

Physicochemical Assessment of Water and Sediments of Santa Barbara Estuary of the Niger Delta, Nigeria

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ABSTRACT

The concentration of water and sediment quality parameters such as Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), pH, Sulphate, Potassium, Calcium, Nitrate, Total Hydrocarbon Concentration (THC), Total Organic Carbon (TOC), and Phosphate was studied between April 2021 to March 2022. The mean concentration of the parameters in the various stations range between 6.70 – 7.04; 29.09 – 29.45 °C; 5.11 – 5.77 mg/l; 75.72 – 81.85 mg/l; 89.23 – 90.97 mg/l; 1.29 – 1.88 mg/l; 2.41 – 2.86 mg/l; 1.53 – 2.14 mg/l; 7.08 – 19.58 mg/l, 0.27 – 0.62 mg/l, and 2.34 – 2.52 mg/l for pH, Temperature, Dissolved Oxygen, Potassium, Calcium, Phosphate, Sulphate, Nitrate, Turbidity, Biological Oxygen Demand, and THC respectively. In sediment, the mean concentration of parameters was between 5.12 – 5.62; 1.73 – 2.36 mg/kg; 3.96 – 5.11 mg/kg; 1.67 – 2.15 mg/kg; 298.90 – 409.40 mg/kg; 419.25 – 491.53 mg/kg; 7.14 – 7.53 %, and 98.94 – 130.55 mg/kg for pH, Nitrate, Sulphate, Phosphate, Calcium, Potassium, TOC, and THC. In water, there was a significant variation across study stations ($p < 0.05$), in the concentration of phosphate, nitrate, and turbidity, but no such variation ($p > 0.05$) occurred in the other parameters. In sediments, there were also spatially significant variations ($p < 0.05$) in the concentrations of pH, Nitrate, Sulphate, and Phosphate. Overall, the concentrations of these parameters were higher in sediments than in water. Hierarchical Cluster Analysis grouped the physicochemical parameters of water and sediments from the study area into three clusters. These findings reflect the dynamic nature of the aquatic environment and the influence of various factors on water and sediment quality.

Keywords: Physicochemical parameter, Sediments Quality, Water Quality, Pollution, Niger Delta.

INTRODUCTION

Water is one of the most utilized natural resources available to man. In its natural state, it is a colorless, odorless, and tasteless liquid composed mainly of Hydrogen and Oxygen (Boyd, 2020). Its quality is determined by human usage and exploitation of resources associated with it, and also the presence of ions and non-ions present in it, which differ based on prevailing environmental factors and biological processes (Van-Wyk et al., 1999; Ward and Tunnel, 2017). The presence and interaction of physical, chemical, and biological parameters are also key determinants of water quality (Patil, 2012; Vasistha and Ganguly, 2020). These ions and non-ions present are important determinants in the structure and composition of phytoplankton and benthic macroinvertebrates (Dalu et al., 2017; Sharma et al., 2020). Factors such as vegetation, human activities, soil type, climate, and geology are significant to its quality (Chaudhry and Malik, 2017). No one parameter effectively determines a good water quality; rather, a composition of different characteristics effectively determines its quality (Ward and Tunnel, 2017). As a result of its importance and its continuously changing state, which most times are often undesirable, and is due to human pressure, its ability to self-purify has been diminished, thus monitoring of the aquatic environment becomes essential (Khanna et al., 2011; Burt et al., 2014).

The aquatic environment is delicate, hence susceptible to changes at the slightest intrusion. This delicate system is important at a domestic level, useful for agricultural and industrial water supply systems, important for aquaculture and fisheries production, and for the overall wellness of the ecosystem (Boyd, 2020). For the effective functioning of man, the ecosystem, communities, and economies, clean and safe water is a necessity (Aniyikaiye et al., 2019; Matta et al., 2015). Water quality can be assessed through the study of the physico-chemical and biological parameters of the water (Sellam et al., 2019; Ustaoglu and Tepe, 2019).

There has been an issue with the decline in water quality globally (Lintern et al., 2018; Matta et al., 2015), and the decline of water quality is one of the most prevalent environmental issues (Custodio et al., 2021). This decline is in part due to agricultural, urban, and industrial activities, domestic sources, municipal sewage treatment plants, surface runoff, atmospheric deposition, and changes in land use (Ferrante et al., 2015; Fierro et al., 2017; Liyanage and Yamada, 2017; Wurtsbaugh et al., 2019). In Nigeria, the release of industrial wastewater into water bodies is primarily the source of pollution in the country's rivers, compromising water quality and disrupting the microbial and aquatic flora, as well as the release of solid waste into water bodies, together with crude oil spills, all lead to the deterioration of water quality, and this may ultimately lead to a health crises (Galadima et al., 2011; Kanu and Achi, 2011; Omokaro et al., 2024). These substances released into the aquatic environment cause changes in physiological conditions that affect the organism's immunity, and the impact of these may be deleterious (Enujiugha and Nwanna, 2004). A benchmark of toxicological values determines the criteria for water quality, and these values are different for different water quality parameters (Lawson, 2011).

The contamination of sediments can lead to significant losses in species and biodiversity (Luoma, 1990; Markovic, 2003), as well as harmful food chain reactions affecting benthic communities and upper trophic levels (McGrath et al., 2019). These communities face extreme challenges due to increasing ocean pollution (Taylor et al., 2019). Coastal areas not only serve as habitats for aquatic organisms

but also play a critical role in the global carbon cycle. They can either contribute organic matter to the open ocean or function as carbon sinks by accumulating materials in sediments (Azevedo et al., 2007). Once contaminants enter the environment, they interact with sediments, the water column, and organisms. These interactions are governed by physical and chemical processes, leading to various outcomes such as the chemical release, immobilization, or transformation of contaminants into more reactive forms or byproducts that are accessible to organisms (NRC, 2003). Benthic organisms, which live in or on sediments (Wokoma and Umesi, 2017), comprise the largest single ecosystem in terms of spatial coverage, as they are found in oceans (Snelgrove, 1997). Their structure and abundance are influenced by physical and biological factors (Govindan, 2002). Benthic organisms play a vital role in the cycling and recycling of nutrients within the aquatic ecosystem, acting as a link between inaccessible nutrients in detritus and valuable protein sources for fish (Andem et al., 2012). Oil pollution related to sedimentation has been shown to negatively impact benthic macrofauna. Baguley et al. (2015) observed decreased evenness and diversity of benthic organisms near wellheads during the Deepwater Horizon spill. Similarly, Fisher et al. (2016) reported a decline in sediment infauna diversity and noted that recovery was slow one year after the disaster. The loss of functional diversity among benthic organisms significantly affects ecosystem function (Waldbusser et al., 2004); however, responses of benthic communities to petroleum-related disturbances vary between different locations (Olsen et al., 2007). Sediment type is a crucial factor in the distribution of benthic macrofauna (Mwakisunga et al., 2020), and the zonation of benthic organisms is determined by sediment characteristics (Fresi et al., 1983).

Different water and sediment quality parameters have different acceptability criteria. These acceptability criteria are determined either by an international standard or a national one, and a deviation from the standard could imply the introduction of a foreign body to the ecosystem.

MATERIALS AND METHODS

Water and sediment samples were collected from the Santa Barbara estuary monthly between April 2021 to March 2022. Samples for the determination of other physico-chemical variables were collected, preserved, and transported to the laboratory by standard procedures. The samples were collected from four sampling stations, labeled 1-4, with the following respective geographical coordinates: - Station 1: 04° 31' 59.6" N, 006° 30' 00.2" E; Station 2: 04° 32' 02.8" N, 006° 30' 18.6" E; Station 3: 04° 31' 51.7" N, 006° 30' 28.5" E, and Station 4: 04° 32' 07.9" N, 006° 30' 42.5" E. The water samples were analyzed in situ and ex-situ, and sediments were analyzed ex-situ only to determine the quality of the Santa Barbara River of the Niger Delta. Sediment samples were collected using the processes described in Hart and Zabbey (2005). The presence of certain water quality parameters, such as Dissolved Oxygen, pH, Turbidity, and Temperature, was measured using a Hanna 98594 in situ test kit, while others were carried out ex-situ. For the parameters analysed ex situ, the Hach DR/890 colorimeter and the GBC Avanta Ver 1.33 AAS were used to test for the presence of metals like calcium and potassium. Biochemical oxygen demand (BOD) was determined by the 5-day BOD test.

QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

The purity of the elemental standards was assessed using Atomic Absorption Spectroscopy (AAS). The accuracy of the prepared standards was verified with certified reference materials, and the analytical procedure was performed in triplicate. All instruments utilized were calibrated with calibration standards, and the analytical process included the use of blanks and repeated measurements. Additionally, all reagents used during the testing were of high purity.

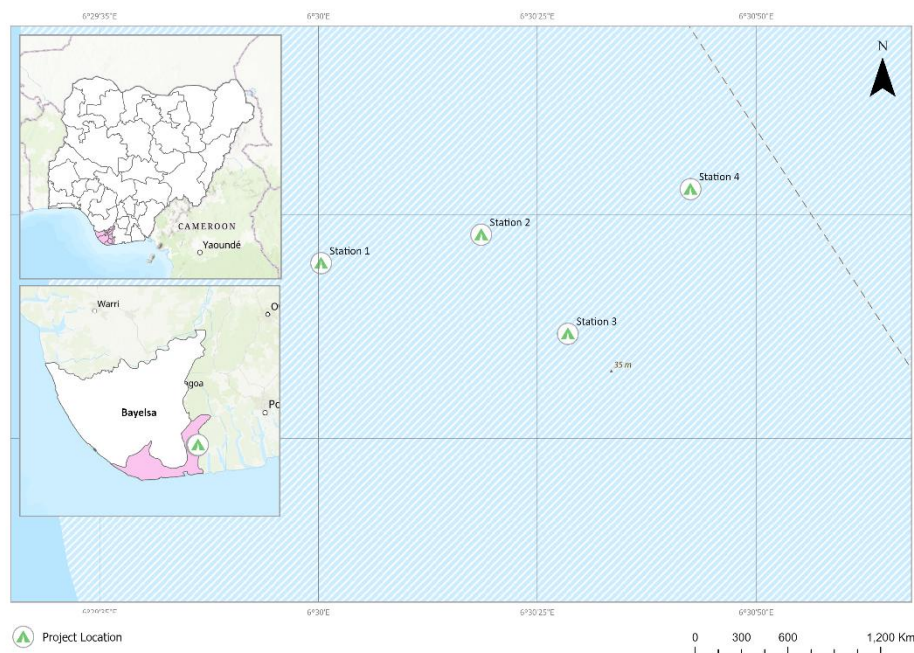


Figure 1: Map of the Study Area

STUDY AREA

Sampling Station 1

This station is situated at the entrance of the Santa Barbara River with a latitude and longitude of $04^{\circ} 31' 59.6''$ N and $006^{\circ} 30' 00.2''$ E on the global positioning system. The station is housing a pipeline running through it and a sparse vegetation of mangrove plants. Notable organisms found in this station are the mudskippers, periwinkles, and different varieties of crabs on the mudflat.

Sampling Station 2

This station is directly opposite a fishing camp called “Shellkiri”, which means Shell land in the Nembe Ijaw dialect. The name of the settlement comes from the fact that the SPDC used to be the operator of OML 29, which is now operated by Aiteo. The station is located at a latitude and longitude of $04^{\circ} 32' 02.8''$ N and $006^{\circ} 30' 18.6''$ E on the global positioning system.

Sampling Station 3

This station is located on a latitude and longitude of $04^{\circ} 31' 51.7''$ N and $006^{\circ} 30' 28.5''$ E on the global positioning system and is rich with a luxuriant mangrove vegetation together with sparse vegetation of *Nypa* palm.

Sampling Station 4

Located close to this station is a small fishing settlement with about four families, and this location has a collection of very tall mangrove trees. It is located at a latitude and longitude of $04^{\circ} 32' 07.9''$ N and $006^{\circ} 30' 42.5''$ E on the global positioning system.

DATA ANALYSIS

Physicochemical parameters of water and sediments were analyzed using MS Excel software. Hierarchical Cluster Analysis was performed on both water and sediment parameters. Additionally, Pearson Correlation and Analysis of Variance (ANOVA) tests were conducted with significance set at $p < 0.05$, using IBM SPSS 20 software.

RESULT

Physico-Chemical Parameters of Water

The results of the physicochemical analysis for the study area reveal significant findings across various parameters, detailed in the accompanying tables.

The highest average potassium concentration was detected at Station 4, with a mean of 81.85 ± 57.18 mg/L, whereas Station 2 recorded the lowest concentration at 75.72 ± 52.95 mg/L. Monthly comparisons indicated that July had the highest potassium level (134.61 ± 11.57 mg/l), while November showed the lowest (10.12 ± 1.41 mg/l). Notably, there was a sharp decline in potassium levels from September to December 2021. Although the analysis revealed significant monthly variations ($p < 0.05$), the spatial distribution showed no significant differences among the stations ($p > 0.05$).

Similar to potassium, the calcium concentrations also varied significantly by month ($p < 0.05$) but not by station ($p > 0.05$). The peak calcium level was observed in June (114.15 ± 1.89 mg/l), with the lowest concentration recorded in September (50.07 ± 6.74 mg/l). Station 4 displayed the highest mean calcium level (90.97 ± 27.85 mg/l), while Station 1 had the lowest (89.23 ± 32.77 mg/l).

Phosphate levels demonstrated both temporal (between months) and spatial (between stations) variations, indicated by significant differences found in the analysis ($p < 0.05$). The highest phosphate concentration occurred in October (2.08 ± 0.63 mg/l) and the lowest in July (1.18 ± 0.38 mg/l). Station 4 recorded the highest calcium level (1.88 ± 0.42 mg/l) and Station 1 the lowest (1.29 ± 0.31 mg/l).

Sulphate concentrations across study stations showed no significant variation ($p > 0.05$), while significant monthly variations ($p < 0.05$) were observed. The maximum sulphate level was recorded in Station 1 (2.86 ± 0.89 mg/l), with the lowest in Station 2 (2.41 ± 0.34 mg/l). The month of April 2021 had the highest sulphate concentration (3.70 ± 0.68 mg/l), and March 2022 had the lowest (1.95 ± 0.19 mg/l).

Nitrate levels were highest in July 2021 (2.60 ± 0.29 mg/l) and lowest in May 2021 (1.28 ± 0.50 mg/l). Station 4 recorded the peak nitrate concentration (2.14 ± 0.38 mg/l), whereas Station 1 had the lowest (1.53 ± 0.67 mg/l). The analysis revealed significant differences ($p < 0.05$) between months and among stations.

Station 4 showed the highest turbidity level (19.58 ± 4.68), while Station 3 was the least turbid (7.08 ± 2.53). The month of July 2021 had the least turbidity (6.75 ± 3.86), while February 2022 saw the highest turbidity (16.75 ± 5.79). Turbidity was generally higher in drier months and lower in the rainy season. Significant spatial variations were found, although no significant temporal variations were noted.

BOD levels ranged from 2.22 to 2.64. November 2021 had the highest BOD (2.64 ± 0.14), and May 2021 had the lowest (2.22 ± 0.08). Station 2 recorded the highest BOD mean (2.52 ± 0.20), while Station 3 had the lowest (2.34 ± 0.19). While temporal variations were significant ($p < 0.05$), spatial variations among stations were not ($p > 0.05$).

Physico-Chemical Parameters of Sediments

The total organic carbon value recorded was highest in November 2021, with a mean and standard deviation of 7.79 ± 0.21 , and the lowest total organic carbon on record was in May 2021, with a mean and standard deviation of 6.75 ± 0.37 . Station 2 had the most TOC (7.53 ± 0.38), while the least station with TOC was at station 3, with a mean and standard deviation of 7.14 ± 0.31 . There was a significant variation ($P < 0.05$) for TOC values in the various stations and months.

The month of March 2022 had the record level of potassium (789.03 ± 283.06 mg/kg), and October recorded the least quantity (207.73 ± 81.37) of potassium in the sediment. The months of January to May had a considerably higher amount of potassium in sediments as opposed to the amount of potassium recorded from June to December. Also, station 1 had the largest amount of potassium, with a mean and standard deviation of 491.53 ± 305.45 mg/kg, and station 2 recorded the least amount (419.25 ± 276.70 mg/kg) of potassium. The amount of potassium recorded in the stations was not spatially different, as there was no significant difference ($P > 0.05$) between the stations. The same was not true for the amount of potassium recorded in the different months, as they were significantly different ($P < 0.05$) from one another, as revealed by the analysis of variance test conducted between the months of study. A significant variation exists between October and April, January, February, and March.

The amount of calcium recorded in the sediments during the study period showed no significant variation ($P > 0.05$) both spatially and temporally. Be that as it may, station 4 had the largest amount of calcium (409.40 ± 387.18), and station 3 had the least (298.90 ± 90.46). August 2021 had the record (474.21 ± 81.94) quantity of calcium during the study, and October had the least amount (220.10 ± 126.33). The months of September to December 2021 recorded the lowest amount of calcium during the study.

The mean value of the most concentrated sediment with phosphate was sediments from station 2, with a mean and standard deviation of 2.15 ± 0.26 , and station 4 had the least concentration of phosphate in sediments (1.67 ± 0.47). The month of January 2022 recorded the highest concentration of phosphate (2.50 ± 0.11), while May 2021 recorded the lowest amount (1.41 ± 0.28). The months of November to December witnessed a consecutive increase in phosphate levels in sediments. The concentration of phosphate varied significantly ($P < 0.05$) between the stations, and the same variation ($P < 0.05$) was recorded between the months of study.

Sulphate levels were highest in station 2 as revealed by the mean and standard deviation (5.11 ± 0.93), whilst station 4 had the lowest amount of sulphate (3.96 ± 0.91). The month of September had the largest amount (5.38 ± 0.12) of sulphate in sediment collected from the study area, and the month of July had the least amount (3.86 ± 0.61) of sulphate. There was no significant difference ($P > 0.05$) in the amount of sulphate recorded during the months of study; the same was untrue for the amount of sulphate recorded in the various stations, as they varied significantly ($P < 0.05$).

The level of nitrate in sediments differed significantly ($P < 0.05$) both within the months of study and among the different study stations. No significant variations between the months of study, but a significant variation was recorded between stations 4 and 1, and between stations 4 and 2. The highest mean and standard deviation (2.36 ± 0.33) value of sulphate in the various stations was recorded in station 2, while station 4 recorded the least mean and standard deviation (1.73 ± 0.57) of the sulphate present in the sediments of the study stations.

The pH level recorded during the duration of this study varied significantly ($P < 0.05$) spatially and temporally. There was no significant interaction between the levels of pH recorded during the months of study, but it showed significant variations between pH levels across the different study stations.

Station 2 had a record pH and standard deviation of 5.62 ± 0.27 , while station 3 recorded the least pH with a value of 5.12 ± 0.49 . March 2022 had the record of the highest pH (5.67 ± 0.19), and April 2021 had the lowest pH level (4.99 ± 0.39). A careful examination of the pH values recorded in the different months of the study shows a steady increase in pH level from July 2021 to March 2022.

Cluster Analysis

A hierarchical clustering analysis was used to study the clustering patterns of physicochemical parameters in sediments and water from the study area. In water and sediments, three clusters were formed as shown in the dendrogram above, with a rescaled distance of 25 (Figure 2, 3). Physicochemical parameters in the same cluster are homogeneous, while those in a separate cluster are heterogeneous.

In water, there was a significant positive correlation between potassium and calcium at $p < 0.01$ level. This relationship may be the reason why both parameters are in the same cluster (Figure 4). There was also a positive correlation between THC and Turbidity, between Phosphate and Sulphate, and a negative correlation between pH and BOD (Figure 4, Table 5); all of which are members of cluster 2. There was, however, an interaction between members of cluster 2 and cluster 1. This possible interaction may be influenced by the negative correlation between Temperature and pH, and a positive relationship between Temperature and Turbidity. In sediments however, the only interaction between physicochemical parameters was between the positive correlation phosphate and pH (Table 6), all these are clustered together.

Table 1: Mean concentration of physico-chemical parameters of water samples from the different study stations

	Station 1	Station 2	Station 3	Station 4	NESREA Standard (2011)
pH	6.70 ± 0.64^a	6.84 ± 0.72^a	6.90 ± 0.73^a	7.04 ± 0.66^a	6.5 – 8.5

Temperature (°C)	29.45 ± 2.32 ^a	29.09 ± 2.32 ^a	29.35 ± 2.26 ^a	29.42 ± 2.71 ^a	
D.O (mg/L)	5.23 ± 1.11 ^a	5.24 ± 1.12 ^a	5.77 ± 1.81 ^a	5.11 ± 0.90 ^a	
Potassium (mg/L)	76.27 ± 55.70 ^a	75.72 ± 52.95 ^a	76.47 ± 56.82 ^a	81.85 ± 57.18 ^a	50.00
Calcium (mg/L)	89.23 ± 32.77 ^a	89.66 ± 28.30 ^a	89.61 ± 27.85 ^a	90.97 ± 27.85 ^a	180
Phosphate (mg/L)	1.29 ± 0.31 ^a	1.70 ± 0.44 ^{ab}	1.50 ± 0.35 ^{ab}	1.88 ± 0.42 ^b	3.5
Sulphate (mg/L)	2.86 ± 0.89 ^a	2.41 ± 0.34 ^a	2.60 ± 0.70 ^a	2.43 ± 0.57 ^a	100
Nitrate (mg/L)	1.53 ± 0.67 ^a	1.63 ± 0.67 ^{ab}	1.83 ± 0.23 ^{ab}	2.14 ± 0.38 ^b	9.1
Turbidity (NTU)	11.25 ± 3.77 ^{ab}	11.83 ± 3.99 ^b	7.08 ± 2.53 ^a	19.58 ± 4.68 ^c	
B.O.D (mg/L)	2.42 ± 0.15 ^a	2.52 ± 0.20 ^a	2.34 ± 0.19 ^a	2.44 ± 0.22 ^a	3.0
THC (mg/L)	0.62 ± 0.92 ^a	0.27 ± 0.40 ^a	0.44 ± 0.42 ^a	0.64 ± 0.71 ^a	

*Parameters with the same superscript are not significantly different (p>0.05).

Table 2a: Mean and standard deviation of physico-chemical parameters of water samples between April 2021 to March 2022.

	pH	Temp.(°C)	D.O (mg/L)	Potassium (mg/L)	Calcium (mg/L)	Phosphate (mg/L)	Sulphate (mg/L)	Nitrate (mg/L)	Turbidity (NTU)	B.O.D (mg/L)	THC (mg/L)
April	7.13 ± 0.05 ^{cd}	28.15 ± 0.13 ^{bc}	7.13 ± 0.05 ^c	122.68 ± 10.12 ^b	112.18 ± 0.77 ^c	2.04 ± 0.31 ^a	3.70 ± 0.68 ^d	1.93 ± 0.35 ^{ab}	13.75 ± 9.43 ^a	2.61 ± 0.23 ^a	0.78 ± 0.16 ^a
May	7.85 ± 0.20 ^f	29.74 ± 0.55 ^d	6.56 ± 0.34 ^{bc}	50.52 ± 7.48 ^a	82.66 ± 7.39 ^b	1.38 ± 0.30 ^a	2.19 ± 0.11 ^a	1.28 ± 0.50 ^a	12.50 ± 6.45 ^a	2.22 ± 0.08 ^a	0.09 ± 0.10 ^a
June	7.39 ± 0.13 ^{df}	27.16 ± 0.18 ^{ab}	4.25 ± 0.13 ^a	125.26 ± 35.01 ^b	114.15 ± 1.89 ^c	1.80 ± 0.40 ^a	3.45 ± 0.73 ^{cd}	1.90 ± 0.26 ^{ab}	8.25 ± 5.96 ^a	2.36 ± 0.09 ^a	0.018 ± 0.02 ^a
July	7.43 ± 0.41 ^{df}	26.21 ± 0.61 ^a	4.80 ± 0.22 ^{ab}	134.61 ± 11.57 ^b	109.57 ± 7.29 ^c	1.18 ± 0.38 ^a	2.55 ± 0.35 ^{abc}	2.60 ± 0.29 ^b	6.75 ± 3.86 ^a	2.24 ± 0.12 ^a	0.01 ± 0.00 ^a
August	7.53 ± 0.26 ^{df}	26.67 ± 0.47 ^a	5.48 ± 0.51 ^{abc}	134.96 ± 18.42 ^b	111.02 ± 6.60 ^c	1.28 ± 0.31 ^a	2.58 ± 0.30 ^{abc}	1.88 ± 0.39 ^{ab}	9.50 ± 3.11 ^a	2.39 ± 0.18 ^a	0.01 ± 0.00 ^a
September	7.10 ± 0.03 ^{cd}	26.89 ± 0.61 ^{ab}	5.19 ± 0.26 ^{abc}	13.36 ± 1.32 ^a	50.07 ± 6.74 ^a	1.38 ± 0.30 ^a	2.17 ± 0.27 ^a	1.48 ± 0.75 ^{ab}	12.50 ± 5.44 ^a	2.38 ± 0.39 ^a	0.29 ± 0.31 ^a

*Parameters with the same superscript are not significantly different (p>0.05).

Table 2b: Mean and standard deviation of physico-chemical parameters of water samples between April 2021 to March 2022

	pH	Temp.(°C)	D.O (mg/L)	Potassium (mg/L)	Calcium (mg/L)	Phosphate (mg/L)	Sulphate (mg/L)	Nitrate (mg/L)	Turbidity (NTU)	B.O.D (mg/L)	THC (mg/L)
October	6.07 ± 0.31 ^{ab}	32.25 ± 0.37 ^c	6.56 ± 2.58 ^{bc}	11.49 ± 1.28 ^a	50.36 ± 5.08 ^a	2.08 ± 0.63 ^a	3.20 ± 0.60 ^{bcd}	1.83 ± 0.54 ^{ab}	12.00 ± 6.88 ^a	2.43 ± 0.20 ^a	0.70 ± 0.59 ^a
November	5.77 ± 0.12 ^a	29.30 ± 0.53 ^{cd}	4.99 ± 0.39 ^{ab}	10.12 ± 1.41 ^a	50.99 ± 4.77 ^a	1.50 ± 0.22 ^a	2.60 ± 0.25 ^{abc}	2.28 ± 0.34 ^{ab}	11.50 ± 4.20 ^a	2.64 ± 0.14 ^a	0.07 ± 0.10 ^a
December	7.08 ± 0.15 ^{cd}	32.15 ± 0.55 ^c	5.60 ± 0.43 ^{abc}	11.90 ± 1.94 ^a	59.01 ± 2.73 ^a	1.68 ± 0.28 ^a	2.36 ± 0.20 ^a	1.85 ± 0.52 ^a	15.00 ± 3.16 ^a	2.42 ± 0.18 ^a	1.93 ± 1.08 ^b
January	6.05 ± 0.17 ^{ab}	33.15 ± 1.22 ^c	5.58 ± 0.41 ^{abc}	96.40 ± 12.17 ^b	113.27 ± 5.33 ^c	1.53 ± 0.49 ^a	2.12 ± 0.25 ^a	1.55 ± 0.55 ^{ab}	16.50 ± 6.81 ^a	2.49 ± 0.09 ^a	0.50 ± 0.22 ^a
February	6.41 ± 0.29 ^b	30.20 ± 0.26 ^d	4.32 ± 0.88 ^a	115.67 ± 24.99 ^b	112.22 ± 7.85 ^c	1.68 ± 0.46 ^a	2.01 ± 0.25 ^a	1.40 ± 0.42 ^a	16.75 ± 5.79 ^a	2.50 ± 0.05 ^a	0.75 ± 0.39 ^a
March	6.62 ± 0.31 ^{bc}	30.05 ± 0.17 ^d	3.58 ± 0.72 ^a	114.59 ± 42.21 ^b	112.91 ± 2.40 ^c	1.58 ± 0.32 ^a	1.95 ± 0.19 ^a	1.35 ± 0.35 ^a	14.25 ± 4.86 ^a	2.49 ± 0.07 ^a	0.76 ± 0.40 ^a

*Parameters with the same superscript are not significantly different (p>0.05).

Table 3: Mean and Standard deviation of physico-chemical parameters in sediments from in the different stations between April 2021 to March 2022.

	Station 1	Station 2	Station 3	Station 4
pH	5.23 ± 0.40 ^a	5.62 ± 0.27 ^b	5.12 ± 0.49 ^a	5.28 ± 0.16 ^{ab}
Nitrate (mg/kg)	2.25 ± 0.20 ^b	2.36 ± 0.33 ^b	1.95 ± 0.45 ^{ab}	1.73 ± 0.57 ^a
Sulphate (mg/kg)	4.69 ± 0.50 ^{ab}	5.11 ± 0.93 ^b	4.28 ± 0.50 ^a	3.96 ± 0.91 ^a
Phosphate (mg/kg)	2.05 ± 0.34 ^{ab}	2.15 ± 0.26 ^b	1.98 ± 0.31 ^{ab}	1.67 ± 0.47 ^a
Calcium (mg/kg)	339.58 ± 102.23 ^a	331.75 ± 181.92 ^a	298.90 ± 90.46 ^a	409.40 ± 387.18 ^a
Potassium (mg/kg)	491.53 ± 305.45 ^a	419.25 ± 276.70 ^a	421.59 ± 294.90 ^a	465.35 ± 286.31 ^a
TOC (%)	7.40 ± 0.49 ^a	7.53 ± 0.38 ^a	7.14 ± 0.31 ^a	7.14 ± 0.37 ^a
THC (mg/kg)	122.90 ± 128.06 ^a	113.14 ± 128.80 ^a	98.94 ± 117.30 ^a	130.55 ± 153.21 ^a

*Parameters with the same superscript are not significantly different (p>0.05).

Table 4a: Mean and Standard deviation of physico-chemical parameters in sediments from April 2021 to March 2022.

	TOC (%)	Potassium (mg/kg)	Calcium (mg/kg)	Phosphate (mg/kg)	Sulphate (mg/kg)	Nitrate (mg/kg)	pH	THC (mg/kg)
April	7.31 ± 0.95 ^{ab}	733.90 ± 215.76 ^{bc}	431.30 ± 44.71 ^a	1.86 ± 0.48 ^{abc}	5.08 ± 2.19 ^a	1.95 ± 0.55 ^a	4.99 ± 0.39 ^a	296.53 ± 48.20 ^d
May	6.75 ± 0.37 ^a	577.12 ± 235.40 ^{abc}	348.83 ± 121.04 ^a	1.41 ± 0.28 ^a	4.65 ± 0.27 ^a	1.75 ± 0.13 ^a	5.02 ± 0.38 ^a	0.65 ± 0.99 ^a
June	7.33 ± 0.40 ^{ab}	323.31 ± 33.90 ^{ab}	457.27 ± 89.30 ^a	1.86 ± 0.32 ^{abc}	4.25 ± 0.92 ^a	1.83 ± 0.28 ^a	5.23 ± 0.33 ^a	2.27 ± 4.45 ^a
July	7.48 ± 0.21 ^{ab}	282.02 ± 48.62 ^a	472.50 ± 82.51 ^a	1.91 ± 0.39 ^{abc}	3.86 ± 0.61 ^a	2.10 ± 0.61 ^a	5.02 ± 0.34 ^a	2.01 ± 1.42 ^a
August	7.44 ± 0.37 ^{ab}	312.31 ± 52.27 ^a	474.21 ± 81.94 ^a	1.85 ± 0.26 ^{abc}	4.94 ± 0.50 ^a	1.80 ± 0.26 ^a	5.14 ± 0.30 ^a	2.51 ± 1.03 ^a
Sept.	7.08 ± 0.35 ^{ab}	221.99 ± 95.58 ^a	223.60 ± 130.22 ^a	1.54 ± 0.24 ^{ab}	5.38 ± 0.12 ^a	2.45 ± 0.13 ^a	5.13 ± 0.15 ^a	3.06 ± 0.57 ^a

*Parameters with the same superscript are not significantly different (p>0.05).

Table 4b: Mean and Standard deviation of physico-chemical parameters in sediments from April 2021 to March 2022.

	TOC (%)	Potassium (mg/kg)	Calcium (mg/kg)	Phosphate (mg/kg)	Sulphate (mg/kg)	Nitrate (mg/kg)	pH	THC (mg/kg)
Oct.	7.28 ± 0.16 ^{ab}	207.73 ± 81.37 ^a	220.10 ± 126.33 ^a	2.16 ± 0.10 ^{bc}	4.12 ± 0.81 ^a	1.83 ± 0.39 ^a	5.33 ± 0.30 ^a	388.09 ± 62.47 ^c
Nov.	7.79 ± 0.21 ^b	215.50 ± 64.95 ^a	221.71 ± 126.29 ^a	1.90 ± 0.28 ^{abc}	3.91 ± 0.71 ^a	1.85 ± 0.73 ^a	5.40 ± 0.59 ^a	218.11 ± 59.77 ^{cd}
Dec.	7.60 ± 0.33 ^{ab}	215.70 ± 47.26 ^a	229.98 ± 135.44 ^a	2.00 ± 0.30 ^{abc}	4.31 ± 0.40 ^a	1.88 ± 0.64 ^a	5.51 ± 0.41 ^a	164.31 ± 41.80 ^{bc}
Jan.	7.19 ± 0.05 ^{ab}	766.57 ± 295.27 ^c	427.37 ± 464.29 ^a	2.50 ± 0.11 ^c	4.85 ± 0.20 ^a	2.50 ± 0.16 ^a	5.64 ± 0.28 ^a	122.70 ± 26.03 ^b
Feb.	7.23 ± 0.10 ^{ab}	748.02 ± 216.12 ^c	222.45 ± 77.72 ^a	2.36 ± 0.04 ^c	4.38 ± 0.08 ^a	2.43 ± 0.22 ^a	5.66 ± 0.19 ^a	113.97 ± 17.74 ^b
Mar.	7.14 ± 0.05 ^{ab}	789.03 ± 283.06 ^c	409.57 ± 504.60 ^a	2.19 ± 0.19 ^{bc}	4.40 ± 0.17 ^a	2.53 ± 0.17 ^a	5.67 ± 0.19 ^a	84.48 ± 22.26 ^b

*Parameters with the same superscript are not significantly different (p>0.05).

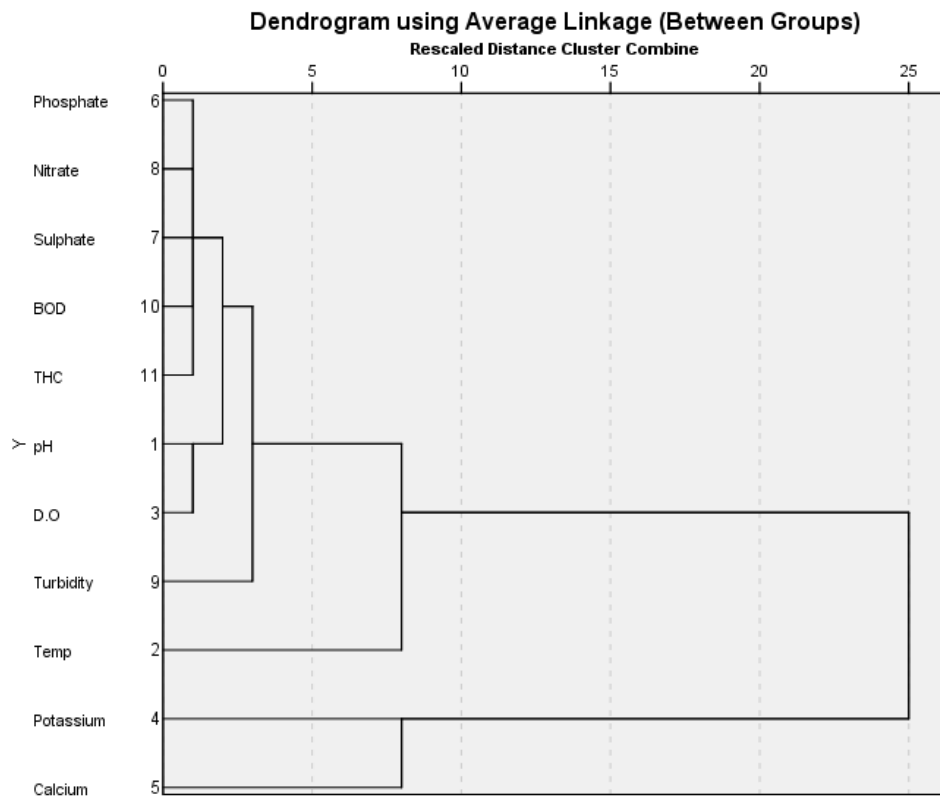


Figure 2: Cluster analysis for physicochemical parameters of water.

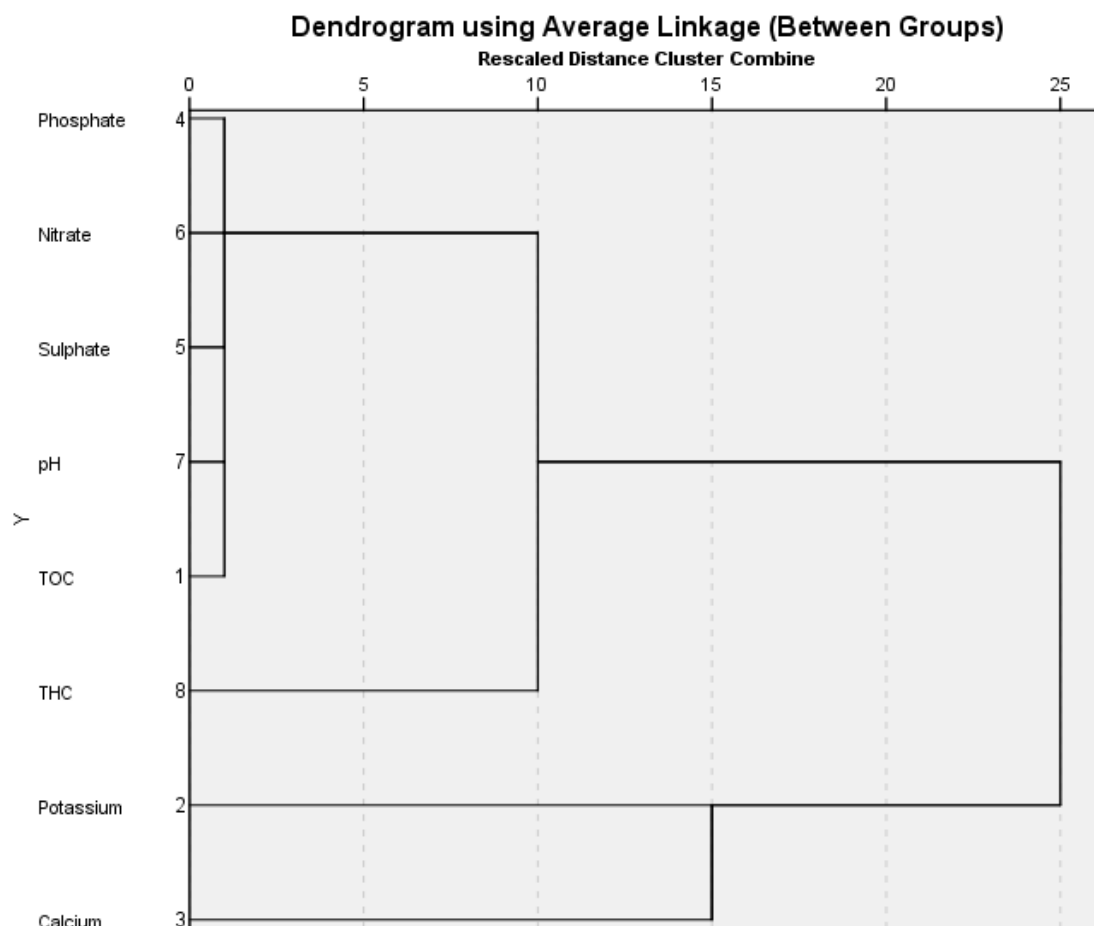


Figure 3: Cluster analysis for physicochemical parameters of sediment.

Table 5: Pearson correlation for physicochemical parameters of Water

Correlations^c

		pH	Temp	D.O	Potassium	Calcium	Phosphate	Sulphate	Nitrate	Turbidity	BOD	THC
pH	Pearson Correlation	1	-.604*	.133	.342	.281	-.351	.113	-.013	-.468	-.714**	-.194
	Sig. (2-tailed)		.037	.681	.277	.376	.264	.727	.969	.125	.009	.546
Temp	Pearson Correlation	-.604*	1	.202	-.418	-.238	.421	-.252	-.384	.737**	.295	.618*
	Sig. (2-tailed)	.037		.529	.177	.457	.173	.430	.217	.006	.353	.032
D.O	Pearson Correlation	.133	.202	1	-.306	-.293	.338	.438	.030	.097	.006	.127
	Sig. (2-tailed)	.681	.529		.333	.356	.283	.154	.926	.764	.986	.694
Potassium	Pearson Correlation	.342	-.418	-.306	1	.971**	-.132	.133	.092	-.221	-.092	-.306
	Sig. (2-tailed)	.277	.177	.333		.000	.683	.681	.776	.491	.776	.334
Calcium	Pearson Correlation	.281	-.238	-.293	.971**	1	-.088	.044	-.058	-.042	-.056	-.215
	Sig. (2-tailed)	.376	.457	.356	.000		.785	.891	.857	.896	.862	.501
Phosphate	Pearson Correlation	-.351	.421	.338	-.132	-.088	1	.632*	-.113	.329	.493	.460
	Sig. (2-tailed)	.264	.173	.283	.683	.785		.027	.727	.297	.104	.132
Sulphate	Pearson Correlation	.113	-.252	.438	.133	.044	.632*	1	.473	-.422	.185	-.101
	Sig. (2-tailed)	.727	.430	.154	.681	.891	.027		.121	.171	.565	.755
Nitrate	Pearson Correlation	-.013	-.384	.030	.092	-.058	-.113	.473	1	-.668*	.031	-.213
	Sig. (2-tailed)	.969	.217	.926	.776	.857	.727	.121		.018	.924	.507
Turbidity	Pearson Correlation	-.468	.737**	.097	-.221	-.042	.329	-.422	-.668*	1	.493	.638*
	Sig. (2-tailed)	.125	.006	.764	.491	.896	.297	.171	.018		.103	.026
BOD	Pearson Correlation	-.714**	.295	.006	-.092	-.056	.493	.185	.031	.493	1	.286
	Sig. (2-tailed)	.009	.353	.986	.776	.862	.104	.565	.924	.103		.368
THC	Pearson Correlation	-.194	.618*	.127	-.306	-.215	.460	-.101	-.213	.638*	.286	1
	Sig. (2-tailed)	.546	.032	.694	.334	.501	.132	.755	.507	.026	.368	

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

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

c. Listwise N=12

Table 6: Pearson correlation for physicochemical parameters of Sediments

Correlations^b

		TOC	Potassium	Calcium	Phosphate	Sulphate	Nitrate	pH	THC
TOC	Pearson Correlation	1	-.494	-.102	.243	-.494	-.280	.135	.300
	Sig. (2-tailed)		.102	.753	.447	.103	.377	.676	.344
Potassium	Pearson Correlation	-.494	1	.315	.420	.290	.534	.354	.003
	Sig. (2-tailed)	.102		.318	.174	.360	.074	.258	.992
Calcium	Pearson Correlation	-.102	.315	1	-.009	.120	-.041	-.324	-.416
	Sig. (2-tailed)	.753	.318		.978	.710	.899	.305	.178
Phosphate	Pearson Correlation	.243	.420	-.009	1	-.266	.490	.803**	.379
	Sig. (2-tailed)	.447	.174	.978		.403	.106	.002	.225
Sulphate	Pearson Correlation	-.494	.290	.120	-.266	1	.282	-.234	-.189
	Sig. (2-tailed)	.103	.360	.710	.403		.375	.464	.557

Nitrate	Pearson Correlation	-.280	.534	-.041	.490	.282	1	.550	-.186
	Sig. (2-tailed)	.377	.074	.899	.106	.375		.064	.563
pH	Pearson Correlation	.135	.354	-.324	.803**	-.234	.550	1	.193
	Sig. (2-tailed)	.676	.258	.305	.002	.464	.064		.548
THC	Pearson Correlation	.300	.003	-.416	.379	-.189	-.186	.193	1
	Sig. (2-tailed)	.344	.992	.178	.225	.557	.563	.548	
**. Correlation is significant at the 0.01 level (2-tailed).									
b. Listwise N=12									

DISCUSSION

This study evaluated the physicochemical parameters of water and sediments along the Santa Barbara estuary of the Niger Delta, Nigeria. Some of the parameters evaluated include: pH, Dissolved Oxygen, THC, TOC, BOD, Calcium, Potassium, Phosphate, Nitrate, and Sulphate. These parameters determine the habitability and productivity of organisms in the aquatic environment.

The pH, which affects the physiology of organisms (Chen and Durbin, 1994; Hansen, 2002), had a mean concentration of 5.77 - 7.85 (Table 2a, b) in water during the months of study and 6.7 – 7.04 in the different study stations. The level of pH in water in this study area is not so different from the levels reported by Ibisi et al. (2017) and Ifelebuegu et al. (2017). The pH of water samples from the various stations where within the approved permissible limit of 6.5- 8.5 set by NESREA. These mean ranges are considered to be ideal for organisms to thrive and function optimally in the aquatic environment (Hansen, 2002; Offem et al., 2011). A range between 8 – 10 is, however, considered unideal (Obahiagbon et al., 2014). The level in sediment, however, ranged from 4.99 – 5.67 and 5.12 – 5.62 in the study stations and months of study, respectively (Table 3; 4a, b). These levels are closer to acidity than the levels recorded in water. These levels are, however, linked to hydrocarbon pollution (Ukpene et al., 2024), and this result is consistent with the reports of Hart and Zabbey (2005); Dirisu and Edwin-Wosu (2022); and Udo et al. (2024), who reported acidic pH in sediments in their studies of sediments in the Niger Delta. The comparatively higher-level mean range of total hydrocarbon concentration (THC) levels in sediments than water in this study further strengthens the argument of Ukpene et al. (2024) that the pH of a medium is affected by oil spills.

The mean THC level recorded in water was 0.27 – 0.64 in the study stations and 0.01 – 1.93 in the different months of the study (Table 1; Table 2a, b), while the range of 98.94 – 130.55 was recorded in sediments from the various stations, and the range of 2.01 – 388.09 was recorded in sediments during the months of study (Table 3; Table 4a, b). Other studies, like Ogeleka et al. (2016) and Kpee and Bekee (2021), have also reported greater levels of THC in sediments than in water.

The low concentration of THC in water reported in this study is consistent with the reports of Oribhabor and Ogbeibu (2009), Ngah et al. (2017), but a far cry from the THC concentrations in water by Ibigoni-Clinton et al (2009), Daka and Moslen (2013), and Gijo et al. (2016). Also, the levels of THC in sediments from this study were far above the levels reported by Ezekiel et al (2011); Ebong and John (2021); Dere-Biemgbo and Oriakpono (2022), and Ebikeme et al. (2023). The greater levels of THC in sediment embolden the sediment as the repository of waste in the aquatic environment (Owoh-Etete et al., 2023).

The temperature of the aquatic environment triggers different physiological responses by different organisms (Fekri et al., 2018; Trombetta et al., 2021; Kazmi et al., 2022; Mei et al., 2022). In this study, the mean temperature level was between 26.67 – 33.15 °C during the months of the study, and 29.09 – 29.45 °C in the different study stations. The mean temperature levels in this study are similar to the levels reported by Bunza et al. (2024). These levels have also been reported to be ideal for the growth and development of plankton, benthic organisms, and fish, although these organisms have different tolerance ranges for temperature (Jain et al., 2013; Fekri et al., 2018; Bunza et al., 2024).

The biological oxygen demand (BOD) level in this study was between 2.22 – 2.64 during the months of the study, and 2.34 – 2.52 in the stations of the study. This concentration is similar to the reports of Komolafe et al. (2014), Dere-Biemgbo and Oriakpono (2022), but less than the level reported by Gijo et al. (2016). An increase in BOD levels has been reported to affect species diversity (Komolafe et al., 2014; Bello et al., 2024), thus, these low levels of BOD in this study area would support the growth of aquatic dwellers, barring any intrusions. Though Komolafe et al. (2014) and Zhao et al. (2020) reported significant seasonal variations in BOD levels from their studies, no significant variation was reported during the months of this study. The permissible limit for BOD as approved by NESREA is 3.0 mg/l, and this level is higher than the level of BOD recorded during this study.

Dissolved oxygen in water from the different stations ranged between 5.11 – 5.77 mg/l. At concentrations above 4.5 mg/l, dissolved oxygen supports the optimal growth of zooplankton (Banerjee et al., 2019), while at concentrations between 8.5 – 10 mg/l, there is usually a low diversity of zooplankton (Ogidi et al., 2024). Based on the aforementioned, this study area is likely to support the growth of zooplankton. Jonah et al (2020) reported a lower level of dissolved oxygen when compared to this study, while other researchers, like Hart and Zabbey (2005), Imachrist et al (2024), and Ogidi et al. (2024), had higher levels of dissolved oxygen in their study area.

In this study, mean nitrate concentrations in sediments were noted between 1.95 - 2.36 mg/kg in the study stations and 1.75 - 2.53 mg/kg during the months of study. The reasons for these low nitrate levels in sediments are a lack of agricultural activity and the presence of petroleum hydrocarbons in sediments (Ifelebuegu et al., 2017; Udoinyang et al., 2023). These two reasons align with this study, as there are no agricultural activities in this study area, and there are high levels of hydrocarbons, as indicated by this study. The concentrations of nitrate in sediments reported by Kartikasari et al (2013), Udoinyang et al (2023), and Jonah et al (2024) are higher than the concentrations reported in this study. In water, the mean concentration of nitrate was between 1.53 - 2.14 and 1.28 - 2.60 mg/l for the study stations and months of study, respectively. The concentration of nitrate in the study area was above the permissible limit of 9.1 mg/l approved by NESREA. The concentrations of nitrate in water, however, are lower than the concentrations reported in sediments. The concentration of nitrate in water is higher in this study than the report of Dere-Biemgbo and Oriakpono (2022), but lower than the report of Adesuyi et al. (2015) and Oladeji (2020).

In this study, however, the mean phosphate levels in sediments ranged between 1.67 - 2.15 mg/kg in the study stations, with monthly concentrations from 1.41 - 2.50 mg/kg, which is not so different from the study of Goodluck (2024), there has also been reports of higher concentration levels of phosphate in sediments when compared to the findings of this study (Tamunotonye et al., 2021; Jonah et al., 2024). However, in water, the concentration of phosphate was between 1.29 - 1.88 mg/l in the stations, and 1.18 - 2.08 mg/l during the months of the study. The concentrations of phosphate in water from this study are less than the concentration in the sediment. The low concentrations of phosphate in water had also been reported by Oladeji (2020) and Dienne et al. (2023). The concentration of phosphate in water was below the permissible level of 3.5 mg/l by NESREA.

The mean potassium concentration in sediments from this study ranged from approximately 421.59 - 491.53 mg/kg across various stations, and 215.50 - 789.03 mg/kg by month. The high concentrations of potassium reported in this study align with previous findings of high potassium concentration in sediments from the Niger Delta (Jason-Ogugbue and Ezekwe, 2020; Okoro and Emegha, 2022; Asunbo and Tanee, 2022) but differ from studies showing lower potassium levels (e.g., Seiyaboh et al., 2017; Ogamba and Nwabueze, 2017). Due to the high concentration of potassium in sediments from this study, they can be used to amend nutrient-deficient soils (Junakova et al., 2021).

In water, the mean concentration of potassium was from 75.72 - 81.85 mg/l between the stations and from 10.12 to 134.96 mg/l during the entire sampling period. Similar high concentrations of potassium in water have been reported by Ezekwe et al (2022) and Ogunbanwo and Faleti (2018). On the contrary, Seiyaboh et al (2016) in their study of the Orashi River reported a far lesser concentration of potassium (1.08 - 8.35 mg/l). The concentration of potassium in water recorded in this study was higher than the approved limit of 50 mg/l for surface water by NESREA.

The concentrations of calcium in water reported by Seiyaboh et al (2016) and Ogbeide and Edene (2023) are lower when compared to the level reported in this study. The mean concentration of calcium in this study ranged between 89.23 and 90.97 mg/l for the different study stations, and between 50.07 and 114.15 mg/l in the different months of the study. The mean calcium concentration in the water was less than the approved permissible concentration of 180 mg/l by NESREA, and this might be grossly less than the concentration needed for aquatic life. These low concentrations across the stations may harm aquatic life in the estuary. The calcium concentrations in sediments from this study ranged from 220.10 - 474.2 mg/kg and 298.90 - 409.40 mg/kg, surpassing those reported in other studies (Ekperusi et al., 2022; Ezekwe et al., 2022). High concentration of calcium in sediment may indicate a robust presence of macroconsumers in the study area (Correa et al., 2018).

The concentrations of sulphate in water reported by Oborie and Osemele (2024); Ogbeide and Edene (2023) are higher when compared to 2.41 - 2.86 mg/l and 2.01 - 3.70 mg/l reported concentrations for the study stations and the months of the study; these concentrations were, however, higher than the concentrations of sulphate reported by Ekperusi et al. (2022). The level of sulphate permissible by NESREA is about 100 mg/l in surface water, but the levels recorded in the stations are a far cry from the permissible level. Thus, there may be an issue of sulphate deficiency in the study area.

In sediments, the concentration of sulphate was 3.96 - 5.11 mg/kg in the study stations, and 3.86 - 5.38 mg/kg during the months of the study. These concentrations were higher when compared to the concentrations in water. The concentrations of sulphates present in sediment reported in the previous studies (Ezekiel et al., 2011; Dere-Biemgbo and Oriakpono, 2022) were higher than those found in this study (Table 3, 4a, b), indicating a possible decrease in organic matter input within the study area.

The turbidity levels recorded during this study ranged from 7.08 to 19.58 NTU for the various stations and from 6.75 to 16.75 NTU for the various months of the study. These concentration levels were higher than those reported by Ogbonna et al. (2021) but lower than the range reported by Ogbeibu et al. (2020). It is noteworthy that Station 4, which holds the record of being the most turbid station, also has the highest concentration of Nitrate and Phosphate when compared with other stations. Thus, an increase in nutrient levels and pollution caused by petroleum hydrocarbons can invariably be linked to an increase in turbidity.

The mean TOC concentrations in this study ranged from 6.75 - 7.79, suggesting that the levels recorded might not yet threaten benthic diversity (Hyland et al., 2005). Unlike previous studies that suggested rainfall affects TOC levels (Al-Hasani et al., 2024), this study did not observe significant monthly variations.

The Hierarchical Cluster Analysis is a tool employed to show the similarity, natural relationship or interactions in a data set that are apparently invisible (Omoleomo et al., 2008; Ogbuagu and Ayoade, 2012). A similar tool has been employed by Raimi and Sawyerr (2022) in the study of groundwater in Obrikom. This analysis revealed the presence of three clusters in water and sediment. These

clusters have been shown to reveal the spatial distribution of chemical components (Omoleomo et al., 2008). The result of the HCA is shown in Figures 2 and 3 for water and sediment samples. In sediments, the first cluster comprised Phosphate, Nitrate, Sulphate, pH, and TOC; the second cluster comprised THC only. In water, however, the first cluster comprised Phosphate, Nitrate, Sulphate, BOD, THC, and pH; the second cluster comprised D.O., Turbidity, and Temperature; while the third cluster contained potassium and calcium in both water and sediment. The clustering pattern for both sediment and water may be an indication that both environments may be polluted from the same source.

CONCLUSION

Due to the pressures from crude oil exploration activities in this area, it is essential to monitor water and sediment quality parameters regularly. These monitoring efforts will help identify any stress within the environment, allowing regulators to take decisive action to limit the release of pollutants. This is crucial, as pollution can have widespread effects on families whose livelihoods depend on the productivity of aquatic ecosystems. Conclusively, the findings indicate that while the Santa Barbara estuary may support a variety of aquatic life, the presence of hydrocarbons may pose challenges that need to be continuously monitored to protect the ecosystem's health.

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