02 (Table 2).Correlation analysis revealed significant positive correlation of TOC with pH during dry season (Table 3). There is a significant difference in TOC levels of sediments during the dry and rainy seasons. An increase in TOC during the dry season may be ascribed to the increased percentage of finer materials in the sediments (clayey and silt sediments), temperature and fast organic matter decay.

3.2.3 Total nitrogen (TN)

Average TN in the sediments varied between 0.12 – 0.37% during the dry season and 0.03 – 0.21% during the rainy season. The variation in the concentration of TN is influenced by the textural nature of the sediments (i.e. percentage of fines). Table 2 shows lower value of TN during the rainy season than the dry season for samples code-named AGM2, OLSW3 and OLSW4. Average total nitrogen obtained for the dry and rainy seasons were 0.24 and 0.13 respectively, with average TN of 0.18 (Table 2). Total nitrogen showed a significant positive correlation with pH and TOC during the dry season but only correlate with TOC during the rainy season (Table 3). The significant difference in total nitrogen levels during the dry and rainy season is perhaps due to the oxidation of dead plant organic matter in the sediments. The lower value of total nitrogen recorded during the rainy season may be ascribed to low quantity of organic matter and low quantity of finer materials which is caused by the winnowing action of waves. Dye (1978) observed high TN content in finer materials and attributed it to trapping of detritus by finer particles, which usually lead to increase in bacterial population. This may also be a reason for the high level of total nitrogen encountered in the present study.

3.2.4 Cation exchange capacity (CEC)

Average cation exchange capacity varied between 10.98 – 24.03cmol$_c$kg^{-1} during the dry season and 9.63 – 20.98% during the rainy season. Table 2 shows low cation exchange capacity during the rainy season and high during the dry season for samples code-named AGM2, OLSW3 and OLSW4. The average cation exchange capacity of sediments for the dry and rainy seasons were 18.91cmol$_c$kg^{-1}and16.25cmol$_c$kg^{-1}respectively, with average CEC of 17.58cmol$_c$kg^{-1} (Table 2). Cation exchange capacity shows strong correlation with all physico-chemical parameters but does not correlate with pH during rainy season (Table 3). There is a significant difference in CEC levels during the dry and rainy seasons. This is ascribed to the differences in the quantity of finer materials and organic matter in the sediments. Cation exchange capacity commonly increases as grain size decreases, but this relation is not true for many stream sands and silts that contain important percentages of rock fragments. Instead, a minimum CEC is measured in the fine-sand to coarse silt range where the fewest clay aggregates occur (Kennedy, 1965).

Table 1: Seasonal variations of sediment composition at the studied areas (*n = 3*)

Dry season							
Sample	Sand (%)		Silt (%)		Clay (%)		Textural class
	Mean	Stdev.	Mean	Stdev.	Mean	Stdev.	
AGM2	11.50	0.29	30.00	0.00	58.25	0.25	Silty clay
OLSW1	59.00	0.00	3.75	0.25	37.50	0.29	Sandy clay
OLSW2	59.75	0.25	4.00	0.00	36.50	0.29	Sandy clay
OLSW3	5.50	0.29	35.50	0.29	58.75	0.47	Clay
OLSW4	5.50	0.29	35.00	0.00	59.25	0.03	Clay
OKCtr	NA						
Rainy season							
Sample	Sand (%)		Silt (%)		Clay (%)		Textural class
	Mean	Stdev.	Mean	Stdev.	Mean	Stdev.	
AGM2	75.95	0.10	4.10	0.06	20.20	0.08	Silty clay
OLSW1	60.20	0.12	3.23	0.22	36.78	0.13	Sandy clay
OLSW2	59.50	0.15	3.43	0.10	36.75	0.19	Sandy clay
OLSW3	75.54	0.24	4.13	0.05	20.08	0.04	Clay
OLSW4	11.45	0.05	46.10	0.04	42.53	0.03	Clay
OKCtr	90.50	0.29	3.98	0.06	6.18	0.10	NA

3.2.5 Total phosphorous (TP)

Total inorganic phosphorus ranged from 5.45 to 23.88µgg^{-1} during the dry season and 4.30 to 24.83µgg^{-1} during the rainy season. Figure 1 shows high value of total phosphorous during the rainy season for samples code-named OLSW1, OLSW2 and OLSW4. Similarly, high total phosphorous was recorded during the dry season for samples code-named AGM2 and OLSW3. The average total phosphorous present in the sediments during the dry and rainy seasons were 16.00µgg^{-1} and 13.23µgg^{-1} respectively, with average total value of 14.61µgg^{-1} (Table 2).

Table 2: Average concentration of physico-chemical parameters for dry and rainy seasons in sediment of the study area

Variables	Mean for dry season	Mean for rainy season	Average for dry and rainy season
pH	5.58	5.44	5.51
TOC (%)	2.84	1.20	2.02
TN (%)	0.24	0.13	0.18
P (µg/g)	16.00	13.23	14.61
CEC(cmol$_c$kg^{-1})	18.91	16.25	17.58
K^+ (cmol$_c$kg^{-1})	1.50	1.32	1.41
Na^+(cmol$_c$kg^{-1})	0.77	0.64	0.70
Ca^{2+}(cmol$_c$kg^{-1})	5.37	3.68	4.52
Mg^{2+}(cmol$_c$kg^{-1})	3.04	2.82	2.93
Mn^{2+}(cmol$_c$kg$_{-1}$)	0.19	0.54	0.37

Total phosphorous correlates with all considered physico-chemical parameters during the dry season but do not correlate with only pH during the rainy season (Table 3). The higher values observed during the dry season may be ascribed to dead organic matter from the top layer. Whereas lower values obtained during the rainy season may be related to the removal of top layer of sediments by heavy floods (Saravanakumar et al., 2008).

Table 3: Pearson's correlation matrix of sediment samples during dry and rainy seasons

	pH	TOC	TN	P	K^+	Na^+	Ca^{2+}	Mg^{2+}	Mn^{2+}	CEC	Sand	Silt	Clay
Dry season													
pH	1												
TOC	0.276	1											
TN	0.346	.980**	1										
P	0.259	.999**	.974**	1									
K^+	0.331	.961**	.963**	.955**	1								
Na^+	0.221	.978**	.966**	.975**	.990**	1							
Ca^{2+}	0.371	.994**	.989**	.991**	.957**	.963**	1						
Mg^{2+}	0.381	.988**	.992**	.983**	.982**	.979**	.994**	1					
Mn^{2+}	0.294	.989**	.975**	.984**	.986**	.993**	.981**	.990**	1				
CEC	0.522	.960**	.968**	.953**	.937**	.924**	.982**	.979**	.958**	1			
Sand	.730*	-0.452	-0.363	-0.47	-0.36	-0.478	-0.36	-0.34	-0.421	-0.195	1		
Silt	0.144	.991**	.963**	.992**	.949**	.981**	.971**	.966**	.979**	.915**	-0.566	1	
Clay	0.64	.915**	.931**	.907**	.902**	.871*	.951**	.949**	.911**	.987**	-0.055	.852*	1
	pH	TOC	TN	P	K^+	Na^+	Ca^{2+}	Mg^{2+}	Mn^{2+}	CEC	Sand	Silt	Clay
Rainy season													
pH	1												
TOC	-0.678	1											
TN	-0.711	.948**	1										
P	-.978**	.738*	0.712	1									
K^+	-0.725	.808*	0.647	.841*	1								
Na^+	-.982**	0.686	0.674	.992**	.778*	1							
Ca^{2+}	-.833*	0.65	0.555	.912**	.824*	.919**	1						
Mg^{2+}	-0.379	0.434	0.265	0.54	.753*	0.497	.750*	1					
Mn^{2+}	-0.643	0.072	0.236	0.54	0.023	0.634	0.516	0.007	1				
CEC	-.786*	.735*	0.682	.870*	.854*	.842*	.918**	.834*	0.372	1			
Sand	0.551	-.900**	-.816*	-0.597	-.751*	-0.523	-0.41	-0.207	0.186	-0.47	1		
Silt	-0.65	.732*	0.639	0.685	.809*	0.606	0.448	0.265	-0.133	0.488	-.900**	1	
Clay	-0.268	.855*	.804*	0.316	0.471	0.267	0.24	0.079	-0.216	0.313	-.848*	0.531	1

Correlation(r) are significant at the 0.05 level (2-tailed); TOC: Total organic carbon; TN: Total nitrogen; pH: Acidity.

3.2.6 Potassium and sodium

Potassium ranged from 0.68 – 2.30$cmol_ckg^{-1}$ during dry season and 0.08 – 3.24$cmol_ckg^{-1}$during rainy season. The amount of potassium was found to be fluctuating during the period of investigation. The average values of potassium in the sediments during the dry and rainy seasons were 1.50$cmol_ckg^{-1}$ and 1.32$cmol_ckg^{-1}$ respectively, with average value of 1.41$cmol_ckg^{-1}$. The maximum value of potassium was obtained in sample code-named OLWS4 during the rainy season. Sodium varies between 0.25 - 1.25$cmol_ckg^{-1}$ during the dry season and 0.08 – 1.27$cmol_ckg^{-1}$ during the rainy season. Average values of sodium for the dry and rainy seasons are 0.77$cmolkg^{-1}$ and 0.64$cmol_ckg^{-1}$ respectively, with average value of 0.70$cmol_ckg^{-1}$.The maximum value of sodium was observed in the sample code-named OLWS4 during the rainy season (Figure 1). Sodium and potassium ions showed significant positive correlations with pH, TOC, TN and P during the dry season but they did not correlate with pH during the rainy season (Table 3).

3.2.7 Calcium, magnesium and manganese

Calcium varied between 2.65 – 7.48$cmol_ckg^{-1}$during dry season and 1.02 – 5.49$cmol_ckg^{-1}$during rainy season. The average value of calcium in the sediment during the dry and rainy seasons were 5.37$cmol_ckg^{-1}$ and 3.68$cmol_ckg^{-1}$ respectively, with average value of calcium which is 4.52$cmol_ckg^{-1}$. The maximum value of calcium was obtained in samples code-named OLWS3 during dry season. Magnesium range from 1.55 – 4.38$cmol_ckg^{-1}$ during dry season and 1.29 – 5.66$cmol_ckg^{-1}$during rainy season. Average magnesium values for the dry and rainy seasons were

3.04cmol$_c$kg^{-1} and 2.82cmol$_c$kg^{-1} respectively, with average value of 2.93cmol$_c$kg^{-1}.

The maximum concentration of magnesium was obtained in sample code-named AGM2 during the rainy season (Figure 1). Calcium and magnesium ions have significant positive correlation with all physico-chemical parameters during the dry season but they did not correlate with only pH during the rainy season. Manganese ranged between 0.07 – 0.30 cmol$_c$kg^{-1} during the dry season and 0.02 – 2.62 cmol$_c$kg^{-1} during the rainy season. Average manganese values for the dry and rainy seasons were 0.19cmol$_c$kg^{-1} and 0.54cmol$_c$kg^{-1} respectively, with average value of 0.37cmol$_c$kg^{-1}. The concentration maxima for manganese was obtained in the sample code-named OLSW3 during rainy season (Figure 1). Manganese ions strongly correlate with all physico-chemical parameters during the dry season but did not correlate with only pH during the rainy season (Table 3).

Table 4: Principal Component Analysis of sediments showing variations in physico-chemical parameters during dry and rainy seasons

	Rainy season				Dry season		
Variables	Comp. 1	Comp. 2	Comp. 3	Communalities	Comp. 1	Comp. 2	Communalities
Sand	-0.97			0.98		0.92	0.99
Clay	0.92			0.85	0.94		0.99
TOC	0.87			0.96	0.99		0.99
TN	0.83		0.42	0.89	0.99		0.98
Silt	0.79			0.74	0.98		0.99
Mg^{2+}		0.98		0.97	0.99		0.99
CEC		0.78	0.48	0.94	0.97		0.99
K^{+}	0.58	0.77		0.97	0.98		0.96
Ca^{2+}		0.72	0.61	0.95	0.99		0.99
Mn^{2+}			0.96	0.98	0.99		0.99
pH	-0.42		-0.81	0.97		0.94	0.99
Na^{+}		0.481	0.78	0.99	0.98		0.98
P	0.44	0.53	0.71	0.98	0.99		0.99
EV	8.43	2.44	1.30		10.90	1.96	
VAR (%)	64.86	18.78	9.97		83.86	15.04	
CVAR (%)	64.86	83.64	93.61		83.86	98.90	

EV =Eigen value, VAR (%) = variance percentage and CVAR (%) = cumulative variance

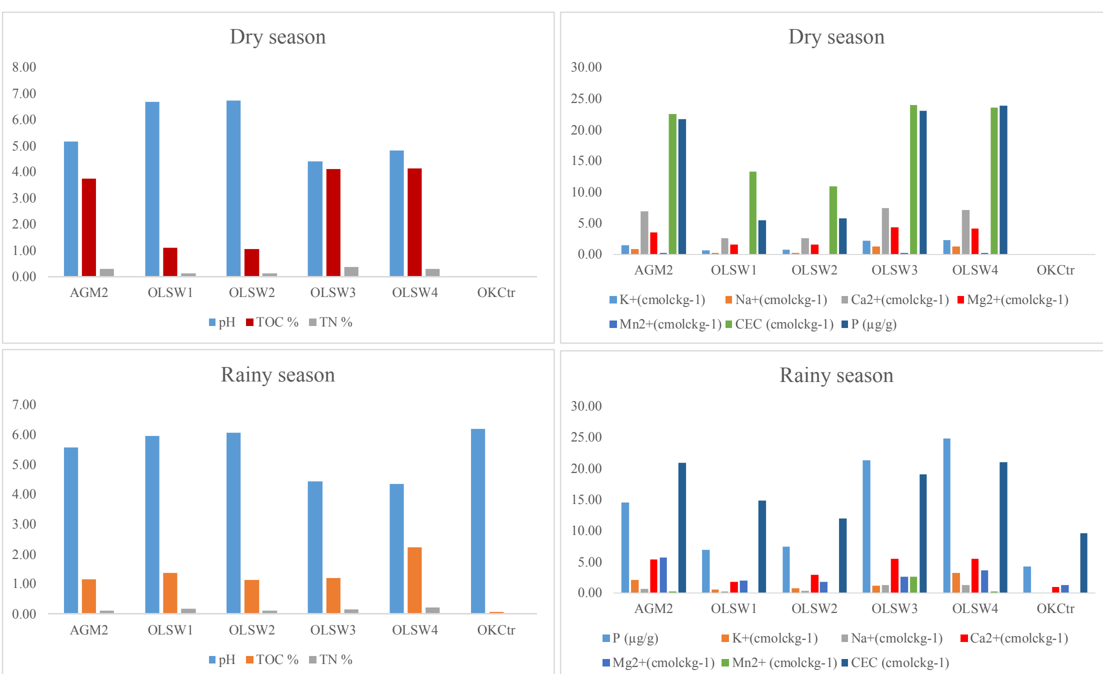

Fig. 1: Seasonal changes of selected physico-chemical parameter levels in the sediments through dry and rainy seasons.

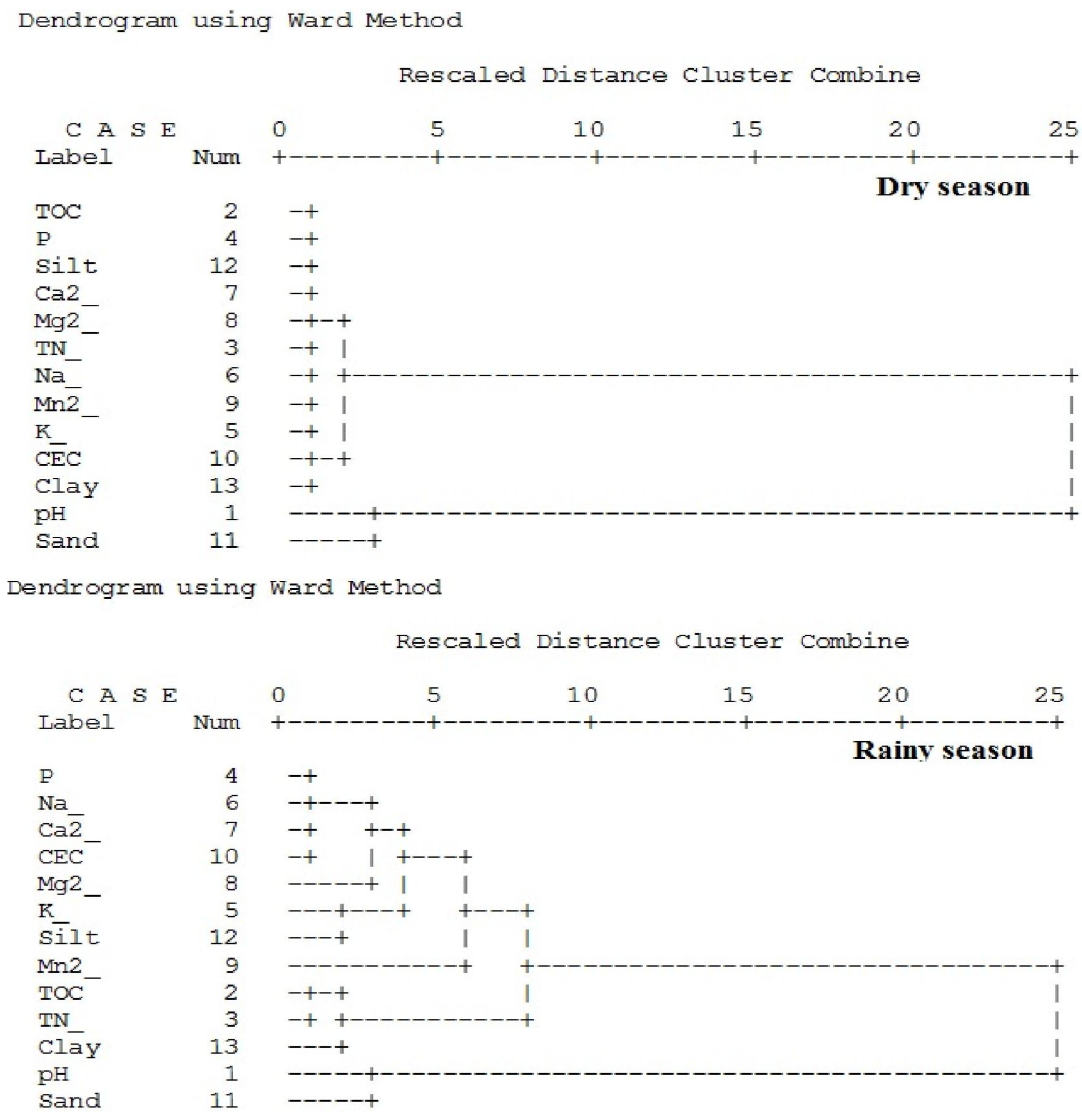

Figure 2: Dendogram cluster analysis of sediments during dry and rainy seasons.

4. Principal Component Analysis of seasonal variation in sediments

The results of output of principal component analysis of sediments collected during the dry and rainy seasons using SPSS version 17 is shown in Table 4. Two components were extracted during the dry season which suggests insufficient physical mixing of sediments. Component 1 contributes 83.86% of the data total variation and comprises of strong positive loadings of silt, Mg^{2+}, Ca^{2+}, Mn^{2+}, K^{+}, TOC, TN, CEC and clay which suggest surface area as the controlling factor. Component 2 contains 15.04% of the data total variation and shows strong positive loadings of pH and sand materials which indicate the pH of the interstitial pore as the controlling factor. Three components were extracted from sediment samples collected during the rainy season. Components 1 showed strong loadings of P, K^{+}, TN, TOC, silt and clay and its represents 64.86% of the total data variation indicating organic matter constituents as the principal factor. Components 2 contains strong loadings P, K^{+}, Na^{+}, Ca^{2+}, Mg^{2+} and CEC and contributes about 18.78% to the total data variation suggesting surface area of the finer component of river sediments.

Components 3 showed positive loadings of P, Na^{+}, Mn^{2+}, Ca^{2+}, TN and CEC and represents 9.97% of the total data variations. This indicated that the data variations are partly controlled by organic matter and surface area. Dendogram cluster analysis corroborated the principal component analysis results by showing two cluster groups; Cluster 1 consists of Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, P, TN, TOC, CEC, silt and clay whereas cluster group 2 comprises of pH and sand (Figure 2). The PCA performed revealed that Fe oxide, Mn oxide, TOC and clay components of the sediments are controlling the metals distribution.

5. Conclusions

Investigative study of the seasonal changes on the physico-chemical characteristics of the sediments in the studied areas revealed that the sediments were mostly composed of sand sized particles with finer materials (i.e. silt and clay). The sand constituents of investigated sediments were higher during the rainy season but the sediments were enriched in silt and clay fractions during the dry season. The pH values of studied sediments were slightly acidic but fall below WHO threshold standards of 6.5 - 8.5. Insignificant differences in pH levels were observed in the sediments during the dry and rainy seasons.

A significant increase in TOC, CEC, TN, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} during the dry season is attributed to increase in the percentage of finer materials (i.e. clay and silt) and organic matter in the sediments. Principal component analysis revealed that the TOC and percentage of fine materials are controlling the varying level of physico-chemical parameters. The cluster groups verified the observed pattern in the principal component analysis.

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