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Application of Correlation Matrix and Analysis of Variance (Anova) in Profiling Surface Water in Nembe Creek of Niger Delta, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Water resource contamination is a major concern in several regions, especially in the Niger Delta, in which the oil exploration activities pose serious risks to human health, water resource and the environment. This present study evaluates the properties of surface water in Nembe Creek. Surface water samples were collected from three (3) control stations and twenty-four (24) sampling stations around the creek during the wet and dry seasons. The samples were subjected to analysis following the standard operating procedures of ASTM and APHA analytical methods. The relationship between the parameters and variations of surface water quality of Nembe creek were determined by using descriptive statistics, Analysis of variance (ANOVA) and Pearson correlation analysis. The results indicated pH had a mean value of 6.67 ± 0.33 (wet season) and 7.21 ± 0.3 (dry season), Electrical Conductivity ranged 200 - 3950 µS/cm (wet season) and 17900 - 25800 µS/cm (dry season), DO ranged between 4.3 - 5.8 (wet season) and 3.9 - 5.6 (dry season), Nitrate had values of 0.007- 0.068 mg/L (wet season) and 0 - 0.007 mg/L (dry season), Sulphate values range 130.58-158.76 mg/L (wet season) and 215.12 - 657.35 mg/L (dry season). Iron range 3.23 - 5.6 mg/L (wet season) and 0.26 - 7.87 mg/L (dry season), Zinc ranged 0.02 - 0.47 mg/L (wet season) and 0.13 -2.22 mg/L (dry season). Across all sampling stations and control areas during the wet season, the values for Total Petroleum Hydrocarbon (TPH), total hydrocarbon Content (THC) and Petroleum Aromatic Hydrocarbon (PAH) were below the detection limit; however, the values varied during the dry season. The Pearson Correlation matrix revealed positive, negative and significant correlations between the pairs of parameters at 95% confidence level. Amongst the sampling and control stations, some parameters had no significant difference (p > 0.05), however some differences were statistically significant (p < 0.05). In conclusion, Nembe Creek is marginally more polluted during the dry season than during the wet season. Most parameters on the Person's Correlation matrix were connected with each other based on the metrics. However, some parameters such as metals, do not significantly correlate with one another, indicating that the sources of contamination may have originated from various places. It is possible that the source may not predominantly originate from oil exploration activities but may involve other natural, geological and anthropogenic activities.

Keywords: Surface water; pearson correlation analysis; heavy metals; physico-chemical; nembe creek; aquatic.

1. INTRODUCTION

Anthropogenic activities such as oil sector operations, manufacturing, and urban wastes have resulted in significant environmental deterioration and pollution in Nigeria's coastal areas, particularly the Niger Delta Basin.

Surface water conveys a reasonable quantity or load of particles in dissolved or particulate form along its path and tributaries [1]. Due to the uncontrolled disposal of urban effluents, runoff, atmospheric deposition, municipal and industrial effluent into these water bodies water quality monitoring and assessment is a critical sustainability concern for surface water [2]. Pollution of these unique sources by numerous anthropogenic and natural sources may not only degrade these ecosystems but also be a threat to public health.

Knowledge of the physico-chemical properties of water is fundamental because they can affect its quality and, thus its suitability for the distribution and production of fish and other aquatic species, directly or indirectly. Variations in water quality parameters caused by pollution have an impact on resident species' quality of life, and these changes are mirrored in the biotic community structure, with the most sensitive species dying off and being replaced by tolerant species. Some species are wiped off, while others are reenforced for survival, while some multiply and decline in number. Water quality others monitoring is crucial for the conservation of water resources for fisheries, water supply, and other uses; it entails evaluating or profiling the physicochemical features of a water body.

Nembe Creek is located in the Niger Delta area of Nigeria, in the Nembe Local Government Area of Bayelsa State. The Nembe Creek field was discovered in the 1970s, which is about 90 km South West of Port Harcourt within a tributary of the Brass River in a typical mangrove

environment. To date, four oil flow stations have been installed in Nembe Creek. Nembe Creek 1, 2 and 3 flow stations were installed in 1977, while Nembe Creek 4 Flow station was installed in 1993. The residents of Nembe are noted for their skill and passion for farming, palm oil milling, local gin production, and fishing as a source of income. As a result, they demand highquality water from the creek. Oil exploration, drilling operations, pipeline installations, flow stations. artisanal refining, refinina. and distribution are just a few of the activities that may pose a risk of spillage that could harm the sediments, surface water, and environment around Nembe Creek [3]. Several oil-producing fields are located along Nembe Creek, which has flow stations or pipes structured across the creek.

According to the Niche news headline from December 2021, the governor of Bayelsa state expressed his displeasure with a spill of an estimated 2 million barrels of crude oil in a river that runs through the Nembe creek. He voiced his disapproval to the well-producing platform operated and managed by one of Nigeria's top indigenous oil companies. The spill harmed flora and fauna of the area, as well as the fishing route, leaving the residents of Nembe distraught. Since then, various organizations and the federal government have begun remediation efforts. The Bayelsa helmsman also condemned the absence of indigenes of host communities from the oil industry's operations, claiming that if indigenes were included in the oil field's operations, they would be better off and would have sought ways to address the problem.

For the same reason, some members of the town indulge in oil bunkering, which is the illegal siphoning or diverting of oil from pipelines and storage facilities. This is against the petroleum resources departments and federal regulatory rules. All of these factors lead to the degrading and deterioration of surface water, harming livelihoods, the environment, and natural receptors. Continuous monitoring of a large number of quality parameters is required for efficient water quality maintenance through appropriate control techniques. However, even when adequate skillful workers and laboratory facilities are available, consistent monitoring of all indicators is a tough and time-consuming task. As a result, in recent years, a statistical correlation-based technique has been employed to establish mathematical relationships for comparing physico-chemical data [4].

Correlation analysis determines how closely two variables are related at any given period. The probability of a relationship between the variables x and y is shown by correlation coefficient values closer to +1 or -1 [5]. This study aims to determine the nature of the linear relationship between the variables and, as a result, gives a prediction mechanism. These data result in three possible definition outcomes for the work that is being done.

- A positive correlation indicates that both variables rise and fall at the same time. The strongest connection for this finding is a coefficient that approaches 1.00.
- When a variable increases, the other decreases, this is known as a negative correlation. This is the expected outcome whenever the coefficient approaches -1.00.
- If the coefficient is 0, the result implies that the two variables do not have any correlation.

Considerable research has been done on statistical analysis to determine surface water quality. However, only a few researchers in Nigeria have carried out this approach [6,7]. Joshi et al., [8] examined the water quality parameters of river Ganga in Haridwar, India using Person's Correlation. In this study, an attempt was made to evaluate the quality of surface water in the study area and, as a result, conduct a correlation study of various physicochemical parameters. This research is needed to update information and identify the effects of anthropogenic activities on Nembe Creek's water quality characteristics.

2. MATERIALS AND METHODS

2.1 Study Area

Nembe is a Local Government Area of Bayelsa State, Nigeria. Its headquarters are in the town of

Nembe the east in of the area at 4°32'22"N 6°24'01"E. It has an area of 760 km² and a population of 130.931 at the 2006 census. Nembe Creek is situated within mangrove swamps in the southwest parts of Bayelsa State, Nigeria. The Nembe Creek has a Trunk Line (NCTL) of 97km, which produces 180,000 barrels of oil per day pipeline was constructed by Roya Dutch Shell plc and is situated in the Niger Delta region of Nigeria. Their major occupations include farming, palm oil milling, local gin making, fishing and trading. The study area map indicates the sampling stations around Nembe creek.

2.2 Surface Water Sampling

Twenty-four (24) water samples were obtained from the water bodies within the project area and from three (3) control points during the wet and dry seasons. Samples were collected using a two (2)-litre plastic container that had been pretreated by washing in dilute hydrochloric acid and rinsed with distilled water. At the sample collection point, the plastic container was rinsed with the relevant sample to be collected. Water samples were taken by submerging the container below the surface and allowing it to overflow. Water quality parameters determined on site (in-situ) include pH, Conductivity, Dissolved oxygen, Total Dissolved Solids, Turbidity and Temperature. Samples were collected and preserved (<4oC) for Anions, Total hardness, and Salinity analysis. Also, samples for BOD5, Heavy metals (acidified using nitric acid pH<2), Total Petroleum Hydrocarbon/Total Hydrocarbon Compounds and Chemical Oxygen Demand (acidified using sulphuric acid pH<2) were collected and preserved separately before onward delivery to the laboratory. All samples were preserved at (< 4°C) and transported in that state to Dukoria laboratory Ltd, Effurun, Delta State, where all ex-situ analyses were carried out in line with adapted standard procedures that were validated (APHA, 2012).

2.3 Methods

The methods of analysis were based on standard operating procedures (SOP) developed and validated in Dukoria Laboratories in accordance with APHA and ASTM procedures. The methods were all adapted from international standard methods presented in Table 2.



Fig. 1. Sampling map of study area

Table 1. Coordinates for the sampling loc	cation and sampling code, refer to Fig. 1
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Sample Code	Sample Type	Eastings	Northings
SW 1	Surface Water	424791.000	50053.000
SW 2	Surface Water	424956.000	50121.000
SW 3	Surface Water	425267.000	49896.000
SW 4	Surface Water	425552.000	49902.000
SW 5	Surface Water	425772.000	49854.000
SW 6	Surface Water	424853.000	50299.000
SW 7	Surface Water	424815.000	50585.000
SW 8	Surface Water	424835.000	50803.000
SW 9	Surface Water	424933.000	51047.000
SW 10	Surface Water	424585.000	50065.000
SW 11	Surface Water	424338.000	50167.000
SW 12	Surface Water	424082.000	50303.000
SW13	Surface Water	423776.000	50079.000
SW14	Surface Water	424067.000	50115.000
SW15	Surface Water	424850.000	49669.000
SW16	Surface Water	424696.000	49470.000
SW17	Surface Water	424646.000	49112.000
SW18	Surface Water	425419.000	49461.000
SW19	Surface Water	425261.000	49615.000
SW20	Surface Water	424474.000	49482.000
SW21	Surface Water	429150.000	50405.000

Sample Code	Sample Type	Eastings	Northings	
SW22	Surface Water	429460.000	50427.000	
SW23	Surface Water	429638.000	50349.000	
SW24	Surface Water	429840.000	50293.000	
SW CTRL1	Surface Water	419280.000	56905.000	
SW CTRL2	Surface Water	436714.000	53918.000	
SW CTRL3	Surface Water	435801.000	43071.000	

Parameters	Analytical Methods
Physico-chemical	
pH	Electronic method (APHA - 4500-H+)
Temperature, ⁰ C	Thermometer (APHA, 2550-B)
Conductivity, µS/cm	APHA 2510 B
Total dissolved solids (TDS), mg/L	APHA 2540-C
Total Suspended Solids (TSS), mg/L	Gravimetric method (APHA-2540-D)
Turbidity, NTU	Nephelometric method (APHA – 2130-B)
Anions	
Salinity (CI-), mg/L	Mohr's Argentometric method (APHA 4500 CI-B)
Nitrate, mg/L	Cadmium Reduction method (ASTM, 2016 -D3867)
Phosphate. mg/L	Ascorbic Acid method (APHA-4500 PO43-)
Sulphate, mg/L	Turbidity method (APHA-4500 SO42-E)
Gross organics	
BOD, mg/L	5 day method (APHA 5210B)
DO, mg/L	APHA – 4500-O C
COD, mg/L	Dichromate method (Reflux) (APHA – 5300 B)
Inorganics	
Calcium, mg/L	Complexometric Titration method
Magnesium, mg/L	Complexometric Titration method
Metals	Atomic Absorption Spectrophotometer (AAS), (APHA 3400)
	Source: APHA, (2017)

2.4 Statistical Analysis

Descriptive statistics and a one-way analysis of variance (ANOVA) was used to compute the significant difference between sampling points at 95% confidence level. Karl-Pearson correlation coefficient (r) was calculated, and correlation for significance has also been tested by applying a t-test. All statistical analyses were performed using SPSS, Kyplot and, Microsoft Excel, of Office 365.

3. RESULTS

The surface water quality of the study areas is presented in Table 3-7 and Figures 2-5 for wet and dry seasons.

3.1 Descriptive Statistics and ANOVA Analysis of Physicochemical and Metal Characteristics of the Surface Water in Nembe Creek

One-way Analysis Of Variance (ANOVA) was conducted to determine the relationship of water quality in the different sampling stations of Nembe Creek. The ANOVA was based on a significance level (α) of 0.05. The result represents the summary of the descriptive statistics for each physicochemical parameter and the statistical difference between the samplings station at 95% confidence interval. In the table of results (Tables 3 and 4), p > 0.05 connotes that at 95% confidence interval, there is no statistically significant difference between the values at various sampling points, while p < 0.05 is an indication that the differences are statistically significant.

The null hypothesis may not be rejected where null hypothesis, H_0 = no statistically significant difference and the alternative hypothesis, H_a = a statistically significant difference in physicochemical water quality parameters among the twenty-four (24) different points in Nembe Creek.

3.1.1 pH

The values for pH ranged between 6.1 - 7.3 and 6.8 - 8.2 for the sampling stations while the

control stations ranged between 6.5 - 7.6 and 7 -7.5 for the wet and dry season respectively. During the wet season in the sampling station, the mean value 6.67± 0.33 was less than the value 6.93 ± 0.5 recorded for the control stations. However, in the dry season, the sampling station had a higher value of 7.21 ± 0.3 when compared to the control station which had a lower value of 7.16 \pm 0.2. The values obtained were within the permissible range of values (6.5-8.5) prescribed as Nigeria Standard for Drinking Water Quality [9] and World Health Organization [10] permissible limits for water quality standard (Table 5). There was no statistical difference between pH at the sampling stations and the control stations (p > 0.05) at 95% confidence interval.

3.1.2 Electrical conductivity

Electrical Conductivity (EC) values range 200 – 3950 μ S/cm with mean value of 485 ± 77 μ S/cm (wet season) and 17900 – 25800 μ S/cm with mean value of 21309 ±22 μ S/cm (dry season) observed in the study area is higher than 270 – 590 μ S/cm with mean value of 480 ± 1.8 (wet season) and 18900 – 21700 μ S/cm with mean value of 20533 ± 25 μ S/cm observed in the control area. There was no significant difference between EC values observed in sampling points and control points (p > 0.05) at 95% confidence limit during the wet and dry seasons.

3.1.3 Total suspended solids (TSS)

The TSS values in the study areas had a range of 45.5 - 89.5 mg/L with mean value of 59 ±10.3 mg/L for the wet season and a range of 0 - 26.5mg/L with mean value of 6.81 ± 4.31 mg/L for the dry season. Compared to the control stations, these values were higher. The control stations were in a range of 18.5 - 26.5 mg/L with a mean value of 22.33 ± 0.5 mg/L for the wet season and 0 - 4 mg/L with a mean value of $2 \pm 0.02 \text{ mg/L}$ during the dry season. TSS obtained in the sampling area was significantly different (p < 0.05) from TSS obtained in the control area in the wet season (TSS in control area < TSS in the study area). No statistical difference was observed between TSS recorded in the study area and the control points during the dry season.

3.1.4 Total dissolved solids (TDS)

The total dissolved solids (TDS) range 128 – 2528mg/L (wet season) and 11456 -16512 mg/L

(dry season) were observed in the study area. The control area TDS ranged from 172.8 -377.6 and 12096 – 13888 mg/L in the wet and dry season, respectively. All the sampling points analyzed, showed no significant difference of TDS values (p > 0.05) at 95% confidence interval. The mean concentration of TDS 310 ± 45 and 13637 ± 14mg/L obtained from the sampling stations was higher than the mean TDS values 290.13 ± 0.6 and 13141± 32 mg/L observed in the control stations in both wet and dry seasons.

3.1.5 Dissolved oxygen (DO)

During the wet season, the dissolved oxygen ranged between 4.3 – 5.8 with a mean value of 5 \pm 0.3 while during the dry season, the range was 3.9 - 5.6 with a mean value of 4.42 ± 0.41 . The control stations had a range of 4.9 - 5.2 with mean value of 5.0 \pm 0.15 and 3.7 - 4.5 with a mean value of 4.0 ± 0.4 during the wet and dry season, respectively. There was no statistical difference between sampling points and control stations for DO values (p > 0.05) at 95% confidence interval in both seasons. Additionally, according to APHA [11], dissolved oxygen concentrations above 5 mg/L are appropriate for the sustenance of a variety of biota. Due to seasonal variations in air temperature, the maximum dissolved oxygen levels were seen during the wet season, which also happened to be the period of lowest surface water temperature.

3.1.6 Salinity

Salinity values range 18 - 32 mg/L and 11.8 - 175mg/L obtained in the study area during wet and dry season, respectively is slightly higher than 15.8 - 21.4mg/L (wet season) and 15 - 23 mg/L (dry season) observed in the control points.. There was a statistical difference (p < 0.05) between the mean of the control station and sampling station in the wet season but none was noted as such in the dry season (p > 0.05).

3.1.7 Biochemical oxygen demand (BOD)

The Biochemical Oxygen demand (BOD) range 0.3 - 5.8 mg/L (wet season) and 1.8 - 5.9 mg/L (dry season) were observed in the study area. The control stations BOD ranged from 0 - 5.2 and 2 - 5.1 mg/L in the wet and dry seasons, respectively. All the sampling points analyzed showed no significant difference of BOD values (p > 0.05) at 95% confidence interval. A higher

BOD level was observed in the dry season (3.42 \pm 0.78) than the wet season (3.35 \pm 1.7).

3.1.8 Chemical oxygen demand (COD)

COD range of 1.5 - 61 mg/L (wet season) and 7.8 - 12.88 mg/L (dry season) was observed in the study area. 8.4 - 61 mg/L (wet season) and 2.6 - 7.2 mg/L (dry season) were obtained in control area. There was no significant difference of COD values (p > 0.05) at 95% confidence interval between the sampling points.

3.1.9 Turbidity

The Turbidity values in the study areas had a range of 48.5 - 197 NTU with mean value of 90.3 ± 3 for the wet season and a range of 0 - 26 NTU with mean value of 8.84 ± 0.9 for the dry season. No statistical difference was observed for turbidity values between sampling points (p > 0.05) at 95% confidence limit. The mean turbidity values of 90.3 ± 3 in the wet season was higher than 8.84 ± 0.9 in the sampling area during the dry season.

3.1.10 Total hardness

During the wet season, the total hardness ranged between 0 - 990 mg/L with a mean value of 231.8 \pm 9 mg/L while during the dry season, the range was 800 – 10400 mg/L with a mean value of 3565 \pm 22 mg/L. The control stations had a range of 410 – 1900 mg/L with mean value of 910 \pm 21 mg/L and 1800 – 3200 mg/L with a mean value of 2500 \pm 99 mg/L during the wet and dry seasons, respectively. There was a statistical difference between sampling points and control stations for Total hardness values (p < 0.05) at 95% confidence interval

16 14 12 10 8 6 4 2 0 pH DO BOD COD • wet season CDry season during the wet season but otherwise in the dry seasons.

3.1.11 Organics (TPH, THC and PAH)

Across all sampling stations and control areas during the wet season, the values for Total Petroleum Hydrocarbon (TPH), total hydrocarbon Content (THC) and Petroleum Aromatic Hydrocarbon (PAH) were so minute that they were below the detection limit (<0.001) of the instrument. During the dry season, TPH values ranged between 0.02 - 1.69 mg/L with a mean value of 0.47 ± 0.4 mg/L in the sampling stations, while the control areas ranged between 0 - 0.24mg/L with a mean value of 0.14 ± 0.02 mg/L. The values for THC were 0.88 - 5.56 mg/L with a mean value of 3.22 ± 0.3 mg/L in the sampling stations, while the control areas ranged between 0 - 0.88 mg/L with a mean value of 0.29 ± 0.02 mg/L. The values for PAH were 0.05 - 0.74 mg/L with a mean value of 0.31 ± 0.02 mg/L in the sampling stations while the control areas ranged between 0.09 - 0.17 mg/L with a mean value of 0.12 ± 0.04 mg/L. There was no statistical difference between sampling points and control stations for the organics (p < 0.05) at 95% confidence interval during the dry seasons.

3.1.12 Anions (chloride, sulphate, nitrate, calcium, magnesium, potassium, sodium)

Chloride values range 24.92 - 449.86 mg/L (wet season) and 6348.03 - 11296.5 mg/L (dry season) observed in the study area is higher than 49.83 - 174.85 mg/L (wet season) and 4198 - 7998 mg/L (dry season) observed in the control area. No statistical difference was observed for chloride values obtained between the sampling points (p > 0.05) at 95% confidence interval.



(a)

(b)





Fig. 2. (a, b, c): Mean result for physico-chemical parameters across the sampling stations in Nembe creek



Fig. 3. Mean concentration of organics (TPH, THC, PAH) across the sampling station in the dry season in Nembe creek

Sulphate values range130.58- 158.76 mg/L (wet season) in the study area is higher than 6.17 - 29.48 mg/L (wet season) obtained from the control points. 215.12 - 657.35 mg/L observed in the study area during the dry season is lower than 62.94 - 858mg/L (dry season) observed in the control. Difference of Sulphate values between sampling stations was statistically significant (p > 0.005) at 95% confidence interval on the wet season but was statistically insignificant in the dry season.

Nitrate values range 0.007- 0.068 mg/L (wet season) and 0 – 0.007 mg/L (dry season) in the study area is relatively within the 0.019 – 0.028

mg/L (wet season) and 0 – 0.002 mg/L (dry season) observed in the control area. Only the wet season showed statistical difference of nitrate values between sampling stations (p > 0.05) at 95% confidence interval.

Calcium range 14.62- 14.62 mg/L (wet season) in the study area is lower than 0 – 43.54 mg/L (wet season) observed in the control. 129.37-231.83 mg/L (dry season) is relatively within the range 115 – 261 mg/L (dry season) observed in the control. No statistical difference of potassium values between sampling stations was observed in this study (p > 0.05) at 95% confidence interval.

Magnesium 2.14 - 224.03 mg/L (wet season) in the study area is higher than 2.49 - 36.49 mg/L(wet season) observed in the control. 471.57 - 760.88 mg/L (dry season) is relatively within the range 401 - 821 mg/L (dry season) observed in the control. No statistical difference of potassium values between sampling stations was observed in this study (p > 0.05) at 95% confidence interval.

Potassium range 0.45 - 8.85 mg/L (wet season) in the study area is higher than 0.6 - 1.32 mg/L(wet season) observed in the control. 40.1 - 57.79 mg/L (dry season) is relatively above the range 42.34 - 48.61 mg/L (dry season) observed in the control. No statistical difference of potassium values between sampling stations was observed in this study (p > 0.05) at 95% confidence interval.

Sodium range 35.51- 701.27 mg/L (wet season) in the study area was higher than 47.93 - 104.75 mg/L (wet season) and 3177.89 - 5202.1 mg/L (dry season) observed in the study area is lower than and 2780.2 - 5739 mg/L (dry season) recorded in the control area. There was no statistical difference of sodium values between sampling points (p > 0.05) at 95% confidence interval.

3.1.13 Heavy metals (iron, zinc, lead, copper, nickel)

Iron (Fe) range 3.23 - 5.6 mg/L (wet season) and 0.26 - 7.87 mg/L (dry season) in the study area

is slightly higher than 2.07 - 4.85 mg/L (wet season) 2.19 - 3.38 mg/L (dry season) obtained in the control stations. There was no statistical difference for Fe values between sampling stations (p > 0.05) at 95% confidence interval.

Zinc (Zn) range 0.02 - 0.47 mg/L (wet season) is more than the range 0.03 - 0.07 mg/L (wet season) observed in the control station and 0.13 - 2.22 mg/L (dry season) in the study area was higher than 0.44 - 0.91 mg/L (dry season) observed in the control station. No statistical difference was observed for Zn values between samplings points (p > 0.05) at 95% confidence interval.

Lead (Pb) values were below the detection limit (<0.01) of the instrument during the wet season. However, in the dry season, the range 0.04 - 2.01 mg/L (dry season) obtained in the study area corresponds with 1 - 2 mg/ L (dry season) observed in the control stations. There was no statistical difference for Cr values between sampling stations (p > 0.05lk) at 95% confidence interval.

Copper (Cu) values was below the detection limit (<0.003) of the instrument during the wet season. However, in the dry season, the range 0.02 - 0.38 mg/L (dry season) obtained in the study area was higher than 0.02 - 0.08 mg/L (dry season) observed in the control stations. The difference of Cu values between sampling stations was statistically insignificant (p > 0.05) at 95% confidence interval.



Fig. 4. Mean concentration of anions (chloride, sulphate, magnesium, sodium, nitrate, potassium, calcium) across the sampling station in Nembe creek



Fig. 5. Mean concentration of Heavy Metals (Iron, zinc, Lead, copper, Nickel) across the sampling station in Nembe creek

	Sampling	g stations	Control	areas	
	Range	Mean ± S.D	Range	Mean± S.D	P value
рН	6.1 – 7.3	6.67±0.33	6.5 - 7.6	6.93 ± 0.5	P > 0.05
Electrical Conductivity, µS/cm	200 – 3950	485 ± 77	270 – 590	480 ± 1.8	P > 0.05
Total Suspended Solids (TSS), mg/L	45.5 – 89.5	59 ±10.3	18.5 - 26.5	22.33 ± 0.5	P < 0.05
Total Dissolved Solids (TDS), mg/L	128 – 2528	310 ± 45	172.8 -377.6	290.13 ± 0.6	P > 0.05
Dissolved Oxygen (DO), mg/L	4.3 – 5.8	5 ± 0.3	4.9 - 5.2	5.0 ± 0.15	P > 0.05
Salinity, %	18 – 32	23 ± 3	15.8 – 21.4	18.9 ± 0.09	P < 0.05
Biochemical Oxygen Demand (BOD), mg/L	0.3 – 5.8	3.35 ±1.7	0-5.2	4.1 ± 0.05	P > 0.05
Chemical Oxygen Demand (COD), mg/L	1.5 – 61	13.8 ± 15	8.4 – 61	26.2 ± 0.08	P > 0.05
Turbidity, NTU	48.5 – 197	90.3 ±3	42 – 95	64.5 ± 2	P > 0.05
Total Hardness, mg/L	0 - 990	231.8 ±9	410 - 1900	910 ± 21	P < 0.05
Organics					
Total Petroleum Hydrocarbon (TPH)	<0.001	<0.001	<0.001	<0.001	<0.001
Total Hydrocarbon Content, (THC)	<0.001	<0.001	<0.001	<0.001	<0.001
Polynuclear Aromatic Hydrocarbon (PAH)	<0.001	<0.001	<0.001	<0.001	<0.001
Anions					
Chloride, (Cl-)	24.92 - 449.86	78.6 ±8	49.83 – 174.85	99.86 ± 6	P > 0.05
Sulphate, (SO42-)	130.58- 158.76	146.71 ± 14	6.17 – 29.48	15.6 ±0.69	p < 0.05
Nitrate, (NO3-)	0.007- 0.068	0.026 ± 0.01	0.019 – 0.028	0.022 ± 0.004	P > 0.05
Calcium, (Ca 2+)	14.62- 14.62	14.62 ±0.10	0 – 43.54	14.51 ± 1.2	0
Magnesium, (Mg2+)	2.14 – 224.03	15.6 ±4.50	2.49 – 36. 49	13.91 ± 1	P > 0.05
Potassium, (K+)	0.45 – 8.85	1.1 ±0.02	0.6 – 1.32	1.01 ± 0.09	P > 0.05
Sodium, (Na+)	35.51- 701.27	86 ±0.03	47.93 – 104.75	80.48 ± 1	P > 0.05
Metals					
Iron, (Fe)	3.23	4.8 ±0.9	2.07 – 4.85	3.25 ± 0.05	P < 0.05
Zn	0.02 - 0.47	0.05 ±0.02	0.03 - 0.07	0.05 ± 0.009	P > 0.05
Lead	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.003	<0.003	<0.003	<0.003	<0.003
Ni	1.56 – 5.51	2.94 ± 0.98	0.5- 1.55	1.12 ± 0.09	P > 0.05

Table 3. Physico-chemical parameters of water in Nembe creek during the wet season

	Sampling	Stations	Control	Control stations				
	Range	Mean	Range	Mean	P value			
рН	6.8 – 8.2	7.21 ± 0.3	7 - 7.5	7.16 ± 0.2	P > 0.05			
Electrical Conductivity, µS/cm	17900 – 25800	21309 ±22	18900 - 21700	20533 ± 25	P > 0.05			
Total Suspended Solids (TSS), mg/L	0 – 26.5	6.81 ± 8.31	0 – 4	2 ± 0.02	P > 0.05			
Total Dissolved Solids (TDS), mg/L	11456 -16512	13637 ± 14	12096 - 13888	13141 ± 32	P > 0.05			
Dissolved Oxygen (DO), mg/L	3.9 – 5.6	4.42 ± 0.41	3.7 - 4.5	4.0 ± 0.4	P > 0.05			
Salinity, %	11.8 – 175	25 ± 3.71	15 – 23	19 ± 0.05	P > 0.05			
Biochemical Oxygen Demand (BOD), mg/L	1.8 – 5.9	3.42 ± 0.78	2 – 5.1	3.5 ± 0.09	P > 0.05			
Chemical Oxygen Demand (COD), mg/L	7.8 – 12.88	10.39 ± 1.20	2.6 – 7.2	9.06 ± 0.05	P > 0.05			
Turbidity, NTU	0-26	8.84 ± 0.9	1 – 7	3.33 ± 0.05	P > 0.05			
Total Hardness, mg/L	800 – 10400	3565 ± 22	1800 - 3200	2500 ± 99	P > 0.05			
Organics								
Total Petroleum Hydrocarbon (TPH)	0.02 - 1.69	0.47 ± 0.4	0 – 0.24	0.14 ± 0.02	P > 0.05			
Total Hydrocarbon Content, (THC)	0.88 – 5.56	3.22 ± 0.3	0-0.88	0.29 ± 0.02 P > 0.05				
Polynuclear Aromatic Hydrocarbon (PAH)	0.05 – 0.74	0.31 ± 0.02	0.09 – 0.17	0.12 ± 0.04	P > 0.05			
Anions								
Chloride, (Cl-)	6348.03 – 11296.5	8380 ± 26	4198 - 7998	6431 ± 19	P < 0.05			
Sulphate, (SO42-)	215.12 – 657.35	380 ± 12	62.94 – 858	526 ± 12	P > 0.05			
Nitrate, (NO3-)	0-0.007	0.003 ± 0.001	0-0.002	0.00066 ± 0	P > 0.05			
Calcium, (Ca 2+)	129.37- 231.83	194.4 ± 2	115 – 261	179 ± 7	P > 0.05			
Magnesium,(Mg2+)	471.57 – 760.88	589 ± 7	401 – 821	582 ± 12	P > 0.05			
Potassium, (K+)	40.1 – 57.79	47.7 ± 5	42.34 - 48.61	45 ± 3	P > 0.05			
Sodium, (Na+)	3177.89 – 5202.1	3858 ± 59	2780.2 – 5739	3867 ± 16	P > 0.05			
Heavy Metals								
Iron, (Fe)	0.26 – 7.87	2.4 ± 0.8	2.19 – 3.38	2.8 ± 0.5	P > 0.05			
Zn	0.13 – 2.22	0.61 ± 0.09	0.44 – 0.91	0.64 ± 0.2	P > 0.05			
Lead	0.04 - 2.01	0.97 ± 0.5	1 - 2	1.37 ± 0.08	P > 0.05			
Cu	0.02 – 0.38	0.15 ± 0.02	0.02 - 0.08	0.05 ± 0.01	P > 0.05			
NI	0.08 - 4.29	1.57 ± 0.05	0.1 – 0.35	0.2 ± 0.05	P > 0.05			

Table 4. Physico-chemical parameters of water in Nembe creek during the dry season

Physico-chemical Parameters	WHO, 2011	NSDWQ, 2007
	(Domestic water)	
рН	6.5 – 8.5	6.5 -8.5
Electrical conductivity, µS/cm	1000	1000
Dissolved Oxygen, mg/L	-	5.0
Turbidty, NTU	5	5
Total suspended solids, mg/L	50	-
Total dissolved solids, mg/L	500	500
Sulphate, mg/L	250	-
Nitrate, mg/L	50	50
Calcium, mg/L	-	-
Sodium, mg/L	200	200
Magnesium, mg/L	-	30
PAH	-	0.007
Iron , mg/L	0.3	0.3
Zinc, mg/L	3	3
Lead, mg/L	0.01	0.01
Copper , mg/L	2	-
Nickel , mg/L	0.03	-

Table 5. Water qua	ality standards
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Nickel (Ni) had values of 1.56 - 5.51 mg/L during the wet season at the study area but recorded lesser values of 0.5- 1.55 at the control stations. Ni values in the range 0.08 - 4.29 mg/L (dry season) observed in the study area was higher than 0.1 - 0.35 mg/L (dry season) observed in the control. No statistical difference of Ni values was observed between points (p > 0.05) at 95% confidence limit.

3.2 Pearson Correlation Matrix and Seasonal Variation

Correlation Pearson correlation coefficients were computed in order to understand the association and relationship of different physical and chemical parameters, including heavy metals of the Nembe Creek. The value of the relationship takes values ranging from -1 to +1, where +1 represents an absolute perfect positive linear relationship, 0 represents no linear relationship, whereas -1 represents an absolute inverse relationship between the bivariates. The sign in front of the correlation coefficient value determines the direction of the relationship. A strong positive correlation between parameters denotes that an increase in one parameter results in a subsequent increase in the other parameter, while a negative correlation between parameters indicates that an increase in one parameter causes the other parameter to decrease (Shroff et al. 2015). The correlation coefficients are presented in the form of matrix, for Nembe Creek, with their statistical

significance at 0.05 alpha levels (p values) for wet and dry seasons, respectively (Tables 6-7).

In this Study, pH showed a moderate positive correlation with electrical conductivity, Salinity, Turbidity, Calcium, potassium and sodium in the dry season and a weak correlation in the wet season. The correlation coefficient value were r = 0.672, -0.52, 0.512, 0.495, 0.672 and 0.794 for the various parameters listed above. The pH contributes to the increase in conductivity. The conductivity of a solution depends on the concentration of all the ions present; the greater their concentrations, the greater the conductivity.

Electrical conductivity showed a strong positive correlation with Total dissolved solids (TDS), Calcium, magnesium, potassium, sodium, and zinc during the wet season with a correlation coefficient value (r = 1, 0.995. 0.9948, 1, 1, 0.999). During the dry season, there was a weak positive correlation between EC and COD, a moderate positive correlation between EC and calcium, strong positive correlation of EC with potassium and sodium. The correlation coefficient value where (r = 0.387, 0.5036, 1,0.8048), The elevated level of EC in the dry season is consistent with the strong correlation of these ions observed shows that the ions may have contributed to the high EC recorded. However, it also implies that as these ions increases, the Electrical conductivity of such sampling area increases.

Table 6. Person correlation matrix of the parameters in the different sampling stations in Nembe creek during wet season

	рН	EC	TSS	TDS	DO	Salinity	BOD	COD	Turbidity	Total Hardness	TPH	PAH	Sulpahte	Nitrate	Calcium	Mg	К	Na	Fe	Zn	Pb	Cu	Ni
pН	1																						
Ec	-0.252	1																					
TSS	0.163	-0.115	1																				
TDS	-0.252	1	-0.115	1																			
DO	-0.224	-0.075	-0.515	-0.076	1																		
Salinity	-0.131	-0.055	-0.052	-0.056	0.04	1																	
BOD	0.071	-0.08	0.017	-0.08	0.13	-0.087	1																
COD	-0.264	-0.081	-0.15	-0.081	-0.03	-0.113	-0.361	1															
Turbidity	0.049	-0.285	0.079	-0.285	0.08	0.141	-0.177	-0.12	1														
Total	-0.122	-0.062	0.358	-0.062	-0.23	-0.092	-0.185	-0.139	0.616	1													
Hardness																							
TPH	0	0	0	0	0	0	0	0	0	0	1												
PAH	0	0	0	0	0	0	0	0	0	0	0	1											
Sulphate,	-0.203	-0.246	0.159	-0.24	-0.07	0.450	-0.037	0.185	0.021	0.019	0	0	1										
Nitrate	-0.074	0.109	-0.105	0.1094	0.266	-0.272	0.3009	-0.199	-0.01	-0.23	0	0	-0.114	1									
Calcium	-0.251	0.995	-0.139	0.995	-0.06	-0.055	-0.055	-0.06	-0.296	-0.07	0	0	-0.247	0.103	1								
Magnesium	-0.262	0.9948	-0.16	0.9948	-0.05	-0.048	-0.053	-0.054	-0.29	-0.07	0	0	-0.244	0.106	0.999	1							
Potassium	-0.253	1	-0.115	1	-0.08	-0.056	-0.08	-0.081	-0.285	-0.06	0	0	-0.246	0.109	0.995	0.995	1						
Sodium	-0.252	1	-0.115	1	-0.08	-0.056	-0.08	-0.081	-0.285	-0.06	0	0	-0.246	0.109	0.995	0.995	1	1					
Iron	-0.01	0.137	0.0251	0.137	-0.02	0.645	-0.008	-0.172	0.326	0.023	0	0	0.007	-0.09	0.124	0.134	0.137	0.137	1				
Zinc	-0.25	0.999	-0.111	0.999	-0.07	-0.047	-0.082	-0.079	-0.291	-0.07	0	0	-0.235	0.12	0.994	0.994	1	1	0.144	1			
Lead	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1		
Copper	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	
Nickel,	0.078	-0.11	0.7129	-0.11	-0.4	-0.255	0.0779	-0.091	-0.239	0.321	0	0	0.209	-0.33	-0.12	-0.14	-0.11	-0.11	-0.35	-0.12	0	0	1

Table 7. Person correlation matrix of the parameters in the different sampling stations in Nembe creek during dry season

	рН	EC	TSS	TDS	DO	Salinity	BOD	COD	Turbidity	Total Hardness	TPH	PAH	Sulpahte	Nitrate	Calcium	Mg	к	Na	Fe	Zn	Pb	Cu	Ni
pН	1																						
Ec	0.672	1																					
TSS	-0.14	-0.078	1																				
TDS	0.672	1	-0.078	1																			
DO	-0.23	-0.289	0.1718	-0.29	1																		
Salinity	-0.52	-0.285	0.4633	-0.28	0.385	1																	
BOD	0.037	0.2619	0.0963	0.262	-0.67	-0.038	1																
COD	0.183	0.387	0.2054	0.387	-0.08	-0.316	0.055	1															
Turbidity	0.512	0.2941	0.0663	0.294	-0.25	-0.346	0.035	0.212	1														
Total	0.278	0.1082	-0.116	0.108	0.032	-0.117	-0.136	-0.09	0.168	1													
Hardness																							
TPH	-0.06	-0.065	0.0916	-0.06	0.146	0.1931	-0.299	0.175	-0.04	-0.211	1												
PAH	0.113	-0.076	0.1175	-0.08	0.146	0.2137	-0.425	-0.02	-0.01	-0.057	0.496	1											
Sulphate,	-0.04	-0.25	0.0433	-0.25	-0.14	-0.197	0.26	-0.11	0.212	0.3625	-0.51	-0.129	1										
Nitrate	-0.1	0.1265	-0.067	0.126	0.269	0.2959	-0.348	-0.32	-0.21	0.1135	-0.13	0.0478	-0.115	1									
Calcium	0.495	0.5036	-0.1	0.504	-0.23	-0.084	0.13	-0.07	0.304	0.1301	0.273	-0.134	-0.359	-0.039	1								
Mg	0.305	0.0771	-0.07	0.077	0.308	0.0707	-0.171	-0.08	0.091	0.0201	0.132	0.3112	0.0505	0.0709	0.289	1							
кĭ	0.672	1	-0.078	1	-0.29	-0.284	0.262	0.387	0.294	0.1084	-0.06	-0.076	-0.25	0.1264	0.504	0.077	1						
Na	0.794	0.8048	-0.169	0.805	-0.32	-0.347	0.274	0.195	0.419	0.1597	0.119	-0.013	-0.202	-0.091	0.748	0.406	0.805	1					
Fe	-0.08	-0.042	0.1735	-0.04	0.119	0.0923	0.147	0.157	0.071	-0.241	-0.13	0.2242	0.4122	-0.371	-0.37	0.091	-0.04	-0.17	1				
Zn	-0.03	-0.007	0.4249	-0.01	0.298	0.2401	-0.121	0.32	0.18	-0.116	0.043	0.0783	-0.19	-0.002	-0.09	0.095	-0.01	-0.029	0.05	1			
Pb	-0.15	0.0223	0.1865	0.022	0.156	0.0909	-0.083	0.088	0.101	-0.237	0.099	0.2446	0.0068	0.3736	-0.26	0.298	0.022	0.0066	-0.029	0.261	1		
Cu	0.089	-0.042	0.0028	-0.04	-0.18	-0.094	0.04	-0.25	-0.16	0.1525	-0.1	-0.229	-0.207	-0.102	0.198	-0.244	-0.04	-0.034	-0.409	-0.34	-0.541	1	
Ni	0.06	0.3509	-0.057	0.351	-0.3	0.0675	0.394	-0.04	-0.002	-0.352	-0.06	-0.073	-0.261	0.1273	0.241	0.116	0.351	0.2408	0.058	-0.04	0.224	-0.099	1

TSS had a moderate negative correlation with Dissolved oxygen (r = -0.515) and a moderate positive correlation with Nickel (r = 0.7129) in the wet season. This illustrates that as the TSS increases, the DO decreases. This implies that TSS might have contributed to the depletion of oxygen in the wet season. During the dry season, TSS had a weak positive correlation with Salinity (r = 0.4633) and Zinc (r = 0.4249).

TDS had a strong positive correlation with calcium, magnesium, potassium, sodium and zinc with coefficient values of (r = 0.995, 0.9948, 1, 1, 0.999) in the wet season. This shows that these salts contributed to the TDS of the surface water in these study. There was also a moderate and strong positive correlation with calcium, potassium, sodium during the dry season (r = 0.504, 1, 0.805).

In the wet season, DO exhibit weak positive correlation. No significant correlation was observed between DO and other parameters. However, in the dry season, there was a weak positive correlation between DO and Salinity with a coefficient of (r = 0.385).

Salinity exhibited weak positive correlation with Sulphate (r = 0.450) in the wet season. However, during the dry season, there was a weak correlation with all parameters.

While these parameters were weakly correlated with others in the wet season, during the dry season, BOD showed a weak negative correlation with PAH (r = =-0.425). COD showed a weak positive correlation with potassium (r = 0.387). Turbidity showed a weak positive correlation with sodium (r = -0.419). TPH showed a weak positive correlation with PAH (r = 0.419).

In the wet season, calcium showed strong positive correlation with magnesium, potassium, sodium and zinc with coefficient values of (r = 0.999, 0.995, 0.995, 0.994). This infers that they may be from the same pollution source. Source of calcium may be from natural sources or rocks from geological activities. In the dry season, calcium exhibited a moderate positive correlation with potassium (r = 0.504). This shows that as Calcium values increases, magnesium, potassium, sodium and zinc also exhibit increase in their values.

In the wet season, magnesium showed a strong positive correlation with potassium, sodium and zinc with coefficient values of (r = 0.995, 0.995,

0.994). In the dry season, magnesium exhibited weak positive correlation with sodium (r = 0.406).

Potassium exhibited a weak correlation in the wet season but in the dry season was strongly correlated with sodium with an r value of 0.805. Iron was negatively correlated with copper with a coefficient of (r = -0.409) while lead was also negatively correlated with copper with a coefficient of (r = -0.541).

4. DISCUSSION

This study also took into account the seasonal variations in these parameters caused by pollution (agricultural runoff, such as the application of fertilizers, insecticides, and herbicides), mixed farming, deforestation, oil operations, and bunkering activities, as well as other climatic factors like wind and rainfall and their effects on Nembe Creek. According to Okoro and Diejomaoh (2022), the activities in river basins are the main factors affecting the water quality of aquatic systems. The pH values were within the usual range of 7.0-8.5 and were typically indicative of a tidal brackish water environment, as indicated by Ajao and Fagade (2002), in accordance with WHO criteria for domestic use of water. Additionally, the seasonal variation was consistent with the findings of an earlier study in the Bonny Estuary by Onojake et al. (2015), with the greatest values obtained during the dry season and the lowest values during the rainy season. The pH of the surface water may be inclined towards being slightly acidic in the wet season due to increased rates of photosynthetic activity in aquatic plants, leachate drainage, or rainfall during the wet season (Ansa 2005). As a result, the pH seems to be ideal for a wide range of aquatic species and domestic uses.

A valuable indicator for geographical and/or temporal changes is provided by electrical conductivity and total dissolved solid values. In the rainy season, electrical conductivity and total dissolved solids were found to be much lower (Tables 3 and 4); this may be because the water becomes more diluted as volume increases. However, water evaporation and an increase in ion concentration during the dry season lead to an increase in electrical conductivity and TDS. This supports the conclusions reached by Magami et al (2014). The correlation matrix also revealed a substantial link between EC and TDS, suggesting that TDS may have had a significant role in the elevated level of EC. Total dissolved solids (TDS) levels were higher than is recommended for brackish water in the observed values [12]. This is a sign of organic contamination from anthropogenic sources such as sewage from homes, septic tanks, and farming operations [13]. The seasonal variations in TSS were significantly different from each other as the values of the wet season were higher than the dry season in the study area. This may be due to the presence or deposition of silt, clay, plankton, organic wastes, and inorganic precipitates during the wet season.

The samples were collected from May through October, which fell within the wet season. This typically occurs during the rainy season in West Africa, when large amounts of freshwater are released into coastal, brackish, or estuarine waters, lowering or diluting the water. Rainfall is said to have the potential to dilute brackish water and reduce salinity, according to Mclusky [14]. This attributed to the low values of salinity discovered in this study in the wet season.

In the rainy season, the DO levels were in line with the WHO standard; however, during the dry season, a minor decline was seen. Depletion of the DO in the water results from the addition of organic or inorganic components that require oxygen. Fish and other advanced aquatic species are at risk because of this. The distribution of plants and fauna is controlled by the concentration of DO. Additionally, all aquatic life forms require it, particularly the organisms that carry out the self-purification of natural waters.

According to this study, the water quality and marine life would be severely threatened if more organic and inorganic elements were added into Nembe Creek. The BOD was often higher during the dry season than the wet, which may be related to the slower water flow and the buildup of waste from anthropogenic activities. Since the concentration recorded suggests the minimal activity of bacteria in the breakdown of organic contaminants, the reduced levels have little impact on the water quality and marine life, hence is clean or slightly polluted. Similar studies by Ngah et al. [15] demonstrated this assertion. The lack of significant seasonal fluctuations could be attributed to surface runoff and organic pollutant influx. The results of Tanimu [16] and Hassan et al. [17] 's studies on the Tudun Wada-Makera Drain, River Kaduna, and Hussainiya River are in agreement with this. Greater temperatures, saline conditions, and putrefaction

of materials dumped into rivers could all contribute to the higher BOD during the dry season. The water body appeared to be given relatively that clean the ROD measurements during the wet and dry seasons were within the range of 10 mg/L recommended by World Health Organization (WHO) and Nigerian Standard for Drinking Water Quality (NSDQW). This therefore indicates minimum anthropogenic activities in the study area. In contrast to the seasonal trend observed in this study, higher BOD values in the wet season was reported by loryue et al, (2018) from River Mkomon in Kwande Local Government Area, Nigeria.

Salinity levels were higher during the dry season than the wet season according to seasonal variation. This may be triggered by intense sunlight, which enhances the rate of water evaporation from the water's surface, making it saltier and more saline. The wet season was found to have greater turbidity levels than the dry season. This was most likely caused by waste produced by municipal activities in the river, excessive levels of natural erosion and runoff from the surroundings, and oil drilling activity.

Surface water hardness was found to be higher during the dry season (Tables 3 and 4), which could be explained by an increase in salt concentration caused by the water level being lowered and the wind's impact, which promotes the resuspension of calcium and magnesium ions in the sediment. The components of artificial fertilizer derived from alkaline earth metals, such as NPK, NH₃, NO₃, etc., as well as pesticides and herbicides from catchment area runoff, may be responsible for the hardness during the rainy season.

One of the main contaminants that are routinely released into the coastal waters during oil petroleum exploration activities are hydrocarbons. In comparison to the control stations, the values of the organics for Nembe Creek show higher concentrations of PAH, TPH, and THC during the dry season than during the rainy season. This may be due to the existence of bacteria that reduce hydrocarbons and the dilution of surface water during the rainy season, which causes the organics to become apparent during the dry season. Nembe Creek's elevated hydrocarbon concentration is a result of human activity, mainly illegal oil bunkering and marine vessel maintenance. High hydrocarbon concentration degrades oxygen by reducing gaseous diffusion through the oil's surface film. which has significant effects on the local flora and wildlife (Osuji et al., 2004). According to a previous study, the absence of PAH during the rainy season is due to a relationship between the number of rings and the solubility of the PAHs in a medium [18]. Additionally, Karlsson and Viklander's prior work from [19], which stated that PAHs with more rings are less soluble and those with fewer rings are more soluble, supports this discovery. As a result, these PAHs may be below detection limits during the rainy season. The findings of this study showed that the features of the various points/locations from which the samples were obtained greatly influenced the PAH, TPH, and THC contamination in dry and wet seasons. Regardless of the season, the dredging, bush burning, illegal oil bunkering, and boating at the locations helped to clarify why certain areas had high PAHs levels while others have low levels (dry or rainy season).

The existence of elevated concentrations of anions during the dry season, such as chloride, sulfate, calcium, magnesium, potassium, and sodium, points to increasing levels of organic pollution during such a season, which can be linked to increased sewage contamination and agricultural waste [20] Additionally, in this study, nutrients like nitrate were statistically different and more abundant during the rainy season. Around Nembe Creek. Small farms are maintained by several homes, and manure or nitrogenous fertilizer are administered to these domestic farms. It is thought that during the rainy season, when agricultural activity is at its peak, the majority of the applied fertilizers utilized by these farmers are washed away to pollute shallow and deep rivers. The decomposition of dead plants, animals, and other species adds to the organic matter in the soil, which is then carried into water bodies, especially during rainy seasons. These could also account for the higher nitrate concentrations in the rainy season in this study as compared to the dry season. However, the sulfate source in this study might come from soil, weathering of gypsumcontaining rocks, iron sulfide, or other sulfide compounds.

Due to the input of surface run off from hill torrents and agricultural wastes, the concentration of iron was found to be extremely high in water samples obtained from several sampling stations during the wet season [15]. Zinc (Zn) levels found in sampling locations and control sites during the dry season were below the permitted limit of 3 mg/L for domestic water

set by the World Health Organization [10] and the Nigeria Standard for Drinking Water Quality [9]. The Nigeria Standard for Drinking Water Quality from and the World Health [9] Organization both consider lead (Pb) concentrations obtained in sampling areas and control areas during the dry season to be above the permissible limit of 0.01 mg/L. (2011). This suggests that lead concentrations in the research were influenced by humans. Lead area concentrations in aquatic systems can increase as a result of human activities like unlawful bunkering and surface runoff that flushes fertilizer into bodies of water [21,22]. This was affirmed by Owamah [23], who reported an increased concentration of lead in a petroleumimpacted River as a result of anthropogenic activities. Owamah [23] asserts that surface water with such a range of Pb concentrations is not safe for domestic use due to the potential health risks. The copper (Cu) concentrations found in this study during the wet and dry seasons are within the safe drinking water standard of 2 mg/L set by the World Health Organization [10]. (Table 5). Cu's low value suggests that manmade environmental impact is minimal. Nickel concentrations increased during the rainy season, which may have been brought on by surface runoff from industrial waste and trash from dredging low-grade ores. It was discovered that because nickel is more mobile in soil, it has the tendency of contaminating the aquifer [22,24] In order to identify malicious increases brought on by anthropogenic input and prevent potential public health effects on those who consume water and marine life in the research region, the parameters that were over the standard limit need to be continuously monitored.

5. CONCLUSION

According to the findings of the present study, Nembe Creek is marginally more polluted during the drv season than during the wet season. Most parameters on the Person's Correlation matrix were found to be somewhat connected with one another according to the investigation of correlations between water quality metrics. However, it has been noted that some indicators, including metals and other physicochemical parameters, do not significantly correlate with one another, indicating that the sources of contamination may come from various places. It is possible that the source may not predominantly originate from oil exploration activities but may involve other natural, geological and anthropogenic activities. From correlation analysis, the negative relationship with other parameters reveals a slightly high organic pollution resulting from anthropogenic activities in the creek. The minimum PAH, THC, and TPH concentrations in the creek are also consistent with the effects of oil exploration and illegal oil bunkering activities. When evaluating additional changes brought on by nature or man in these rivers, the data collected in this river could be utilized as a baseline and reference point.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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