__Original Research Article__

Assessment of physicochemical characteristics of waters in Santa Barbara River, Bayelsa State, Nigeria.

Abstract

Effluents received by surface water increase the concentration of heavy metals and nutrients in the water to a level that is harmful to the aquatic organism and pose a health risk to humans. Water samples were collected from 20 sampling stations along the Santa Barbara River during the wet and dry seasons. Total suspended solids, polyaromatic hydrocarbons, and sodium were the only parameters that showed a statistical difference between values obtained in the control and study area ($p > 0.05$) at 95% confidence interval. Some of the results observed in this study are: pH varied between 5.9 – 7.2 and 7.06 – 8.20; Electrical conductivity, 260 – 1020 µS/cm and 15710 – 17760 µS/cm; biological oxygen demand, 1.0 – 3.2 mg/L and 2.0 – 8.60 mg/L; polynuclear Aromatic hydrocarbons, 0.03 – 0.16 mg/L and 0.11- 0.53 mg/L ; Lead 0.51- 1.53 mg/L and 0.1 – 3.19 for wet and dry season respectively. Pearson correlation shows a significant correlation among the measured parameters. The results of Polyaromatic hydrocarbons, lead, chromium and sulphate observed indicated anthropogenic influence on the water quality that may be due to the use of lead in fishing neat, combustion of coal, combustion of fossil fuel, and waste discharge into the River. Impact mitigation measures is therefore recommended to improve the water quality of the River.

Keywords: Effluent, Heavy metals, Surface water, Santa Barbara.

INTRODUCTION

Surface water is a natural resource used extensively for irrigation, recreation, domestic use, and other purposes. Globally, surface water bodies are the primary dump site for the disposal of effluents (Olalekan and Ezugwu, 2017). Industries, agricultural activities, and human settlements are the primary source of waste (Mateo – sagasta et al., 2017). The waste received by water bodies increases the concentration of heavy metals and nutrients to a level harmful to the aquatic organism and poses a health risk to humans.

Surface water bodies are vulnerable to pollutants because there are a variety of tropic levels present, through which pollutants bioaccumulate in the bodies of aquatic organisms (Forstner and Wittmann, 1979). Heavy metals become toxic when bioaccumulated above the permissible limit. The safety and quality of fish are crucial for human health because fish is a rich source of protein (Noman et al. 2022). Water quality, therefore, determines the survival of aquatic organisms.

Water quality is measured by assessing water's physical, chemical, and biological characteristics against standards used to determine water use for various purposes (Nitasha and Sanjiv, 2014). Fishes in water bodies with DO concentration of 0.3 mg/L can die if exposed to this concentration for a long time. Water bodies should have at least 1.0mg/L of dissolved oxygen to sustain the aquatic organisms. DO of 5.0 mg/L is adequate (Ekubo and Abowei, 2011). Chemical oxygen demand (COD) and biological oxygen demand (BOD) are important pollution indicators in the water quality assessment used to estimate the amount of oxygen used up in the degradation of organic matter present in the aquatic system (Edori and Nna, 2018). Polyaromatic hydrocarbons (PAHs) are toxic organic compounds that persist in the environment. PAHs bioaccumulate in the bodies of aquatic organisms when it enters the food chain (Liu et al., 2013). Heavy metals are metals and metalloids with a relatively high density in the ranges of 3.5 - 7gcm^{-3}; these metals are poisonous even at low concentrations (Sanjay, 2014). Heavy metal pollution in the environment is a global challenge because it is toxic at low concentrations; however, heavy metals such as copper, zinc, iron, chromium, and manganese have a biological function. Above optimum concentration in the environment, essential heavy metals become toxic. Metals such as Arsenic, lead, and cadmium is non-essential and have no biological function (Forstner and Wittmann, 1979; Aghoghovwia et al., 2018). A high concentration of heavy metals in humans can damage the liver, kidney, and brain; and in severe cases, it can cause cancer (Sanjay, 2014).

Santa Barbara River is a fishing site in Bayelsa state, Nigeria. The River is known for its rich biodiversity; oysters, periwinkles, crayfish, crabs, and shrimps are some aquatic species harvested from the River. Fishing is the main occupation of the inhabitants of the community. Fishes are harvested and Sold to Urban areas like Bassambiri, Nembe town, and Port Harcourt. The people are also involved in petty trade, processing fish harvested (drying and the removal of shells), and farming on a small scale. The communities in the Santa Barbara locality are crude oil-producing communities.

Since the discovery of crude oil in the Niger Delta, its exploration has negatively impacted the environment (Nwachoko et al., 2021). The disadvantages of oil exploration include Oil spillage, gas flaring, and the chemicals used in oil processing (Collins and Jurgen, 2008). Oil spillage results in the discharge of heavy metals and hydrocarbons into receiving surface water, groundwater, and soil (Ordinioha and Brisibe, 2013). Crude oil can spill into the environment via leaks from pipelines, accident discharge, discharge from urban settlements, and refineries (Collins and Jurgen, 2008).It is necessary to evaluate the impact of oil exploration and other human activities on the water quality of the Santa Barbara River to preserve the River's rich biodiversity. This study gives an insight into the physicochemical characteristics of the Santa Barbara River to ascertain anthropogenic influence on the water quality

Material and methods

Study Area

The River is a fishing site in the Nembe Local Government Area of Bayelsa state. The town of Nembe is the headquarters of Nembe Local Government Area (LGA). Nembe LGA had a total population size of 130 966 at the 2006 population census. Santa Barbara River flows into the Atlantic Ocean. Many communities in the Santa Barbara River are rural. Figure: 1 is the map showing the sampling points along the Santa Barbara River

Sample collection

Surface water sampling was done in two seasons (wet and dry seasons) following standard methods and procedures. The month of November to March represents the dry season, while April to October represents the wet season. A total of 20 sampling stations along the Santa Barbara River were selected close to operational oil and gas facilities. The control points were areas where there is minimum influence from industrial activities. pH, Conductivity, Dissolved oxygen, Total Dissolved Solids, Turbidity, and Temperature were determined in-situ. Samples for BOD5, Heavy metals, and chemical oxygen demand were collected separately. Heavy metals were acidified with nitric acid pH < 2. Chemical Oxygen Demand was acidified with sulphuric acid pH < 2. All samples were preserved at < 4^{o}C and delivered in that state to Dukoria laboratory Ltd, Effurun in Delta state.

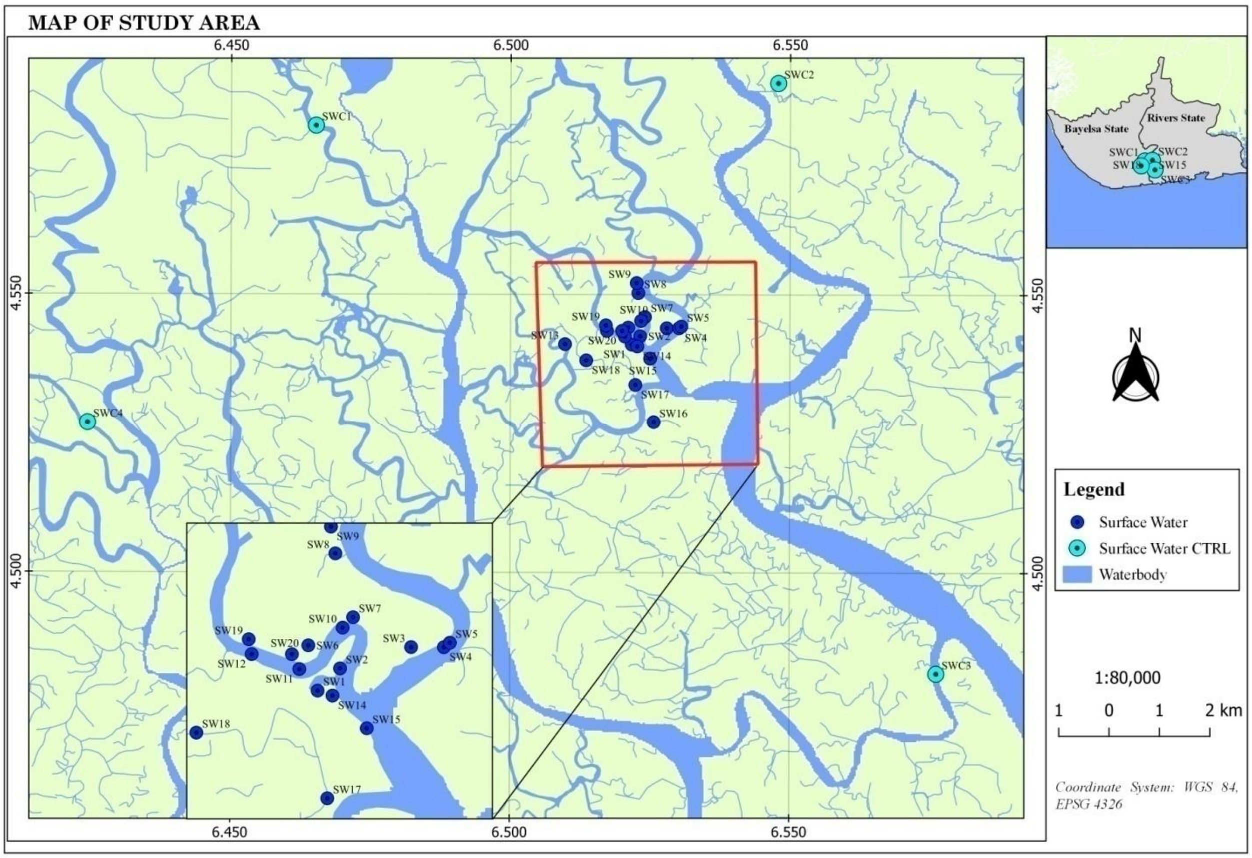

Figure1: Map showing the sampling points in the study area.

Laboratory Analysis

All ex-situ analyses were done based on APHA, (1998) standard procedures developed and validated in Dukoria Laboratories. The analytical methods adapted are presented in Table 1

Statistical Analysis

The physicochemical results were subjected to Descriptive statistics analyses to compute the mean and standard deviation. Pearson correlation analysis determined the relationship between the parameters measured. One–way analysis of variance (ANOVA) was applied to determine the significant difference between the sampling and control area at 95% confidence level. Microsoft Excel, Office 365 was used to compute all statistical Analyses.

Analytical Methods

Table 1: Analytical methods for the parameters analyzed in this study

Parameters	Analytical Methods
Physico-chemical	
pH	Electronic method (APHA - 4500-H+)
Total dissolved solids (TDS), mg/L	APHA 2540-C
Conductivity, µS/cm	APHA 2510 B
Total Suspended Solids (TSS), mg/L	Gravimetric method (APHA-209-D)
Turbidity, NTU	Nephelometric method (APHA – 2130-B)
Anions	
Sulphate, mg/L	Turbidity method (APHA-426C SO42-E
Nitrate, mg/L	Cadmium Reduction method (ASTM, 2016 -D3867)
Gross organics	
DO, mg/L	APHA – 4500-O C
COD, mg/L	Dichromate method (Reflux) (APHA – 5300 B)
BOD, mg/L	5 day method (APHA 5210B)
Inorganics	
Magnesium, mg/L	APHA3500
Metals	Atomic Absorption Spectrophotometer (AAS), (APHA 3000)

PAHs	Polynuclear Aromatic Hydrocarbons (APHA 6440)

Source: APHA, (2012)

Results and Discussions

The result of the descriptive statistics of physicochemical parameters of surface water from Santa Barbara River in the wet and dry seasons is summarized in Table 2 and Table 3, respectively. P > 0.05 in Table 2 and Table 3 represents differences that are statistically insignificant between sampling and control points at 95% confidence interval. P> 0.05 connotes statistical significance between sampling points and control points at 95% confidence interval.

Table 2: Physicochemical parameters of surface water in Santa Barbara during the wet season.

Physico-chemical parameters	**Study area Range**	**Study area mean ± S.D**	**Control area mean ± S.D**	**P value**	**Control area Range**
pH	5.9 – 7.2	6.44± 0.30	6.83 ± 0.41	P < 0.05	6.3 – 7.30
Electrical Conductivity, µS/cm	260 – 1020	526 ± 234.05	348 ±271	P > 0.05	240 – 564
Total Suspended Solids (TSS), mg/L	9 – 162.50	51.53 ± 36.62	138 ±68.57	P < 0.05	67.5 -225
Total Dissolved Solids (TDS), mg/L	166 – 653	336.65 ± 149.88	1003.5 ±173	P > 0.05	26 – 361
Dissolved Oxygen (DO),	4.9 – 5.8	5.33 ± 0.19	5.23 ±0.12	P > 0.05	5.1 – 5.4

mg/L					
Salinity, %	14.7 – 27.40	20.71 ± 3.47	17.9 ±2.82	P > 0.05	14.2 – 21
Biochemical Oxygen Demand (BOD), mg/L	1.00 – 3.2	2.00 ± 3.21	2.475 ±1.83	P > 0.05	1.2 -5.20
Chemical Oxygen Demand (COD), mg/L	7.8 – 14.80	11.96 ± 1.99	8.30 ± 2.43	P < 0.05	5.1 – 10.80
Turbidity, NTU	10 – 23.50	17.59 ± 4.04	13.50 ± 6.60	P > 0.05	6 – 30
Organics, mg/L					
Polynuclear Aromatic Hydrocarbon (PAHs)	0.03 – 0.16	0.09 ± 0.03	0.03± 0.02	P < 0.05	0.01 – 0.05
BTEX	<0.005	<0.005	<0.005	-	<0.005
Anions (mg/L)					
Sulphate, (SO42-)	1.97 – 133	54.61 ± 33.37	29.26 ± 13.92	P > 0.05	19.63 – 49.78
Nitrate, (NO3-)	0.01 – 0.04	0.02 ± 0.01	0.021 ± 0.01		0.01 – 0.05
Cations (mg/L)					
Calcium, (Ca 2+)	3.31 – 21.70	6.15 ± 0.94	13.47 ± 14.03	P > 0.05	6.05 – 34.51
Magnesium,(Mg2+)	7.06 – 30. 87	14.71 ± 1.28	17.87 ± 15.38	P > 0.05	5.32 – 40
Sodium, (Na2+)	46.05 – 181	93.39 ± 9.29	278.37 ± 182	P < 0.05	7.21 – 1001
Heavy Metals (mg/L)					
Iron, (Fe)	0.629 – 9.05	1.92 ± 0.39	2.52 ± 0.37	P > 0.05	1.97 – 2.74
Zinc, (Zn)	0.05 – 0.19	0.09 ± 0.01	0.28 ± 0.50	P > 0.05	0.01 – 1.04
Chromium, (Cr)	13.23 – 44.73	28.56 ± 1.86	23.26 ± 5.34	P > 0.05	20.29 – 31.26
Lead, (Pb)	0.51 – 1.53	1.19 ± 0.12	<0.01	-	<0.01
Copper, (Cu)	0.05 – 2.17	0.29 ± 0.11	0.23 ± 0.007	P > 0.05	0.22 – 0.24
Cadmium, (Cd)	<0.002	<0.002	<0.002	-	<0.002
Mercury, (Hg)	<0.001	<0.001	<0.001	-	<0.001
Vanadium, (V)	<0.001	<0.001	<0.001	-	<0.001

Nickel (Ni)	<0.010	<0.010	0.41 ± 0.12	-	0.01 – 0.56
Barium (Ba)	<0.005	< 0.005	< 0.005	-	<0.005

Note, S.D – standard deviation, BTEX - benzene toluene ethylbenzene

Table 3: Physicochemical parameters of surface water in Santa Barbara during the dry season.

Physico- chemical parameter	**Study area Range**	**Study area Mean ± S.D**	**Control area mean ± S.D**	**P – value**	**Control area Range**
pH	7.06 – 8.20	7.59 ± 0.28	7.48 ± 25	P > 0.05	7.22 – 7.76
Electrical Conductivity, µS/cm	15710 - 17760	16569 ± 636	15615 ± 3435	P > 0.05	11220 – 19600
Total Suspended Solids (TSS), mg/L	0.00 – 17	5.38 ± 3.84	3.88 ± 0.85	P > 0.05	3 – 5
Total Dissolved Solids (TDS), mg/L	7046 – 8876	8275± 408	7804 ± 1712	P > 0.05	5624 – 9802
Dissolved Oxygen (DO), mg/L	2.5 – 4.80	3.91 ± 0.67	4.05 ± 1.05	P > 0.05	2.52 – 4.80
Salinity, %	25 – 32	29.14± 1.97	26.25 ± 1.25	P < 0.05	25 – 28
Biochemical Oxygen Demand (BOD), mg/L	2 – 8.60	4.95 ± 2.31	4.4 ± 3.05	P > 0.05	2.30 – 8.90
Chemical Oxygen Demand (COD), mg/L	6.9 – 13.20	9.23 ± 1.68	9.25 ± 1.08	P > 0.05	7.8 – 10.30
Turbidity, NTU	0.00 – 18	3.35 ± 4.51	1.75 ± 2.21	P > 0.05	0.00 – 5.00
Organics (mg/L)					
Polynuclear Aromatic Hydrocarbon (PAHs)	0.11 – 0.53	0.25 ± 0.12	0.08 ± 0.02	P < 0.05	0.07 – 0.11
BTEX	<0.005	<0.005	<0.005	-	<0.005
Anions (mg/L)					
Sulphate, (SO42-)	7.87 – 3769	701 ± 574	647 ± 216	P > 0.05	374 – 8367
Nitrate, (NO3-)	0.001 – 0 .07	0.01 ± 0.02	0.003 ± 0.002	P > 0.05	0.001 – 0.006

Cations (mg/L)					
Calcium, (Ca^{2+})	123.43 – 220.07	166 ± 24.07	168 ± 41.31	P > 0.05	118.11 – 217.95
Magnesium,(Mg^{2+})	16.91 – 21.30	19.86 ± 0.98	18.73 ± 4.11	P > 0.05	13.5 – 23.52
Sodium, (Na^{2+})	1954.56 – 2462.20	2295 ± 113	2165 ± 475.16	P > 0.05	1560 – 2719
Heavy Metals (mg/L)					
Iron, (Fe)	0.29 – 5.59	2.09 ± 1.23	1.09 ± 0.65	P > 0.05	0.11 – 1.44
Zinc, (Zn)	0.51 – 1.57	0.80 ± 0.23	0.82 ± 0.22	P > 0.05	0.573 – 1.02
Chromium, (Cr)	<0.006	<0.006	<0.006		<0.006
Lead, (Pb)	0.1 – 3.19	1.85 ± 0.83	2.06 ± 0.53	P > 0.05	1.49 – 2.65
Copper, (Cu)	0.03– 0.19	0.12 ± 0.04	0.13 ± 0.08	P > 0.05	0.02 – 0.20
Cadmium, (Cd)	0.01 – 0.68	0.12 ± 0.20	0.11 ± 0.01	P > 0.05	0.09 – 0.12
Mercury, (Hg)	<0.001	<0.001	<0.001		<0.001
Vanadium, (V)	<0.001	<0.001	<0.001		<0.001
Nickel (Ni)	0.18 – 1.24	0.64 ± 0.32	0.66 ± 0.49	P > 0.05	0.17 – 1.13
Barium (Ba)	<0.005	<0.005	<0.005	-	<0.005

Note, S.D – standard deviation, BTEX - benzene toluene ethylbenzene

Pearson correlation matrix and seasonal variation

Tables 4 and Table 5 shows the correlation coefficient (r) of the physicochemical parameter, with their statistical significance at 0.05 alpha levels (p values) for wet and dry seasons.

Correlation coefficients show the correlation between variables and compute the statistical significance between water quality variables. The correlation coefficient (r) has values between +1 and -1. A strong positive correlation between parameters denotes that an increase in one parameter results in a subsequent increase in the other. A negative correlation between parameters indicates that an increase in one parameter causes the other parameter to decrease (Shroff et al. 2015). +0.8 to + 1.0 and -0.8 to -1.0 represents strong positive and negative correlation respectively; +0.5 to + 0.8 and -0.5 to -0.8 represents moderate positive and negative correlation respectively; + 0.0 to + 0.5 and -0.0 to -0.5 are for weak positive and negative correlation respectively, between variables (Shroff et al, 2015; Lencha et al, 2021).

In this study, pH correlated negatively with salinity values r = - (0.481) at 0.05 alpha levels during the wet. There was no significant correlation between pH and other parameters during the dry season.

Electric conductivity (EC) showed strong positive correlation with K^+, Na^{2+} and Zn values (r = +0.999, r = + 0.999 and r = + 0.999 respectively) at $p < 0.05$, and weak negative correlation with DO with value r = - 0.408 at $p < 0.05$(wet season). During the dry season, EC showed strong positive correlation with K^+, $Na^{2+,}$ $Mg^{2+,}$ TDS values (r = + 0.833, r = 0.833 r = 0.833, r = 0.833 respectively) at $p < 0.05$, moderate positive correlation with Ca2+ value r = -0.613 at $p < 0.05$, weak positive correlation with Ni value r = + 0.451 $p < 0.05$, and weak negative correlation with COD, TSS and turbidity values (r = - 0.415, - 0.482 – 0.440) at $p < 0.05$.

Total suspended solids (TSS) showed moderate positive correlation with BOD values (r = + 0 .732) at $p < 0.05$ (wet season). During the dry season, TSS showed moderate positive correlation with turbidity values (r = + 0.748) at $p < 0.05$ (dry season).

Total dissolved solids (TDS) showed strong positive correlation with Zn, K+ and Na^{2+} values (r = + 0.999, r = + 1, r = + 1 respectively) at $p < 0.05$, and weak negative correlation with

DO value r = - 0.409 at $p < 0.05$ (wet season). TDS showed strong positive correlation with EC, $Mg^{2+,}$ K+ and Na^{2+} with values (r = + 0.833, + 0.999, + 1, + 1 respectively) at $p < 0.05$ (dry season).

Table 4: Correlation matrix showing the relationship between the measured physicochemical parameters in the wet season

	pH	EC	TSS	TDS	DO	Salinity	BOD	COD	Turbidity	PAHs	SO42-	NO3-	Ca 2+	Mg2+	K+	Na2+	Fe	Zn	Cr	Cu
pH	1																			
EC	-0.266	1																		
TSS	*-0.037*	*-0.158*	*1*																	
TDS	-0.266	**0.999**	-0.158	1																
DO	-0.235	**-0.408**	-0.136	**-0.409**	1															
Salinity	**-0.481**	0.317	0.390	0.317	-0.175	1														
BOD	-0.089	-0.036	**0.732**	-0.036	-0.095	0.087	1													
COD	0.019	-0.002	0.108	-0.001	0.159	-0.021	0.082	1												
Turbidity,	0.207	0.046	-0.365	0.046	-0.031	-0.319	-0.291	0.064	1											
PAHs	0.194	0.015	-0.001	0.015	0.041	-0.132	-0.056	-0.252	0.260	1										
SO42-	-0.010	-0.018	-0.130	-0.018	-0.176	0.135	-0.374	-0.174	0.057	-0.088	1									
NO3-	-0.112	0.001	0.101	0.001	0.089	-0.164	0.005	0.203	-0.310	-0.289	-0.031	1								
Ca 2+	0.300	-0.119	-0.0478	-0.119	-0.013	-0.280	-0.052	-0.066	0.441	0.344	-0.116	**-0.415**	1							
Mg2+	0.344	0.214	-0.125	0.214	-0.360	-0.293	-0.153	-0.025	0.221	0.379	-0.096	-0.255	0.557	1						
K+	-0.266	**0.999**	-0.158	**1**	**-0.409**	0.317	-0.036	-0.001	0.046	0.015	-0.018	0.001	-0.112	0.214	1					
Na2+	-0.266	**0.999**	-0.158	**1**	-0.409	0.317	-0.036	-0.001	0.046	0.015	-0.018	0.001	-0.119	0.214	1	1				
Fe	0.376	-0.274	-0.140	-0.274	0.136	-0.337	-0.260	-0.025	0.227	0.505	-0.063	-0.255	**0.818**	**0.662**	-0.274	-0.274	1			
Zn	-0.266	**0.999**	-0.158	**0.999**	**-0.409**	0.317	-0.036	-0.001	0.047	0.013	-0.019	0.004	-0.119	0.214	**0.999**	**0.999**	-0.275	1		
Cr	0.089	0.074	0.049	0.074	-0.036	-0.132	0.243	0.331	0.171	0.267	-0.285	0.021	-0.218	0.139	0.074	0.074	0.005	0.075	1	
Cu	0.585	-0.199	-0.173	-0.200	0.039	**-0.416**	0.051	-0.126	0.148	0.155	-0.118	-0.174	0.041	-0.124	-0.199	-0.200	-0.024	-0.200	-0.08	1

Values in bold are statistically different from 0 at 0.05 level(two tail)

Table 5: Correlation matrix showing the relationship between the measured physicochemical parameters in the dry season

	pH	EC	TSS	TDS	DO	Saliniyy	BOD	COD	Turbidity	PAH	SO42-	NO3-	Ca 2+	Mg2+	K+	Na2+	Fe	Zn	Pb	Cu	Cd	Ni
pH	1																					
EC	-0.121	1																				
TSS	0.387	**-0.482**	1																			
TDS	-0.141	**0.833**	-0.288	1																		
DO	-0.095	0.179	-0.034	0.241	1																	
Salinity	-0.240	-0.063	0.253	0.079	0.074	1																
BOD	0.164	-0.420	0.267	-0.397	**-0.846**	0.004	1															
COD	-0.113	**-0.415**	0.268	-0.325	**-0.699**	0.136	**0.885**	1														
Turbidity	0.402	**-0.440**	**0.748**	-0.287	0.026	0.049	0.201	0.079	1													
PAH	-0.172	0.013	0.198	0.081	**0.444**	0.108	-0.137	0.030	0.184	1												
SO42-	-0.158	0.217	0.033	0.196	0.380	-0.114	-0.394	**-0.476**	0.079	0.226	1											
NO3-	-0.010	0.373	-0.313	0.225	-0.384	-0.263	0.026	-0.041	-0.195	-0.326	-0.132	1										
Ca 2+	-0.143	**0.613**	-0.157	**0.448**	0.185	-0.178	-0.33	**-0.401**	-0.145	0.077	**0.509**	0.183	1									
Mg2+	-0.142	**0.833**	-0.289	**0.999**	0.241	0.081	-0.398	-0.325	-0.287	0.081	0.196	0.225	**0.448**	1								
K+	-0.141	**0.833**	-0.288	**1**	0.241	0.079	-0.397	-0.324	-0.287	0.081	0.196	0.225	**0.448**	**0.999**	1							
Na2+	-0.141	**0.833**	-0.288	**1**	0.241	0.079	-0.397	-0.325	-0.287	0.081	0.196	0.225	**0.448**	**0.999**	1	1						
Fe	0.083	0.175	0.244	0.085	0.227	-0.131	-0.273	-0.171	0.245	0.254	0.045	0.042	0.242	0.084	0.085	0.085	1					
Zn	0.222	-0.291	0.171	-0.316	-0.066	-0.180	0.087	0.029	0.119	-0.255	-0.063	-0.062	0.035	-0.318	-0.316	-0.316	0.365	1				
Pb	0.186	328	-0.112	0.286	0.286	-0.288	-0.155	-0.255	-0.058	0.030	0.189	-0.126	**0.435**	0.285	0.286	0.286	-0.150	0.105	1			
Cu	-0.345	-0.006	-0.041	0.028	-0.075	-0.096	-0.008	-0.097	0.106	-0.238	0.236	0.259	**0.469**	0.028	0.028	0.028	-0.220	0.137	0.345	1		
Cd	**-0.442**	040	-0.385	0.019	0.292	-0.045	-0.296	-0.279	-0.180	-0.085	0.189	-0.126	0.292	0.020	0.018	0.019	-0.191	0.003	0.155	0.302	1	
Ni	-0.335	**0.451**	-0.319	0.211	0.329	-0.063	-0.339	-0.367	-0.316	0.283	**0.511**	-0.230	**0.625**	0.212	0.212	0.211	0.063	-0.056	**0.536**	0.221	**0.418**	1

Values in bold are statistically different from 0 at 0.05 level(two tail

Dissolved oxygen (DO) showed weak negative correlation with K^+ and Zn values (r = - 0.409, r = - 0.409 respectively) at $p < 0.05$ (wet season). During the dry season, DO showed strong negative correlation with BOD values (r = - 0.846) at $p < 0.05$, moderate negative correlation with COD value r = - 0.699 at $p < 0.05$ and weak positive correlation with PAH value r = + 0.444 at $p < 0.05$.

Salinity showed weak negative correlation with Copper values (r = - 0.416) at $p < 0.05$ during the wet season. No significant correlation between salinity and other parameters during the dry season.

Biological Oxygen demand (BOD) shows strong positive correlation with COD values (r = + 0.885) and strong negative correlation with DO value (r = - 0.846) at $p < 0.05$ during the dry season. There was a strong positive correlation between BOD and TSS during the wet season.

Chemical Oxygen demand (COD) showed strong positive correlation with BOD value (r = + 0.899) , weak negative correlation with sulphate, EC and calcium values (r = - 0.476, - 0.415 and r = - 0.401 respectively) and moderate negative correlation with DO values (r = - 0.699) in the dry season. No significant correlation was observed between COD and other parameters determined in this study during the wet season.

Sulphate correlation withcalcium r = + 0.509 and Nickel (+0.511) at $p < 0.05$ in the dry season. In this study, no significant correlation was between sulphate values and other parameters determined during the wet season.

Nitrate showed weak positive correlation with calcium values (r = + 0.415) at $p < 0.05$ during the wet season. No significant correlation was between nitrate and other parameters during the dry season.

Calcium showed weak positive correlation with nitrate values (r = 0.415) and strong positive correlation with Iron values (r = 0.818) during the wet season. Calcium had weak positive correlation with $Mg^{2+,}$ $Cu^{2+,}$ Pb, K^{2+} , TDS, and Na^{2+} with values (r = + 0.448, + 0.469, + 0.435, + 0.448, + 0.448), moderate positive correlation with EC, sulphate and Ni with values (r = + 0.613, + 0.509, + 0.625) and weak negative correlation with COD with value r = - 0.476 during the dry season.

Strong positive moderate correlation was observed between magnesium and Fe values (r = + 0.662 $p < 0.05$ during the wet season. Magnesium values showed strong positive correlation with EC and TDS values (r = + 0.833 and + 0.999 respectively) at $p < 0.05$ during the dry season.

There was no significant correlation between Pb^{2+} values and other parameters during the wet season. Weak positive correlation was found between Pb^{2+} and calcium values (r = 0.435) at $p < 0.05$ during the dry season.

Sodium showed strong positive correlation with Zn, EC and TDS values (r = + 0.999, + 0.999, +1) at $p < 0.05$ during the wet season. There significant correlation was observed between Na^{2+} and EC, TDS, Ca and Magnesium values (r = 0.833, + 1, +0.448, +0.999 respectively) during the dry season.

Cd showed weak correlation with pH value (r = - 0.442) at $p < 0.05$ during the dry season.

Nickel showed a weak positive correlation with EC and Cd values (r =0.451 and 0.418) and a moderate positive correlation with Sulphate, Lead, and calcium values (r = 0.511, + 0.536, and 0.625)during the dry season,

Physicochemical parameters of the surface water

pH

pH values observed in the study area ranged from 5.9 – 7.2 and 7.06 – 8.20, with mean values of 6.44 ± 0.30 and 7.59 ± 0.28 during the wet and dry seasons. pH in the control area ranged from 6.3 – 7.30 and 7.22 – 7.76, with average values of 6.83 ± 0.41 and 7.48 ± 25 during the wet and dry seasons. 6.5 – 9.0 is the ideal pH range for fish growth (Heydarnejad, 2012). The values observed in this study are within this optimum range for fish in aquatic systems. Lawrence et al. (2020) reported pH values of 6.29 – 6.71 in similar brackish water environment.

Electrical Conductivity (EC)

Electrical Conductivity (EC) values measured in the study area were between 260 – 1020 µS/cm and 15,710 – 17,760 µS/cm, with mean values of 526 ± 234.05 µS/cm and 16,569 ± 636 µS/cm during the wet and dry seasons respectively. The EC values measured in the control stations ranged from 240 – 564 µS/cm and 11, 220 – 19,600 µS/cm, with the mean value of 348 ± 271 µS/cm and 15615 ± 3435 µS/cm during the wet and dry seasons respectively. There was no significant difference between EC values observed in sampling points and control points ($p > 0.05$) during the wet and dry seasons. Higher concentration of EC was recorded during the dry season (Figure 2) A high EC concentration indicates elevated soluble salt concentration in the water column (Taylor et al. 2018). The strong positive correlation between EC and K^{+}, $Na^{2+,}$ Ca, $Mg^{2+,}$ and total dissolved solids show that these salt ions may have contributed to the elevated

EC concentration in the study area during the dry season. The seasonal variation observed may be due to seawater mixing with the River (Edori et al. 2019). Ngah et al. (2017) reported higher EC values in the range of 13,663 – 25,325 µS/cm (wet season) and 19,773 – 24,052 µS/cm (dry season) from Elechi creek in upper Bonny Estuary, River state, Nigeria. Edori et al. (2019) reported 26, 100 - 27,200 µS/cm from Silver River, Southern Ijaw, Bayelsa State, Niger Delta, Nigeria.

Figure 2: Mean concentration of electrical conductivity from the study area

Total suspended solids (TSS)

Total Suspended Solids observed in the study area ranged from 9 – 162.50 mg/L and 0.00 – 17 mg/L, with mean values of 51.53 ± 36.62 mg/L and 5.38 ± 3.84 mg/L in the wet and dry seasons. TSS recorded in the control area ranged from 67.5 – 225 mg/L and 3 – 5 mg/L with mean values of 138 ± 68.57 mg/L and 3.88 ± 0.85 mg/L during the wet and dry seasons. There was a significant statistical difference between TSS values observed in the study and control area ($p < 0.05$) during the wet season (Figure 3). In the dry season, there was no significant statistical difference between TSS values obtained in the study and control area ($p > 0.05$). The Moderate positive correlation between TSS and biological oxygen demand (BOD) in the wet season is an indication that organic matter is a constituent of TSS in the water column. Increased surface runoff caused by heavy rainfall may have washed organic matter into the water body. Edori and Nna, (2018) reported a similar low concentration of 7.31mg/L from New Calabar River, Port Harcourt, Nigeria.

Figure 3: Mean concentration total suspended solids fromthe study area

Total Dissolved Solids (TDS)

The Total Dissolved Solids values in the study area ranged from 166 – 653 mg/L and 7046 – 8876 mg/L, with an average concentration of 336.65 ± 149.88 mg/L and 8275± 408 mg/L during the wet and dry seasons. TDS measured in the control area varied between 26 – 361 mg/L (wet season) and 5624 – 9802 mg/L (dry season), with mean concentrations of 1003.5 ±173 mg/L and 7804 ± 1712 mg/L. There was no statistically significant difference between TDS recorded in the sampling and control points ($p > 0.05$) in both seasons. Inorganic salts are the main constituents of total dissolved solids in aquatic systems (Ustaoğlu and Tepe, 2019). The strong positive correlation between TDS and ions of inorganic salts such as Zn, K^{+}, and Na^{2+} (wet season) and Mg2+, K+ and Na^{2+} (dry season) infers that these ions contributed to the TDS concentration observed in both seasons. Brackish water usually contains TDS between 500 mg/L to 48000 mg/L (Peter, 2011). The TDS concentration obtained in this study and control area during the dry season is within the stipulated concentration often measured in a brackish water environment. Woke and Umesi, (2018) reported comparable to 2657± 24.4 mg/L in a study conducted in the New Calabar River in Port Harcourt, Niger Delta. Ngah et al. (2017) reported higher TDS values in the range of 11,700 mg/L to 26,250 mg/L in a study conducted in Elechi Creek in the Upper Bonny Estuary in Rivers State.

Figure 4: mean concentration of total dissolved solids from the study area.

Dissolved oxygen (DO)

Dissolved Oxygen (DO) values measured in the study area varied between 4.9 – 5.8 mg/L and 2.5 – 4.80 mg/L, with average values of 5.33 ± 0.19 mg/L and 3.91 ± 0.67 mg/L during the wet and dry seasons. DO values observed in the control area ranged from 5.1 – 5.4 mg/L and 2.52 – 4.80 mg/L, with mean values of 5.23 ± 0.12 mg/L and 4.05 ± 1.05 mg/L for the wet and dry seasons. There was no statistical difference between DO values recorded in the study and control area ($p > 0.05$) in both seasons. The correlation between chemical oxygen demand, biological oxygen demand, and polyaromatic hydrocarbons show that organic matter and PAHs in the water column may be responsible for oxygen depletion observed in the dry season. Microbes utilize oxygen in the degradation of PAHs and organic matter in aquatic systems (Boyd et al. 2005; Edori and Nna, 2018). Wokoma and Njoku, (2017) reported values in the range of 3.22 ± 0.02 – 6.42 ± 0.02mg/L in a study carried out in the lower Sombreiro River in Niger Delta, Nigeria.

Salinity

The salinity concentration observed in the study stations ranged from 14.7 – 27.40 % and 25 – 32 %, with average concentrations of 20.71 ± 3.47 % and 29.14± 1.97 % in the wet and dry seasons. The control area salinity values varied from 14.2 – 21% and 25 – 28 %, with mean values of 17.9 ±2.82 % and 26.25 ± 1.25 % during the wet and dry seasons. High salinity during the dry season corroborates with the concentration of electrical conductivity and total dissolved solids observed. The lower salinity measured in this study during the wet season may be due to the dilution effect of total dissolved salts in the water column caused by increased rain falls (Nithunya et al, 2018). Salinity values obtained in this study suggest a brackish water environment. Salinity higher than 1 % is brackish or marine, while salinity values lower than 1% is characteristics of a freshwater environment (Ezekiel et al. 2011).

Biochemical oxygen (BOD)

Biochemical oxygen (BOD) concentration in the sampling stations varied between 1.00 – 3.20 mg/L and 2 – 8.60 mg/L, with a mean concentration of 2.00 ± 3.21 mg/L and

4.95 ± 2.31 mg/L during the wet and dry seasons. BOD values obtained in the control stations ranged from 1.2 -5.20 mg/L and 2.30 – 8.90 mg/L, with mean values of 2.475 ± 1.83 mg/L and 4.4 ± 3.05 mg/L in the wet and dry seasons respectively. There was no significant statistical difference between BOD values obtained in the sampling and the control stations ($p > 0.05$) in the wet and dry seasons. Unpolluted natural water bodies have a BOD value of 5 mg/L or less (Ioryue et al, 2018). The study area had BOD values of less than 5mg/L in both seasons. In contrast to the seasonal trend observed in this study, Ioryue et al. (2018) reported higher BOD values in the wet season. Edori and Nna (2018) reported corresponding BOD values in the range of 4.28 ± 1.08-6.11 ± 1.33 mg/L with a mean concentration of 4.92 mg/L.

Chemical oxygen demand (COD)

Chemical oxygen demand (COD) values observed in the sampling stations were between 7.8 – 14.80 mg/L and 6.9 – 13.20 mg/L, with average COD values of 11.96 ± 1.99 mg/L and 9.23 ± 1.68 mg/L in the wet and dry seasons. The control area ranged from 5.1 – 10.80 mg/L and 7.8 – 10.30 mg/L, with mean values of 8.30 ± 2.43 mg/L and 9.25 ± 1.08 mg/L in the wet and dry seasons. There was a statistical difference between COD values observed in the sampling points and control points ($p < 0.05$) during the wet season. The study area had higher values (Figure 5). No statistical difference between COD values in the sampling and control points ($p > 0.05$) in the dry season. A significantly weak negative correlation between sulphate, calcium and electric conductivity suggests that they contributed to the COD values measured in the study area during the dry season. COD in surface water usually varies between 20mg/L or less for unpolluted water bodies to 200mg/L for water bodies receiving effluents (Chapman, 1996). The COD values observed in this study is that of an unpolluted environment. Emoyanaet al. (2008) reported a higher range of 40.88 - 52.64 mg L from a study conducted in River Ijana, Ekpan, in Delta State, Nigeria.

Figure 5: Mean concentration of chemical oxygen demand in study area

Turbidity (NTU)

Turbidity values measured in the study area were between 10 – 23.50 NTU and 0.00 – 18 NTU, with mean values of 17.59 ± 4.04 NTU and 3.35 ± 4.51 NTU in the wet and dry seasons. Turbidity values obtained in the control area ranged from 6 – 30 NTU and 0.00 – 5.00 NTU, with mean values of 13.50 ± 6.60 NTU and 1.75 ± 2.21 NTU for the wet and dry seasons. No statistically significant difference between turbidity values was recorded in the sampling point and control points in the wet and dry seasons ($p > 0.05$). Higher turbidity values was observed in the study area during the wet season (Figure 6).The high turbidity values observed in the wet season may be due to increased surface runoff caused by heavy rainfall. Seiyaboh et al. (2016) reported similar turbidity values of 22.17 - 31.23 NTU in a study conducted in River Orashi in Eastern Niger Delta, Nigeria.

Figure 6. Mean concentration of turbidity from the studyarea

Polynuclear Aromatic Hydrocarbon (PAHs)

Polynuclear Aromatic Hydrocarbon (PAHs) concentration in the study area varied between 0.03 – 0.16 mg/L and 0.11 – 0.53 mg/L with mean concentration of 0.09 ± 0.03 mg/L and 0.25 ± 0.12 mg/L in the wet and dry seasons respectively. The control stations had PAHs values in the range of 0.01 – 0.05 mg/L and 0.07 – 0.11 mg/L with mean concentration of 0.03± 0.02 mg/L and 0.08 ± 0.02 mg/L. PAHs values in the study area were statistically different from values obtained in the control area ($p < 0.05$) during the wet and dry seasons. The elevated PAHs values recorded in this study may be due to incomplete coal combustion, wood, garbage burning, fish drying, roasting, and fossil fuel combustion (Davies and Abolude, 2016). High PAHs values observed in this study are comparable to 0.008 – 0.249 mg/L reported by Nwineewii and Abiye, (2015) in a study conducted in some creeks in South East Rivers State, Niger Delta.

Sulphate

Sulphate values in the study area ranged from 19.63 – 49.78 mg/L and 7.87 – 3769 mg/L, with an average sulphate concentration of 54.61 ± 33.37 mg/L and 701 ± 574 mg/L in the wet and dry seasons. Sulphate measured in the control area ranged from 19.63 – 49.78 mg/L and 374 – 8367 mg/L, with mean values of 29.26 ± 13.92 mg/L and 647 ± 216 mg/L for the wet and dry seasons. No statistical difference was between sulphate concentration observed in the sampling and control stations ($p > 0.05$) in both seasons (Figure 7). The moderate positive correlation between sulphate, calcium, and nickel, observed in the dry season, suggests that they may have originated from a similar pollution source. Sources of sulphate in surface water may be due to washing clothes in the river with synthetic fertilizer, sewage infiltration, and the weathering of rocks (Huiwei and Qianqian, 2019). Wokoma and Njoku, (2017) reported corresponding Sulphate values in the range of 309±7.0 - 988±8.0mg/L from Lower Sombreiro River, Niger Delta. Vincent-Akphua et al. (2015) reported sulphate concentration of 115 – 654 mg/L from a study conducted in Bodo Creek in the Niger Delta.

Figure 7: mean concentration of sulphate in the studyarea

Nitrate

Nitrate values ranged from 0.01 – 0.04 mg/L and 0.001 – 0 .07 mg/L in the study area with average nitrate values of 0.02 ± 0.01 mg/L and 0.01 ± 0.02 mg/L during the wet and dry seasons. Nitrate values obtained in the control area ranged from 0.01 – 0.05 mg/L and 0.001 – 0.006 mg/L with an average nitrate value of 0.021 ± 0.01 mg/L and 0.003 ± 0.002 mg/L in the wet and dry seasons. There was no significant statistical difference between values obtained in the sampling stations and the control stations ($p > 0.05$) during the wet and dry seasons. The nitrate in surface water hardly excessed 0.1 mg/L, but when influenced by human activity, iron concentration can get up to 5 mg/L and over 200 mg/L in extreme cases (Chapman, 1996) . Excess nitrate causes eutrophication which impedes the growth and survival of aquatic organisms due to the depletion of oxygen in the water body (Lawrence et al. 2020). Wokoma and Njoku (2017) reported a higher range of 0.05 ± 0.1 – 7.75 mg/L from Lower Sombreiro River, Niger Delta.

Calcium

Calcium concentration in the study area varied from 3.31 – 21.70 mg/L and 123.43 – 220.07 mg/L, with mean values of 6.15 ± 0.94 mg/L and 166 ± 24.07 mg/L in the wet and dry seasons. The control area had calcium concentrations in the range 6.05 – 34.51 mg/L and 118.11 – 217.95 mg/L , with a mean concentration of 13.47 ± 14.03 mg/L and 168 ± 41.31 mg/L during the wet and dry seasons. There was no statistical difference between calcium values observed in the study area and control area ($p > 0.05$) during the wet and dry seasons. Calcium occurs naturally in surface water (Potasznik and Szymczyk, 2015). In this study calcium was higher during the dry season (Figure 8). The positive correlation observed between $Mg^{2+,}$ $Cu^{2+,}$ Pb, K^{2+} , TDS, and

Na^{2+} EC, sulphate, Ni and calcium during the dry season infers that they may be from similar source such as weathering of rocks in the catchment (Potasznik and Szymczyk, 2015). Evaporation caused by elevated temperature associated with the dry season may have also contributed to the elevated calcium recorded (Ojok et al. 2017). Akintoye et al. (2014) reported higher mean values of 297.3 mg/L and 260.10 mg/L for the wet and dry seasons in a study conducted in Etche River, Niger Delta.

Figure 8: mean concentration of calcium from the study area

Sodium

Sodium values observed in the study area ranged from 46.05 – 181 mg/L and 1954.56 – 2462.20 mg/L, with average value of 93.39 ± 9.29 mg/L and 2295 ± 113 mg/L in during the wet and dry seasons. Sodium concentration in the control area varied between 7.21 – 1001 mg/L and 1560 – 2719 mg/L with mean values of 278.37 ± 182 mg/L and 2165 ± 475.16 mg/L during the wet and dry seasons. There was a significant statistical difference between Sodium concentration obtained in the study area and the control area in the wet season ($p < 0.05$). No statistical difference was found between sodium values obtained in the study area and control area ($p > 0.05$) during the dry seasons. Higher sodium concentration was recorded in study area during the dry season (Figure 9). Pearson correlation showed a strong positive correlation between sodium, electrical conductivity, total dissolved solids, Zn, and magnesium in the wet and dry seasons; this indicates that similar factors may have contributed to their concentration in the water column. The high concentration of sodium observed in this study during the dry season may be attributed to seawater intrusion and weathering of rocks (Nganje et al. 2017; Ukpatu et al. 2018). Seawater has high concentration of soluble salt (Napaporn et al. 2021). A lower mean concentration of 716.0 mg/L was reported by Ukpatu et al. (2018) from Okoro River Estuary in South-Eastern Nigeria

Figure 9: Mean concentration of sodium in study area

Magnesium

Magnesium concentration varied from 7.06 – 30. 87 mg/L and 16.91 – 21.30 mg/L with mean values of 14.71 ± 1.28 mg/L and 19.86 ± 0.98 mg/L in the study area during the wet and dry seasons. The control stations had magnesium values in the range of 5.32 – 40 mg/L and 13.5 – 23.52 mg/L, with mean values of 17.87 ± 15.38 mg/L and 18.73 ± 4.11 mg/L during the wet and dry seasons. There was no significant statistical difference between magnesium concentration observed in the study area and control area ($p > 0.005$) during the wet and dry seasons. Magnesium is naturally present in high concentrations in surface water; it is a component of chlorophyll and participates in enzymatic reactions (Potasznik and Szymczyk, 2015). The strong positive correlation between magnesium and iron in the wet season and with total dissolved solids (TDS) and electrical conductivity (EC) during the dry season suggest that similar factors may have contributed to their concentration in the water body. The leaching of magnesium from rocks that contain carbonate and ferromagnesium minerals and organic matter present in the water body are the principal source of magnesium in aqueous systems (Chapman, 1996). A higher magnesium value of 71.22 mg/L(wet season) and 63.19 mg/L (dry season); were reported by Akintoye et al. (2014).

Figure 10: mean concentration of magnesium in the study

Heavy metals in surface water

Iron (Fe)

Iron (Fe) concentration in the study area ranged from 0.629 – 9.05 mg/L (wet season) and 0.29 – 5.59 mg/L (dry season) with mean values of 1.92 ± 0.39 mg/L and 2.09 ± 1.23 mg/L for the wet and dry seasons. Fe values ranged between 1.97 – 2.74 mg/L (wet season) 0.11 – 1.44 mg/L (dry season) with average values of 2.52 ± 0.37mg/L and 1.09 ± 0.65 mg/L was recorded in the control stations. There was no significant statistical difference between Fe values obtained in sampling and control stations ($p > 0.05$) during the wet and dry seasons. Olu et al. (2019) reported similar values of 1.94 ± 0.49 mg/L from surface water in the Soku Oil Field Area, Niger Delta. Numbere, (2017) reported Lower values of 0.37 mg/L in a study conducted on surface water in some mangrove forest areas in the Niger Delta.

Zinc (Zn)

Zinc (Zn) concentration recorded in the study area ranged from 0.05 – 0.19 mg/L (wet season) and 0.51 – 1.57 mg/L (dry season) with mean concentrations of 0.09 ± 0.01 mg/L and 0.80 ± 0.23. Zinc concentration in the control area was between 0.01 – 1.04 mg/L (wet season) and 0.57 – 1.02 (dry season) with average concentrations of 0.28 ± 0.50 mg/L and 0.82 ± 0.22 mg/L respectively. No significant statistical difference between Zn values obtained in the samplings and control points was observed ($p > 0.05$) during the wet and dry seasons. Zinc in the surface water is usually in low concentration because the controlling mineral in water bodies have low solubility (Boyd, 2015). Elevated concentration in water bodies is due to the impact of human activities. The zinc values observed in this study are comparable to low values in the range of 0.04 to 0.09 mg/L reported by Ngah, (2017) in a study conducted in Elechi Creek in the Upper Bonny Estuary in Rivers State, Nigeria.

Chromium (Cr)

Chromium concentration in the study area ranged from 13.23 – 44.73 mg/L (wet season) with a mean concentration of 28.56 ± 1.86 mg/L. The control area had Cr values in the range of 20.29 – 31.26 mg/L (wet season) with a mean concentration of 23.26 ± 5.34 mg/L. Cr was below detection at < 0.006 in the study area and control stations during the dry season. No significant statistical difference between the Cr concentrations recorded in the sampling and the control area ($p > 0.05$). The elevated chromium level found in this study may be due to ashes from the combustion of coal and municipal waste (Tumolo et al. 2020). Pearson correlation did not show any significant correlation between chromium and other measured physicochemical parameters in this study. Lower chromium of 0.172 mg/L was reported by Nwineewii and Edem (2014) from a study on surface water in Niger Delta.

Lead (Pb)

Lead values obtained in the samples collected from the study area ranged from 0.51 – 1.53 mg/L (wet season) and 0.1 – 3.19 mg/L (dry season) with mean concentration of 1.19 ± 0.12 mg/L and 1.85 ± 0.83 mg/L respectively. Lead was not detected in the control area during the wet season, while lead values in the range of 1.49 – 2.65mg/ L with a mean value of 2.06 ± 0.53 mg/L were recorded in the dry season. There was no statistical difference between lead values obtained in the sampling and control stations ($p > 0.05$) during dry seasons. The elevated lead concentration observed in this study may be due to domestic waste washed into the River, leads used as weights for fishing nets, pipes in old jetties, and boats painted with lead-containing paints (Olu et al. 2019). The findings in this study are comparable lead values of 1.77 ± 0.16mg/L, 1.84 ± 0.07 mg/L, and 1.83 ± 0.1 mg/L reported by Emuedo (2014) from studies conducted in swamps situated in Nembe (Bayelsa state), Okrika (Rivers state) and Okpare (Delta states) respectively. Olu et al. (2019) reported 0.64 ± 0.11 mg/L from surface water in Soku Oil Field Area, Niger Delta. Madilonga et al. (2021) reported the range of 0.05 – 0.07 mg/L from a study conducted in Mutangwi River, South Africa.

Copper (Cu)

Copper (Cu) values recorded in the study area ranged from 0.05 – 2.17mg/L and 0.03– 0.19 mg/L with average concentration of 0.29 ± 0.11 mg/L and 0.12 ± 0.04 mg/L during the wet and dry seasons respectively. Copper concentration in the control area varied from 0.22 – 0.24 mg/L and 0.02 – 0.20 mg/L with average concentration of 0.23 ± 0.007 mg/L and 0.13 ± 0.08 mg/L during the wet and dry seasons respectively. No statistical difference between copper concentration obtained in the sampling and control area was observed ($p > 0.05$) during the wet and dry seasons. According to Boyd, (2015), copper is usually present in low quantity because the controlling minerals in water bodies have low solubility. A high concentration in natural waters is an indication of anthropogenic influence. Imasuen and Egai (2013) had similar values of < 0.001 - 0.48 mg/L in a study conducted on surface water in Aguobiri community, Bayelsa state. Dan et al. (2014) reported 0.05 ± 0.01 (wetseason) and 0.02 ± 0.004(dry season) in a study conducted in Qua – Iboe River Estuary and adjoining creeks, South-south Nigeria.

Cadmium

Cadmium in the study and control area was below the detection limit at < 0.002 during the wet season. During the dry season, Cadmium values in the study area ranged from 0.01 – 0.68 mg/L (dry season) with a mean concentration of 0.12 ± 0.20 mg/L, while the control area had cadmium values in the range of 0.09 – 0.12 mg/L (dry season) with a mean concentration of 0.11 ± 0.01mg/L. No statistical difference between cadmium concentrations in the study and control area was obtained ($p > 0.05$). Aghoghovwia et al. (2018) reported cadmium values in the range of 0.002 – 0.011 mg/L with mean values of 0.007 mg/L from Nun River around Gbarantoru and Tombia Towns in Bayelsa State, Nigeria.

Nickel (Ni)

Nickel (Ni) was below the detection limit in the study area at < 0.010 during the wet season but showed values in the range of 0.01 – 0.56 mg/L with a mean concentration of 0.41 ± 0.12 mg/L in the control area. Nickel values ranged from 0.18 – 1.24 mg/L with mean values of 0.64 ± 0.32 mg/L in the study area. Nickel values ranged from 0.17 – 1.13 mg/L, with a mean value of 0.66 ± 0.49 mg/L in the control area during the dry season. No statistical difference between Ni values was observed in the study and control area ($p > 0.05$) during the wet and dry seasons. Wokoma and Njoku, (2017) similar values in the range of 0.008 ± 0.004 – 0.596 ± 0.01 mg/L .Nwineewii and Edem, (2014) reported mean values of 0.441 mg/L and 1.338 mg/L for wet and dry seasons were reported by Nwineewii and Edem, (2014).

Mercury, Barium, benzene toluene ethylbenzene (BTEX) and Vanadium were below detection limits in the sampling and control area during the wet and dry seasons.

Conclusion

This study examines the water quality of the Santa Barbara River. The results of the physical-chemical parameters revealed higher concentrations during the dry season compared to the wet season. The elevated concentration of dissolved solids, salinity, electrical conductivity, calcium, sulphate and sodium during the dry season may be due to seawater mixing with the River and increased concentration of ions in the water column caused by reduced rainfall. The levels of dissolved solids, salinity, electrical conductivity, and sodium values suggest a brackish water environment.

The heavy metal measured in this study revealed that high concentration of Lead and Chromium. Heavy metals did not show a strong positive correlation with each other; this infers that they are not from a similar source of pollution. A very high concentration of lead and chromium observed in both seasons is suggestive that these heavy metals may bioaccumulate in the tissues of aquatic organisms after a long period. Lead is a very toxic metal that can cause oxidative stress and reproductive and growth disorders in fish. An elevated level of chromium in fish can cause sluggishness and bronchial and renal tumors.

The high concentrations of Electrical conductivity, sodium, total dissolved solids, lead, chromium and sulphate observed in this study may be as a result of the burning of coal, combustion of fossil fuel, seawater intrusion, burning of garbage, use of lead as weight in fish nets, increased surface runoff, municipal waste discharge, and the use of paints containing Lead to paint boats. -Further investigation of the exceedances is recommended in order to profer impact mitigative measures of these pollutants to the environment.

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