

Assessment and Spatio-seasonal Variation of Physiochemical Parameters and Heavy Metals in the Warri River, Delta State, Nigeria

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Abstract This study assessed some physiochemical and heavy metal parameters of Warri River in relation to the Nigeria Standard for Drinking Water Quality/Nigeria Industrial Standard (NSDWQ/NIS 554:2015) and World Health Organization (WHO) guidelines for surface water. The study was done for two seasons (dry and wet season) and at five sampling points (SP), to ascertain how seasonal and location variation affect thirteen (13) physiochemical parameters and seven (7) heavy metals. The sampling and analysis were conducted in accordance with the American Public Health Association (APHA). There was a significant spatial variation ($p < 0.05$) in average values of pH, EC, TDS, Turb, TSS, SO_4^{2-} , NO_3^- , Cl^- , TP, and TN, while there was a significant seasonal variation ($p < 0.05$) in the average values of pH, WT, O&G, COD, and TP in Warri River. The total average value of EC, TDS, SO_4^{2-} , Cl^- and Turb exceeded NSDWQ/NIS and WHO limits for both seasons, especially from SP 3 to SP 5. The concentrations of Pb, Fe, and Ni exceeded the NSDWQ/NIS and WHO limits for both seasons, while Cd was not detected. The results showed that the mean concentrations of metals ranked (high to low) $Fe > Zn > Ni > Cu > Pb > Cr$ during both seasons. There was significant spatial variation ($p < 0.05$) but no seasonal significant variation for all of the analysed heavy metals in Warri River. As a result, governments and other responsible authorities must monitor industrial effluent discharged into Warri River.

Keywords Heavy metals, Physiochemical parameters, Warri River, Sampling points

1. Introduction

Water is the most abundant substance on the earth's surface, and all forms of life require it to survive. Hence, this life-saving resource must be treated as a natural treasure [41,81]. Water pollution and deterioration, on the other hand, are on the rise as a result of urbanisation and industrialisation, especially in developing countries that rely on surface and groundwater for direct drinking and irrigation [43]. The rate at which pollutants are discharged into water bodies exceeds the rate at which water bodies self-purify, which is a major source of concern [63]. In this regard, water quality is assessed in terms of both the immediate condition and the long-term duration.

Surface water quality is influenced by a number of natural and anthropogenic processes. Natural processes include rock weathering, evapotranspiration, wind-driven depositions, soil leaching, hydrological run-off, and

biological processes. Anthropogenic processes include agricultural practices, industrialisation, urbanisation, household sewage, and other man-made activities. This often leads to an imbalance in the ecosystem and generates pollutants that can alter the physicochemical and biological parameters that influence the growth of living organisms in surface water. However, these parameters are seasonal and climatic in nature [75,51,18,59,77].

Warri town is located on the banks of the Warri River in southern Nigeria and is an oil hub. The city boasts a modern seaport that acts as a cargo transit point between the Niger River and the Atlantic Ocean, but it is currently inactive [6]. Along the Warri River, there are oil wells, flow stations, and tank farms, all of which are involved in activities like oil exploration, field development, production operations, transportation, storage, and distribution. Heavy metal pollution may also be linked to crude oil exploitation (drilling), transportation, and other industrial processes [58]. These activities have the potential to worsen the river's water quality over time; hence, it's critical to keep an eye on the pollution levels. Pollution owing to an increase in oil spillages through vandalism, pipeline maintenance, aged facilities, accidents, and illegal bunkering have all also

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become major concerns [60,35]. The degree of pollution is generally assessed by studying the physical, chemical and biological characteristics of the bodies of water, which are prone to change owing to different kinds of pollution, seasonal fluctuation, water extraction, etc. [76,56,73]. Thus, the need to study the physicochemical characteristics of Warri River to determine the quality and its effects on aquatic environment have direct consequences on man and the ecosystem in general.

1.1. Study Area



Figure 1. Tank farm along Warri River

Warri River is one of four major coastal rivers in terms of commercial importance in the Niger Delta, Nigeria. It originates from around Utagba Uno and flows through areas of freshwater swamps, mangroves, and ridges of coastal sand [2,4]. It extends between latitudes $5^{\circ} 21' - 6^{\circ} 00' N$ and longitudes $5^{\circ} 24' - 6^{\circ} 21' E$, covering an area of about 255 sq km with a range of about 150 km. It drains a number of tributaries that join the rivers Forcados and Escravos in

the lower Niger Delta via Jones Creek, which then flows into the Atlantic Ocean. With a mean annual rainfall of roughly 3000mm, the area enjoys tropical humidity of the semi-hot equatorial type [25,47,50]. Other activities along the interconnected network of fresh water aquifers include auto mechanic workshops; fishing; timber logging; river ports; crude oil and refined fraction loading and offloading (Figure 1); rubber processing; and sand mining operations. Local traders' markets and jetties are also found along Warri's main river.

1.2. Specific Objectives

1. Determined the concentration of physicochemical and heavy metals (HM) parameters for dry and wet season
2. Compared the spatial and seasonal variation of the sampling points
3. Compared all of the Warri River water's measured parameters, with the World Health Organization [83] and the Nigeria Standard for Drinking Water Quality/Nigerian Industrial Standards 554:2015 [45] surface water guideline to determine the degree of contamination or effect of effluent discharged
4. The average mean (\bar{X}), standard deviation (SD), and Pearson's correlation (r) value were calculated using SPSS version 25 and MS Excel 2016 to indicate the degree of physicochemical and HM relationship
5. Analysis of variance (ANOVA) using SPSS, version 25 was employed to perform a test of significance at $p < 0.05$, in order to determine the seasonal and spatial variation in the physicochemical parameters and heavy metals concentration

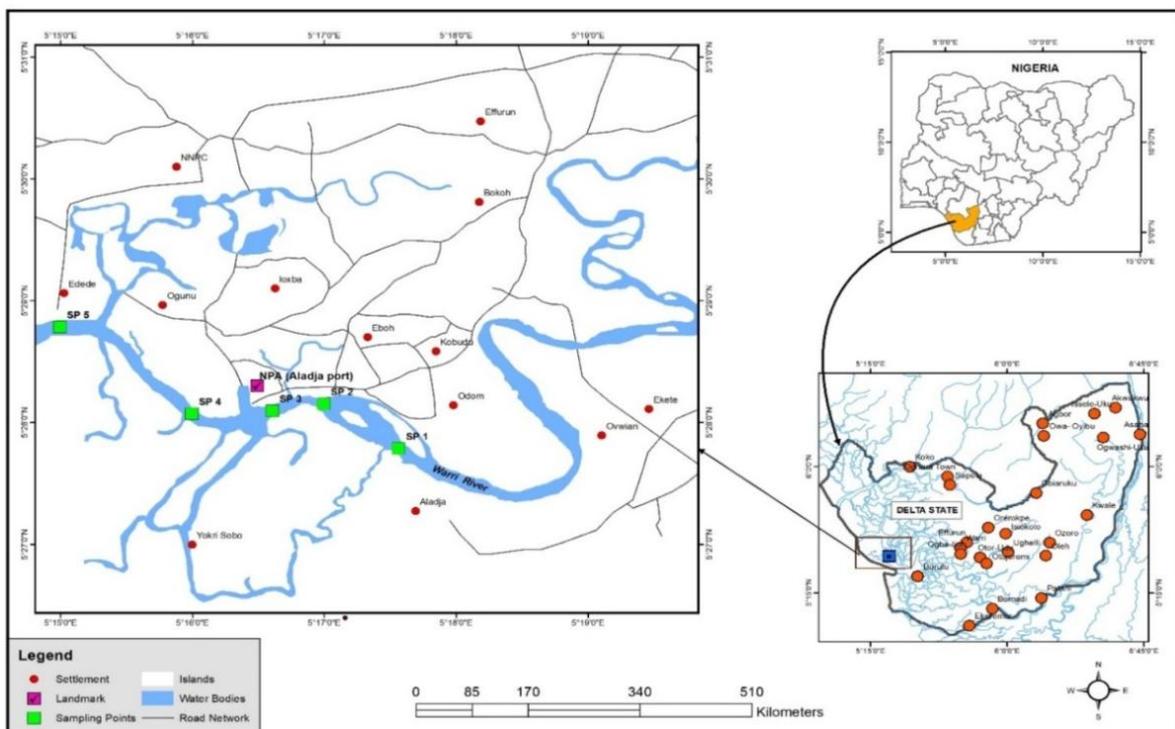


Figure 2. Map of study area indicating sampling points along Warri River (developed from ArcGIS Pro)

2. Methodology

2.1. Water Sample Collection

Water samples from five sampling points (SPs) were collected in triplicate into sterile bottles. The sampling strategy was designed to cover 18.67 km between SP 1 and SP 5 (Table 1 and Figure 2). Surface water sampling was carried out on a seasonal basis, namely during dry season (08 December, 2021) and wet season (17 June, 2021) between 0900 hrs and 1200 hrs. A total of 30 water samples were collected from the sampling points (15 samples from each season).

In-situ parameters were determined and, after which, collected samples were placed in coolers with ice bags to keep samples at 2°C prior to analysis. Samples for heavy metals were acidified with 1mL of Nitric acid (1:1 concentrated HNO₃ to H₂O). All sampling, preservation, and transportation of the water samples were based on the standard principles and procedures for physicochemical characteristics of surface water samples [10].

2.2. Laboratory Analysis of Water Samples

In-situ physicochemical parameters: pH, water temperature (WT), dissolved oxygen (DO), electric conductivity (EC) and total dissolved solids (TDS) were measured. pH and WT were determined using a pHep4 Pocket pH & mercury glass thermometer, respectively. However, the pH was later validated in the laboratory using model PHS-25, Searchtech Instruments, England. EC and TDS were measured using TDS, pH, EC, and Temperature 4 in 1 Kit, but the EC was confirmed using DDS-11A, Serchtech Instruments, England. DO was measured using YSI 550A DO meter.

The following parameters were determined: turbidity (turb), total soluble solid (TSS), oil and grease (O&G), biological oxygen demand (BOD), chemical oxygen demand (COD), sulphate (SO₄²⁻), nitrate (NO₃⁻), chloride (Cl⁻), total phosphorous (TP), total nitrogen (TN). And heavy metals (HM) such as; copper (Cu), lead (Pb), zinc (Zn), iron (Fe), nickel (Ni), cadmium (Cd) and chromium (Cr).

These analyses were carried out at Jacio Environmental Limited, Effurun, Delta State, Nigeria. All water sample

analyses were conducted according to the approved standard analytical methods by American Public Health Association [13] (Table 2). Each analysis was carried out three times, and the average value was obtained. Laboratory quality assurance and quality control approaches, including the use of standard operating procedures, were used to ensure the analytical data integrity, calibration with standards, analysis of reagent blanks, recovery of known additions, and analysis of replicates.

3. Result and Discussion

3.1. Physicochemical Parameters

A pH range of 6.5-9.0 is ideal for most aquatic species. Aquatic organisms are stressed and can reduce reproduction when the pH of water is too high or low. The pH of chemical parameter and heavy metal in water can affect their solubility and toxicity [27,16]. The pH values of water samples from Warri River varied from 5.15 to 7.10 in dry season and between 5.49 and 7.23 in wet season. SP 5 showed higher mean value (7.10 ± 0.10) during wet season while the lowest average pH value (5.23 ± 0.08) was found at SP 3 in dry season (Table 3 and 4). The mean pH across all SP during the dry season (6.01 ± 0.54) and wet season (6.53 ± 0.46) indicated that Warri River is slightly acidic in both seasons (Table 5). This could be as a result of acid rain caused by indiscriminate gas flaring from the Warri Refinery and flow stations in the area, as recorded by Efe and Mogborukor [19]. The dry season mean pH was found to be lower than the WHO and NSDWQ/NIS limit range, while the wet season mean pH was within the limit range. The low pH may be due to dissolved SO_x, NO_x, CO_x, and H₂S gases overtime through wet deposition (precipitation) or dry deposition (as gases or particles) as a result of acid rain and gravity, respectively. There was a significant spatial and seasonal variation ($p < 0.05$) in average pH values in Warri River (Table 5). Okoye and Iteyere [48], Aghoghovwia [5], and Kaizer and Osakwe [39] results agree with the slightly acidic pH values of the Warri River.

Table 1. Sampling point description and coordinates

Sampling Point	GPS Coordinates	Description
SP 1	5°30'48.452"N 5°43'49.822"E	Nigerian Ports Authority (NPA), along old Warri port Jetty
SP 2	5°31'4.224"N 5°42'43.419"E	Warri River flowing along Warri Refining and Petrochemical Company (WRPC)
SP 3	5°32'1.950"N 5°41'9.569"E	Warri River flowing along Matrix Tank Farm, Iffie Community
SP 4	5°31'59.912"N 5°38'59.649"E	Warri River flowing along Ajuju-Batan Community
SP 5	5°31'32.332"N 5°35'46.568"E	Warri River flowing along Batan Flow Station, Batan

Table 2. Analytical test methods and equipment for physicochemical parameters [10]

Parameter	Test method	Method	Equipment (model)
pH	APHA 4500-H ⁺	Electrometric	model PHS-25, Searchtech Instruments
EC	APHA 2510B	Electrometric	DDS-11A, Searchtech Instruments
TDS	APHA 2540C	Gravimetric	Extech EC500
WT	APHA 2550 B	Electrometric	Glass Thermometer
Turb	APHA 2130B	Nephelometric	HACH 2100P Turbidimeter
DO	APHA 4500-O-G	Membrane Electrode	Smart sensor AR8210 DO meter
TSS	APHA 2540D	Gravimetric	S. Mettler FA2104 Electronic Balance
O&G	ASTM D3921	Infrared Spectroscopy	InfraCal 2 Analyzer
BOD	APHA 5210B	5-day BOD Test	Membrane Electrode
COD	APHA 5220C	Closed reflux Colorimetric	Hach 45600 COD Reactor
SO ₄ ²⁻	APHA 4500 SO ₄ ²⁻ E	Turbidimetric Method	752N Model UV VIS Spectrophotometer
NO ₃ ⁻	APHA 4500E	Screening Method	752N Model UV VIS Spectrophotometer
Cl ⁻	APHA 4500-Cl-B	Argentometric Titrimetric Method	-
TP	APHA 4500-P-E	Ascorbic Acid Colorimetric	752N Model UV VIS Spectrophotometer
TN	APHA 4500-N-C	Kjeldahl Method	752N Model UV VIS Spectrophotometer
HM	APHA 3111B	Flame-AAS	Varian SpectraAA-600, Flame Atomic Absorption Spectroscopy (AAS)

EC is a measure of water's capacity to conduct electrical current and is determined by the existence of free ions in the water as well as the number of salts dissolved in it [27]. The EC values, measured in microsiemens per centimetre ($\mu\text{s}/\text{cm}$), ranged from 290.00 to 7357.00 $\mu\text{s}/\text{cm}$ in dry season and between 278.00 and 6914.00 $\mu\text{s}/\text{cm}$ in wet season. SP 5 showed the highest mean value ($7100.00 \pm 235.00 \mu\text{s}/\text{cm}$) during dry season, while the lowest average EC value ($284.00 \pm 5.35 \mu\text{s}/\text{cm}$) was found at SP 3 in wet season (Table 3 and 4). The overall mean EC value during dry season was $2182.80 \pm 2508 \mu\text{s}/\text{cm}$ and wet season was $2139.80 \pm 2425.88 \mu\text{s}/\text{cm}$. There is a significant variation in mean EC value among the sampling points ($p < 0.05$), while there was no seasonal significant difference ($p > 0.05$) in mean EC value in Warri River (Table 5). The dry and wet season mean EC value across all SP was found to be higher than the WHO and NSDWQ/NIS limit (Table 5), especially from SP 3 to SP 5 (Table 3 & 4). This indicates high dissolved salts and inorganic materials such as alkalis, chlorides, sulfides and carbonate compounds in the river. This could be as a result of produced water discharge from flow stations in to the river [36] or the intrusion of highly saline water from the Focardos River into the fresh water. Also, the sudden rise in EC from SP 3 to 5 indicates the source of dissolved ions is in the vicinity. This high EC values was also recorded by Okoye and Iteyere [48] and Ezekiel *et al.* [24].

TDS describes the inorganic salts, organic matter, and other dissolved materials present in water and affect the pH of the body of water, which in turn may influence the overall health of many aquatic species [79,11]. The TDS from the water samples, measured in milligram per litre (mg L^{-1}), varied from 157.00 to 3956.00 mg L^{-1} in dry season and between 156.00 and 3872.00 mg L^{-1} in wet season. SP 5

recorded the highest mean values ($3905.00 \pm 42.92 \text{ mg L}^{-1}$) during dry season, while the lowest average TDS value ($159.00 \pm 2.94 \text{ mg L}^{-1}$) was found at SP 1 in wet season (Table 3 and 4). During the dry and wet seasons, the overall mean TDS concentration was $1200.20 \pm 1379.70 \text{ mg L}^{-1}$ and $1198.20 \pm 1358.55 \text{ mg L}^{-1}$, respectively. These values exceeded the WHO and NSDWQ/NIS limits (Table 5). This has reduced the clarity of the water, which has contributed to a decrease in photosynthesis and led to an increase in water temperature. The increase in temperature, in turn, leads to a high dissolution rate of dissolved minerals. High TDS was expected because of the high EC recorded, and also at a significance level of 0.01 the EC and TDS of different source of water were found to be correlated in all types of water [17]. On the contrary, the TDS results reported by Umedum *et al.* [73] and Aghoghovwia [5] were low. There is a significant variation in mean TDS value among the sampling points ($p < 0.05$), while there was no significant seasonal difference in mean EC value in the Warri River (Table 5).

WT is a governing factor in aquatic habitat dynamics because it interferes with organism metabolism, influences reproduction, speeds up chemical processes, and accelerates organic matter breakdown. It can raise metabolic oxygen demand, affecting numerous species when combine with lower oxygen solubility. The rate of microbial activity is likewise increased when temperature rise [21,49,70]. The WT, measured in degree Celsius ($^{\circ}\text{C}$), observed varied from 25.5 to 30.4 $^{\circ}\text{C}$ in dry season and between 25.1 and 28.1 $^{\circ}\text{C}$ in wet season. SP 1 showed the highest mean values ($28.90 \pm 0.75^{\circ}\text{C}$) during the dry season, while the lowest average WT value ($26.40 \pm 1.11^{\circ}\text{C}$) was found at SP 4 in wet season (Table 3 and 4). As expected, WT were highest during dry seasons and lowest during wet seasons. The average total of WT in dry season was $28.22 \pm 1.42^{\circ}\text{C}$, while during wet

season it was $26.98 \pm 0.77^\circ\text{C}$. There were no significant differences ($p > 0.05$) in WT among the sampling points. Nevertheless, the seasonal trends in the distribution of WT showed significant changes ($p < 0.05$) (Table 5).

Table 3. Physicochemical parameters concentration of Warri River during dry season

Parameters	SP 1	SP 2	SP 3	SP 4	SP 5
pH					
$\bar{X} \pm \text{SD}$	6.06 ± 0.11	6.13 ± 0.39	5.23 ± 0.08	5.87 ± 0.10	6.75 ± 0.32
Range	5.90 – 6.15	5.63 – 6.59	5.15 – 5.33	5.80 – 6.01	6.33 – 7.10
EC ($\mu\text{s}/\text{cm}$)					
$\bar{X} \pm \text{SD}$	305.00 ± 14.72	649.00 ± 21.97	1106.00 ± 71.93	1754.00 ± 106.98	7100.00 ± 235.00
Range	290.00 – 325.00	627.00 – 679.00	1045.00 – 1207.00	1613.00 – 1872.00	6789.00 – 7357.00
TDS (mg/L)					
$\bar{X} \pm \text{SD}$	165.00 ± 8.64	358.00 ± 5.35	608.00 ± 92.92	965.00 ± 66.59	3905.00 ± 42.92
Range	157.00 – 177.00	352.00 – 365.00	512.49 – 733.91	896.00 – 1055.00	3851.00 – 3956.00
WT ($^\circ\text{C}$)					
$\bar{X} \pm \text{SD}$	28.90 ± 0.75	28.70 ± 1.00	27.70 ± 1.58	27.60 ± 2.06	28.20 ± 0.64
Range	28.10 – 29.90	27.80 – 30.10	26.00 – 29.80	25.50 – 30.40	27.70 – 29.10
Turb (NTU)					
$\bar{X} \pm \text{SD}$	6.10 ± 0.65	7.80 ± 0.99	5.60 ± 0.67	8.40 ± 0.71	9.40 ± 0.92
Range	5.30 – 6.90	6.70 – 9.10	4.70 – 6.30	7.90 – 9.40	8.70 – 10.70
DO (mg/L)					
$\bar{X} \pm \text{SD}$	7.00 ± 0.08	6.80 ± 1.88	6.90 ± 0.50	7.10 ± 0.84	6.40 ± 0.16
Range	6.90 – 7.10	4.20 – 8.60	6.20 – 7.30	5.98 – 8.00	6.20 – 6.60
TSS (mg/L)					
$\bar{X} \pm \text{SD}$	2.21 ± 0.04	2.71 ± 0.25	1.96 ± 0.08	2.96 ± 0.10	3.93 ± 0.06
Range	2.15 – 2.25	2.41 – 3.03	1.85 – 2.02	2.87 – 3.10	3.86 – 4.00
O&G (mg/L)					
$\bar{X} \pm \text{SD}$	2.34 ± 0.02	2.92 ± 0.05	1.51 ± 0.30	2.99 ± 0.13	2.67 ± 0.31
Range	2.31 – 2.36	2.86 – 2.98	1.21 – 1.91	2.81 – 3.11	2.23 – 2.93
BOD (mg/L)					
$\bar{X} \pm \text{SD}$	2.40 ± 0.22	1.60 ± 0.33	2.13 ± 1.12	2.10 ± 0.96	1.87 ± 0.13
Range	2.10 – 2.60	1.14 – 1.90	1.28 – 3.72	0.74 – 2.80	1.76 – 2.05
COD (mg/L)					
$\bar{X} \pm \text{SD}$	12.93 ± 4.81	8.20 ± 0.61	11.54 ± 0.45	14.10 ± 0.37	13.13 ± 0.53
Range	6.20 – 17.10	7.36 – 8.80	11.00 – 12.11	13.70 – 14.60	12.40 – 13.60
SO_4^{2-} (mg/L)					
$\bar{X} \pm \text{SD}$	16.37 ± 0.85	92.95 ± 5.43	102.46 ± 18.63	273.80 ± 11.81	584.50 ± 62.30
Range	15.34 – 17.42	85.42 – 98.00	77.38 – 122.00	261.00 – 289.50	512.40 – 664.40
NO_3^- (mg/L)					
$\bar{X} \pm \text{SD}$	1.13 ± 0.05	1.16 ± 0.04	1.61 ± 0.10	1.42 ± 0.14	2.08 ± 0.05
Range	1.07 – 1.19	1.11 – 1.21	1.47 – 1.72	1.24 – 1.53	2.01 – 2.124
Cl^- (mg/L)					
$\bar{X} \pm \text{SD}$	74.98 ± 2.24	149.89 ± 7.39	257.39 ± 47.03	571.82 ± 20.40	1584.50 ± 46.05
Range	72.93 – 78.10	141.49 – 159.48	193.04 – 304.13	543.00 – 587.35	1523.00 – 1633.80
TP (mg/L)					
$\bar{X} \pm \text{SD}$	0.89 ± 0.33	0.91 ± 0.20	1.43 ± 0.07	1.01 ± 0.26	1.63 ± 0.08
Range	0.56 – 1.35	0.70 – 1.17	1.33 – 1.49	0.65 – 1.21	1.52 – 1.70
TN (mg/L)					
$\bar{X} \pm \text{SD}$	1.90 ± 0.13	1.92 ± 0.03	2.12 ± 0.09	2.05 ± 0.15	3.90 ± 0.04
Range	1.80 – 2.08	1.89 – 1.95	2.01 – 2.22	1.84 – 2.20	3.86 – 3.96

Table 4. Physicochemical parameters concentration of Warri River during wet season

Parameters	SP 1	SP 2	SP 3	SP 4	SP 5
pH					
$\bar{X} \pm SD$	6.42 \pm 0.14	6.67 \pm 0.09	6.54 \pm 0.41	5.90 \pm 0.33	7.10 \pm 0.10
Range	6.29 – 6.61	6.56 – 6.77	6.00 – 6.99	5.49 – 6.30	7.00 – 7.23
EC ($\mu\text{s}/\text{cm}$)					
$\bar{X} \pm SD$	284.00 \pm 5.35	597.00 \pm 2.160	1378.00 \pm 10.23	1540.00 \pm 10.71	6900.00 \pm 17.05
Range	278.00 – 291.00	595.00 – 600.00	1366.00 – 1391.00	1526.00 – 1552.00	6876.00 – 6914.00
TDS (mg/L)					
$\bar{X} \pm SD$	159.00 \pm 2.94	334.00 \pm 7.87	772.00 \pm 2.45	862.00 \pm 15.12	3864.00 \pm 9.93
Range	156.00 – 163.00	323.00 – 341.00	769.00 – 775.00	841.00 – 876.00	3850.00 – 3872.00
WT ($^{\circ}\text{C}$)					
$\bar{X} \pm SD$	27.60 \pm 0.46	27.40 \pm 0.57	26.90 \pm 0.36	26.40 \pm 1.11	26.60 \pm 0.16
Range	27.00 – 28.10	26.60 – 27.90	26.60 – 27.40	25.10 – 27.80	26.40 – 26.80
Turb (NTU)					
$\bar{X} \pm SD$	4.90 \pm 0.16	8.40 \pm 0.25	7.90 \pm 0.09	9.10 \pm 0.02	11.80 \pm 0.78
Range	4.70 – 5.10	8.05 – 8.60	7.78 – 7.97	9.07 – 9.13	10.80 – 12.70
DO (mg/L)					
$\bar{X} \pm SD$	7.40 \pm 0.29	7.10 \pm 0.10	7.20 \pm 0.04	6.70 \pm 0.41	6.30 \pm 0.80
Range	7.10 – 7.80	6.96 – 7.20	7.15 – 7.25	6.20 – 7.20	5.25 – 7.20
TSS (mg/L)					
$\bar{X} \pm SD$	1.43 \pm 0.09	2.98 \pm 0.10	2.31 \pm 0.04	3.56 \pm 0.15	4.41 \pm 0.19
Range	1.30 – 1.50	2.85 – 3.10	2.27 – 2.36	3.35 – 3.71	4.18 – 4.64
O&G (mg/L)					
$\bar{X} \pm SD$	1.83 \pm 0.20	ND	ND	1.62 \pm 0.18	1.92 \pm 0.12
Range	1.56 – 2.05	ND	ND	1.47 – 1.88	1.76 – 2.01
BOD (mg/L)					
$\bar{X} \pm SD$	2.13 \pm 0.13	2.20 \pm 0.02	1.90 \pm 0.09	1.50 \pm 0.12	2.40 \pm 0.08
Range	2.00 – 2.30	2.18 – 2.22	1.78 – 2.01	1.40 – 1.67	2.30 – 2.50
COD (mg/L)					
$\bar{X} \pm SD$	17.00 \pm 0.57	15.86 \pm 0.37	15.93 \pm 0.58	13.47 \pm 1.31	17.17 \pm 0.78
Range	16.20 – 17.50	15.36 – 16.22	15.24 – 16.65	12.30 – 15.30	16.20 – 18.10
SO_4^{2-} (mg/L)					
$\bar{X} \pm SD$	12.64 \pm 0.23	84.37 \pm 1.12	96.28 \pm 2.17	234.89 \pm 7.24	558.70 \pm 5.55
Range	12.37 – 12.92	82.79 – 85.22	93.28 – 98.34	225.92 – 243.65	553.50 – 566.40
NO_3^- (mg/L)					
$\bar{X} \pm SD$	0.84 \pm 0.04	0.91 \pm 0.06	2.40 \pm 0.17	1.16 \pm 0.07	1.89 \pm 0.10
Range	0.79 – 0.88	0.86 – 0.99	2.16 – 2.55	1.06 – 1.22	1.75 – 1.97
Cl^- (mg/L)					
$\bar{X} \pm SD$	66.61 \pm 1.29	105.90 \pm 2.82	284.95 \pm 1.25	498.00 \pm 11.57	1205.36 \pm 21.95
Range	64.87 – 67.96	102.40 – 109.30	283.44 – 286.51	482.90 – 511.00	1185.20 – 1235.88
TP (mg/L)					
$\bar{X} \pm SD$	0.68 \pm 0.03	0.72 \pm 0.06	0.99 \pm 0.07	0.90 \pm 0.10	1.28 \pm 0.05
Range	0.63 – 0.71	0.63 – 0.78	0.89 – 1.05	0.79 – 1.03	1.23 – 1.34
TN (mg/L)					
$\bar{X} \pm SD$	1.61 \pm 0.09	1.53 \pm 0.17	3.49 \pm 0.02	2.23 \pm 0.18	3.21 \pm 0.04
Range	1.51 – 1.72	1.29 – 1.67	3.48 – 3.51	1.10 – 2.43	3.16 – 3.26

ND: Not Detected

Turb is a measurement of water cloudiness which is a result of TSS, dissolved organic matter, microbial growth etc. Turb is one of the most significant characteristics in water

analysis because it decreases light penetration and hence hinders photosynthesis of submerged plants and algae. Fish production may suffer as a result [67,28]. The values of

Turb, measured in Nephelometric Turbidity Unit (NTU), in samples ranged from 4.70 to 10.70 NTU in dry season and between 4.70 and 12.70 NTU in wet season. SP 5 recorded the highest mean Turb values (11.80 ± 0.16 NTU) and SP 1 recorded the lowest average (4.90 ± 0.16 NTU), both during wet season. The mean Turb in dry and wet season was 7.46 ± 1.63 NTU and 8.42 ± 2.25 NTU respectively (Table 3 and 4), and these were slightly higher than the WHO and NSDWQ limits (Table 5). This could be as a result of the many domestic, anthropological, and industrial wastes from the town and along the river being all channelled into the Warri River. Okoye et al. [48], and Ovonramwen [55] also recorded similar Turb. An increase in dissolved minerals and frequent movement of boats, barges, and vessels at low tide during the dry season could disturb the sediment, clay, and silt particles of the river at the time of sampling and could also lead to an increase in turbidity. An increase in the growth of microorganisms due to decomposing organic matter could contribute to higher turbidity during the dry season [54]. There is a significant variation in mean Turb value among the SP ($p < 0.05$), while there was no seasonal significant difference in mean Turb value in Warri River (Table 5).

DO is a crucial sign of water pollution and a water quality metric. The low dissolved oxygen level in surface water implies microbial pollution or chemical deterioration [22,28]. The DO content of the examined water samples from Warri River varied from 4.20 to 8.60 mg L⁻¹ in dry season and between 5.25 and 7.80 mg L⁻¹ in wet season. During the wet season, SP 1 (7.40 ± 0.29 mg L⁻¹) had the highest mean value and SP 5 (6.30 ± 0.80 mg L⁻¹) had the lowest mean value (Table 4). The mean DO for the dry season was 6.84 ± 0.98 mg L⁻¹ while the for the wet season was 6.94 ± 0.58 mg L⁻¹. There was no significant spatial and seasonal variation ($p > 0.05$) in the average DO values in Warri River (Table 5). The DO concentration recorded implies the river is less polluted by organic matters. These results were similar to a study recorded in Umedum et al. [73], Tesi et al. [71], Okoye et al. [48], and Aghoghovwia [5].

TSS is defined as the amount of fine particulate matter (< 2 microns in size) that remains in suspension in water [15]. TSS concentration in the water sample varied from 1.85 to 4.00 mg L⁻¹ in dry season and between 1.30 and 4.64 mg L⁻¹ in wet season. The highest mean value was observed in SP 5 (4.41 ± 0.19 mg L⁻¹) and the lowest mean value was recorded at SP 1 (1.43 ± 0.09 mg L⁻¹) during the wet season (Table 4). There is a significant variation in mean TSS value among the sampling points ($p < 0.05$), while there was no significant seasonal difference in mean TSS value in Warri River (Table 5). The average TSS for both dry and wet season was 2.75 ± 0.70 and 2.94 ± 1.03 mg L⁻¹ respectively, which is within the NSDQW limit. This could be due to the river's constant flow into the Atlantic Ocean and the absence of sandmining at sampling points. Umedum et al. [73] also recorded low TSS, while high TSS was recorded by Idomeh et al. [34] and Tesi et al. [71].

O&G includes Fats, lubricant and motor oils, waxes, fuels, total petroleum hydrocarbons, and other related elements

present in water that form thin films on the water because they do not readily mix with water. This film depletes the oxygen level in the surface water by not allowing the atmospheric oxygen to dissolve in the water, thereby wreaking havoc on aquatic life [20]. The O&G concentration varied from 1.21 to 3.11 mg L⁻¹ in dry season and between 1.47 and 2.05 mg L⁻¹ in wet season. SP 4 showed the highest O&G mean concentration (2.99 ± 0.13 mg L⁻¹) and the lowest average O&G concentration (1.51 ± 0.30 mg L⁻¹) was found at SP 3 in dry season (Table 3 and 4). The dry season average O&G concentration was 2.49 ± 0.58 mg L⁻¹ and 1.79 ± 0.21 mg L⁻¹ during the wet season. Similar O&G results were recorded by Arimoro et al. [12], while high O&G was recorded by Okoye and Iteyere [48]. There were no significant differences ($p > 0.05$) in O&G among the sampling points. Nevertheless, the seasonal trends in the distribution of O&G showed significant changes ($p < 0.05$) (Table 5).

BOD is the amount of dissolved oxygen required by bacteria and other microorganisms to decompose and break down organic matters that are aerobically degradable in 1 litre of water. BOD is an indicator of levels of organic pollution and is useful in managing pollution control of streams and assessing their self-purification capacity [24,31,14]. The BOD value varied from 0.74 to 3.72 mg L⁻¹ in dry season and between 1.40 and 2.50 mg L⁻¹ in wet season. The highest mean value was observed in SP 1 (2.40 ± 0.22 mg L⁻¹) during dry season, while the lowest mean value was recorded at SP 4 (1.50 ± 0.12 mg L⁻¹) during the wet season (Table 3 and 4). The average BOD concentration during the dry and wet season was 2.02 ± 0.74 and 2.03 ± 0.32 mg L⁻¹, respectively. This low BOD concentration means the river has a low content of organic matter and has low counts of microbial organisms [71]. There was a significant spatial and seasonal variation ($p < 0.05$) in average BOD values in Warri River (Table 5). Tesi et al. [71], Okoye and Iteyere [48], and Idomeh et al. [34] recorded considerably higher BOD.

COD is the amount of dissolved oxygen required to oxidise chemical, organic, and inorganic materials in water. It's a method for determining how much organic matter has contaminated water [66]. The range of values obtained for COD in the water samples from Warri River varied from 6.20 to 17.10 mg L⁻¹ in dry season and between 12.30 and 18.10 mg L⁻¹ in wet season. SP 5 showed the highest mean concentration (17.17 ± 0.78 mg L⁻¹) during the wet season and the lowest average COD concentration (8.20 ± 0.61 mg L⁻¹) was found at SP 2 in dry season (Table 3 and 4). The mean COD values during the dry season was 11.980 ± 3.01 mg L⁻¹ and wet season was 15.89 ± 1.54 mg L⁻¹ for the Warri River. As expected, the BOD was lower than the COD, but the high COD result indicated that the water samples contained more inorganic matters. There were no significant differences ($p > 0.05$) in COD among the sampling points. Nevertheless, the seasonal trends in the distribution of COD showed significant changes ($p < 0.05$) (Table 5). Similar COD values were recorded by Tesi et al. [71], Okoye and Iteyere [48].

SO₄²⁻ can be present in practically all natural water bodies,

either naturally (leached from sulphate-bearing soils and rocks) or as a result of municipal/industrial emissions [7,53]. The SO_4^{2-} concentration of water samples varied from 15.34 to 664.40 mg L^{-1} in dry season and between 12.37 to 566.40 mg L^{-1} in wet season. The highest mean value was observed in SP 5 ($584.50 \pm 62.30 \text{ mg L}^{-1}$) during dry season and the lowest mean concentration of SO_4^{2-} was recorded at SP 1 ($12.64 \pm 0.23 \text{ mg L}^{-1}$) during the wet season (Table 3 and 4). The total average concentration in dry ($214.02 \pm 205.62 \text{ mg L}^{-1}$) and wet ($197.38 \pm 194.51 \text{ mg L}^{-1}$) seasons fell within the standard limit for WHO but not NSDWQ/NIS (Table 5). However, during both seasons, SP 4 and SP 5 exceeded WHO and NSDWQ/NIS (Table 3, 4 & 5). Firstly, this could be as a result of discharged effluent from sewage treatment plants on boat house and produced water from flow stations. Secondly, the high sulfate value could also be attributed to the intrusion of dissolved solids containing sulfate from highly saline water body. Thirdly, the flared gases may have been washed down from the atmosphere through rainfall (acidic rain) or as a result of gravity. There was a significant variation in mean SO_4^{2-} value among the sampling points ($p < 0.05$), while there was no seasonal significant difference in mean SO_4^{2-} value in Warri River (Table 5). There is no record of excess sulfate in any article on Warri River to corroborate the findings of this study.

NO_3^- is a stronger indicator of the potential of a sewage, manure, or industrial discharge source since they impact aquatic plant and animal development, dissolved oxygen, temperature, and other indicators [82,3]. The NO_3^- concentration from the water samples varied from 1.07 to 2.12 mg L^{-1} in dry season and between 0.79 and 2.55 mg L^{-1} in wet season. The highest mean value was observed in SP 3 ($2.40 \pm 0.17 \text{ mg L}^{-1}$) and the lowest mean value was recorded at SP 1 ($0.84 \pm 0.04 \text{ mg L}^{-1}$) during the wet season. In the dry season, the overall mean concentration of NO_3^- was $1.48 \pm 0.36 \text{ mg L}^{-1}$ while in wet season, it was $1.44 \pm 0.62 \text{ mg L}^{-1}$ (Table 3 and 4), both of which were below the WHO and NSDWQ/NIS standards (Table 5). This could be as a result of the lack of tanneries, farming, and minimal domestic sewage discharge along the river. Hence, the Warri River is not NO_3^- contaminated. There was a significant variation in mean NO_3^- value among the sampling points ($p < 0.05$), while there was no seasonal significant difference in mean NO_3^- value in Warri River (Table 3). Umedum *et al.* [73], Kaizer and Osakwe [39], Okoye and Iteyere [48] all recorded similar low NO_3^- concentrations, whilst Tesi *et al.* [71] and Aghoghovwia [5] recorded high NO_3^- concentrations.

Cl^- in water bodies can come from a variety of sources, including natural sources (soil), municipal or industrial sewage, and chlorine-treated sewage effluents, and it is frequently used as a chemical pollution indicator for sewage contamination [80,42,78]. The Cl^- concentration varied from 72.93 to 1633.80 mg L^{-1} in dry season and between 64.87 and 1235.88 mg L^{-1} in wet season. The highest mean value was observed in SP 5 ($1584.50 \pm 46.05 \text{ mg L}^{-1}$) during the dry season, while the lowest mean value was recorded at SP 1 ($66.61 \pm 1.29 \text{ mg L}^{-1}$) during the wet season

(Table 3 and 4). The overall average Cl^- for dry and wet seasons was $527.72 \pm 555.76 \text{ mg L}^{-1}$ and $432.16 \pm 415.82 \text{ mg L}^{-1}$ respectively, but they both exceeded the WHO and NSDWQ/NIS limits (Table 5). This could be due to indiscriminate dumping of solid and highly chlorinated sewage wastes from barge houses, tank farms, and flow stations along the river, as well as other anthropogenic activities. Produced water contains salts which are primarily chlorides and sulfides of calcium, magnesium, and sodium. Therefore, treated produced water that is discharged into the river may contain high levels of chlorides [44,36]. Also, the high chloride value could also be attributed to the intrusion of dissolved solids containing chloride from a highly saline water body. There is a significant variation in mean Cl^- value among the sampling points ($p < 0.05$), while there was no seasonal significant difference in mean Cl^- value in Warri River (Table 5). SP 1 and SP 2 recorded similar Cl^- concentration by Umedum *et al.* [73] and Tesi *et al.* [71], while very high concentration recorded in SP 3 – SP 5 was not recorded by any article on Warri River.

The sum of orthophosphate, polyphosphate, and organic forms of phosphorus is referred to as total phosphorus (TP). In unpolluted bodies of water, total phosphorus is an essential element for plants and algae growth, but when there is too much of it in the water, it can hasten eutrophication (accelerated plant growth, algal blooms, low dissolved oxygen) [26,1,61]. The concentration of TP varied from 0.56 to 1.70 mg L^{-1} in dry season and between 0.63 and 1.34 mg L^{-1} in wet season. SP 5 showed higher mean values ($1.63 \pm 0.08 \text{ mg L}^{-1}$) during dry season while the lowest average TP value ($0.68 \pm 0.03 \text{ mg L}^{-1}$) was found at SP 1 in wet season (Table 3 and 4). The mean TP values during the dry season was $1.17 \pm 0.37 \text{ mg L}^{-1}$ and $0.92 \pm 0.23 \text{ mg L}^{-1}$ during wet season. Low TP could be further confirmed by the absence of aquatic vegetation on the Warri River, with the exception of a few plants that were flushed into the river from stagnant water following heavy rain during wet seasons. There was a significant spatial and seasonal variation ($p < 0.05$) in average TP values in Warri River (Table 5).

Nitrate (NO_3^-), nitrite (NO_2^-), organic nitrogen, and ammonia are all parts of total nitrogen (TN). Total nitrogen is a key contributor to eutrophication of water bodies, which in high concentration disturbs ecology and results in harmful algal blooms, oxygen depletion, and biodiversity loss, among other issues [85]. The concentration of TN varied from 1.80 to 3.96 mg L^{-1} in dry season and between 1.29 and 3.51 mg L^{-1} in wet season. SP 5 showed the highest mean values ($3.90 \pm 0.04 \text{ mg L}^{-1}$) during dry season, while the lowest average TN value ($1.53 \pm 0.17 \text{ mg L}^{-1}$) was found at SP 2 in wet season (Table 3 and 4). During the dry season, the mean TN was $2.38 \pm 0.77 \text{ mg L}^{-1}$, and $2.41 \pm 0.82 \text{ mg L}^{-1}$ during the wet season. This concentration may have been caused by sewage effluents from small villages, but there was no runoff from land where manure or chemical fertilizer had been applied or stored. There is a significant variation in mean TN value among the sampling points ($p < 0.05$), while there was no seasonal significant difference in mean TN value in Warri River (Table 5).

The correlation matrix for the estimated physicochemical parameters in Warri River during the dry and wet season are shown in tables 6 and 7, respectively. During the dry season, there was a strong and positive correlation between (EC and TDS, $r = 0.998$), (EC and TSS, $r = 0.883$), (EC and SO_4^{2-} , $r = 0.964$), (EC and Cl^- , $r = 0.991$), (EC and TN, $r = 0.977$), (TDS and TSS, $r = 0.881$), (TDS and SO_4^{2-} , $r = 0.959$), (TDS and Cl^- , $r = 0.990$), (TDS and TN, $r = 0.979$), (Turb and TSS, $r = 0.907$), (TSS and SO_4^{2-} , $r = 0.914$), (TSS and Cl^- , $r = 0.903$), (TSS and TN, $r = 0.816$), (SO_4^{2-} and Cl^- , $r = 0.986$), (SO_4^{2-} and TN, $r = 0.892$) and (Cl^- and TN, $r = 0.945$).

During the wet season, there was a strong and positive correlation between (EC and TDS, $r = 1.000$), (EC and Turb, $r = 0.830$), (EC and SO_4^{2-} , $r = 0.971$), (EC and Cl^- , $r = 0.979$), (EC and TP, $r = 0.888$), (TDS and Turb, $r = 0.830$), (TDS and SO_4^{2-} , $r = 0.971$), (TDS and Cl^- , $r = 0.979$), (TDS and TP, $r = 0.889$), (Turb and TSS, $r = 0.963$), (Turb. and SO_4^{2-} , $r = 0.893$), (Turb. and Cl^- , $r = 0.863$), (TSS and SO_4^{2-} , $r = 0.892$), (TSS and Cl^- , $r = 0.846$), (BOD and COD, 0.870), (SO_4^{2-} and Cl^- , $r = 0.992$), (SO_4^{2-} and TP, $r = 0.869$), (NO_3^- and TN, $r = 0.956$), (Cl^- and TP, $r = 0.900$) and (TP and TN, $r = 0.833$).

Table 5. Standard limit and ANOVA relation of physicochemical parameters at different sampling points and different seasons

Parameters	Dry Season			Wet Season			ANOVA		Standard Limits	
	Mean	Range	Std. Dev.	Mean	Range	Std. Dev.	SP	Seasonal	WHO	NSDWQ/NIS
pH	6.01	5.151-7.1	0.54	6.53	5.49-7.23	0.46	SS*	SS*	6.5-8.5	6.5 - 8.5
EC ($\mu\text{s}/\text{cm}$)	2182.80	290.00-7357.00	2508.92	2139.80	278.00-6914.00	2425.88	SS*	NSS	NS	1000.00
TDS (mg/L)	1200.2	157.00-3956.00	1379.70	1198.20	156.00-3872.00	1358.55	SS*	NSS	1000.00	500.00
WT ($^{\circ}\text{C}$)	28.22	25.50-30.40	1.42	26.98	25.10-28.10	0.77	NSS	SS*	NS	Ambient
Turb (NTU)	7.46	4.70-10.70	1.63	8.42	4.70-12.70	2.25	SS*	NS	5	5
DO (mg/L)	6.84	4.20-8.60	0.98	6.94	5.25-7.80	0.58	NSS	NSS	NS	NS
TSS (mg/L)	2.75	1.85-4.00	0.70	2.94	1.30-4.64	1.03	SS*	NSS	30	NS
O&G (mg/L)	2.49	1.21-3.11	0.58	1.79	1.47-2.05	0.21	NSS	SS*	NS	NS
BOD (mg/L)	2.02	0.74-3.72	0.74	2.03	1.40-2.50	0.32	NSS	NSS	NS	NS
COD (mg/L)	11.98	6.20-17.10	3.01	15.89	12.30-18.10	1.54	NSS	SS*	NS	NS
SO_4^{2-} (mg/L)	214.02	15.34-664.40	205.62	197.38	12.37-566.40	194.51	SS*	NSS	250.00	100.00
NO_3^- (mg/L)	1.48	1.07-2.12	0.36	1.44	0.79-2.55	0.62	SS*	NSS	50.00	50.00
Cl^- (mg/L)	527.72	72.93-1633.80	555.76	432.16	64.87-1235.88	415.82	SS*	NSS	250.00	250.00
TP (mg/L)	1.17	0.56-1.70	0.37	0.92	0.63-1.34	0.23	SS*	SS*	NS	NS
TN (mg/L)	2.38	1.80-3.96	0.77	2.41	1.29-3.51	0.82	SS*	NSS	NS	NS

NS: Not Specified NSS: Not statistically significant SS: Statistically significant *(asterisk): $p < 0.05$ Range value: min – max

Table 6. Correlation matrix of the physicochemical parameters during dry season

	pH	EC	TDS	WT	Turb	DO	TSS	O&G	BOD	COD	SO_4^{2-}	NO_3^-	Cl^-	TP	TN
pH	1.000														
EC	0.628	1.000													
TDS	0.636	0.998	1.000												
WT	0.054	-0.082	-0.048	1.000											
Turb	0.540	0.697	0.679	-0.154	1.000										
DO	0.124	-0.171	-0.178	-0.577	-0.317	1.000									
TSS	0.742	0.883	0.881	-0.003	0.907	-0.271	1.000								
O&G	0.514	0.161	0.158	0.152	0.630	-0.076	0.536	1.000							
BOD	0.064	-0.012	-0.034	-0.578	-0.051	0.456	-0.073	0.027	1.000						
COD	0.060	0.244	0.242	-0.316	0.202	0.122	0.186	-0.019	0.372	1.000					
SO_4^{2-}	0.573	0.964	0.959	-0.142	0.787	-0.142	0.914	0.288	-0.021	0.291	1.000				
NO_3^-	0.252	0.784	0.765	-0.339	0.513	-0.157	0.581	-0.094	0.049	0.266	0.763	1.000			
Cl^-	0.616	0.991	0.990	-0.099	0.729	-0.162	0.903	0.216	-0.004	0.290	0.986	0.781	1.000		
TP	0.296	0.762	0.762	-0.080	0.283	-0.239	0.516	-0.293	0.018	-0.136	0.651	0.68	0.721	1.000	
TN	0.639	0.977	0.979	-0.035	0.594	-0.169	0.816	0.064	-0.008	0.202	0.892	0.744	0.945	0.798	1.000

Bold values indicate the correlation is significant at the 0.05 level

Table 7. Correlation matrix of the physicochemical parameters during wet season

	Ph	EC	TDS	WT	Turb	DO	TSS	O&G	BOD	COD	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	TP	TN
pH	1.000														
EC	0.549	1.000													
TDS	0.550	1.000	1.000												
WT	0.287	-0.342	-0.339	1.000											
Turb	0.352	0.830	0.830	-0.399	1.000										
DO	-0.098	-0.598	-0.597	0.620	-0.586	1.000									
TSS	0.281	0.788	0.788	-0.419	0.963	-0.623	1.000								
O&G	0.467	0.352	0.349	-0.300	0.077	-0.126	0.021	1.000							
BOD	0.706	0.441	0.440	0.102	0.141	-0.158	0.069	0.704	1.000						
COD	0.484	0.293	0.292	0.032	-0.090	0.054	-0.210	0.744	0.870	1.000					
SO ₄ ²⁻	0.417	0.971	0.971	-0.408	0.893	0.657	0.892	0.22	0.281	0.103	1.000				
NO ₃ ⁻	0.285	0.472	0.472	-0.290	0.424	-0.123	0.244	0.265	0.042	0.143	0.379	1.000			
Cl ⁻	0.410	0.979	0.979	-0.419	0.863	-0.646	0.846	0.236	0.262	0.124	0.992	0.454	1.000		
TP	0.407	0.888	0.889	-0.269	0.799	-0.506	0.714	0.105	0.196	0.092	0.869	0.714	0.900	1.000	
TN	0.305	0.600	0.601	-0.265	0.534	-0.260	0.370	0.125	-0.002	0.073	0.532	0.956	0.607	0.833	1.000

Bold values indicate the correlation is highly significant at the 0.05 level

3.2. Heavy Metal

Cu is a critical micronutrient for a variety of metabolic activities in both prokaryotic and eukaryotic organisms. Despite the fact that copper is a necessary component of human metabolism, overly high dosages cause significant mucosal irritation and corrosion, as well as widespread capillary damage, hepatic and renal damage, and central nervous system irritation, which leads to melancholy [42,62,65]. The concentration of Cu in the water under study ranged from a minimum of 0.011 mg L⁻¹ (SP 1) to a maximum of 0.075 mg L⁻¹ (SP 5), both during the dry season across the sampling points (Table 8 and 9). The mean concentration of Cu during dry season was 0.035 ± 0.019 mg L⁻¹ with values ranging from 0.011 to 0.075 mg L⁻¹, while during wet season was 0.029 ± 0.016 mg L⁻¹ with values ranging from 0.012 to 0.062 mg L⁻¹. Similar results were recorded by Aghoghovwia et al. [6], Okoye and Iteyere [48], Ama et al. [9] and Kaizer and Osakwe [39]. The Cu concentration did not exceed WHO and NSDWQ/NIS limits (Table 10).

Pb is spread throughout the environment as a direct result of human activities such as paints, gasoline, and other lead-based products. It is also in the air, in the form of particles, and can be dissolved by rain or the earth's gravitational pull. The quantity of Pb dissolved in surface waters is determined by the pH of the water and the concentration of dissolved salts in the water [70,84,46]. Pb is a non-essential, and poisonous metal that has been linked to a number of disorders affecting the brain, central nervous system, brain, and kidneys [38,69]. The concentration of Pb varied from 0.012 to 0.052 mg L⁻¹ in dry season and between 0.017 and 0.042 mg L⁻¹ in wet season. SP 5 showed the highest mean Pb values (0.040 ± 0.011 mg L⁻¹) during dry season while the lowest concentration (0.020 ± 0.002 mg L⁻¹) was found at SP 4 in wet season. Pb was not detected in SP1 & 2 during dry season and SP1, 2 & 3

during wet season (Table 8 and 9). The mean Pb concentration during dry season was 0.032 ± 0.012 mg L⁻¹ and 0.029 ± 0.010 mg L⁻¹ during wet season (Table 10). Similar results were observed by Aghoghovwia et al. [6], Ama et al. [9], and Kaizer and Osakwe [39]. Pb concentration exceeded WHO and NSDWQ/NIS limits (Table 10). This might be caused by flaking paint from ships, boat homes, and old buildings washing down the river [8].

Zn is an essential trace element that plays a key role in the physiological and metabolic process of many organisms, it is a component of proteins as well as greater number of enzymes [64,57]. Bacteria, plants, and animals, including humans, require this trace element to survive. It's also a metal with a low concentration in surface water due to its limited mobility from rock weathering or natural sources [37]. High concentration of Zn leads phytotoxicity, reproduction problem, and brain disorder [74]. The concentration of Zn during dry season ranged from 0.040 to 1.017 mg L⁻¹ and the average concentration across the SP was 0.455 ± 0.295 mg L⁻¹. The concentration of Zn during wet season ranged from 0.036 to 1.641 mg L⁻¹ and the average concentration across the SP was 0.370 ± 0.397 mg L⁻¹. The highest concentration of Zn was recorded at SP 1 (0.747 ± 0.086 mg L⁻¹) (Table 8) during dry season while the lowest average concentration was measured at SP 4 (0.180 ± 0.103 mg L⁻¹) (Table 9) during wet season. Okoye and Iteyere [48] also recorded close results. Zn concentration did not exceed WHO and NSDWQ/NIS limits (Table 10).

Fe is a naturally occurring metal that plays a significant role in the environment since it is linked to a variety of abiotic and biotic processes. Natural deposits, industrial wastes, iron ore refinement, and corrosion of iron-containing metals can all release Fe into the water [68]. Although, Fe is a necessary nutrient for most species, too much of it can harm the liver, pancreas, and heart in humans [16]. The mean concentration of Fe during dry season was 1.326 ± 0.660

mg L⁻¹, with values ranging from 0.645 to 2.960 mg L⁻¹ while during the wet season was 1.061 ± 0.535 mg L⁻¹, with values ranging from 0.390 - 2.050 mg L⁻¹. The highest mean concentration across SP was recorded at SP 5 (2.480 ± 0.347 mg L⁻¹) during the dry season, ranging from 2.150 – 2.960 mg L⁻¹, while the lowest mean concentration across SP was recorded at SP 4 (0.664 ± 0.275 mg L⁻¹) during wet season, ranging from 0.441 – 1.052 mg L⁻¹ (Table 8 and 9). Fe concentration exceeded WHO and NSDWQ/NIS limits (Table 10). Apart from natural deposits of Fe in the river,

iron and Steel industry at Aladja discharged effluents into the river, numerous iron alloy machineries and equipment are on, moving, and buried in this river, abandoned jetty, barges, and unpainted vessels parked by the water side are continually subjected to electrochemical reaction (corrosion), which results in rust flaking off iron metal into the river. Similar results were recorded by Tesi et al. [71] and Aghoghovwia et al. [6], low concentrations by Kaizer and Osakwe [39], Umedum et al. [73], whilst high concentrations were recorded by Okoye and Iteyere [48].

Table 8. Heavy metals concentration of Warri River during dry season

Parameters	SP 1	SP 2	SP 3	SP 4	SP 5
Cu (mg/L)					
$\bar{X} \pm SD$	0.011 ± 0.000	0.026 ± 0.006	0.027 ± 0.007	0.029 ± 0.001	0.066 ± 0.008
Range	0.011 – 0.011	0.021 – 0.035	0.019 – 0.037	0.028 – 0.031	0.055 – 0.075
Pb (mg/L)					
$\bar{X} \pm SD$	ND	ND	0.024 ± 0.009	0.031 ± 0.008	0.040 ± 0.011
Range	ND	ND	0.012 – 0.035	0.021 – 0.041	0.025 – 0.052
Zn (mg/L)					
$\bar{X} \pm SD$	0.747 ± 0.086	0.425 ± 0.166	0.282 ± 0.034	0.088 ± 0.350	0.732 ± 0.204
Range	0.632 – 0.84	0.203 – 0.603	0.254 – 0.330	0.040 – 0.120	0.547 – 1.017
Fe (mg/L)					
$\bar{X} \pm SD$	0.802 ± 0.134	1.049 ± 0.296	1.244 ± 0.171	1.057 ± 0.116	2.480 ± 0.347
Range	0.645 – 0.973	0.813 – 1.466	1.006 – 1.398	0.924 – 1.207	2.150 – 2.960
Ni (mg/L)					
$\bar{X} \pm SD$	0.018 ± 0.000	0.032 ± 0.006	0.019 ± 0.002	0.044 ± 0.008	0.106 ± 0.006
Range	0.018 – 0.018	0.024 – 0.039	0.017 – 0.021	0.037 – 0.055	0.098 – 0.113
Cd (mg/L)					
$\bar{X} \pm SD$	ND	ND	ND	ND	ND
Range	ND	ND	ND	ND	ND
Cr (mg/L)					
$\bar{X} \pm SD$	ND	ND	0.013 ± 0.003	0.037 ± 0.004	0.014 ± 0.001
Range	ND	ND	0.011 – 0.017	0.031 – 0.040	0.013 – 0.016

ND: Not Detected

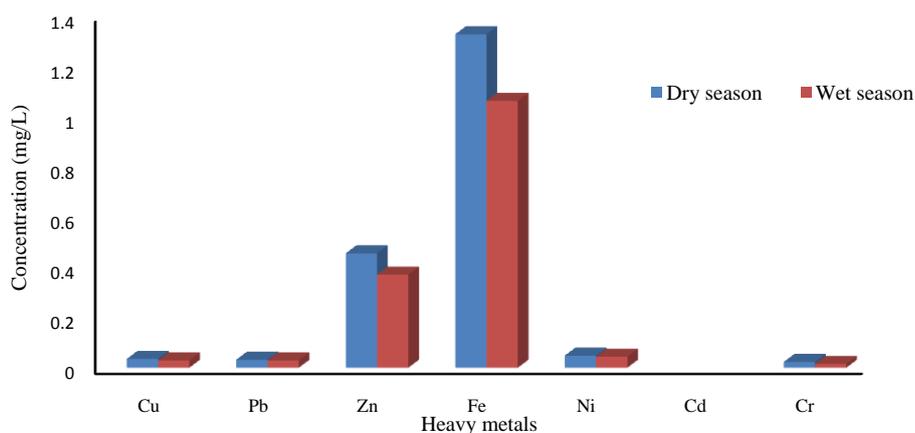


Figure 3. Heavy metals concentration during dry and wet season

Table 9. Heavy metals concentration of Warri River during wet season

Parameters	SP 1	SP 2	SP 3	SP 4	SP 5
Cu (mg/L)					
$\bar{X} \pm SD$	0.012 \pm 0.003	0.022 \pm 0.003	0.018 \pm 0.005	0.031 \pm 0.012	0.047 \pm 0.015
Range	0.012 – 0.012	0.018 – 0.024	0.013 – 0.023	0.022 – 0.047	0.026 – 0.062
Pb (mg/L)					
Mean	ND	ND	ND	0.020 \pm 0.002	0.038 \pm 0.003
Range	ND	ND	ND	0.017 – 0.022	0.036 – 0.042
Zn (mg/L)					
$\bar{X} \pm SD$	0.875 \pm 0.554	0.318 \pm 0.271	0.281 \pm 0.096	0.180 \pm 0.103	0.195 \pm 0.062
Range	0.348 – 1.641	0.122 – 0.701	0.208 – 0.417	0.036 – 0.272	0.112 – 0.263
Fe (mg/L)					
$\bar{X} \pm SD$	0.951 \pm 0.136	0.953 \pm 0.234	0.763 \pm 0.281	0.664 \pm 0.275	1.973 \pm 0.060
Range	0.759 – 1.051	0.623 – 1.130	0.39 – 1.069	0.441 – 1.052	1.904 – 2.050
Ni (mg/L)					
$\bar{X} \pm SD$	0.023 \pm 0.000	0.039 \pm 0.100	0.034 \pm 0.013	0.029 \pm 0.006	0.079 \pm 0.012
Range	0.023 – 0.023	0.029 – 0.049	0.016 – 0.045	0.021 – 0.036	0.063 – 0.093
Cd (mg/L)					
$\bar{X} \pm SD$	ND	ND	ND	ND	ND
Range	ND	ND	ND	ND	ND
Cr (mg/L)					
$\bar{X} \pm SD$	ND	0.011 \pm 0.001	ND	ND	0.020 \pm 0.001
Range	ND	0.010 – 0.012	ND	ND	0.018 – 0.021

ND: Not Detected

Table 10. Standard limit and ANOVA relation of heavy metal at different sampling points and different season

Parameters	Dry Season			Wet Season			ANOVA		Standard Limits	
	Mean	Range	Std. Dev.	Mean	Range	Std. Dev.	SP	Seasonal	WHO	NSDWQ/NIS
Cu (mg/L)	0.035	0.011 -0.075	0.019	0.029	0.012 – 0.062	0.016	SS*	NSS	2.000	1.000
Pb (mg/L)	0.032	0.012 -0.052	0.012	0.029	0.017 – 0.042	0.010	SS*	NSS	0.010	0.010
Zn (mg/L)	0.455	0.040 -1.017	0.295	0.370	0.036 – 1.641	0.397	SS*	NSS	3.000	3.000
Fe (mg/L)	1.326	0.645 -2.960	0.660	1.061	0.390 - 2.050	0.535	SS*	NSS	0.300	0.300
Ni (mg/L)	0.048	0.017- 0.113	0.035	0.044	0.016 - 0.093	0.024	SS*	NSS	NS	0.020
Cr (mg/L)	0.023	0.011 - 0.040	0.012	0.015	0.010 - 0.021	0.005	SS*	NSS	NS	0.050

NS: Not specified NSS: Not statistically significant SS: Statistically significant *(asterisk): $p < 0.05$ Range value: min – max

Ni is an important trace element for aquatic organisms, but higher concentrations can be toxic. It could be derived from both natural and anthropogenic activity. Ni pollution can come from a variety of sources, including industry, the usage of liquid and solid fuels, as well as municipal and industrial waste [29]. At high concentrations, nickel limits the growth of algae [23]. The concentration of Ni from water samples varied from 0.017 to 0.113 mg L⁻¹ in dry season and between 0.016 and 0.093 mg L⁻¹ in wet season. The mean concentration of Ni during the dry season was 0.048 \pm 0.035 mg L⁻¹ and 0.044 \pm 0.024 mg L⁻¹ during wet season. SP 5 showed the highest mean Ni values (0.106 \pm 0.006 mg L⁻¹) while the lowest mean of Ni (0.018 \pm 0.000 mg L⁻¹) was found at SP 1, both in dry season, across all SP (Table 8 and 9). Ni concentration exceeded WHO and NSDWQ/NIS limits (Table 10). This could be as a result of industrial and domestic wastes discharged in to the river.

Cd is the one most commonly found heavy metals and is

uniformly distributed in trace amounts in the earth's crust and is highly toxic and responsible for several cases of food poisoning [32]. Small quantities of Cd cause adverse changes in the arteries of human kidneys [30]. Cd enters water through industrial discharges or the deterioration of galvanized pipes and can be present in groundwater from a wide variety of sources in the environment and from industry [33]. Cd was not detected in any of the sampling points for both seasons.

Cr is a heavy metal that may be found in nature, but only in a mixed condition with oxidation states ranging from +2 to +6. Cr can enter natural streams by weathering of Cr-containing rocks, direct discharge from industrial operations, or soil leaching [72,40]. The valence state of Cr determines its toxicity to plants. Whilst Cr (VI) is very toxic and mobile, Cr (III) is not. Cr toxicity in contaminated water bodies has detrimental consequences for human health (carcinogen), as well as plant dry matter production,

photosynthesis, and mineral nutrition [52]. The average concentration of Cr during dry season was 0.023 ± 0.012 mg L⁻¹ and ranged from 0.011 to 0.040 mg L⁻¹. The highest concentration of Cr during dry season was recorded at SP 4 (0.037 ± 0.004 mg L⁻¹), ranged from 0.031 to 0.040 mg L⁻¹ while the lowest average concentration of Cr was measured at SP 3 (0.013 ± 0.003 mg L⁻¹), ranged from 0.011 – 0.017 mg L⁻¹. The average concentration of Cr during wet season was 0.015 ± 0.005 mg L⁻¹ and ranged from 0.010 to 0.021 mg L⁻¹. The highest concentration of Cr during wet season was recorded at SP 5 (0.020 ± 0.001 mg L⁻¹), ranged from 0.018 to 0.021 mg L⁻¹ while the lowest average concentration of Cr was measured at SP 2 (0.011 ± 0.001 mg L⁻¹), ranged from 0.010 – 0.012 mg L⁻¹ (Table 8 and 9). Cr concentration did not exceed WHO and NSDWQ/NIS limits (Table 10).

Table 11. Correlation matrix of the Heavy metals during wet season

	Cu	Pb	Zn	Fe	Ni	Cr
Cu	1.000					
Pb	0.221	1.000				
Zn	0.477	0.199	1.000			
Fe	0.918	0.191	0.372	1.000		
Ni	0.918	0.471	0.542	0.864	1.000	
Cr	-0.422	-0.010	-0.638	-0.534	-0.019	1.000

Bold values indicate the correlation is highly significant at the 0.05 level

Table 12. Correlation matrix of the Heavy metals during wet season

	Cu	Pb	Zn	Fe	Ni	Cr
Cu	1.000					
Pb	0.401	1.000				
Zn	-0.344	0.277	1.000			
Fe	0.521	0.950	-0.119	1.000		
Ni	0.571	0.847	-0.323	0.917	1.000	
Cr	0.675	0.339	-0.309	0.926	0.882	1.000

Bold values indicate the correlation is highly significant at the 0.05 level

The mean concentration of the metals in the studied river, varied in the order of Fe > Zn > Ni > Cu > Pb > Cr (Figure 3). Heavy metal concentrations were greater during the dry season than during the rainy season. The maximum concentration of most metals during the dry season is owing to the river's gentler flow during the dry season, as well as the fact that water volume has decreased, causing dissolved metals to be at greater concentration levels with industrial and municipal discharge into the river remaining unchanged. There was significant variation ($p < 0.05$) in the mean values across the sample stations in Warri River for all of the analysed heavy metals, but there was no seasonal significant variation in mean value ($p > 0.05$) (Table 10). The correlation coefficient matrix among the selected heavy metals was presented in Tables 11 and 12. Strong significant correlations between the heavy metals during the dry season (Table 11) were Fe and Cu ($r = 0.918$), Ni and Cu ($r = 0.918$), Fe and Ni ($r = 0.864$), which could indicate the same or

similar source input. Strong significant correlations between the heavy metals during the wet season (Table 12) were Fe and Pb ($r = 0.950$), Ni and Pb ($r = 0.847$), Ni and Fe ($r = 0.917$), Cr and Fe ($r = 0.926$), Cr and Ni ($r = 0.882$), which could indicate the same or similar source input.

4. Conclusions and Recommendations

The assessment result of surface water samples from Warri River for physicochemical parameters and heavy metals revealed a significant contamination as one travels down from SP 1 to SP 5. The high concentration of EC, TDS, SO₄²⁻, Cl⁻ and Turb followed this trend and could be as a result of more dense industrial activity as you travel down the river, mostly during the dry season. The concentration of the aforementioned physicochemical parameters exceeded the standard allowable limits of NSDWQ/NIS and WHO from SP 3 to SP 5, which confirms the presence of inorganic salts, organic matter, and other dissolved materials in Warri River. Fe is quite abundant in the earth's crust; hence, natural waters always contain a variable concentration of Fe. Hence, the high concentration of Fe could be as a result of the geological make-up of the river bed and/or industrial activities along the river. The concentrations of Fe, Pb and Ni exceeded the NSDWQ/NIS and WHO standard limits, while Cd was not detected for both seasons. As a result, the government and other responsible authorities should take necessary remedial action and endorse further research into other physical, chemical, and unassessed biological parameters of serious environmental concern, as well as the identification of possible sources of high EC. However, more research is needed to separate the natural and anthropogenic contributions to the chemical and biological state of Warri River.

Declaration of Competing Interest

The authors have no conflict of interest.

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