NUTRITIONAL RICHNESS OF SEDIMENTS FROM CRUDE OIL IMPACTED IKO RIVER ESTUARY, EASTERN OBOLO L.G.A, NIGERIA

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ABSTRACT

This was a longitudinal study that lasted twelve calendar months;and conducted in three selected stations along the course of a crude oil impacted Iko river estuary, Eastern Obolo LGA, Akwa Ibom State, Nigeria.Standard protocols were followed in collection and analysis of sediment samples. There were spatio-temporal variations in total hydrocarbon content (THC): lowest value (101.40 mgkg^{-1}) recorded at Station 2 in October while the highest value (219.60 mgkg^{-1}) was obtained at Station 1 in April; dry season mean value of 162.31 ± 22.67 mgkg^{-1}was significantly ($p<0.05$) higher than that of wet season (137.19 ± 34.59 mgkg^{-1}). The levels of Total Nitrogen (TN) in the study area were quite low, with values that ranged from 0.19 - 0.50 %, 0.20 - 0.44 % and 0.15 - 0.046 % in Station 1, 2 and 3 respectively with no significant differences observed irrespective of seasons. Levels of Ammonium ions (NH_4^+) recorded in the sediments were 2.28 - 5.11 mgkg^{-1}, 2.96 - 6.01 mgkg^{-1} and 2.41 - 5.72 mgkg^{-1} in Station 1, 2 and 3 respectively. Nitrate (NO_3^-) lowest value of 11.60 mgkg^{-1} was recorded in Station 2 while the highest value of 36.00 mgkg^{-1}was recorded in Station 3. Wet season $NO_3^{-\ mean}$ value was higher (27.51 ± 4.62 mgkg^{-1}) than that of the dry season (18.38 ± 4.06 mgkg^{-1}). Phosphate levels in sediments were not significantly different among stations and seasons. The mean concentrations of Sulphate in sampling stations were 48.53 ± 4.62 mgkg^{-1}, 36.96 ± 6.93 mgkg^{-1} and 42.25 ± 5.98 mgkg^{-1} for Stations 1, 2 and 3 respectively. There was no remarkable spatial variation in the Chloride levels of the sediments. Nevertheless, influence of season was significant ($p< 0.05$) as dry season mean value of 173.16 ± 12.53 mgkg^{-1} exceeded that of wet season (131.78 ± 20.76 mgkg^{-1}). Both negative and positive associations between pollutants and nutritive salt levels in the sediments were recorded across sampling stations irrespective of the season. From the results, it can be concluded that higher level of nutritive salts were in the sediments at seasons where hydrocarbon contamination of the sediment was lowest.

KEYWORDS: Sediments, Hydrocarbon pollution, Nutritive salts, spatio-temporal, Iko river estuary

INTRODUCTION

Sediment quality is a good indicator of pollution in water column, where it tends to concentrate the heavy metals and other organic pollutants (Amadi *et al*., 2017). According to Wang *et al*. (2012), sediments act as non-point source of pollution and have the potential to release the sediment-bound organic pollutants and other toxicants to overlying waters and in turn adversely affect aquatic organisms. As such, sediments can be sensitive indicator for monitoring contaminants in aquatic environment. As mentioned earlier, sediments are often polluted with various kinds of hazardous and toxic substances, including petroleum hydrocarbon. These accumulate in sediments through various pathways including disposal of effluents, terrestrial runoff and leachate carrying chemicals originating from numerous urban, industrial and agricultural activities, as well as atmospheric deposition. The pollutants concentrations in the sediment indicate the situation in the water body at the time of sampling (Ravera *et al.*, 2003). Several studies (Amadi *et al.*, 2017) have shown that sediment characteristics can vary considerably over short distances in nearshore marine environments, due primarily to differences in waves and tidal action, the extent of shoreward and alongshore drift, and proximity of potential sediment sources such as nearshore reefs, coastal cliffs and estuaries. Furthermore, within estuaries, other factors, such as the amount of rainfall that an estuarine catchment receives, the morphology and number of adjoining rivers and the extent of catchment

vegetation and the type of bedrock also play an important role in influencing the sediment mineralogy and grain sizes. Sediments in rivers are an essential habitat as well as important nutrient source for aquatic organisms. It is broadly recognized that sediments play a major role for the health of the aquatic ecosystems as they provide a habitat to many organisms and support to all aquatic fauna. Sediments also represent the part where the vast majority of the most dangerous, persistent and accumulation-prone pollutants are deposited. Aquatic sediments are main sink for various pollutants like pesticides, heavy metals which also play a significant role in the remobilization of contaminants in aquatic systems under favourable environmental conditions and interactions between water and sediments (Saeed and Shaker, 2008; Wang *et al*., 2012; Amadi *et al*., 2017). The analysis of sediments is an important part in the evaluation of the quality of the total aquatic ecosystem. Sediments apart from being the sources of many pollutants and trace substances of low solubility and low degree of degradability also store pollutants over long periods of time with regards to their chemical persistence and the biochemical and physico-chemical characteristics of the substrata (Adeyemo *et al.*, 2008).

Apart from influencing the feeding strategies of benthic species, a sediment with poor nutritive salt value may suppress photosynthetic activity of phytoplankton, algae and macrophytes. Such nutritive salts include Nitrate salt, Sulphate salts, phosphate salts, Ammonium salts, Chloride

salts, etc. Poor status of these nutrients in sediments may lead to fewer photosynthetic organisms available to serve as food sources for many invertebrates. As a result, overall invertebrate numbers may also decline which may lead to decrease in fish populations. Nonetheless, clay and organic rich sediment may clog pipes and machinery, which may be costly to repair. In addition, sediment may interfere with essential functions of organisms. Some zooplankton suffer decline due to clogged feeding mechanism (Adeyemo *et al.*, 2008). Likewise, fish may suffer clogging and abrasive damage to gills and other respiratory surfaces. Abrasion of gill tissues triggers excess mucous secretion, decrease resistance to disease and a reduction or complete cessation of feeding (Adeyemo *et al.*, 2008). Suspended sediments may also affect predator-prey relationships by inhibiting predators' visual abilities.

It has become very imparative to monitor the nutritive status of sediments in water bodies in the face of crude oil polltion as such pollution has been shown to have the potential of rendering highly nutritive sea foods scarce in availability. This will help to elucidate the possible mechanism that crude oil pollution reduces the availabilty of fish and other sea foods in the water ecosystem. This work was therefore designed to achieve this objective in Iko River Estuary, Eastern Obolo L.G.A, Nigeria.

MATERIALS AND METHODS
The Study Area

Iko River Estuary in Eastern Obolo Local Government Area of Akwa Ibom State is located within the Niger Delta area of Nigeria between latitude 7° 30' N and 7° 45'N and longitude 7° 30' E and 7° 40' E (Figure 1). The Iko River estuary has semi-diurnal tides and a shallow depth ranging from 1 to 7 m at flood and ebb tide; and is more than 20 km long with an average width of about 16 m. Iko River takes its course from Qua Iboe River catchments and drains directly into the Atlantic Ocean at the Bight of Bonny (Benson and Etesin, 2008). The estuary has adjoining creeks, channels and tributaries which is significant in the provision of suitable breeding site for the diverse aquatic resources that abound in the area, good fishing ground for artisanal fisherman as well as petroleum exploration and production activities. Part of the river also drains into Imo River Estuary, which opens into the Atlantic Ocean at the Bight of Bonny (Benson and Etesin, 2008).

Soft dark mudflats, usually exposed during low tide, mangrove swamps, shoals and sandbars, characterize the river's shoreline. The area is characterized by a humid tropical climate with rainfall reaching about 3,000 mm per annum (Benson and Etesin, 2008). The area has distinct wet and dry seasons. The wet season begins in April and last till October, while the dry season begins in November till March. A short period of draught is usually experienced in July and August, while a period of harmattan characterized by cold dry winds and lower temperatures normally occurs between December and February. The mean annual daily evaporation of the area is 4.6 mm per annum. The hydrology of Iko River is affected by tides, although seasonal influences which are related to the climate regime are

evident. The estuary constitutes a major inlet to the land and is often utilized by inhabitants as the main transport route. It is a multi-use resource with fishery as the most dominant. The estuary also serves as the receiving water body for domestic and industrial wastes (Essien *et al*., 2008).
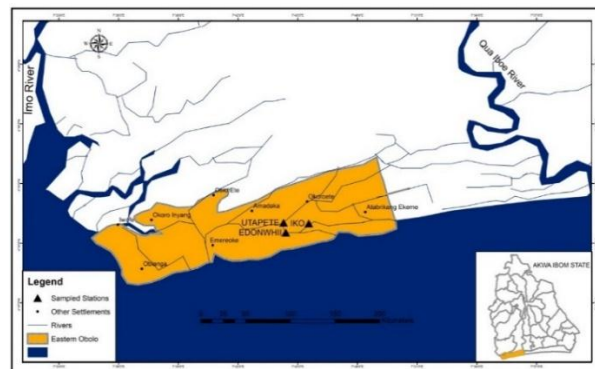

Figure 1: Map Of the South Akwa Ibom State showing the sampled stations (Source: Ministry of Lands and Town Planning, Akwa Ibom State (2008).

Sampling Procedure

The study area was demarcated into three stations for sampling. The sampling stations designated as Station 1 (ST 1) - Utapete, located near an abandoned well-head; Station 2 (ST 2) - Iko, where dredging activities took place; and Station 3 (ST 3) - Edonwhii, which opens into the Atlantic Ocean, were subjectively categorized. Sampling was carried out monthly such that months covering peak period of wet and dry seasons were inclusive.

Sample collection and Preparation

Sediment samples were collected by scooping (using a short core sampler, Kajak corer" model 13.030) the top 1-5 cm of intertidal mudflats; mixed together for homogeneity and the subsamples transferred into polytene bags. All sediments samples were oven dried at 80 - 100°C, gently crushed and sieved to collect the < 63 μ grain size. Accurately weighed (1.0 g) samples of sieved sediments were treated with 10 ml of 0.25 M HNO_3, heated to dryness and thereafter, 10 ml of 0.25 M HNO_3 and 3.0 ml of $HClO_4$ added. Sample solutions were obtained by leaching residues with 4.0 ml of HCL and thereafter filtered and diluted with distilled water to 100 ml mark. Analysis of sediment samples for pollutants and nutritive salts was done as described below (APHA, 2005).

Determination of organic carbon level in sediments
Total organic carbon (TOC)

The organic carbon content of the sediment was determined by the Walkey-Wet method. In this procedure, 1 g of each sediment sample was weighed into Erlenmeyer flask. Twenty millilitres of concentrated H_2SO_4 was added and swirled gently for a minute. Thereafter, 10 ml of $K_2Cr_2O_7$ was added and mixed thoroughly. This was allowed to stand for 20-30 minutes. The suspension was diluted with 100 ml distilled water, treated with 5 drops of diphenylamine indicator and then titrated with ferrous ammonium sulphate to light blue end point. Blank titration was run using the same procedure but with no sediment sample used

(Jackobson, 1992). The organic carbon content level was estimated thus:

$$\text{Organic Carbon} = (B - T) \times 0.003 \times 0.5 \times 100 \times 1.33$$

Where: B = Blank titre and T = Sample titre

Total nitrogen (TN)
The Total Nitrogen in the sediment was determined using the Macro-Kjeldahl techniques of Jackobson (1992). In this procedure, 5 g of air-dried sediment (passed through a 2 mm sieve) was measured and transferred to 500 ml Kjeldahl flask. Through a funnel, one heap spoon (about 11 g) of digestion mixture was added to the flask. Twenty millilitres of concentrated H_2SO_4 was added and swirled gently until the content was thoroughly mixed. The flask was placed on Kjeldahl digestion apparatus and heated at low heat for four hours until frothing ceased or organic matter was destroyed as evidenced by the light grey colour. It was further heated for 30 minutes. The heat was turned off, flask removed and capped immediately with beaker and left to cool.

During the cooling process, 25 ml of 4 % boric acid (plus methyl orange pH indicator) and 25 ml distilled water were introduced into the flask. The flask was placed under the condenser of the distillation apparatus such that the end of the tube was below the level of H_3BO_3. The cooling water in the condenser was turned on and allowed to run. After cooling, 250 ml of distilled water was added to the Kjeldahl flask and the content mixed thoroughly. The flask was tilted to an angle of 45° and 75 ml of 40 % NaOH added so that it ran down the side to the bottom of the flask without mixing. Two to three pieces of zinc metal were added and the flask immediately attached to the distillation apparatus and distillation commenced. The heat was turned low and the content of the flask swirled to mix. About 200 ml of the distillate was obtained in the receiving flask. The receiving flask was then lowered such that the receiving tube was above the level of the solution in the flask and detached from the apparatus. The distillate was titrated against standard acid until the blue colour disappeared. A blank titration was carried out with no soil sample. The percentage nitrogen in the soil sample was calculated as in Equation 1;

$$\%N = \frac{T - B \times Na \times 1.4}{S} \quad \text{Equation 1}$$

Where:
T = Sample titration (ml)
B = Blank titration (ml)
Na = Normality of acid used
S = Sample weight (g)

Determination of Nutritive Salts Contents, Nitrate (NO_3^-)
Nitrate content in water and sediment samples was determined calorimetrically by uv/visible HACH spectrophotometer (APHA, 2005). The method is based on a yellow complex formation between brucine sulphate and nitrate in the presence of H_2SO_4 acid. The measurement was taken at a wavelength of 410 nm. Prior to analysis of the samples, the equipment was calibrated with working standards from analytical grade potassium nitrate salt.

Instrument Calibration: Appropriate volumes (2.0, 4.0, 6.0, 8.0 and 10.0 ml) of nitrate working solution were measured into a series of tubes to cover the range 10 to 50 µg NO_3^-. These contents in the tubes were mixed by swirling in a cold-water bath. This was followed by addition of 10.0 mL H_2SO_4 and then 0.5 mL of brucine sulphanilic acid reagent, and heated in a 100 °C water bath for 25 minutes. The rack of tubes was immersed in the cold-water bath and allowed to cool to room temperature. Then, the absorbance of the solution was read at 410 nm using a visible spectrophotometer (HACH DR 3800 SC) and units of values obtained were recorded in mgl^{-1}. Blank determination was done following the same procedure. Deionized water was used in place of nitrate working solution.

Phosphate (PO_4^{2-})
The phosphate content in water and sediments samples was determined by the ascorbic acid method as described in APHA (2005). This method involved a mixture of ascorbic acid, antimony potassium tartrate, H_2SO_4 and ammonium molydate as a combined reagent. Fifty millilitres of sample were pipette to a conical flask followed by 98% ethanol and 2.5 ml of combined reagents. A period of 30-minute s was allowed for the development of blue colour before absorbance was read at 880 nm using the atomic absorption spectrophotometer (HACH DR 3800 SC) and units of values obtained were recorded in mgl^{-1}.

Instrument calibration: Standard solutions of 0, 4, 8, 10, 12, 14 and 20 mgl^{-1} concentrations were prepared from the stock standard solution and treated in same way as the samples for colour development. The calibration curve was plotted by reading the absorbance of the standard solutions after colour development using a visible spectrophotometer (HACH DR 3800 SC).

Sulphate (SO_4^{2-})
The sulphate content of the water and sediment samples was determined turbidimetrically with ultra violet HACH spectrophotometer (HACH DR 3800 SC) at wavelength of 425 nm (APHA, 2005). The method is based on precipitation of sulphate ion in an acetic acid medium with barium chloride (precipitating agent). The reaction, formed barium sulphate crystals of uniform size. Light absorbance of the barium sulphate suspension was measured and the SO_4^{-2} concentration in mgl^{-1} was determined by comparison with standards. Prior to analysis of the samples, the equipment was calibrated with sulphate working standards prepared from standard sodium sulphate salts.

Preparation of calibration standards and blanks: To five 50 mL glass stoppered standard flasks (four for standards and one for the blank), 10, 20, 30 and 40 mL of the standard sulphate solution were added to the four standard flasks and deionized water was added to the fifth standard flask. About 2.0 ml of the conditioning reagent was added to all five standard flasks and final volume made up to the 50 mL mark. A blank sample was similarly prepared by substituting 100 ml of deionised water for the water sample. The absorbance of the different solutions was measured using a visible spectrophotometer (HACH DR 3800 SC) at 425 nm.

Chloride
Chloride in sediment and water samples was determined titrimetrically by the silver-nitrate method or Argentometric

method (APHA, 2005). The method required titrating an aliquot portion of water sample or sediment suspension in the presence of potassium chromate as indicator to brick red end point with silver nitrate. Prior to sample analysis silver nitrate solution was standardized with sodium chloride. Fifty millilitres of the water sample were pipette into a 100 ml conical flask and 1.0 ml of potassium chromate indicator was added. Standard silver nitrate solution was then titrated against the sample, a few drops at a time, until the first permanent reddish coloration appeared. A blank titration was also carried out.

Calculation:

$$\text{Conc. of chlorides (mgL}^{-1}) = \frac{(V_s - V_b) \times \text{Normality} \times 35.45 \times 1000}{\text{volume of sample taken (mL)}}$$

Where, V_s = volume of $AgNO_3$ required by sample (ml)
V_b = volume of $AgNO_3$ required by the blank (ml)
Equivalent weight of chlorine = 35.45

Ammonium (NH_4^+)
Ammonium (NH_4^+) in water and sediment samples was determined with the HACH Spectrophotometer using the Nessler reagent (Radojevic and Bashkin, 1999). Essentially, the Nessler reagent (K_2HgI_4) reacts under strong alkaline condition with the ammonia present in the sample to a yellow solution in direct proportion to the ammonia concentration. Measurements were made at a wavelength of 425 nm.

Calibration: Appropriate volumes (2.0, 4.0, 6.0, 8.0 and 10.0 ml) of working ammonium solution were measured into a series of tubes to cover the range 0.1 to 1.0 µg NH_4^+. These tubes and its contents mixed by swirling in a cold-water bath. After cooling at room temperature, the absorbance of the solution was read at 425 nm using a visible spectrophotometer (HACH DR 3800 SC) and results obtained were recorded in mgl⁻¹. Blank determination was done following the same procedure using deionized water. A calibration curve was plotted from the readings.

Data Analysis
All data were analysed using Statistical Package for Social Sciences (SPSS) software, version 21. Percentage analysis, ANOVA and Fisher's exact tests were used as appropriate.

RESULTS
Spatio-temporal result of sediment physicochemistry
The spatio-temporal result of sediment physicochemistry is presented in Tables 1 and 2. Values of pH ranged from 6.21 - 6.58 in Station 1, 6.27 - 7.18 in Station 2, 6.23 - 7.11 in Station 3 and were statistically significant ($P < 0.05$). Seasonal variations in pH revealed slightly higher mean values in the dry season (6.78 ± 0.40) than the wet season (6.42 ± 0.23). Electrical conductivity levels observed for the intertidal sediment varied between stations with mean of 1708.70 ± 697.76 µs/cm in Station 1, 1497.40 ± 472.22 µs/cm in Station 2, and 1384.36 ± 606.39 µs/cm in Station 3. Electrical conductivity during the dry season was higher than the wet season though the difference was insignificant ($P > 0.05$). Mean values of salinity were: 26.72 ± 5.35 %, 23.56 ± 6.12 % and 27.64 ± 6.50 % for Stations 1, 2 and 3 respectively. Minimal variations in stations and season were

observed in the salinity of sediments in the study area. Generally, higher values were recorded in the dry season (31.94 ± 2.44 %) than in the wet season (21.71 ± 3.91 %) with the highest value of 35.20 % recorded in the month of February in Station 3. Total Hydrocarbon Content (THC) ranged from 117.30 - 219.60 mgkg⁻¹ in Station 1, 101.40 - 192.30 mgkg⁻¹ in Station 2 and 110.60 - 203.80 mgkg⁻¹ in Station 3 (Table 8). There was spatial variation in THC as the lowest value of 101.40 mgkg⁻¹ was recorded in Station 2 in October while the highest value of 219.60 mgkg⁻¹ was obtained in Station 1, in April. However, seasonal variations of THC were significant ($P < 0.01$) with dry season mean value of 162.31 ± 22.67 mgkg⁻¹ higher than that of wet season (137.19 ± 34.59 mgkg. Mean values of Total Organic Carbon (TOC) were: 11.93 ± 2.74 %, 13.39 ± 2.39 % and 14.65 ± 4.53 % for Stations 1, 2 and 3 respectively. The values of TOC in Iko Estuary varied in space and season with higher values observed during the dry season (16.54 ± 2.51 %) than in the wet season (11.02 ± 1.76 %). The levels of Total Nitrogen (TN) in the study area were quite low. In Station 1, values ranged between 0.19 - 0.5 %, Station 2 (0.20 - 0.44 %) and in Station 3 (0.15 - 0.046 %) and no significant differences were observed among the stations. Similarly, seasonal variation showed no remarkable differences. Mean wet season value was 0.39 ± 0.07 % while that of dry season was (0.24 ± 0.04 %). The Phosphate (PO_4^{2-}) level was generally high across the sampling stations. The mean concentration of PO_4^{2-} in sediment was 41.21 ± 8.78 mgkg⁻¹ in Station 1, 35.13 ± 8.44 mgkg⁻¹ in Station 2 and 38.63 ± 8.69 mgkg⁻¹ in Station 3. Station 1 had the highest value of 51.5 mgkg⁻¹ in October while Station 2 had the least value of 24.60 mgkg⁻¹ in January. Phosphate levels in sediment were not significantly different among stations and seasons. Nitrate (NO_3^-) lowest value of 11.60 mgkg⁻¹ was recorded in Station 2 in February while the highest value of 36.00 mgkg⁻¹ was recorded in Station 3 in July. Significant difference ($P < 0.05$) was observed in NO_3^- between Stations but none between seasons. Wet season NO_3^- mean value was higher (27.51 ± 4.62 mgkg⁻¹) than that of the dry season (18.38 ± 4.06 mgkg⁻¹).

The Sulphate level in the sediment of Iko River Estuary was generally high and varied across the study sites and periods, though not significantly. The mean concentrations of Sulphate in sampling stations were: 48.53 ± 4.62 mgkg⁻¹, 36.96 ± 6.93 mgkg⁻¹ and 42.25 ± 5.98 mgkg⁻¹ for Stations 1, 2 and 3 respectively. Low levels of Ammonium ions (NH_4^+) was recorded in the sediments and values obtained ranged between 2.28 - 5.11 mgkg⁻¹ in Station 1, 2.96 - 6.01 mgkg⁻¹ in Station 2 and 2.41 - 5.72 mgkg⁻¹ in Station 3 (Table 8). Analysis of variance (ANOVA) showed significant spatial ($P < 0.05$) and temporal ($P < 0.01$) differences. There was no remarkable spatial variation in the Chloride levels of the sediments (Table 8). Nevertheless, influence of season was significant ($P < 0.05$) as dry season mean value of (173.16 ± 12.53 mgkg⁻¹) exceeded that of wet season (131.78 ± 20.76 mgkg⁻¹).

Table 1: Physical and Chemical Characteristics of the Sediments in Iko Estuary

Parameters	Station 1 Range Min – Max	X±SD	Station 2 Range Min - Max	X±SD	Station 3 Range Min – Max	X±SD	Significance (2- tail)
PH	6.21-6.58	6.31±0.11	6.27-7.17	6.74±0.35	6.23-7.11	6.67±0.38	P<0.05
EC (μs/cm)	964.80-2947.50	1708.70±697.76	912.60-2092.60	1497.40±472.22	920.10-2118.30	1384.36±606.39	
Salinity (%)	20.10-34.20	26.72±5.35	15.30-32.70	23.56±6.12	17.60-35.20	27.64±6.50	
THC (mg/kg)	117.30-219.60	156.14±35.62	101.40-192.30	139.09±31.14	110.60-203.80	147.75±31.51	
TOC (%)	8.60-16.70	11.93±2.74	10.10-17.70	13.39±2.39	8.30-20.60	14.65±4.53	
T.N (%)	0.19-0.50	0.35±0.11	0.20-0.44	0.31±0.09	0.15-0.46	0.33±0.10	
PO_4^{2-} (mg/kg)	28.00-51.50	41.21±8.78	24.60-48.20	35.13±8.44	26.10-50.20	38.63±8.69	
NO_3^- (mg/kg)	19.50-35.40	25.85±5.75	11.60-30.20	19.90±6.78	18.70-36.00	25.38±4.81	p<0.05
SO_4^{2-} (mg/kg)	41.30-54.10	48.53±4.62	27.30-47.50	36.96±6.93	35.10-51.80	44.25±5.98	p<0.001
NH_4^+ (mg/kg)	2.28-5.11	3.49±1.00	2.96-6.01	4.54±0.90	2.41-5.72	4.05±1.01	p<0.05
Cl^- (mg/kg)	123.80-193.20	160.16±26.71	101.80-166.50	138.25±24.73	113.00-191.00	148.65±27.53	

Table 2: Variations in Sediment Physicochemical Parameters in Relation to Seasons in Iko River Estuary

Parameters	Wet Season Mean±SD	Range Min-Max	CV	Dry Season Mean±SD	Range Min – Max	CV	ANOVA Test F-Value	P-Value
PH	6.42±0.23	6.23-7.05	3.66	6.78±0.40	6.21-7.15	5.96	10.84	
EC (μs/cm)	1236.38±528.90	118.2-2312.90	42.79	1941.45±427.54	1327.20-2947.50	22.02	18.13	
Salinity (%)	21.71±3.91	15.30-30.80	18.02	31.94±2.44	26.10-35.20	7.64	79.66	
THC (mgkg^{-1})	137.19±34.59	101.4-219.60	25.21	162.31±23.67	129.20-201.70	14.58	5.90	P<0.01
TOC (%)	11.02±1.76	8.30-14.70	15.97	16.54±2.51	12.50-20.60	15.22	59.89	
T.N (%)	0.39±0.07	0.22-0.50	18.34	0.24±0.04	0.15-0.32	20.19	52.17	
PO_4^{2-} (mgkg^{-1})	44.64±5.17	31.70-51.50	11.60	29.48±3.16	24.60-36.10	10.72	101.17	
NO_3^- (mgkg^{-1})	27.51±4.62	16.80-36.00	16.81	18.38±4.06	11.60-23.60	22.08	37.62	
SO_4^{2-} (mgkg^{-1})	47.14±6.24	29.10-54.10	13.25	37.79±5.56	27.30-47.80	14.72	21.44	
NH_4^+ (mgkg^{-1})	3.62±0.99	2.28-5.14	27.31	4.59±0.86	3.01-6.01	18.77	9.18	P<0.01
Cl^- (mgkg^{-1})	131.78±20.76	101.80-171.60	15.75	173.16±12.53	155.20-193.20	7.23	47.07	P<0.05

Table 3: Pearson Product Moment Correlation of Physicochemical Parameters of Sediments in Station 1

	pH	EC	Salinity	THC	TOC	TN	PO_4^{2-}	NO_3^-	SO_4^{2-}	NH_4^+	CL^-
pH	1										
EC (µs/cm)	-.586*	1									
Salinity (%)	-.622*	.801**	1								
THC (mgkg-1)	-.496	.925**	.705*	1							
TOC (%)	-.549	.694*	.940**	.555	1						
T.N (%)	.596*	-.804**	-.968**	-.682*	-.956**	1					
PO_4^{2-}(mgkg-1)	.596*	-.804**	-.968**	-.682*	-.956**	.496	1				
NO_3^- (mgkg-1)	.767**	-.755**	-.920**	-.665*	-.878**	.920**	.907**	1			
SO_4^{2-}(mgkg-1)	.543	-.507	-.865**	-.390	-.888**	.880**	.958**	.853**	1		
NH_4^+(mgkg-1)	-.503	.917**	.691*	.868**	.572	-.652*	-.536	-.578*	-.411	1	
Cl^-(mgkg-1)	-.647*	.842**	.963**	.777**	.900**	-.934**	-.919**	-.895**	-.850**	.789**	1

**. Correlation is significant at the 0.01 level (2-tailed).   *. Correlation is significant at the 0.05 level (2-tailed).

Table 4: Pearson Product Moment Correlation of Physicochemical Parameters of Sediments in Station 2

	PH	EC	Salinity	THC	TOC	TN	PO_4^{2-}	NO_3^-	SO_4^{2-}	NH_4^+	CL^-
pH	1										
EC (µs/cm)	.101	1									
Salinity (%)	.622*	.737**	1								
THC (mgkg-1)	.010	.934**	.594*	1							
TOC (%)	.655*	.609*	.747**	.639*	1						
T.N (%)	-.581*	-.774**	-.887**	-.721**	-.895**	1					
PO_4^{2-}(mgkg-1)	-.528	-.791**	-.944**	-.645*	-.768**	.941**	1				
NO_3^- (mgkg-1)	-.564	-.813**	-.914**	-.691*	-.793**	.953**	.941**	1			
SO_4^{2-}(mgkg-1)	-.256	-.892**	-.794**	-.867**	-.786**	.908**	.861**	.894**	1		
NH_4^+(mgkg-1)	.051	.910**	.695*	.845**	.554	-.627*	-.707*	-.658*	-.791**	1	
Cl^-(mgkg-1)	.410	.851**	.933**	.737**	.769**	-.939**	-.970**	-.947**	-.930**	.759**	1

**. Correlation is significant at the 0.01 level (2-tailed).   *. Correlation is significant at the 0.05 level (2-tailed).

Table 5: Pearson Product Moment Correlation of Physicochemical Parameters of Sediments in Station 3

	PH	EC	Salinity	THC	TOC	TN	PO_4^{2-}	NO_3^-	SO_4^{2-}	NH_4^+	CL^-
pH	1										
EC (µs/cm)	.642*	1									
Salinity (%)	.723**	.847**	1								
THC (mgkg-1)	.258	.825**	.709**	1							
TOC (%)	.864**	.834**	.920**	.534	1						
T.N (%)	-.569	-.890**	-.832**	-.909**	-.735**	1					
PO_4^{2-}(mgkg-1)	-.738**	-.804**	-.927**	-.582*	-.942**	.752**	1				
NO_3^- (mgkg-1)	-.659*	-.727**	-.847**	-.583*	-.748**	.698*	.735**	1			
SO_4^{2-}(mgkg-1)	-.792**	-.653*	-.747**	-.395	-.876**	.663*	.896**	.603*	1		
NH_4^+(mgkg-1)	.328	.809**	.725**	.932**	.600*	-.893**	-.680*	-.520	-.516	1	
Cl^-(mgkg-1)	.675*	.863**	.923**	.807**	.837**	-.910**	-.865**	-.858**	-.730**	.834**	1

**. Correlation is significant at the 0.01 level (2-tailed).   *. Correlation is significant at the 0.05 level (2-tailed).

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*Udoinyang et al: Nutritional Richness of Sediments from Crude Oil
Impacted Iko River Estuary, Eastern Obolo L.G.A, Nigeria
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Spatial assessments of the relationship between crude oil pollution indicators and Nutritive salts in sediment

Tables 3 - 5 are data of the Pearson correlation matrix for sediment physicochemical variables. In Station 1, Total Hydrocarbon Content exhibited negative associations (P<0.01) with PO_4^{2-}, NO_3^-; and their correlation coefficients were: r = -0.95, r = -0.87 respectively. Positive associations also existed between THC and NH_4^+ (r = 0.86, P < 0.01), Cl^- (r = 0.77, P < 0.01). Similarly, in Station 2, THC also correlated negatively with PO_4^{2-} (r = -0.64, P < 0.05), NO_3^- (r = -0.69, P < 0.05) and SO_4^{2-} (r = -0.86, P < 0.01). Positively, THC related strongly with NH_4^+ (r = 0.84, P < 0.01) and Cl^- (r = 0.73, P < 0.01). Strong positive associations (P < 0.01) existed between Total Hydrocarbons (THC) and NH_4^+ (r = 0.93) as well as with Cl^- (r = 0.80) in Station 3. Again, THC correlated negatively with PO_4^{2-} (r = -0.58, P < 0.05) and NO_3^- (r = -0.58, P < 0.05). Total organic carbon (TOC) showed a strong but negative affinity (P < 0.01) with TN (r = -0.95), PO_4^{2-} (r = -0.95), NO_3^- (r = -0.87), SO_4^{2-} (r = -0.88), silt (r = -0.77) and clay (r = -0.79); but related positively with Cl^- (r = 0.90) and sand (r = 0.93) in Station 1. A similar trend was also observed in Station 2 where TOC exhibited strong but negative associations (P < 0.01) with PO_4^{2-} (r = -0.76), NO_3^- (r = -0.79) and SO_4^{2-} (r = -0.78). Again, TOC related positively with Cl^- (r = 0.76). Whereas in Station 3, TOC correlated positively with NH_4^+ (r = 0.60, P < 0.05) and Cl^- (r = 0.83, P<0.01) but negatively with PO_4^{2-} (r = -0.94), NO_3^- (r = - 0.74) and SO_4^{2-} (r = -0.87). The correlation between Total Nitrogen (TN) and NO_3^- (r = 0.92, P < 0.01) was strong and positive in Station 1 as well as that of Total Nitrogen and SO_4^{2-}, silt and clay. Their correlation coefficients were: r = 0.88, r = 0.86 and r = 0.77 respectively. Total Nitrogen also related negatively with NH_4^+ (r = -0.65, P < 0.05), Cl^- (r = -0.93, P < 0.01) and sand (r = -0.96, P < 0.01). However, in Station 2, Total Nitrogen also correlated positively (P < 0.01) with PO_4^{2-} (r = 0.94), NO_3^- (r = 0.95), SO_4^{2-} (r = 0.90) and silt (r = 0.93); while the negatively correlated parameters were those of TN and NH_4^+ (r = -0.62, P < 0 .05), Cl^- (r = -0.93, P < 0.01), and sand (r = -0.91, P < 0.01). Total Nitrogen showed a strong but negative correlation (P<0.01) with NH_4^+ (r = -0.89), Cl^- (r = -0.91), and sand (r = -0.83) in Station 3. Significant positive correlation existed between Total Nitrogen and PO_4^{2-} (r = 0.75, P < 0.01), NO_3^- (r = 0.69), SO_4^{2-} (r = 0.66, P < 0.05), silt (r = 0.89, P < 0.01) and clay (r = 0.61, P < 0.05).

The analysis also revealed significant (P < 0.01) positive relationship between Nitrate and SO_4^{2-} (r = 0.85). Nitrate also exhibited negative correlation with NH_4^+ (r = -0.57, P < 0.05) and Cl^- (r = -0.89, P < 0.01) in Station 1. Similarly, in Station 2, Nitrate correlated positively with SO_4^{2-} (r = 0.89, P < 0.01). Significant negative associations also existed between NO_3^- and NH_4^+ (r = -0.65, P < 0.05) as well as with Cl^- (r = -0.94, P < 0.01). In Station 3, NO_3^- correlated significantly and positively with SO_4^{2-} (r = 0.60, P < 0.05); but had inverse relationship between NO_3^- and Cl^- (r = -0.85, P < 0.01). A strong significant inverse relationship between SO_4^{2-} and with Cl^- (r = -0.85, P < 0.01) was recorded in Station 1. Sulphate in Station 2 related negatively with NH_4^+ (r = -0.79, P < 0.01), Cl^- (r = -0.93, P < 0.01). Nevertheless,

in Station 3, Sulphate significant negative relationship was with Cl^- (r = -0.73, P < 0.01). Ammonium ion had a weak positive relationship with Cl^- (r = 0.78, P < 0.01) in Station 1; but positively correlated with Cl^- in Station 2 (r = 0.75, P < 0.01) and Cl^- in Station 3 (r = 0.83, P < 0.01).

Temporal assessments of the relationship between crude oil pollution indicators and Nutritive salts in sediment.

Tables 6 and 7 show the results of seasonal assessments of correlations between crude oil pollution indicators and Nutritive salt levels in sediments. The analysis revealed that the relationship between THC and NH_4^+ (r = 0.57) and between THC and Cl^- (r = -0.52) were weak during the dry season; whereas THC exhibited a strong positive relationship with NH_4^+ (r = 0.66, P < 0.01) and Cl^- (r = 0.90, P < 0.01) during the wet season. Besides, strong inverse associations existed between THC and PO_4^{2-} (r = -0.64) as well as with NO_3^- (r = -0.56) during the wet season.

A significant but negative relationship during the wet season were those between TOC and PO_4^{2-} (r = - 0.76, P < 0.01), NO_3^- (r = -0.58, P < 0.01) and SO_4^{2-} (r = -0.53, P < 0.05). whereas, a significant positive (P < 0.01) relationship was recorded between TOC and NH_4^+ (r = 0.63).

Total Nitrogen (TN) in the dry season had no significant co-relationship with any other physiochemical parameters but in the wet season, it showed both positive and negative significant relationships. The positive ones were those between TN and PO_4^{2-}, NO_3^- and SO_4^{2-}; their correlation coefficient values were r = 0.86, P < 0.01, r = 0.74, P < 0.01 and r = 0.54, P < 0.05 respectively. While the negative correlation (P < 0.01) were those between TN and NH_4^+ (r = -0.72) and Cl- (r = -0.59).

During the dry season phosphate correlated positively with NO_3^- (r = 0.56, P < 0.05), SO_4^{2-} (r = 0.66, P < 0.01) and Cl^- (r = 0.54, P < 0.05). However, in the wet season, significant positive correlations (P < 0.01) existed between PO_4^{2-} and NO_3^- (r = 0.72) and SO_4^{2-} (r = 0.80). Also, inverse relationship was shown between PO_4^{2-} and NH_4^+ (r = -0.86). Correlation between NO_3^- and SO_4^{2-} was a strong positive (r = -0.76, P < 0.01) during the dry season. Sulphate only correlated negatively with NH_4^+ (r = -0.63) during the wet season and in the dry season, it showed a strong positive correlation (P < 0.01) with Cl^- (r = 0.70). In the wet season, NH_4^+ correlated with Cl^- (r = 0.51) and sand (r = 0.62), but in the dry season no significant co- relationship was established. Chloride showed significant relationships (P < 0.01) with silt (r = -0.69) and clay (r = 0.63) during the dry season but related inversely with silt only (r = -0.90, P < 0.01) during the wet season.

DISCUSSION

Sediment which provides habitat for a wide range of benthic and epi-benthic organisms also serves as the ultimate sink of contaminants in the aquatic systems because of their variable physical and chemical properties (Praveena *et al*., 2007). These contaminants (organic and inorganic compounds) may easily, slowly or poorly degrade under natural conditions.

Table 6: Pearson Product Moment Correlation of Physicochemical Parameters of Sediment (Dry Season)

	pH	EC	Salinity	THC	TOC	TN	PO_4^{2-}	NO_3^-	SO_4^{2-}	NH_4^+	CL^-
PH	1										
EC (μs/cm)	-.459	1									
Salinity (%)	-.100	.256	1								
THC (mgkg^{-1})	-.377	.851**	.142	1							
TOC (%)	.541*	-.125	.396	-.037	1						
T.N (%)	.009	-.312	.232	-.382	.135	1					
PO_4^{2-}(mgkg^{-1})	-.529*	.503	.280	.660**	-.071	-.145	1				
NO_3^- (mgkg^{-1})	-.372	.175	.626*	.267	.345	.228	.563*	1			
SO_4^{2-}(mgkg^{-1})	-.811**	.482	.490	.387	-.190	.191	.661**	.760**	1		
NH_4^+(mgkg^{-1})	.393	.529*	-.064	.570*	.064	-.467	.019	-.352	-.371	1	
Cl^-(mgkg^{-1})	-.724**	.516*	.300	.526*	-.123	-.255	.540*	.507	.704**	-.136	1

**. Correlation is significant at 0.01 levels (2-tailed).   *. Correlation is significant at 0.05 levels (2-tailed).

Table 7: Pearson Product Moment Correlationof Physicochemical Parameters of Sediment in Iko Estuary (Wet Season)

	pH	EC	Salinity	THC	TOC	TN	PO_4^{2-}	NO_3^-	SO_4^{2-}	NH_4^+	CL^-
pH	1										
EC (μs/cm)	-.205	1									
Salinity (%)	-.228	.627**	1								
THC (mgkg^{-1})	-.345	.884**	.845**	1							
TOC (%)	.299	.536*	.410	.519*	1						
T.N (%)	-.004	-.710**	-.638**	-.792**	-.861**	1					
PO_4^{2-}(mgkg^{-1})	.116	-.624**	-.359	-.642**	-.762**	.861**	1				
NO_3^- (mgkg^{-1})	.054	-.615**	-.358	-.568**	-.585**	.745**	.728**	1			
SO_4^{2-}(mgkg^{-1})	.077	-.341	.134	-.245	-.538*	.548*	.802**	.622**	1		
NH_4^+(mgkg^{-1})	-.254	.651**	.424	.660**	.639**	-.729**	-.866**	-.566**	-.636**	1	
Cl^-(mgkg^{-1})	-.355	.797**	.902**	.908**	.322	-.597**	-.414	-.414	-.007	.515*	1

**. Correlation is significant at 0.01 levels (2-tailed).   *. Correlation is significant at 0.05 levels (2-tailed).

There were spatial and seasonal variations in the pH of the sediments. The mean pH value of the sediment in Iko River estuary was 6.57. This result compares favourably with earlier reports of Smith (1996) as well as that of Daka and Moslen (2013) which considers that sediments are generally acidic. Contrasting results was obtained in Minichinda stream by Braide *et al*. (2004), who reported on alkaline sediment. The higher acidic sediment characteristics in Station 2 than Stations 1 and 3 could be attributed to the presence of mangrove vegetation which adds to the organic (humic) acid content of the sediment through defoliation and decay of leaves and other plant parts. Daka and Moslen (2013) affirmed that mangrove sediment is often acidic with acidity varying between 3.5 and 4.5. The pH values of sediments were higher during the dry season months and lower during the wet season months. The fluctuations in pH values during the different seasons were attributed to factors like removal of CO_2 by photosynthesis through bicarbonate degradation, dilution of waste with freshwater, reduction in salinity and temperature, and decomposition of organic matters.

Electrical conductivity of sediment varied between 1708 μs/cm in Station 1, 1497 μs/cm in Station 2 and 1384 μs/cm in Station 3. Mean values of conductivity in Stations 2 and 3 were relatively lower than in Station 2. The higher EC in Station 1 could be attributed to the high degree of anthropogenic activities such as waste disposal and agricultural run-off. This is similar to the findings of Ezekiel *et al*. (2011) (40-1940 μs/cm) in Sombreiro River but inconsistent with that of Sikoki and Veen (2004), who reported extremely low values of 3.8 - 10.0 μs/cm in the Shiroro reservoir. Seasonality profile of EC in the study area showed higher dry season values than its wet season counterpart across the stations. High dry season EC values were perhaps due to increased concentration of dissolved solids, relatively high flow of water, increased evaporation and input sewage. Aktaruzzaman *et al*. (2013) averred that dissolved solids could directly influence water conductivity, the higher the dissolved solids, the higher the conductivity. The minimal EC values observed in the wet season could be linked to dilution with rain water.

Spatial variation in sediment salinity showed elevated salt condition in all the three stations which may be ascribed partly to the finer particulate composition of grain size distribution of the sediment and to the salt excretory habit of mangrove trees (Prahl and Carpenter, 1983). In addition to exuding salts, mangroves also have the ability to exude sulphides from their tissues. This sometimes results in elevated poor water concentration of salts in localities where poor flushing area is common. The high salinity levels is indicative of a high concentration of total dissolved salts which in turn suggests that a contaminant plume from chemical pollutants (e.g. crude oil) towards the sediment is enhanced by the tidal waves. Freshwater run-off increased during the wet season, leading to a decrease in salinity. Variation in sediment salinity would certainly influence the existence, diversity and distribution of microphytes including the protists, in the estuarine mangrove ecosystem. Changes in salinity can cause changes in the relative diversity and abundance of organisms. Such changes may lead to degradation of the food and energy in the ecosystem.

Natural sources and anthropogenic activities are pathways through which hydrocarbon enters the marine environment. These natural sources include petroleum seeps, forest fires and post depositional transformation of biogenic precursors while the anthropogenic sources are from urban run-off, industrial effluents, sewage disposal, oil production and transportation activities. Levels of THC in the sediment were appreciably high with mean value ranging from 101.40 - 219.60 mgkg⁻¹, and Station 1 recorded the highest value more than Stations 2 and 3. The high concentrations observed in Station 1 may be ascribed to petroleum seeps from the abandoned oil well-head located in this station. The moderately high levels in Stations 2 and 3 could perhaps be due to the bunkering activities in this estuary in addition to the physicochemical properties of the sediment, which gave the hydrocarbon a strong affinity for particulate or organic matter. Similar observations have been made by Ezekiel *et al*. (2011) in Sombreiro River, Daka and Moslen (2013) in Azuabie Creek of the upper Bonny Estuary and Ezekiel *et al*. (2013) in Amassoma flood-plain. This report deviated from the findings of Davies and Tawari (2010) who recorded lower level of THC in Trans-okpoka Creek, upper Bonny Estuary.

The hydrocarbon levels in sediments also exhibited marked seasonality with higher values observed in the dry season. This may be ascribed to the presence of commercial activities with corresponding increase in transportation (motorized boats) within the estuary in the dry months and tidal effects not excluded. Lower levels of THC during the wet season may be linked to input of storm water during the wet season. Comparatively, levels of THC in sediment conforms to earlier reports that sediments serve as the ultimate sink of contaminants in the aquatic ecosystems (Awofolu *et al.*, 2005). The effects of hydrocarbon-laden sediments and overlying water on aquatic biota have attracted considerable attention. Petroleum hydrocarbons in polluted sediments have been closely correlated with alterations in detoxification enzymes in fishes, tissue abnormalities and reproductive hormones of flat fishes (Truscott *et al.,* 1992). Moles and Norcross (1998) also observed increases in fin erosion, liver lipidosis, gill hyperlasia and gill parasite coupled with decreased in macrophage aggregates in juvenile flat fishes exposed to oil-laden sediments. Dublin-Green (1990), noted that, continuous releases of petroleum effluents and chronic pollution, apart from causing measurable changes in the physicochemical parameters of an aquatic ecosystem, also sharply reduced species diversity, eliminated sensitive species, changed the location of significant biotype boundaries and increased the relative abundance of pollution tolerant species. Furthermore, Chinda and Braide (2003) averred that the presence of hydrocarbons in water have adverse effect on phytoplankton community structure and abundance.

Total organic carbon provides a measure of how much organic matter occurs in sediment. It also buffers the sediment, improves sediment structure, stimulates biological

activity and absorbs mineral nutrients. It is the main source of energy for soil organism. High percentage of organic carbon was recorded in station 3 (14.65 %) owing to the high rate of freshwater inflow enriched with organic debris from land run-off. Moderately high percentage of organic carbon in Station 1 (11.93 %) and Station 2 (13.39 %) could primarily be attributed to input from the mangrove in form of dead leaves and decaying prop roots. This supports the report of Smith (1996) that organic enrichment of mangrove sediment in the intertidal zone is from leaf litter derived from mangrove trees and from detritus. The percentage of total organic carbon observed in Iko River Estuary (8.30 - 20.60 %) show good correspondence with that of Ekeh (2005) (3.68 - 26.07 %) in Amadi and Nwaja Creek of the upper Bonny Estuary. Nevertheless, this was at variance with the reports of Ezekiel *et al*. (2011) where a range of 2.02 - 4.13 % was given for Sombreiro River; as well as that of Daka and Moslen (2013) where the range of 0.84 - 2.16 % was documented for Azuabie Creek of the upper Bonny Estuary. Organic matter decomposition may be attributed to the spatial variation in organic content. Sediment is a major site for organic matter decomposition which is largely carried out by bacteria.

The total organic carbon content of sediments also gives an idea of the origin of the sediment material. Organic carbon levels less than 12 % by weight of sediment samples imply that sediment material is derived from mineral source, while concentrations above 12 % suggest that sediments originated from decayed organic sources. This implies that the total organic content of the sediment of dry season (16.54 %) was mainly derived from decayed organic debris. However, during the wet season, the values recorded (11.02 %) were slightly below 12 %, an indication that hydrocarbons may have contributed to the organic load of the Iko River Estuary during this period. The levels of Total Nitrogen across the stations were quite low (0.31 - 0.35 %). The low nitrogen levels of Iko River estuary may be traced to frequent cases of crude oil pollution in the region. The presence of crude oil in sediment has been reported (Udosen, 2001), to hinder the availability of nitrogen and phosphorus to plants including microphytes. Shukla and Chandel (2008) also reported that the nitrogen content in surface mineral soils is about 0.02-0.5 % and that soil nitrogen occurs as part of organic molecule.

The total nitrogen contents recorded for both seasons showed marked variations during the wet (0.39 %) and dry seasons (0.24 %). This marked seasonality regime was expected considering the fact that tidal influence and terrestrial runoff might have contributed to the high load of nitrogen from agricultural and sewage effluent discharges. Naturally, major nutrients such as nitrogen, phosphorus and potassium are limiting or lacking or better still low in sediment because plants use large amounts for their growth and survival.

Phosphates and nitrates normally give an indication of the nutrient level in the study area. Variations across the sampling stations were observed in the concentration of these nutrients. Nutrient levels were found to be generally higher in Stations 1 and 3 than in Station 2. Domestic wastes input and surface run-off could be the possible explanation for the high levels of nutrients recorded at these stations. However, the mean concentration (28.0 - 38.63 $mgkg^{-1}$) of phosphates observed in this study compares favourably to the range value of (0.29 - 244 $mgkg^{-1}$) obtained by Braide *et al.* (2004) and (13.43 - 26.31 $mgkg^{-1}$) recorded by Ezekiel *et al.* (2013). These findings were at variance with the views of Daka and Moslen (2013) (0.5 - 8.10 $mgkg^{-1}$). Similarly, the nitrates values (19.90 - 25.85 $mgkg^{-1}$) observed in this study deviated from the reports of Ezekiel *et al.* (2011) (2.6 - 4.1 $mgkg^{-1}$), Daka and Moslen (2013) (2.32 - 7.84 $mgkg^{-1}$) and Ezekiel *et al.* (2013) (2.46 - 4.17 $mgkg^{-1}$); all in the Niger Delta region of Nigeria. Seasonal variations were observed in the concentration of phosphates and nitrates with exceptionally higher values during the wet season. Phosphates and nitrates are components of agricultural fertilizers commonly used by farmers in the Niger-Delta area. These fertilizers may be leached into the rivers during the wet season and can account for the increased concentration in Iko River during the wet season. Bay *et al.* (2003) averred that urban storm water runoff is a major source of contaminants to southern California's coastal waters and was responsible for the detectable toxicity of Ballona Creek.

The concentrations of SO_4^{2-}, NH_4^+ and Cl^- in the sediments of Iko River Estuary varied across the stations and were remarkably higher during the dry season except for SO_4^{2-} which recorded higher concentration in the wet season. Elevated wet season concentration of SO_4^{2} may be ascribed to the allochthonous sources of nutrients into the estuary, which may have been trapped by the sediments as insoluble complexes. Crude oil pollution has also been associated with increase in nutritive salts and salinity levels of aquatic systems (Rhykered *et al*., 1995) and may have contributed to the high concentrations of SO_4^{2}, NH_4^+ and Cl^- levels in the sediments during the dry season.

The nutritive value of the sediment and the organic matter composition mayexplain the dynamics in the benthic community structure found in Iko river estuary

CONCLUSION

Understanding the condition of estuaries is critical if Nigeria is to develop effective plans to maintain, manage and restore them. It has been found in the present study that the sediments of Iko River Estuary is laden withhydrocarbon and other organic pollutants; as well as with nutritive salts such asPO_4^{2-}, NO_3^-, SO_4^{2-}, NH_4^+ and Cl^-salts. Associations between pollutants and nutritive salt levels in the sediments were established.Spatio-temporal distributions were recorded in the study. Higher level of nutritive salts were recorded in the wet season whereas the hydocarbon contents of the sediments were higher in the months of the dry season.

REFERENCES

Adeyemo,O. K., Adedokun, O. A., Yusuf, R.K. and Adeleye, E.A. (2008). Seasonal Changes in Physico-Chemical Parameters and Nutrient load of River Sediments in Ibadan City, Nigeria. *Global Network on Environmental Science and Technology Journal*,2: 326-336.

Aktaruzzaman, M., Mohammed, S. H., Abu, N. M. F., Mohammed, J. U., Syed, H. R., Mohammed, A. Z. C., Mohammed, K. A., Zeenath, F. and Mohammed A. H. (2013). Water and Bottom Sediments Quality of Brackish Water Shrimp Farms in Kaliganjupazile, Satkhira, Bangladesh. *Soil Environment,*.32 (1): 29-35.

Amadi, A.N., Olasehinde, P.I., Obaje, N.O., Unuevho, C.I., Yunusa, M.B., Keke, U. and Ameh, I.M. (2017) . Invest igat ing the Qual i ty of Groundwater from Hand-dug Wells in Lapai, Niger State, North-central Nigeria using Physico-chemical and Bacter iological Parameters. *Minna Journal of Geoscience*, 1(1), 77 – 92.

American Public Health Association (APHA) (2005). Standard methods for the examination of water and waste water. Washington, DC: American Public Health Association.

Awofolu, O. R., Mbolekwa, L., Mtshemla, V.and Fatoki, O. S. (2005). Levels of Trace Metals in Water and Sediment from Tyume River and the effects on an Irrigated Farm Land. *Water South Africa,* 31: 87 – 94.

Bay, S., Jones, B. H., Schiff, K. and Washburn, L. (2003). Water Quality Impacts of Storm-Water Discharges to Santa Monica Bay. *Marine Environmental Research,* 56:205-223.

Benson, Nsikak U. and Etesin, Usoro M. (2008). Metal contamination of surface water, sediment and Tympanotonus fuscatus var. radula of Iko River and environmental impact due to Utapete gas flare station, Nigeria. *Environmentalist*, 28:195–202.

Braide, S.A., Izonfuo, W. A. L., Adakwu, P. U., Chinda, A. C. and Obinwo, C. C. (2004).Water Quality of Mini-Ewa Stream, A Swamp Forest Stream Receiving Non-Point Source Waste Discharge in Eastern Niger Delta. *Nigeria Science Afric*a, 3(1): 1-8.

Chinda, A. C. and Braide, S. A. (2003). Epipelic Algae of Tropical Estuary: Case of Stable and Invariable Seasonally Community. *Polish Journal of Ecol*ogy.51(1):91-99.

Davies, O.A. and Tawari, C. C. (2010). Season and Tide Effects On Sediment Characteristics of Trans-Okpoka Creek, Upper Bonny Estuary, Nigeria. *Agriculture and Biology Journal of North America*, 1(2): 89-96.

Daka, E and Moslen, M. (2013). Spatial and Temporal Variation of Physico-Chemical Parameters of Sediment from Azuabie Creek of the Upper Bonny Estuary, Niger Delta.*Research Journal of Environmental and Earth Sciences*.5(4):219-228.

Dublin-Green, C.O. (1990). The Foraminiferal Fauna of the Bonny Estuary: A Baseline Study. Nigerian Institute of Oceanography, *Marine Res*ources.64:12-18.

Ekeh, C. A. (2005). The Study of Plankton in Amadi andNwaja Creek of the Upper Bonny Estuary. Unpublished M.Sc. Thesis, Rivers State University of Science andTechnology, Port-Harcourt, Nigeria, 180 pp.

Essien J. P., Antai, S. P. and Benson, N. U. (2008). Microalgae Biodiversity and Biomass Status in Qua Iboe Estuary Mangrove Swamp, Nigeria. *Aquatic Ecology.*42:71-81.

Ezekiel, E. N., Hart, A.I. and Abowei, J. F. N. (2011).The Sediment Physical and Chemical Characteristics in Sombreiro River, Niger Delta, Nigeria.*Research Journal of Environmental and Earth Sciences*.3(4):341-349.

Ezekiel, E., Abowei, J. and Charles, E. (2013). Effects of flooding on Amassoma flood plain sediments Niger Delta. *Applied Science Report*. 4(1):173–180.

Ferraro, S. P. and Cole, F.A. (1992). Taxonomic Level Sufficient for Assessing a Moderate Impact on Macrobenthic Communities in Puget Sound, Washington USA.*Canadian Journal of Fisheries and Aquatic Science.*49:1184-1188.

Grosheva, E. I., Voronskaya, G. N. and Pastukhove, M. V. (2000). Trace Element Bioavailability in Lake Baikal. *Aquatic Ecosystem. Health Management.* 3:229 – 234.

International Fertilizer Development Center (IFDC-Africa) (1996). Restoring and Maintaining the Productivity of West Africa Soil: Key to Sustainable Development. Miscellaneous Fertilizer Studies No. 1494 Pp.

Jackobson, S. T. (1992). Chemical Reaction and Air Change during the Decomposition of Organic Matter. *Resources Conservation and Recycling.*6: 529 -539.

King, R. P. and Jonathan, G. E. (2003). Aquatic Environmental Perturbations andMonitoring: African Experience.USA. 166 pp.

Moles, A. and Norcoss, B.L. (1998). Effects of Oil-Laden Sediments on Growth and Health of Juvenile Flatfishes.*Canandian Journal of Fishery and Aquatic Sci*ence.55:605 – 610.

Nordstrom, K. F. (1992). Estuarine Beaches. Essex. England. Elsevier Science Publishers Ltd. 225pp

Palmer, M. A., Ambrose, R. F. andPoff, N. L. (1997). Ecological Theory andCommunity Ecology. *Restoration Ecology,*5(4): 291-300.

Prahl, F. G. and Carpenter, R. (1983). Polycyclic Aromatic Hydrocarbon (PAH)-Phase associated in Washington Coastal Sediment. *Geochim-Cosmodium Acta,*47:1013-1023.

Praveena, S. M., Radojevic, M., Abdullah, M. H. And Aris, A. Z. (2007). Application of Sediment quality. guidelines in the Assessment of Mangrove Surface Sediment in Mengkabong Lagoon, Sabah, Malaysia.*Global Journal and Environmental Res*ources,**1**(3): 96-102.

Radojevic, M. and Bashkin, V. N. (1999). Assessment of Pollutants in Water and Sediment Samples in Lake Chad, Baga, North Eastern Nigeria. "*Practical Environmental Analysis," The Royal Society of Chemistry,Cambridge*," p. 466.

Ravera R. C., Beone,G.M., Dautas,M. and Lodigiani, P. (2003). Trace Element concentrations in Freshwater Mussels and Macrophytes as related to those in their environment. *Journal of Limnology*. **291**:61-70.

Rhykered, R. I., Weaver, R.W. and Mclnnes, K. J. (1995). Influence of Salinity on Bioremediation ofOil in Soil. *EnvironmentalPollution,*90:127-130.

Shukla, R. S. and Chandel, P. S. (2008). Plant Ecology including Ethnobotany and Soil Science, *S.*Chand publisher, New Delhi: 544pp.

Sikoki, F. D. and Veen, J. V. (2004). Aspects of Water Quality and the Potential for Fish Production of Shiroro Reservoir, Nigeria.*Livestock System Sustainable Development.* 2: 1- 7.

Truscott, B., Idler, D. R. and Fletcher, G. L. (1992). Alternation ofReproductive Steroids of Male Winter Flounder (*Pleuronectesamericanus*) Chronically Exposed to Low Levels ofCrude Oil in Sediments. *Canadian Journal of Fish and Aquatic Science*.49: 2190-2195.

Udosen, E. D.(1994). Level of Toxic Metals in *Telfairia occidentalis* from a paint industry environment. *Journal of Applied Chemistry and Agricultural Research,*1: 35-42.

Vignier, V., Vandermeulen, J. H. and Fraser, A.J. (1992). Growth and Food Conversion by Atlantic Salmon pair during 40 days Exposure to Crude Oil. *Transaction of American Fishery Society*. 121:322-332.

Wang, C., Niu, Z., Li, Y., Sun, J. and Wang, F. (2011). Study on heavy metal concentrations in river sediment through the total amount evaluation method. *Journal of Zhejiang University SCIENCE,* 12(5): 399-404.

Young, G. C. and Palter, I. C. (2001). Influence of exceptionally high Salinities, Marked Variations in Freshwater discharge and opening of Estuary Mouth on the Charateristics of the Ichthyofauna of a Normally-Closed Estuary.