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ASSESSMENT OF SEASONAL VARIATIONS OF HYDROCHEMICAL SIGNATURES OF SURFACE WATER QUALITY USING MULTIVARIATE STATISTICAL METHODS

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ABSTRACT

Analyses of forty water samples from rivers and their tributaries were conducted to evaluate the effect of seasonality on chemistry of the Eastern Niger Delta drainage basin. Results show the waters to vary from acidic to alkaline nature across seasons. Definitive anion compositions indicates the waters to be of Cl – SO_4 type in both dry and wet seasons with an increase of anthropogenic pollution indicators (NH_4 – NO_3) in the wet season. Application of multivariate statistical interpretation modules (correlation, factor and cluster analyses) reveals variations in hydrochemical status to be dominantly controlled by natural processes (water-rock reactions and water mixing) and to degree anthropogenic activities.

Keywords: water quality, geogenic and anthropogenic inputs, correlation and factor analysis, Nigeria

INTRODUCTION

Rivers and their catchment constitute an important part of the natural environment and play an integral part in the sustainability and livelihood of communities in the vicinity of such river basins. Their status consequently affects the health and well being of humans, animals and plants that depend on this natural resource. The quantity and quality of surface water within a region is usually controlled by natural processes (precipitation rate, weathering and erosion processes) and anthropogenic effects (urban, industrial and agricultural activities as wells as marine transportation). This places a demand for assessment of water quality as key to strategic resource management and sustainable development planning in both developed and developing countries such as Nigeria. This is however best achieved using scientific modules as is the interest of this paper.

Background geochemistry is an important tool with which to evaluate the hydrochemistry of the surface and ground water and to plan the maintenance of water quality. The chemical composition and characteristics of surface and ground waters have been shown to vary with seasonal regimes (Pejman et al., 2009; Ekwere, 2010 and Garizi et al., 2011). This is usually associated with variations in precipitation, surface run-off, groundwater flow, interception and abstraction of river discharge (Vega et al., 1998; Pejman et al., 2009 and Garizi et al., 2011). Ouyang et al., (2006) concludes that influx of pollutants from series of transport pathways (storm water run-off, discharge from ditches and creeks, vadose zone leaching, groundwater seepage and atmospheric deposition) are seasonally controlled. This makes it apparent to consider seasonal variations in attempts to establish surface water quality monitoring programs and hazard prognosis.

The application of multivariate statistical techniques has proven its usefulness in the interpretation of complex data matrices in seasonal water quality assessment in a variety of localities including Nigeria. This is evident in the works of; Edet & Offiong, (2003), Pejman et al., (2009), Ekwere, (2010) and Garizi et al., (2011). The current study has an interest of providing background data set, as deduced from statistical approaches, for future assessment under conditions of climate change and population growth. Observed seasonal pattern of water will serve in optimizing management strategies and facilitate a continuum for improved understanding of surface water resources.

Description of study area

The study area designated Eastern Niger Delta stretches the coastal plain physiographic province, extending eastwards from Ikot Abasi to Calabar area and spanning the shorelines of Akwa-Ibom and Cross River States of south-eastern Nigeria. The study area is about 200km long and about 55km wide, delimited by longitudes 7º 30 – 8º 15 E and latitudes 4º 30 - 4º 40 N (Fig. 1).

The study area is built of Tertiary and Quaternary sediments referred to as Coastal Plain Sands of the broader Niger Delta basin (Short & Stauble, 1967). The sediment fill of this formation consists of alternating sequences of gravel, sand, silt, clay and alluvium sourced from three major geologic units on the hinterlands. These are; (1) the Precambrian Oban Massif Complex made up of migmatites-gneisses, granites, schists, para-schists, pegmatites and a host of other ultra-mafic rock suites (Ekwueme, 2003), (2) Cretaceous sedimentary fill known as the Calabar Flank, composed of limestones, sandstones, shales and marls (Reijers, 1996) and (3) the lower Benue Trough (Anambra Basin) of post-Cretaceous sediments (shales, sandstones, siltstones and limestones) with associated Pb-Zn sulphide mineralization (Dessauvagie, 1975).

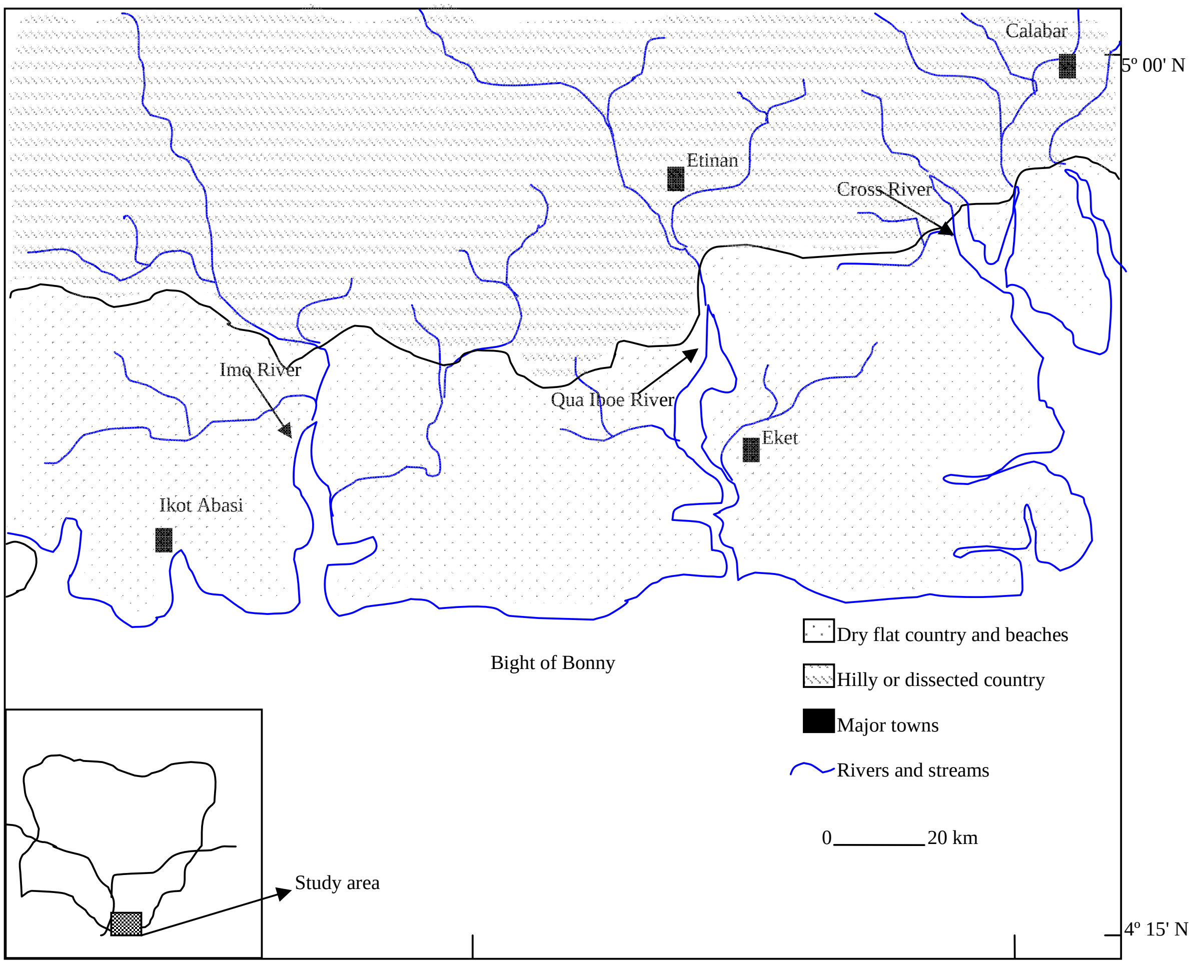

Fig. 1 Map of Niger Delta Basin showing sampled rivers; inset index map of Nigeria (modified from Elueze et al., 2009)

Another source of sediments into the study area is the Cross River Delta (Rio Del Rey Basin), Reijers (1996) and Elueze et al., (2009). The three major rivers in this study (Imo, Qua-Iboe and Cross River) and their tributaries drain the aforementioned geologic units on the hinterlands. Thus the differences in chemical composition, porosity and permeability, and origin of the different rock units and their associated sediments will influence the composition of the water which drains through them.

The area lies within a morphological enclave of flat and low-lying terrain constituting part of the coastal lowland/ Niger Delta region of southern Nigeria with elevations ranging from less than 10m at the coastal fringe to about 80m northwards.

The study area receives an average rainfall of about 254mm annually within two distinct seasons; dry and wet seasons. Mean annual air temperature and relative humidity are 26.8ºC and 84.6% respectively (Edet & Worden, 2009). The land use in the study area is of built-up urban setting, forests and croplands.

METHODS

The Imo, Qua-Iboe and Cross Rivers and their tributaries drain about 70% of the eastern arm of the Niger Delta; hence their assessment can be used to define the surface water quality of the study area. Forty water samples were collected from the rivers and associated streams between the period of June 2008 to February 2009, to cover for variations within the two major seasons viz wet and dry. Two samples were collected from each location in 75cl polyethylene bottles. The sample bottles were soaked in 10% HNO_3 for 24 hours and rinsed several times with de-ionized water prior to use. At the sampling locations, the bottles were thoroughly rinsed with aliquots of the sampled waters, prior to collection. One sample from each location was preserved by acidifying to pH ca.2 with 0.5ml of concentrated HNO_3 acid for trace metals analysis. Field measurements included temperature, electrical conductivity, total dissolved solids, dissolved oxygen, pH and Eh were carried out using standard field equipment (PHT-027 multi-parameter water quality probe). Prior to measurement of pH, the electrode was calibrated using pH 6.88 and 4.01 buffer solutions at a similar temperature to the water samples. The same meter and an ionode ORP electrode were used to measure Eh.

Chemical analyses were carried out for the major ion concentrations of water samples using the standard procedures recommended by APHA (1995). Trace metal contents were also determined by atomic absorption spectrometry (AAS).

RESULTS AND DISCUSSION

Results from analysis of selected parameters (physical and chemical) for the dry and wet seasons are presented in Tables 1&2 respectively. These also show statistical deductions from data set (mean and standard deviation). Maximum water temperature and higher mean value is recorded in the dry season as expected in this humid tropical setting. Results suggest acidic – alkaline waters for the rivers marked by pH ranges of 6.30-7.18 and 5.60-6.78 for the dry and wet seasons respectively. However acidity of the waters increases in the wet season with a mean pH of 6.11. This may be attributed to acidic conditions initiated by higher precipitation with increased weathering of silicate, carbonate and sulphide minerals as well as atmospheric contributions (Ekwere, 2010). Total dissolved solids (TDS) increases in the wet season due to weathering intensity and commensurately electrical conductivity (EC) increases along.

Oxygen is probably the most important chemical constituent of surface water chemistry, as all aerobic organisms require it for survival. Dissolved oxygen (DO) shows mean value differences across sampling seasons. The decrease in the wet season can be linked to increase in marine biota population and higher demands for the resource. Mean values for Eh do not show any remarkable difference between the two sampling seasons, just as alkalinity doesn't too, though it is higher in the wet season.

The trend of dominance of major nutrients in the waters are; $Cl^- > NH_4 > SO_4 > NO_3 > PO_4$ for the dry season and $Cl^- > NO_3 > NH_4 > SO_4 > PO_4$ in the wet season. The definitive anions for water quality, shows that the waters are of Cl – SO_4 type. The average contents of Cl, SO_4 and PO_4 are higher in the dry season. This difference is attributable to concentration of solutes resulting from higher temperature regimes and evaporation during the dry season and dissolution effects from influx of surface run-off in the wet season. Ammonium (NH_4) and nitrate (NO_3) contents increase during the wet season and this is related to wash-off from crop lands which have been enhanced with fertilizers. These fertilizers have urea (NH_3 compound) and nitrate as major constituents.

A wide range of metals may be found in rivers from natural sources where metal ores are present in the rocks over which the river flows or in the aquifers feeding water into the river. However many rivers have an increased load of metals because of industrial activities which include mining and quarrying and the processing and use of metals. Trace elements (Pb, Zn, Cd, Cr, As and Ni) compositions, as shown from analyses do not vary significantly across sampling seasons. Iron contents are however higher in the dry season than in the wet seasoning. Part of the drainage basin catchment includes the Precambrian basement of the Oban Massif, dominated by ultra-mafic and mafic rock suites that are hosts to most trace and rare metals species as revealed from hydrogeochemical modelling (Ekwere, 2010). Economic activities of mining and quarrying within the basement complex are also responsible for disaggregation and mobilization with the release of soluble species of these metals. Cross River and Qua Iboe rivers drain most of the urbanized and industrial settlements within the study area. These areas have the presence of large and small scale processing and production industries, automobile repair and service shops and a wide variety of artisanal industries, which may serve as sources of trace metal release from their effluents into the environment.

A plot of total alkalinity versus Cl^{-} + SO_4^{2-} (Figure 2), shows most points plotting below the equiline across seasons. However two locations from the dry season and one from the wet season plot in proximity to the equiline. This indicates that salinities of majority of the waters are related to precipitation and seawater mixing across shorelines rather than water-rock interactions.

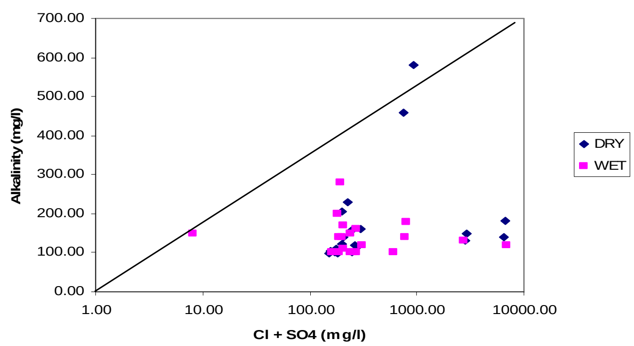

Figure 2. Plot of alkalinity vs Cl+SO_4 for different samples across sampling seasons

Correlation analysis

Correlation analyses were performed (Tables 3&4) in order to indicate the sufficiency of one parameter to predict another. Only correlation coefficients of r = or > 0.50 were considered significant for interpretation. In the dry season temperature exhibited a strong positive correlation with Eh (0.58), PO_4 (0.72) and Cr (0.65). Other strong positive correlations within the same season were between pH- Eh, Cr; Cl – SO_4; PO_4, NH_4 and NO_3 (Table 3). The metals show positive correlations between Pb – Cd – Cr and Fe – Ni in the dry season.

In the wet season (Table 4), strong positive correlations exist between temperature – Eh, Fe; pH – Eh; Cl – SO_4; TDS – As, Cr; Pb – Zn, Cd and Cr. This series of correlations across sampling seasons represent strong chemical association, non-competitive correlations between ions of same or varying charges and valence number and other physical parameters (Aris et al., 2007). The strong positive correlation between major components of seawater (Cl-SO_4) indicates seawater influence on the salinity of the waters. Also correlations between anthropogenic indicators (NH_4-NO_3-PO_4) suggest some form of pollution on water chemistry largely from agricultural fertilizer use on crop lands and effluents/waste disposal (Edet & Worden, 2009). Trace metal correlations indicate a dominance of geogenic relations (Elueze et al., 2009). However the variations of relationships may indicate the complexity of the hydrochemical components of natural waters as they contain dissolved and suspended substances of mineral origin (Aris et al., 2007).

Factor analysis

From computed data, four factors were determined to have controls on the nature of the waters in both the dry and wet seasons (Tables 5&6). Only factor loadings of score >0.40 were considered for interpretation.

The four factors from the dry season accounted for a total variance of 69.38% of the data set. Factor 1 (Temp, EC, Cl, SO_4, PO_4, NH_4 and NO_3) controlled 24.80% of total data variance. This factor shows the effect of physical parameter (temperature) on availability of principal components of surface water quality, relative to mineral dissolution and water mixing across water interfaces. Imprints of anthropogenic indices are evidence within this factor. Factor 2 (Temp, TDS, DO, PO_4, Pb, Cd, Cr and Fe) accounted for 21.33% of data variance. The factor represents input of geogenic sourcing (mineral dissolution) controlled by prevalent temperature regime (Ekwere, 2004). Factor 3 (pH, Eh, SO_4, Cd) and factor 4 (Pb-Zn) also represent geogenic influence on water chemistry with an imprint of mineralization of the lower Benue Trough (Ekwere and Elueze, 2012).

In the wet season, the four factors accounted for about 67% of total data variance. Factor 1 (Temp, pH, EC, DO, Eh, Cr, Pb, Zn, Cd, Ni and Fe) accounted for about 25% of total data variance. This factor reflects the effect of physical conditions on water-rock reactions and release of soluble mineral species (Ekwere, 2010). It is a natural factor related to the lithogenic composition of the study area. Factor 2 (TDS, DO, Cl, SO_4, PO_4, NH_4, Cr and As) represented about 18% of data variance reflecting influence of natural processes of mineral dissolution, water mixing and anthropogenic effects of waste/sewage disposal and agricultural activities. Factor 3 (Alkalinity, PO_4, Pb, Zn, Ni) and factor 4 (EC, Alkalinity, NH_4, NO_3, As, Fe) together represented about 23% of total data variance. They reflect the interplay of natural and anthropogenic elements in quality of surface waters.

From the assessment, temperature, total solids and principal nutrients (Cl, SO_4, NO_3 and NH_4) are the most significant parameters contributing to water quality variations in the dry and wet seasons of the study area. Nitrate, phosphate and ammonium with strong positive loadings in the dry season are significant to water quality variation indicating inorganic nutrients from croplands and sewage (Pejman et al., 2009). Their influence is reduced from dilution effects in the wet season. Presence of trace metal loadings as significant parameters, confirms dominance of water-rock reactions and dissolution effect in the wet season.

Table 1 Results of analysis of physico-chemical parameters for samples from dry season

sample	Temp.	pH	EC	TDS	DO	Eh	Alkalinity	Cl^-	SO_4	PO_4	NH_4	NO_3	Pb	Zn	Cd	Cr	As	Fe	Ni
L1	32.01	7.04	35.02	941.00	53.38	1852.00	120.70	195.10	2.18	1.64	1.68	1.48	0.06	0.05	0.05	0.04	0.01	4.04	0.02
L2	30.40	7.18	2182.00	815.00	40.92	1954.00	580.00	925.00	6.80	1.20	18.40	2.62	0.08	0.07	0.03	0.04	0.02	2.87	0.02
L3	30.60	7.04	63.10	1652.00	46.42	1800.00	114.90	280.43	1.81	0.14	1.71	1.88	0.04	0.04	0.02	0.04	0.03	6.48	0.06
L4	29.00	6.82	28.00	1654.00	44.18	1192.00	158.00	242.62	4.82	0.60	1.82	1.95	0.07	0.05	0.05	0.03	0.01	6.72	0.04
L5	29.50	6.85	14.03	1438.00	42.08	1186.00	102.20	164.02	8.64	0.82	2.60	2.08	0.09	0.06	0.03	0.02	0.02	1.22	0.04
L6	30.60	6.65	2263.01	681.00	48.60	1401.00	180.48	6660.14	14.76	1.62	22.61	8.50	0.04	0.03	0.04	0.02	0.02	6.81	0.06
L7	30.40	6.30	9.00	816.00	44.62	1192.00	109.30	170.85	4.63	0.86	1.62	1.28	0.05	0.07	0.02	0.02	0.01	7.34	0.04
L8	28.40	6.40	12.01	2043.00	30.56	1273.00	228.01	220.40	6.42	0.09	1.82	1.53	0.06	0.08	0.04	0.01	0.02	5.88	0.06
L9	29.80	6.90	122.00	81.00	35.52	1242.00	160.20	290.20	8.32	0.12	21.83	4.20	0.03	0.08	0.04	0.03	0.02	2.24	0.03
L10	30.80	6.98	6324.20	52.00	31.62	1401.00	150.01	2942.68	8.92	1.24	19.15	6.08	0.04	0.07	0.02	0.03	0.03	1.64	0.05
L11	30.00	6.98	30.00	645.00	39.26	1730.00	99.60	179.20	1.08	0.21	0.78	1.29	0.03	0.03	0.01	0.02	0.04	3.04	0.01
L12	29.80	7.10	2044.00	71.00	35.99	2000.00	460.00	752.00	3.40	0.17	14.20	1.85	0.05	0.05	0.01	0.02	0.01	2.66	0.01
L13	30.00	6.94	55.00	1155.00	40.49	2000.00	101.80	250.16	0.10	0.02	0.32	0.89	0.02	0.02	0.02	0.02	0.01	5.46	0.03
L14	28.00	6.79	22.00	125.00	38.29	1150.00	139.00	206.00	2.98	0.01	0.63	1.06	0.04	0.03	0.02	0.02	0.03	5.62	0.02
L15	29.00	6.72	11.00	1026.00	35.07	1069.00	98.10	148.00	4.63	0.01	1.40	1.10	0.04	0.04	0.02	0.01	0.01	0.23	0.02
L16	30.00	6.80	2084.00	622.00	44.50	2000.00	140.00	6401.10	10.73	0.82	18.42	7.31	0.01	0.05	0.01	0.01	0.01	1.16	0.01
L17	29.00	6.80	7.00	513.00	40.32	1089.00	103.10	151.93	3.86	0.04	0.71	0.92	0.03	0.05	0.01	0.01	0.02	6.32	0.02
L18	28.80	6.79	9.00	159.00	28.82	1256.00	207.00	199.20	3.78	0.04	0.09	1.03	0.03	0.41	0.02	0.01	0.01	4.99	0.04
L19	29.60	6.70	107.00	506.00	30.29	1239.00	120.11	260.18	4.20	0.04	17.91	3.11	0.01	0.05	0.01	0.01	0.01	1.16	0.01
L20	29.00	6.72	220.00	30.00	0.48	1196.00	130.00	2832.67	6.78	0.18	18.11	4.02	0.02	0.02	0.01	0.01	0.01	1.48	0.03
Mean	29.74	6.83	782.07	751.25	37.57	1461.10	175.13	1173.59	5.44	0.49	8.29	2.71	0.04	0.07	0.02	0.02	0.02	3.87	0.03
SD	0.94	0.22	1560.23	601.02	10.87	349.13	124.84	2007.14	3.56	0.56	8.98	2.23	0.02	0.08	0.01	0.01	0.01	2.34	0.02

*All values in ppm, except temperature, EC and Eh in º C, µS/cm and mV respectively

Table 2 Results of analysis of physico-chemical parameters for samples from wet season

Sample	Temp.	pH	EC	TDS	DO	Eh	Alkalinity	Cl^-	SO_4	PO_4	NH_4	NO_3	Pb	Zn	Cd	Cr	As	Fe	Ni
L1	28.60	5.79	780.00	824.00	0.56	1720.00	100.00	184.34	1.21	0.10	0.83	7.68	0.05	0.05	0.04	0.03	0.03	0.73	0.08
L2	28.70	6.20	1490.00	826.00	0.62	2000.00	140.00	765.72	2.57	0.11	14.08	6.88	0.05	0.07	0.04	0.03	0.04	0.90	0.10
L3	25.00	6.12	340.00	1660.00	0.74	1237.00	100.00	255.24	3.15	0.06	0.33	8.63	0.02	0.03	0.01	0.01	0.02	1.18	0.03
L4	25.00	5.81	320.00	1225.00	0.42	1143.00	140.00	198.52	3.34	0.10	0.56	8.05	0.04	0.04	0.03	0.02	0.02	1.08	0.08
L5	26.40	5.79	120.00	5750.00	1.24	1063.00	100.00	155.98	5.03	0.09	1.20	10.82	0.04	0.04	0.04	0.02	0.03	0.48	0.07
L6	27.80	6.44	1730.00	7068.00	1.08	2000.00	100.00	594.14	8.64	0.08	16.20	10.93	0.02	0.02	0.01	0.01	0.10	0.27	0.03
L7	27.30	5.70	210.00	915.00	1.26	1083.00	100.00	235.80	4.15	0.09	0.64	8.17	0.03	0.05	0.03	0.01	0.02	0.34	0.06
L8	27.40	5.72	500.00	3005.00	0.78	1253.00	200.00	175.84	4.73	0.09	0.09	9.38	0.03	0.04	0.02	0.01	0.03	0.36	0.05
L9	25.30	5.60	240.00	1224.00	1.28	1194.00	110.00	205.20	3.41	0.10	18.60	8.60	0.03	0.02	0.01	0.02	0.00	2.19	0.01
L10	26.80	6.12	710.00	709.00	0.96	2000.00	100.00	265.16	5.79	0.16	20.00	8.63	0.02	0.04	0.02	0.02	0.02	0.07	0.05
L11	28.90	6.78	788.00	746.00	0.43	1840.00	140.00	188.36	2.26	1.10	0.64	9.60	0.03	0.08	0.04	0.07	0.01	0.06	1.02
L12	29.00	6.40	1588.00	727.00	0.37	1620.00	180.00	787.60	3.56	0.19	18.06	8.68	0.08	0.09	0.06	0.07	0.06	0.07	1.10
L13	27.00	6.50	380.00	1260.00	0.41	1400.00	120.00	305.24	3.25	1.06	0.39	8.80	0.01	0.01	0.03	0.03	0.05	0.01	2.05
L14	26.20	6.80	360.00	1445.00	0.36	1244.00	170.00	204.60	4.36	0.40	1.04	8.05	0.06	0.08	0.05	0.04	0.01	0.06	0.16
L15	27.20	5.60	300.00	530.00	0.42	1164.00	150.00	7.04	1.09	1.28	1.28	12.84	0.02	0.01	0.02	0.06	0.01	0.05	0.41
L16	28.20	6.70	1846.00	690.00	0.46	1800.00	120.00	6841.42	8.68	0.04	18.24	12.98	0.06	0.05	0.03	0.03	0.06	0.04	1.24
L17	27.60	5.90	240.00	755.00	0.51	1483.00	160.00	265.44	4.75	0.07	0.69	10.12	0.01	0.02	0.05	0.04	0.04	0.08	0.20
L18	28.20	5.72	600.00	2730.00	0.48	1353.00	280.00	185.94	5.74	0.03	1.07	11.36	0.06	0.06	0.05	0.01	0.06	0.10	0.32
L19	26.30	5.80	280.00	920.00	0.75	1290.00	150.00	235.41	3.48	1.12	22.40	8.80	0.02	0.03	0.04	0.03	0.02	0.04	2.27
L20	27.70	6.70	8204.00	305.00	0.57	1600.00	130.00	2721.62	6.00	0.20	30.00	9.60	0.04	0.01	0.06	0.05	0.01	0.02	0.10
Mean	27.23	6.11	1051.30	1665.70	0.69	1474.35	139.50	738.93	4.26	0.32	8.32	9.43	0.04	0.04	0.03	0.03	0.03	0.41	0.47
SD	1.24	0.42	1769.94	1769.53	0.31	323.29	44.54	1548.25	2.03	0.43	9.98	1.64	0.02	0.02	0.02	0.02	0.02	0.56	0.69

*All values in ppm, except temperature, EC and Eh in º C, µS/cm and mV respectively

Table 3 Correlation matrix for water samples from dry season

	Temp	pH	EC	TDS	DO	Eh	ALK	Cl	SO_4	PO_4	NH_4	NO_3	Pb	Zn	Cd	Cr	As	Fe	Ni
Temp	1.00																		
pH	.39	1.00																	
EC	.18	.15	1.00																
TDS	.01	-.20	-.47	1.00															
DO	.49	.18	-.55	.40	1.00														
Eh	.58	.62	.09	.05	.35	1.00													
ALK	.06	.40	.20	-.12	-.01	.43	1.00												
Cl	.24	-.08	.57	-.23	.00	.21	.02	1.00											
SO_4	.09	-.24	.46	-.12	-.03	-.18	.11	.78	1.00										
PO_4	.72	.12	.32	.05	.46	.26	.17	.50	.53	1.00									
NH_4	.27	.15	.65	-.49	-.26	.15	.36	.65	.70	.34	1.00								
NO_3	.32	-.03	.60	-.28	-.02	.11	.02	.92	.86	.53	.82	1.00							
Pb	.10	.13	-.16	.49	.35	-.04	.40	-.30	.09	.42	-.24	-.26	1.00						
Zn	-.21	-.07	-.14	-.20	-.15	-.17	.13	-.15	-.05	-.14	-.17	-.17	-.03	1.00					
Cd	.22	-.03	-.24	.47	.41	-.09	.06	-.06	.24	.48	-.05	.06	.60	.01	1.00				
Cr	.65	.60	.01	.18	.49	.42	.28	-.15	-.11	.50	.06	-.01	.49	-.19	.52	1.00			
As	.03	.26	.04	-.01	.13	.02	-.08	-.05	-.04	-.01	-.07	.03	.08	-.19	-.09	.30	1.00		
Fe	-.04	-.30	-.37	.35	.39	-.07	-.08	-.13	-.20	.04	-.45	-.24	.15	.10	.32	.18	.10	1.00	
Ni	.05	-.33	.11	.44	.05	-.26	-.14	.14	.33	.22	-.07	.20	.29	.17	.46	.19	.19	.50	1.00

* Temp – temperature, ALK - alkalinity

Table 4 Correlation matrix for water samples from wet season

	Temp	pH	EC	TDS	DO	Eh	ALK	Cl	SO_4	PO_4	NH_4	NO_3	Pb	Zn	Cd	Cr	As	Fe	Ni
Temp	1.00																		
pH	.32	1.00																	
EC	.28	.47	1.00																
TDS	-.08	-.08	-.14	1.00															
DO	-.33	-.42	-.14	.48	1.00														
Eh	.64	.54	.33	-.02	-.16	1.00													
ALK	.27	-.11	-.05	-.05	-.48	-.16	1.00												
Cl	.26	.47	.46	-.17	-.20	.33	-.12	1.00											
SO_4	.08	.34	.33	.47	.24	.30	.01	.58	1.00										
PO_4	.03	.12	-.14	-.27	-.34	-.10	.02	-.21	-.47	1.00									
NH_4	.12	.29	.63	-.13	.16	.46	-.18	.46	.41	-.09	1.00								
NO_3	.18	.01	.08	.28	-.09	-.03	.20	.45	.45	.15	.01	1.00							
Pb	.38	.23	.18	-.12	-.30	.10	.36	.34	.07	-.35	.14	-.04	1.00						
Zn	.44	.31	-.17	-.12	-.32	.23	.35	.01	-.11	-.14	-.15	-.28	.74	1.00					
Cd	.48	.32	.39	-.33	-.55	.05	.47	.11	-.08	.02	.07	-.11	.56	.46	1.00				
Cr	.42	.43	.27	-.50	-.54	.19	.03	.10	-.39	.53	.14	.06	.22	.27	.51	1.00			
As	.45	.20	.01	.53	-.04	.43	.15	.26	.58	-.27	.10	.32	.14	.08	.01	-.25	1.00		
Fe	-.52	-.42	-.21	.03	.43	-.24	-.30	-.20	-.28	-.37	-.02	-.39	-.06	-.15	-.49	-.36	-.29	1.00	
Ni	.15	.27	-.09	-.26	-.36	-.04	.09	.21	-.07	.66	.18	.11	-.05	.02	.21	.33	.16	-.42	1.00

*Temp – temperature, ALK - alkalinity

Table 5 Factor loadings of parameters in the dry season

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
Temp.	.482891	.591673	-.272117	.298972
pH	.215252	.322953	-.789462	-.120391
EC	.747009	-.285999	-.039584	-.198089
TDS	-.399858	.555976	.351197	.102921
DO	-.065006	.766984	-.017405	.387378
Eh	.300894	.385793	-.641639	.188428
ALK	.265544	.215970	-.374952	-.677253
Cl	.840397	-.124079	.276475	.252670
SO_4	.761428	-.031374	.543667	-.130123
PO_4	.635086	.607306	.165509	.005766
NH_4	.886874	-.201112	-.045064	-.149300
NO_3	.918375	-.078924	.284652	.167340
Pb	-.127828	.693532	.138926	-.529496
Zn	-.204498	-.160968	.114625	-.465833
Cd	.010934	.702657	.423145	-.249721
Cr	.169055	.821521	-.299823	-.086040
As	.003669	.184198	-.104124	.210801
Fe	-.377514	.408692	.397681	.163135
Ni	.038864	.340902	.713520	-.104405
Eigenval.	4.713	4.054	2.837	1.578
% var.	24.80	21.33	14.93	11.60
Cuml.EV	4.713	8.767	11.603	13.181
Cuml.%	24.80	46.14	61.07	69.38

Table 6 Factor loadings of parameters in the wet season

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
Temp	-.737788	-.086365	.189274	.128202
pH	-.701838	-.172511	-.202667	-.177492
EC	-.501457	-.328634	-.242354	-.464169
TDS	.310116	-.594551	.193520	.439519
DO	.666849	-.456712	-.024813	-.160927
Eh	-.537887	-.392834	-.085283	-.211139
ALK	-.325262	.227443	.480664	.447428
Cl	-.533219	-.496416	-.213004	-.154301
SO_4	-.209273	-.888234	-.017262	.154497
PO_4	-.162294	.598244	-.624378	.336460
NH_4	-.337639	-.438540	-.362121	-.486821
NO_3	-.202330	-.355524	-.265591	.595162
Pb	-.539247	-.007826	.644679	-.216961
Zn	-.473982	.227890	.679048	-.079288
Cd	-.708676	.303127	.300849	-.066571
Cr	-.624908	.511036	-.266454	-.157525
As	-.299763	-.615222	.181395	.467549
Fe	.662715	-.008921	.184716	-.489605
Ni	-.412079	.271814	-.476861	.326712
Eigenval.	4.841	3.482	2.382	2.127
% var.	25.48	18.33	12.54	11.19
Cuml. EV	4.841	8.324	10.705	12.832
Cuml. %	25.48	43.81	56.345	67.54

Cluster analysis

Cluster analysis was applied to find out the similarity groups between the controlling factors. Four primary and one secondary unique factor loadings characterize the variation of data set in both the dry and wet seasons (Table 7). These factors had loading scores of greater than +/- 0.50. Cluster analysis results group these unique factors into four statistically meaningful clusters. These clusters determine the oblique factors for hierarchical analysis. Cluster 1 constitutes of P1 and P2, cluster 2 (P1 and P3), cluster 3 (P1 and P4) and cluster 4 (P1 and S1) in the dry season. The clusters and component factors are the same in the wet season as in the dry period.

Table 7 Secondary (S) and primary (P) unique factors

Season	S1	P1	P2	P3	P4
Dry	Temp, pH, Eh, Cr	EC, Cl, SO_4, PO_4, NH_4, NO_3	Temp, DO	TDS, Pb, Cd, Fe, Ni	Alkalinity
Wet	Temp, Cd, Cr, Fe	PO_4, Fe, Ni	pH, EC, Eh, Cl, NH_4	Alkalinity, Pb, Zn, Cd	TDS, SO_4, NO_3, As

CONCLUSION

This study shows that natural processes; water-rock reactions and water mixing, exerts a recognizable control on the chemical status of the Eastern Niger Delta drainage basin. Physical parameters; temperature, pH, TDS and EC are season dependent and their propensity for variations affects the chemical characteristics of the waters. Principal anion contents reveal the waters to be Cl – SO_4 type both in the dry and wet seasons. Major and trace element concentrations are within background levels reflecting lithogenic origin from the catchment geology.

Application of multivariate statistical methods; correlation, factor and cluster analyses, elucidate controlling factors of water chemistry and variation trends across seasons. Correlations reveal strong interrelation between physical and chemical components on water quality in the dry and wet seasons. Factor analysis establishes four explicable factors to be responsible for hydrochemical variations in the dry and wet seasons forming four similarity clusters within the sampling periods.

However it is important to note the presence and increasing industrial operations and their anthropogenic inputs within the catchment, though their effects may not be alarming on water quality at present. This current research may thus serve as a baseline for future hydro-environmental monitoring for flora and fauna population growth and diversity as a platform for sustainable development and resource management.

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