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Assessing the Impacts of Coastal Activities on the Water Quality of Qua Iboe River Estuary, South-South, Nigeria.

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Abstract: Studies on the impacts of coastal activities on water quality of Qua Iboe River Estuary in Akwa Ibom State, South- South Nigeria was conducted for 12 months (between May 2015 and April 2016) with the aim of Understanding the current sources of contaminants concentration in the system and provide a model which allows policy-makers and local actors to design programs and policies to improve the existing practices and mitigate future problems. Water samples were collected monthly in five stations along the estuary and analyzed using standard procedures. Mean values obtained for physico-chemical parameters of water samples in wet and dry season were as follows: pH (7.69±0.29 and 7.79±0.38), temperature (26.19±0.05 and 26.72±0.08 ^{o}C), electrical conductivity (34562.59±8905.32 and 35049.25±9058.56 µs/cm), total dissolved solids (17949±469.71 and 17964.84±46.83.07 mg/l), dissolve oxygen (6.20±0.09 and 5.97±0.12 mg/l), chlorides (10391.06± 2811.82 and 10703.90±2811.82 mg/l), turbidity (23.58±3.77 and 25.31±4.74 NTU), total suspended solids (40.98±5.78 and 43.43±4.00 mg/l), bicarbonate (84.29±20.75 and 92.68±22.85 mg/l), alkalinity (68.86±16.94 and 75.32±18.53mg/l), biochemical oxygen demand (2.15±0.15 and 2.07±0.44 mg/l), chemical oxygen demand (145.56±38.08 and 129.60±33.82mg/l), total hydrocarbon content (6.55±2.09 and 6.62±2.33 mg/l) total organic carbon content (8.42±3.06 and 9.44±3.47 mg/l), nitrate (28.45±7.00 and 29.00±7.08 mg/l), phosphate (4.02±1.31 and 4.25±1.38 mg/l), sulphate (2038.57±560.89 and 2160.20±585.28 mg/l) and ammonia (11.28±4.19 and 16.96±4.23 mg/l) respectively. Silicates were below detectable limits in the water samples. Physico-chemical parameters (electrical conductivity, total dissolved solids, chloride, turbidity, chemical oxygen demand, sulphate and ammonia) exceeded the permissible WHO Standard for surface water. Analysis of variance and paired sample t-test revealed significant (p = 0.05) spatial and seasonal variations respectively. Correlation analysis revealed strong positive relationships amongst physicochemical parameters of water. Multivariate analytical techniques (PCA and HCA) imprinted that the estuary is a continuum in environmental block swayed by multiple contamination sources. However, the series of activities evident, coupled with the findings of this study further vindicate the need for proper monitoring and management of our indigenous water bodies.
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1. Introduction

The negative impacts on the natural environment due to various coastal activities are becoming an increasing concern among stakeholders and the public at large. Coastal activities include fishing, farming, dredging, oil exploration and seismic activities, gas flaring and indiscriminate disposal of sewage and domestic wastes. Today the environment has become foul, contaminated, undesirable, and therefore harmful for the health of living organisms, including man due to the negative impact of coastal activities.

Water is essential for life on earth. It is the most naturally occurring mineral compound and its relevance cannot be overemphasized (WHO, 2011). Increasing human population alongside progressive urbanization has led to a replacement of the world's natural environment with an artificial one. Pollution growth is a global problem that affects water, soil and the atmosphere. Almost every environmental issue today has man at the receiving end of the blame. Man has become the principal driver of change on the earth's surface and for the first time, a single biological species rivals or even surpasses the ability of geophysical forces to shape the earth.

In different parts of Nigeria, rivers are used for disposal of refuse, human sewage, and waste waters from residential areas, abattoirs and industries (Fagade *et. al.,* 1993). Storm water runoffs and discharge of sewage into rivers are two common sources of nutrients in aquatic ecosystem that results in their pollution (Sudhira and Kumar, 2000; Adeyemo, 2003). Rapid industrialization has direct and indirect adverse effects on our environment (Nasrullah *et. al.,* 2006). This has led to an increase in generation of industrial effluents which when discharged untreated, would result in water, sediment and seafood contamination (Wakawa *et. al.,* 2008). Environmental degradation, deterioration and underdevelopment are top public issues both at national and international levels (Ekweozor and Agbozu, 2001).

Anthropogenic discharges due to coastal activities in aquatic ecosystems, reduces light penetration and transparency and these have adverse effect on the primary productivity and hence benthic community (Odiete, 1999). In some advanced countries, general monitoring of water quality is done on a regular basis (USEPA, 2014). Abnormal changes in the water quality can easily be detected and appropriate measures taken before the outbreak of epidemics (Wakawa *et. al.,* 2008). Several health stressors significantly deplete the biodiversity of aquatic ecosystems. Biodiversity loss and its effects are predicted to be greater for aquatic ecosystems than for terrestrial ecosystems (Sala *et. al*., 2000).

Research carried out in majority of the cities in Nigeria had discovered that industrial effluent is one of the key sources of surface water pollution in Nigeria (Ekiye and Zejiao, 2010). Industrial effluents when discharged directly into the rivers devoid of prior treatment have ability of escalating water quality parameters. Dada (1997) indicated that less than 10 % of industries in Nigeria treat their effluents before predisposing into the rivers. This has led to elevated load of inorganic metals in most of the water bodies (Wakawa *et. al*. 2008). The consequential effects of this will be on the receiving streams and rivers. The impacts might include water quality mutilation, reduction in fish abundance and effect on water-usage for recreation, industrial and domestic purposes. Elevated phosphate concentrations in these effluents could result into nutrient enrichment of the receiving water bodies thus leading to ecological tragedy.

It is therefore the aim of this study to evaluate the condition of the environment and examine the linkages between coastal activities and the observed status of the environment using multivariate statistical tool in modeling contaminants concentration which will help policy makers in the proper planning and monitoring in the event of pollution.

2.0 Materials and Methods

2.1 Description of study area

The Qua Iboe River Estuary (Figure 1) lies within latitude 4º 40´30´´N and longitude 7º 57´0´´E on the South Eastern Nigeria Coastline. It is a meso-tidal estuary having tidal amplitude of 1m and 3m at neap and spring phases respectively (Uwah *et.al.* 2013). The River originating from Umuahia hills traverses mainly sedimentary terrains of cretaceous to recent ages and develop into extensive meanders before emptying into the Atlantic Ocean. Creeks and channels island are common throughout the length of the estuary while sand bars occur at the mouth as a result of interplay between the long shore drift which runs approximately in a west- east direction (parallel to the shoreline) and the River current. The study area has some coastal plain sands which are not older than the quaternary age; the creeks have younger alluvial covers. Sediments are brought into the estuary by longshore drift, tidal flow, waves and river transport. Coarse to medium-grained sand occurs mostly in the mouth of the estuary and middle of the main channels where the tidal current is strong but most parts of the banks and creeks where the tidal current are weak are characterized by fine sand, silt and clay. The latter has high affinity for pollutants such as hydrocarbon and heavy metals (Uwah *et.al*. 2013).

The climate of the area is characterized by a long wet season usually lasting from May to November and a short period of dry weather from December to April. The QIRE is comprised of tidal creeks (most notably Stubb creek and Douglas creek), lagoons, wetlands, and tributaries fringed with mangrove vegetation made up of species of *Avicennia, Rhizophora* and *Nypa*. The coastal vegetation of the area is mainly thick mangrove swamp. The estuary is also rich with abundance of edible aquatic biota. The dominant shellfishes in the estuary include mangrove oyster, periwinkle, swimming crab, and mussel. These shellfishes are widely consumed by the coastal and estuarine communities in the Niger Delta as a delicacy and dietary protein supplement. The main occupation of the inhabitants includes large scale fishing employing the use of fishing vessels, small scale fishing by artisanal fishermen employing the use of fishing boats, farming activities involving the use of agrochemicals, boat construction, sand excavation for commercial purposes as well as timber logging of mangrove vegetation as fuel wood (Ekwere, *et. al*. 1992).

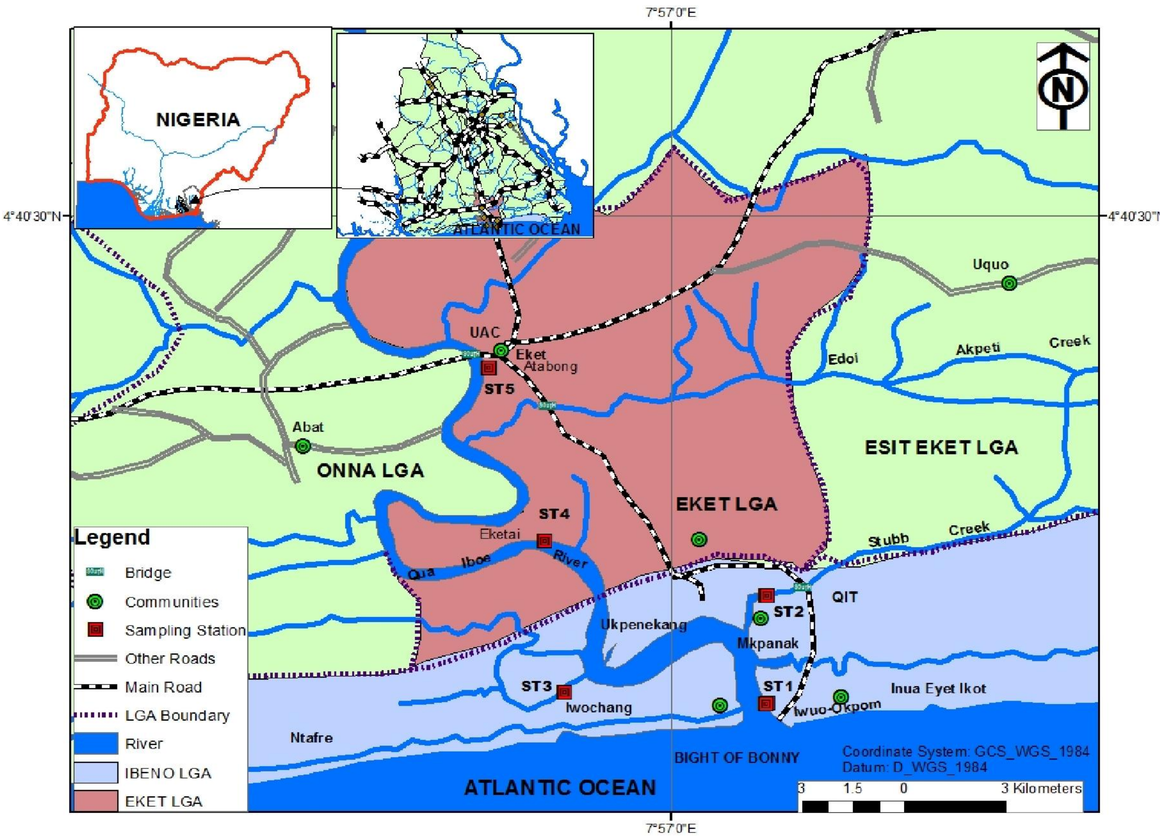

Fig. 1: Map of the study area showing sampling stations in Qua Iboe River Estuary

2.2 Sampling stations

The experimental sites were selected randomly in such a way that four sampling stations were selected with high coastal activities within the estuary and a station with low coastal activities along the River segment.

Station 1

Station 1 is the discharge point; it receives waste from the market and domestic waste from the inhabitants of the community. Other coastal activities in this station include, large scale fishing using fishing vessels, small scale fishing with motorized boats with possible oil and fuel spills from the boat engine and open defecation into the Estuary. Station 1 is a pure mangrove plots comprising of *Avicennia africana* cohabiting with *Achrostichum aureum.* This station is located at Iwuokpom between latitude 4^0 32´ N and longitude 7^0'58' E. (plate 1).

Station 2

Station 2 is the Exxon Mobil - QIT terminal. This is where off-loading of finished petroleum product from ship to pipelines is done and fishing activities is also high in this station. Other coastal activities include, large scale fishing using fishing vessels, small scale fishing with motorized boats with possible oil and fuel spills from the boat engine, gas flaring and disposal of domestic waste from inhabitants of the community into the Estuary. Station 2 is a mixed mangrove vegetation comprising *Nypa fruticans, Avicennia africana, Rhizophora mangle* and *Achrostichum aureum.* This station is located at Mkpanak between latitude 4^0 34´ 09.9'' N and longitude 7^0 58' 32.8'' E (plate 2).

Station 3

This is a commercial station with a large market located at the River side, domestic wastes from human households is being emptied into the River. Other coastal activities in this station include, large scale fishing using fishing vessels, small scale fishing with motorized boats with possible oil and fuel spills from the boat engine, boat construction, disposal of market / domestic waste and open defecation into the Estuary. This is a landing site for fishermen and distribution to other sectors and also a boat park for movement of goods and people within the estuarine communities. Station 3 is a characteristic of mono-specific mangrove vegetation subjugated by *Nypa fruticans* interlaced with few stands of *Elaise guineensis.* The station is located at Iwuochang between latitude 4^0 32´ N and longitude 7^0 55'E. (plate 3).

Station 4

Station 4 is the discharge point; it receives run-off from agricultural farmlands and wood industry sited 1.5 km from the river bank. Fishing activities in this station is minimal employing the use of motorized boat by artisanal fishermen and for transportation of wood with possible oil and fuel spill from the boat engine. Dredging is one of the major coastal activities sited in this station. Station 4 is a secondary swamp forest composed of diverse species such as *Pandanus candelabrum, Elaise guineensis, Pycnathus angolensis, Raphia hookeri, Musanga cercropiodes, Barteria nigritiana, Anthocleista djalonensis* with *Cytrospermum sengalensis, Afzelia nephtytis* and *Smilax anceps* as undergrowth. This station is located at Eketai between latitude 4^0 35' N and longitude 7^0 54'E (plate 4).

Station 5

Station 5 is the discharge point; it receives effluents from urban / drainage discharge, abattoir which is usually flooded during high tide, effluents from auto-mechanic workshop and car wash activities. A fringing vegetation dominated by species such as *Symphonia globulifara, Pandanus candelabrum, Cytrospermum senegalenses, Alstonia boonei, Elaise guineensis and Vossia cuspidate*. This station is located at Atabong between latitude 4^0 38' N and longitude 7^0 54' E (plate 5).

2.3 Sample collections / analysis

Water samples were collected in each of the sampling stations from May 2015 to April 2016. At all times sampling was carried out between 08:00 am and 12:00 noon each sampling day. Water samples for temperature, pH, dissolved oxygen, electrical conductivity, total dissolved solids and turbidity were measured *in situ* according to Standard Methods for Examination of Water and Waste water (APHA, 2005; AOAC, 2000). Water sample for biological oxygen demand, chemical oxygen demand phosphate, chloride, total suspended solids, nitrate and sulphate were collected using 250 ml glass bottle. The sample bottle was filled with water and stoppered under water, ensuring that no air bubble was trap in it. After collection, all samples were stored in ice-packed coolers and transported to the laboratory (Devine Concept Integrated Laboratory, Port Harcourt) for analysis based on the standard method has outlined by (APHA, 2005; AOAC, 2000).

2.4 Data analysis

Statistical package for Social Sciences (SPSS) version 20 was employed to compute Mean, variance and standard error in the data. Also, one-way analysis of variance (ANOVA) and Least Significant Difference (LSD) test were employed to separate significant differences in mean values computed for stations while paired sample t-test was used to compare seasons. The probability level was set at p = 0.05. Correlation analysis tested the association between various parameters along sampling stations. Hierarchical cluster analysis was used for stations classification and source apportionment while principal component analysis was employed to ordinate environmental variables into factor components.

3.0 Results

3.1Physico-chemical parameters

Summary of the data obtained on range values, seasonal mean and standard error on physico-chemical parameters studied between May, 2015 to April, 2016 is presented in Table 1.

Table I: Seasonal range, mean variation, standard error of physico-chemical parameters measured in Qua Iboe River Estuary for wet and dry season (May, 2015 – April, 2016)

Physico-chemical parameters	Units	Range (Wet Season)	Range (Dry Season)	Mean ± S.E (Wet Season)	Mean ± S.E (Dry Season)	WHO Permissible Limit
pH	-	6.54 – 8.15	6.31 – 8.28	7.69 ± 0.29	7.79 ± 0.38	6.5 – 9.0
Temperature	^oC	26.0 – 26.33	26.50 – 26.98	26.19 ± 0.05	26.72 ± 0.08	25 ^oC
Electrical conductivity	µS/cm	28.00 – 49993.33	26.93 – 50978.33	34562.59 ± 8905.32	35049.25 ± 9058.56	1400 µS / cm
Total Dissolve Solids	mg/l	14.40 – 27035.33	14.38 – 26706.17	17949.38 ± 4691.71	17964.84 ± 4683.07	1200 mg / L
Dissolved Oxygen	mg/l	5.97 – 6.47	5.72 – 6.30	6.20 ± 0.09	5.97 ± 0.12	5.0 mg / L
Chloride	mg/l	7.67 – 14611.33	7.50 – 15566.67	10391.06 ± 2677.21	10703.90 ± 2811.82	250 mg / L
Turbidity	NTU	10.35 – 33.88	7.42 – 34.07	23.58 ± 3.77	25.31 ± 4.74	5 NTU
Total Suspended Solids	mg/l	19.97 – 53.07	28.47 – 50.78	40.98 ± 5.78	43.43 ± 4.00	> 10
Bicarbonate	mg/l	1.96 – 114.35	1.71 – 120.28	84.29 ± 20.75	92.68 ± 22.85	-
Alkalinity	mg/l	1.72 – 93.37	1.47 – 97.67	68.86 ± 16.94	75.32 ± 18.53	500 mg /L
Biological Oxygen Demand	mg/l	1.57 – 2.40	1.63 – 2.50	2.15 ± 0.15	2.07 ± 0.14	50 mg / L
Chemical Oxygen Demand	mg/l	0.70 – 226.23	0.67 – 197.17	145.56 ± 38.06	129.60 ± 33.82	80 - 100 mg / L
Total Hydrocarbon	mg/l	0.05 -13.20	0.05 – 14.52	6.55 ± 2.09	6.62 ± 2.33	10 mg / L
Total Organic Carbon	mg/l	0.03 – 18.43	0.03 – 21.47	8.42 ± 3.06	9.44 ± 3.47	-
Nitrate	mg/l	0.67 – 37.93	0.86 – 38.28	28.45 ± 7.00	29.00 ± 7.08	50 mg / L
Phosphate	mg/l	0.03 – 8.24	0.04 – 8.71	4.02 ± 1.31	4.25 ± 1.38	250 mg/ L
Sulphate	mg/l	3.88 – 321.67	3.33 – 3254.83	2038.57 ± 560.89	2106.20 ± 585.28	500 mg / L
Ammonia	mg/l	0.56 – 22.62	0.51 – 23.63	17.28 ± 4.19	16.96 ± 4.23	0.5 mg / L
Silicon	mg/l	BDL	BDL	BDL	BDL	-

Where: S.E = Standard Error, WHO = World Health Organisation, BDL = Below Detectable Limit

3.2 Correlation matrix and hierarchical cluster dendrogram based on physico-chemical parameters (wet season)

During the wet season, significant positive correlation was observed between pairs of Physico-chemical parameters. (Table 2). Similar positive correlation was observed between pairs of Physico-chemical parameters during the dry season (Table 3).

Hierarchical cluster analysis (HCA) was used in the classification of the stations based on similarity of physico-chemical properties into primary groups. Figure 2 and Fig 3 reveal three primary cluster groups for the wet and dry season. During the wet season, cluster group 1 (Iwuochang, QIT and Iwuokpom) comprise of core estuarine habitats, whereas group 2 (Eketai) retains an intermediary gradient while group 3 (Atabong) is an outlier. Similar observation was also recorded for the dry season.

Table 2: Pearson's correlation matrix of physico-chemical parameters in water from Qua Iboe River Estuary (wet season)

	pH	^{0}C	EC	TDS	DO	Cl^-	Turbidity	TSS	HCO_3^-	Alkalinity	BOD	COD	THC	TOC	NO_3^-	PO_4^{3-}	SO_4^{2-}	NH_3
pH	1																	
Temperature	-.274	1																
EC	.993**	-.323	1															
TDS	.988**	-.327	.998**	1														
DO	.586	-.693	.615	.588	1													
Chloride	.988**	-.316	.998**	.994**	.645	1												
Turbidity	.833	.149	.764	.745	.270	.754	1											
TSS	.863	-.035	.796	.774	.409	.786	.980**	1										
Bicarbonate	.999**	-.246	.991**	.984**	.590	.989**	.842	.868	1									
Alkalinity	.998**	-.236	.991**	.984**	.589	.990**	.839	.862	.999**	1								
BOD	.949*	-.437	.959**	.945*	.806	.970**	.698	.765	.952*	.952*	1							
COD	.987**	-.301	.990**	.994**	.520	.980**	.775	.799	.981**	.980**	.915*	1						
THC	.855	-.253	.862	.886*	.218	.831	.651	.653	.837	.834	.698	.922*	1					
TOC	.764	-.021	.755	.782	-.019	.718	.676	.635	.749	.746	.543	.835	.966**	1				
Nitrate	.992**	-.297	.974**	.965**	.590	.966**	.863	.905*	.990**	.987**	.938*	.971**	.838	.748	1			
Phosphate	.842	-.255	.848	.873	.199	.816	.642	.645	.823	.820	.680	.912*	1.000**	.969**	.826	1		
Sulphate	.957*	-.427	.979**	.988**	.579	.970**	.656	.697	.947*	.947*	.917*	.985**	.915*	.797	.933*	.904*	1	
Ammonia	.996**	-.288	.981**	.971**	.616	.977**	.855	.895*	.995**	.993**	.954*	.971**	.821	.726	.998**	.808	.935*	1

* - Significant at P = 0.05; ** - Significant at P = 0.01

Table 3: Pearson's correlation matrix of physico-chemical parameters in water from Qua Iboe River Estuary (dry season)

	pH	^{o}C	EC	TDS	DO	Cl^-	Turbidity	TSS	HCO_3^-	Alkalinity	BOD	COD	THC	TOC	NO_3^-	PO_4^{3-}	SO_4^{2-}	NH_3
pH	1																	
Temperature	.152	1																
EC	.982**	.250	1															
TDS	.977**	.241	.999**	1														
DO	.192	.848	.199	.183	1													
Chloride	.975**	.276	.996**	.997**	.243	1												
Turbidity	.901*	.261	.849	.830	.339	.821	1											
TSS	.892*	.272	.833	.813	.383	.809	.998**	1										
Bicarbonate	.998**	.200	.985**	.979**	.224	.976**	.915*	.906*	1									
Alkalinity	.999**	`z.176	Azz	.974**	.213	.971**	.917*	.908*	1.000**	1								
BOD	.799	.464	.802	.801	.616	.848	.660	.683	.800	.796	1							
COD	.977**	.164	.994**	.996**	.112	.991**	.808	.790	.974**	.971**	.780	1						
THC	.734	-.133	.793	.807	-.387	.767	.493	.445	.724	.720	.354	.836	1					
TOC	.716	-.142	.779	.795	-.396	.758	.453	.405	.704	.699	.358	.826	.998**	1				
Nitrate	.975**	.211	.940*	.928*	.267	.921*	.975**	.969**	.981**	.983**	.744	.916*	.634	.604	1			
Phosphate	.789	-.014	.853	.864	-.269	.829	.571	.525	.785	.779	.437	.883*	.991**	.986**	.702	1		
Sulphate	.926*	.390	.977**	.980**	.292	.986**	.760	.745	.933*	.924*	.846	.967**	.761	.755	.865	.830	1	
Ammonia	.971**	-.057	.931*	.926*	-.015	.908*	.885*	.869	.963**	.968**	.647	.939*	.780	.758	.953*	.812	.834	1

* - Significant at P = 0.05; ** - Significant at P = 0.01

Table 4: Size, percentage total variation and cumulative percentage of correlation matrix of three components in the original data set of contaminants and physico-chemical parameters of Qua Iboe River Estuary (wet season)

Component	Eigen Values	% of Variance	Cumulative %
1	20.933	80.512	80.512
2	3.088	11.875	92.387
3	1.595	6.134	98.521

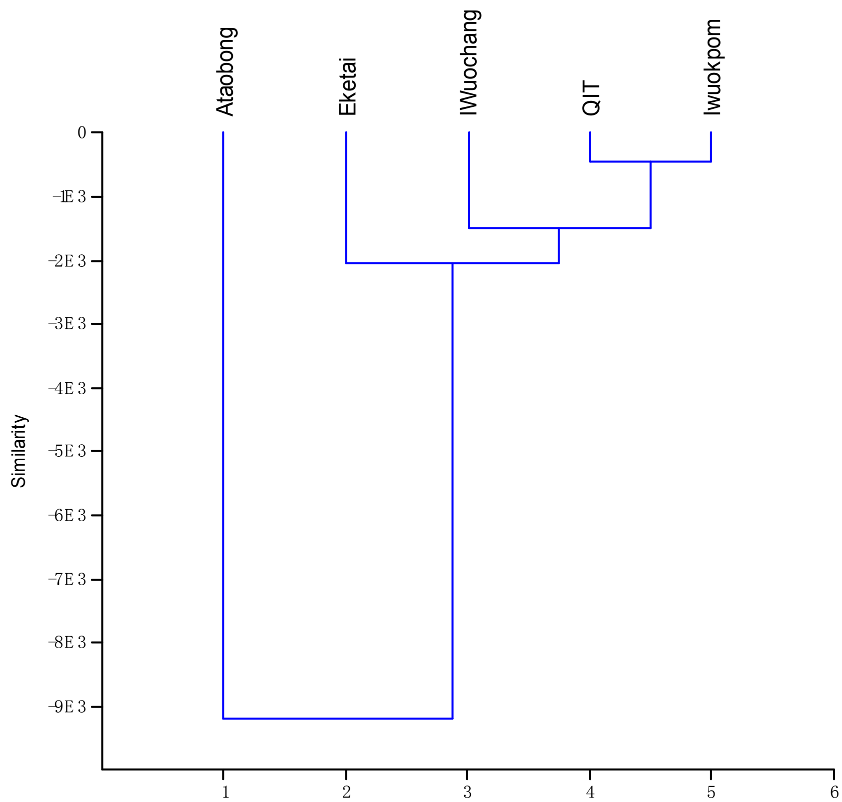

Fig. 2: Dendrogram showing spatial distribution of physico-chemical parameters in water (wet season).

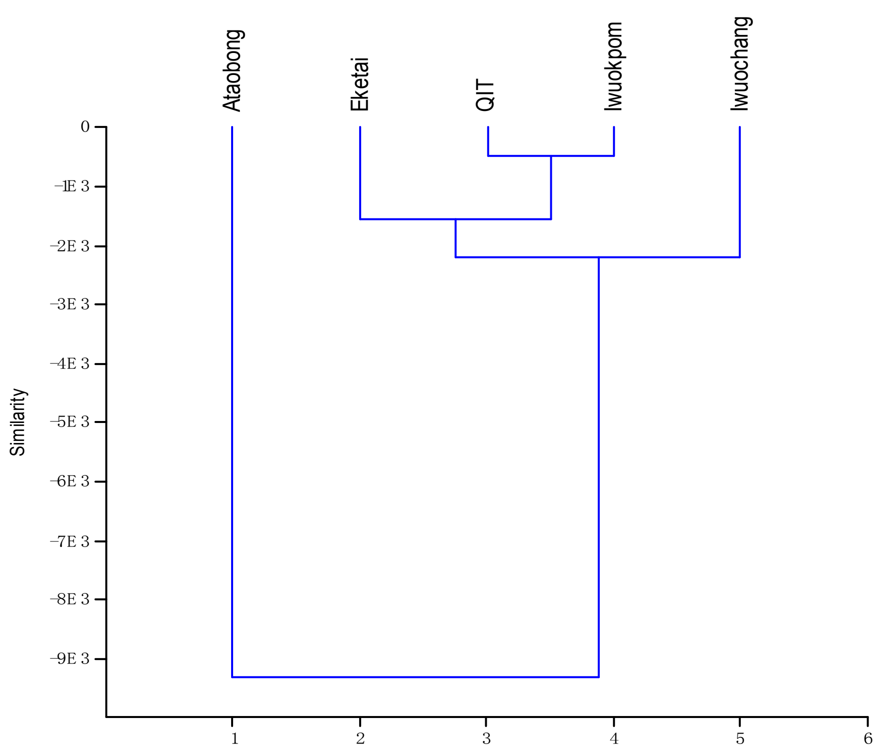

Fig. 3: Dendrogram showing spatial distribution of physico-chemical parameters in water (dry season).

3.4 Ordination of contaminants and physico-chemical parameters for wet and dry season in Qua Iboe River Estuary.

3.4.1 Ordination of contaminants and physico-chemical parameters of study area (wet season)

Ordination of physico-chemical parameters in water by principal component analysis with Varimax rotation distinguished 3 components with the sizes as shown on Table 4. The first component account for 80.51 % of the variations due to physico-chemical parameters in water while component 2 and 3 explained 11.87 % and 6.13 % respectively of the variations in the data. The first component therefore bears vital information required for explaining most of the variations due to physico-chemical parameters in water in this estuary. For convenience, each of these components so identified will have the designation "PC" and their loadings are shown in Table 5.

PC_1 (Primary substrate component): On this component, 13 parameters were spotted with characteristic high loadings. These were: total suspended solids (0.924), ammonia (0.914), alkalinity (0.903), turbidity (0.902), bicarbonate (0.902), nitrate (0.900), pH (0.887), biological oxygen dmand (0.884), chloride (0.860), electrical conductivity (0.847), total dissolved solids (0.817), chemical oxygen demand (0.802) and sulphate (0.726)

PC_2 (Secondary substrate component): In this component, 3 parameters loaded highly. These parameters were total organic carbon (0.879), phosphate (0.823) and total hydrocarbon (0.811).

PC_3 (Tertiary / Residual component): Component 3 had 2 significant loadings. These were temperature (0.934) and dissolved oxygen (0.702).

3.4.2 Ordination of contaminants and physico-chemical parameters of study area (dry season)

Ordination of physico-chemical parameters in water by principal component analysis with Varimax rotation distinguished 3 components with the sizes as shown on Table 6. The first component account for 77.39 % of the variations due to physico-chemical parameters in water while component 2 and 3 explained 15.09 % and 5.60 % respectively of the variations in the data. The first component therefore bears vital information required for explaining most of the variations due to physico-chemical parameters in water in this estuary. For convenience, each of these components so identified will have the designation "PC" and their loadings are shown in Table 7.

PC_1 (Primary substrate component): On this component, 14 variables were spotted with characteristic high loadings. These were: total suspended solids (0.960) nitrate (0.949), turbidity (0.949), alkalinity (0.913), pH (0.906), bicarbonate (0.904), ammonia (0.900), copper (0.880), electrical conductivity (0.817), chloride (0.803), total dissolved solids (0.800), chemical oxygen demand (0.794), biological oxygen demand (0.724) and sulphate (0.719).

PC_2 (Secondary substrate component): In this component, 3 parameters loaded highly. These parameters were TOC (0.899), THC (0.882) and Phosphate (0.860).

PC_3 (Tertiary/Residual component): Component 3 had 2 significant loadings. These were Temperature (0.955) and DO (0.860).

Table 5: Rotated component matrix of contaminants and physico-chemical parameters of Qua Iboe River Estuary (wet Season).

Arameters	Component		
	1	2	3
Zscore: pH	**.887**	.399	.233
Zscore: Temperature	-.069	-.016	**-.934**
Zscore: Elect Conductivity	**.847**	.413	.316
Zscore: TDS	**.817**	.461	.326
Zscore: DO	.628	-.336	**.702**
Zscore: Chloride	**.860**	.366	.324
Zscore: Turbidity	**.902**	.267	-.294
Zscore: TSS	**.924**	.213	-.142
Zscore: Bicarbonate	**.902**	.372	.211
Zscore: Alkalinity	**.903**	.369	.208
Zscore: BOD	**.884**	.156	.432
Zscore: COD	**.802**	.527	.275
Zscore: THC	.546	**.811**	.210
Zscore: TOC	.476	**.879**	-.032
Zscore: Nitrate	**.900**	.370	.212
Zscore: Phosphate	.528	**.823**	.206
Zscore: Sulphate	**.726**	.531	.429
Zscore: Ammonia	**.914**	.339	.222

Table 6: Size, percentage total variation and cumulative percentage of correlation matrix of three components in the original data set of contaminants and physico-chemical parameters of Qua Iboe River Estuary (dry season)

Component	Eigen Values	Total % of Variance	Total Cumulative %
1	20.122	77.392	77.392
2	3.924	15.092	92.484
3	1.457	5.605	98.089

Table 7: Rotated component matrix of contaminants and physico-chemical parameters of Qua Iboe River Estuary (dry Season).

Parameters	Component		
	1	2	3
Zscore: pH	**.906**	.410	.099
Zscore: Temperature	.080	-.005	**.955**
Zscore: Elect Conductivity	**.817**	.541	.202
Zscore: TDS	**.800**	.565	.200
Zscore: DO	.302	-.408	**.862**
Zscore: Chloride	**.803**	.532	.252
Zscore: Turbidity	**.949**	.103	.112
Zscore: TSS	**.960**	.049	.133
Zscore: Bicarbonate	**.904**	.405	.136
Zscore: Alkalinity	**.913**	.391	.113
Zscore: BOD	**.724**	.176	.543
Zscore: COD	**.794**	.589	.131
Zscore: THC	.433	**.882**	-.182
Zscore: TOC	.402	**.899**	-.175
Zscore: Nitrate	**.949**	.269	.106
Zscore: Phosphate	.493	**.863**	-.075
Zscore: Sulphate	**.710**	.594	.372
Zscore: Ammonia	**.900**	.414	-.136

4.0 Discussion

4.1 Seasonal and spatial variation in physico-chemical parameters in water

pH is an index of the hydrogen ion concentration and a very important environmental variable. The spatial variation in pH observed during the studies could probably be due to evapo-transpiration process, rainfall and the chemical and biological processes in the water (Mama and Ado, 2003). The range value of pH recorded in this study is consistent with the report of Akpan (2004) and Adebisi (1981). Seasonal variation was significant with higher pH in the dry season. This could be attributed to enhance photosynthetic activities by phytoplankton and other aquatic plants. Eyesink and Solomon (1981) reported that the uptake of carbon dioxide by algae for photosynthesis and carbon dioxide exchanged flanked by the surface water and atmosphere are accountable for pH increase during the dry season. Val Saraji *et al.* (1995) also recorded elevated pH on days of extreme photosynthetic activity. However, studies by Nweke (2000), Ebere (2002) and Clarke (2005) inveterate elevated pH in dry season than in wet season which agrees with the result of the present findings. The more acidic water in wet season might be owing to the joint effects of abridged sunlight and the inflow of humic substances and organic substance brought in by the rain during runoff. Also, low temperature during the wet season might account for the observed low pH during the period. The seasonality pattern in the pH of Qua Iboe River Estuary is similar to that reported by Akpan (1991) for Qua Iboe River and King and Ekeh (1990) for Nworie stream. However, it is at variance with the patterns found in some other African rivers in which pH increases during the dry season and reduces during the raining season (Egborge, 1971; Adebisi, 1981). Boyd (1981) recommended pH 6.5 - 9.0 for optimum fish production below or above is not desirable for this purpose. The result of this study shows that the pH range was within the recommended range (6.0 – 9.0) which is suitable for aquatic life (WHO, 2011).

During the study, the result obtained shows that the mean surface water temperature fell within the normal temperature range (20 – 40 ^{o}C) as recommended by World Health Organisation (2011).

In estuaries, temperatures are less considerable than variations in salinity and types of substratum in determining distribution patterns and relative abundance of species (Chindah *et. al*. 2005). The observed temperature demonstrated narrow amplitude of spatial variation but did not differ significantly which may be attributed to the time of sampling and the volume of riparian vegetation which may lead to a variation in water temperature between the stations as observed during the study. Similar observations were made by other researchers (Grover and Chrzanowski, 2006). Seasonal variation was significant with higher temperature in the dry season which is in consistent with tropical environments; in dry season, temperature is generally higher than in wet season. This might be ascribed to longer photoperiod and elevated intensity of sunlight. Temperature wheel the cyclic variations of phytoplankton and epiphyton (Grover and Chrzanowski, 2006; Frankovich *et. al*. 2006). According to (WHO, 2011), temperature has significant impact on the growth and activities of ecological life and it greatly affects the solubility of oxygen in water. High water temperature enhances the growth of micro-organisms and may increase problems related to taste, odour, colour and corrosion. It is believed that the difference in temperature values of the water is not unrelated with solar radiation. Sunlight enforces a rise in water temperature in the dry season compared to the wet season values.

The significant increase in conductivity in the dry season is probably owing to high evapo-transpiration process which resulted in the concentration of the ions in the water (Allan, 2001). There was a significant difference between the values in the seasons and stations. This intra-seasonal variability indicates a strong influence of hydrometeorological factors on conductivity levels in the river. Similar influence has been reported by Adebisi (1981) in Ogun River, Nigeria. This seasonality regime is consistent with those of other tropical rivers (Welcomme, 1985; King and Ekeh, 1990; Akpan and Ufodike, 2005). The significant difference observed for Conductivity values of stations and seasons is attributed to coastal activities which resulted in high concentrations of dissolved ions in stations highly impacted with coastal activities. This tends to confirm the views of APHA (2005). APHA (2005) opined that several factors influence electrical conductivity, these include; temperature, ionic mobility and ionic valences.

The total dissolved solid is an index of the amount of dissolved substances from coastal activities into water body. The occurrence of such solutes alters the physical and chemical properties of water. The observed total dissolved solid concentrations during the study were beyond the recommended 1,001-10,000 mg / L for brackish water (McNeely, *et. al*. 1979). This portends organic pollution from coastal activities. The present total dissolved solid range is in harmony with that reported by Edoghotu (1998) in Okpoka Creek. TDS was higher in downstream site because of salt intrusion from the sea and with a significant difference between the seasons and stations. The high dry season value is probably as a result of evapo-crystallisation process and low precipitation signifying low dilution. This result is consistent with the report of Akpan (1991).

Dissolved oxygen is perhaps the most common applied water quality standard. The observed dissolved oxygen concentrations were within the tolerable range recommended by WHO (2011). Dissolved oxygen concentration beyond 4 mg / L is excellent while below 4 mg / L is injurious to aquatic life. Dissolved oxygen levels were higher in the wet season than in the dry season due to the increased current flow that enables the diffusion and mixing of atmospheric oxygen into the water. This finding is consistent with those reported for River Osun (Welcomme, 1979), Zambezi River (Hall *et al*., 1977), Qua Iboe River (Akpan, 1993) who observed that tropical African aquatic systems generally have low DO in the dry season than the wet season. King and Ekeh (1990) in their work on Nworie Stream, Nigeria, attributed the dry season decline in dissolved oxygen concentration to stream stagnation and increased input of organic load into the water (mainly as leaf litter), whose decomposition increases oxygen depletion. On the other hand, some authors have argued the fact that dissolved oxygen does not increase with the rains. Kemdirin and Ejike (1992) argued that dissolved oxygen concentration is high in the dry seasons due to high photosynthetic activities of phytoplankton at this period. They argued that low DO levels during rainy months is likely caused by high aquatic vegetation cover that flourish favourably in the rainy months at the expense of dissolved oxygen used in respiration. On the other hand, the high levels of dissolved oxygen observed in the wet season in all the stations in Qua Iboe River Estuary is in consistent with the work of Chindah and Braide, (2004) in Bonny River, in the Niger Delta who observed that DO concentrations varied between seasons with wet season concentration significantly higher than that of dry season. The low values of DO observed in the dry season were attributed to organic pollution due to coastal activities.

The mean range chloride concentration in Qua iboe River Estuary agrees with the acceptable concentration of less than 19,000 mg/L in brackish water though higher levels may arise (McNeely, 1979). The observed range of chloride concentration in this study is in harmony with those reported by Ebere, (2002) in Okrika Creek. Also, Pillard *et al.*

(2002) reported similar values for Amococadiz oil spill in United States of America. The observe increase in chloride concentrations downstream implies that chloride level is swayed as a result of proximity to the sea. The low mean concentrations of chloride observed in the wet season clarify the effect of dilution through municipal runoffs and precipitation during the wet season. This observation corroborates with findings of Chindah and Braide (2001) and Ebere (2002). The elevated values of chloride observed in this study during the dry season were attributed to influx of allochthonous materials resulting from coastal activities into the water body during the wet season. This observation agrees with the findings of Chindah and Braide (2001) and Ebere (2002).

Turbidity is a fundamental water quality factor owing to sediment loading and the associated effect it will have on the light accessible for phytoplankton and epiphyton growths as well as other aquatic life (IADC, 2007). Turbidity controls the dynamic of phytoplankton (Chen, *et. al*. 2003). The values recorded in this study did not exceed the level found in natural water bodies. Also, the observed turbidity level in this study agrees with the range reported by Asonye *et al.* (2007) for the turbidity of Nigerian rivers, streams and waterways. The observed turbidity might be attributed to plankton abundance. This confirms the views of Swann (2006) which opines that plankton is one of the causes of turbidity. The recorded high dry season turbidity in this study upholds the views of Swann (2006). From this study, turbidity decreased in the wet season was attributed to reduce coastal activities involving the production of suspended materials which resulted to low influx of suspended materials into the estuary through surface run-off. High values of turbidity in the dry season have been reported by George and Atakpa, (2015) which agrees with the result of the present study. It has been reported that high turbidity reduces photosynthesis of phytoplankton, submerged and rooted aquatic vegetation which results to reduce plant growths and in turn suppress fish productivity.

Seasonal variation was significant with higher total suspended solids values recorded in the dry season. Higher dry season values may be attributed to decay of phytoplankton and other submerges plants within the water body. This is inconsistent with works carried out in other rivers: Akpan, (2004) for Qua Iboe River; King and Nkanta, (1991) for Mfangmfang pond, Hall *et al.* 1977, for River Zambezi which reported high TSS values in the wet season. The wet season decrease in the level of total suspended solids was probably due to reduced coastal activities involving the production of suspended materials which resulted to low influx of suspended materials into the estuary through surface run-of.

Seasonal variation was significant with higher bicarbonate values in the dry season than in the rainy season. The pronounced decline of bicarbonate level in the rainy season reported in this study may be attributed to the utilization of carbon dioxide by phytoplankton.

The marked seasonality trend in the levels of total alkalinity (TA) of the estuary was observed to be higher in the dry season than wet season values. The lower value of total alkalinity in the wet season suggests that runoff water contributed to dilution of this parameter in the wet season. The range concentration of alkalinity recorded during the study agrees with those studies on estuarine environment (Nweke, 2000; Ebere, 2002; Dambo, 2000; Chindah and Braide, 2001). However, the observed alkalinity in this estuary might be connected to the natural carbonates, bicarbonates, hydroxide, borates, silicates, phosphates and organic substance concentrations brought into the water body owing to coastal activities.

BOD varied significantly in season with higher mean value recorded in the wet season than dry season. The wet season increase in BOD values was attributed to increased input of decomposable organic matter brought in by surface runoff into the water body arising as a result of coastal activities. These organic matters require oxygen for their biodegradation. The observed wet season high values of BOD are in accordance with those reported by Akpan and Offem (1993) for Cross River Estuary; Akpan (1993) for Qua Iboe River, Nigeria, and Akpan and Akpan (1994). Biological oxygen demand is of fundamental significance in pollution monitoring. The recorded biological oxygen demand during the study is within the acceptable range for aquatic environments. Waters with biological oxygen demand levels below 4 mg / L are regarded clean and those with levels above 10 mg / L are considered as contaminated as they contain large amounts of degradable organic substance (McNeely, 1979). However, the present biological oxygen demand ranges recorded during the study were below that reported by Edoghotu (1998) for Okpoka creek and Hart and Zabbey (2005) for Woji creek. This indicates that the biological oxygen demand load in the present study did not pose a threat to the aquatic environment.

COD is a measure of the ability of water to devour oxygen at some stage in the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. The mean value of COD recorded in this study were beyond WHO, (2011) recommended limits, indicating a heavy load of organic and inorganic pollution due to coastal activities. High mean value of COD was recorded in the wet season which was attributed to high influx of allochthonous materials into the estuary through surface run-off.

Total hydrocarbon did not vary significantly both spatially and seasonally during the study period. Although, mean values recorded were below WHO, (2011) recommended levels for natural waters.

The total organic carbon contents are a combination of dissolved and particulate organic carbon. The recorded range of total organic carbon concentrations during the study was below 1 to 30 mg / L for natural water. Higher levels in water indicate pollution attributed to anthropogenic inputs from coastal activities (Saad, *et. al*., 1994). Water below 3.0 mg / L total organic carbon is held to be moderately clean (McNeely, *et. al*., 1979). The direct discharge of sewage and domestic wastes as a result of coastal activities from the surroundings into the estuary might be attributed to the elevated levels of total organic carbon observed during the study.

The observed mean nitrate value during the study was below 100 mg / L anticipated to be found in natural surface water. Nitrogen is most often limiting in marine systems (Chrzanowski and Grover, 2001). Owing to the facts that molybdenum, phosphorus or energy constraint can be restrictive to nitrogen fixers, which makes for lesser nitrogen fixation (Vitousek and Howarth, 1991). There is also considerably high denitrification in marine sediments. Nitrate concentration did not vary in space and time suggesting similar coastal activities and natural inputs. The results of findings is inconsistent with the reports of Ebere (2002) who reported elevated nitrates levels in rainy seasons with lower levels in dry season.

The recorded phosphate concentrations in this study were higher than the tolerable limit of 0.10 mg / L in flowing waters recommended by USGS (2007). This observation is consistent with the reports of Chindah and Nduaguibe, 2003 and Ebere, 2002). However, coastal activities resulting in deposition of organic matter might be a contributor to the phosphate concentrations in the estuary. The elevated phosphate concentration in the dry season is in accord with the observations of Chindah and Braide (2001). This could be credited to the elevated biomass of phytoplankton and eiphyton in the dry season. Phosphorus helps in bracing the development of algae.

The sky-scraping sulphate level observed in this study is an attribute of brackish water. Ebere (2002) reported that marine waters are identified to restrain comparatively elevated concentrations of sulphate. The observed levels were perhaps from oxidation of organic materials due to high coastal activities in the estuary. Furthermore, it may possibly be an outcome of wet and dry precipitation from burning of fossil fuels. The seasonality regime in the levels of sulphate was characterized by higher dry season levels than the wet season in the estuary. This means that runoff water during the rainy season dilutes the concentration of sulphate ions in the estuary and evapo-crystallization process increase sulphate ion concentration in the water during the dry season.

The mean value of ammonia recorded during the study period exceeded the concentration of below 0.1mg / L found in natural waters (McNeely, *et. al*., 1979). This possibly indicates organic pollution due to coastal activities. The mean ammonia concentration is also beyond the level of 0.02 mg / L unionized ammonia (NH_3) essential for the protection of aquatic life. Fish cannot stand high concentration of ammonia since it reduces the oxygen-carrying capacity of the blood and thus the fish may choke resulting in mortality. The high concentration of ammonia during the study is linked to coastal activities as a result of deliberate discharge of sewage into the water body. The recorded range of ammonia in the present study exceeds the range reported by (Nweke, 2000; Ebere, 2002; Chindah and Nduaguide, 2003; and Obunwo *et al.* 2004) in the Niger Delta. There were no significant spatial and seasonal variations in ammonia concentration, thus suggesting similar coastal activities and natural inputs.

4.2 Multivariate Analysis, nutrient distribution and source apportionment.

The use of correlation analyses in establishing relationships within and between variables, locations and organisms is well established in literature (Benson *et. al.* 2016). Positive correlations between physico-chemical parameters (TDS, EC, Chlorides, Turbidity, TSS, Bicarbonate, alkalinity, nitrate, COD, Nitrate, ammonia and sulphate) denotes that an increase in one of these parameters leads to a corresponding increase in the other. These inter-relationship patterns may arise from high inflow of particulate matter from run-offs, coastal farmlands and release of untreated sewage into the water leading to an increase in organic materials in the water column. This belief stems from the fact of Mahananda *et. al.* (2010) that total suspended solids are composed of carbonates, chlorides, phosphates, bicarbonates and nitrates of calcium, magnesium, sodium, potassium, manganese, organic matter, salt and other particles. This synchronizes the correlation trend. The persistence of sequences of these events could lead to a reduction in oxygen level of the aquatic system due to increasing biological degradation activity or probably a high presence of oxidizable minerals. Also, high TSS values leads to increased turbidity and so impedes optimum light penetration with a reduced net photosynthetic efficiency. The agglomeration patterns observed in the cluster dendrogram representing the physicochemical attributes of the stations in both rainy and dry season assorts the stations in line with salinity gradient and proximity to the ocean. Similar observations have been observed by earlier researchers (Essumang, *et. al.* 2012 and Benson and Essien, 2012).

Principal component analysis yielded a pattern which confirmed hierarchical values and effects of some nutrient variables regrouped into three factor components. The inter-relationships among the vari-factors as judge from their loadings confirmed close relationship between the members of each factor component. Generally, ordination of environmental variables revealed much similarity in growing environmental conditions which influence their distribution pattern. These conditions arise from coastal activities like; massive influx of run-off, poor sewage disposal, motorized boat movement, commercial logging, dredging, agricultural inputs etc. This finding however, deviates remarkably from those of Nirmal-Kumar *et. al.* (2012) who reported 2 factor components from 8 variables in a similar research.

5.0 Conclusion

This study indicates that coastal activities from residential areas and within the water body have cause significant impact on the water quality of Qua Iboe River Estuary with respect to variations observerd in the studied parameters. The physico-chemical parameters studied were below the permissible limit for some parameters while some were within the permissible limits and others were above the permissible limit of World Health Organization for surface water. The physico-chemical parameters recorded at station 5 (Atabong) were below permissible limit of WHO. This implies that coastal activities in this station were minimal showing little or no elevation in the study parameters. The physico-chemical parameters also show seasonality for some of the studied parameters. The seasonality observed in the parameters during the study was attributed to influx of allochthonous materials and dilution as a result of surface run-off during the wet season. Spatial variation in the study parameters was also observed. This was attributed to similar source of pollution, nature of the environment and proximity of the stations to the sea. Direct relationships between pairs of physico-chemical parameters as observed mandates that an increase in one parameter result in a corresponding increase in the other parameter. Dendrograms resulting from hierarchical cluster analysis assorted the stations as a function of salinity gradient. Ordination using principal component analysis of 18 variables yielded three factor components for the wet and dry season. Generally, the pattern of assortment of the variables in both seasons revealed a continuum in physico-chemical parameters / environmental block in which the stations were more or less arbitrary. From the result of findings, the water quality of Qua Iboe River Estuary is seriously impaired by coastal activities resulting from indiscriminate discharge of domestic waste, industrial waste, agricultural run-off and sewage disposal into the estuary. This study vindicates the essence of continuous monitoring of our water bodies as this will help to give vital information on the status of water bodies in Nigeria and to expedite remedial measures in the event of pollution.

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