PRINT ISSN 1119-8362
Electronic ISSN 2659-1502

Full-text Available Online at
https://www.ajol.info/index.php/jasem
http://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 27 (7) 1541-1549 July 2023

Assessment of Physicochemical Parameters of New Calabar and Orashi Rivers Exposed to Open Waste Discharge in Nigeria

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ABSTRACT: Water is an indispensable resource necessary for life sustenance, social and economic development. Nevertheless exposure to untreated wastes undermines the quality of water bodies. This research therefore, assessed the quality of New Calabar and Orashi Rivers in Rivers State of Nigeria, between December 2020 and October 2021. The results revealed that the analysed physiochemical parameters varied across the months and sampling points. The minimum values of pH, DO and BOD were below the World Health Organisation (WHO) limit. Chloride and sulphate in New Calabar River are above the threshold limit, but within acceptable limits in Orashi River. Temperature, EC, TDS, TSS, phosphate and nitrate were within the acceptable limits. The concentrations of EC and chloride were extremely higher in New Calabar River compared to Orashi River. The results also showed that the physicochemical parameters varied between the dry and wet seasons, but both rivers were more polluted in the dry season. The level of physicochemical parameters in the water samples indicated that both rivers are contaminated and not suitable for domestic use. Therefore, it become imperative that the agencies responsible for maintenance of river quality take proactive measures to design, develop and implement strategies that will improve the current state of Orashi and New Calabar Rivers.

DOI: https://dx.doi.org/10.4314/jasem.v27i7.30

Cite this paper as: NWOCHIGOZIRI, E. C; EKPETE, O. A; KPEE, F. (2023). Assessment of Physicochemical Parameters of New Calabar and Orashi Rivers Exposed to Open Waste Discharge in Nigeria. *J. Appl. Sci. Environ. Manage.* 27 (7) 1541-1549

Dates: Received: 12 June 2023; Revised: 21 June 2023; Accepted: 04 July 2023 Published: 30 July 2023

Keywords: Water Quality, Physicochemical Parameters, Assessment, New Calarbar and Orashi Rivers

Water is a valuable asset and it needs extreme protection against contamination. Unfortunately, urbanization, rapid population growth, industrialization and human poor attitudes to the environment have rendered most water sources unfit for human consumption. This is even worst particularly in countries where environmental management and monitoring are at low levels. Clean and quality water is imperative for a healthy living. According to Bhat *et al.* (2018), quality water sustains public health and guarantees economic development. Indeed, the importance of water cannot be underestimated because it is essential in almost all facets of human activities including agriculture for irrigation farming, fabricating and manufacturing industries amongst others. Despite the availability of freshwater, only about 3% is reliable and accessible, and this small percentage is even under pressure from anthropogenic pollution (Taruna and Alankarita, 2013). Globally, an estimate of 450 billion cubic meters of wastewater enters surface water each year through point sources pollution (Taruna and Alankarita, 2013), and the presence of organic and inorganic chemicals, as well as microorganisms in the wastewater contaminate surface water like lakes, rivers, streams, creeks and oceans (Onyegeme-Okerenta *et al.*, 2016). Surface water quality is also affected through unlawful loading of solid wastes into water-bodies (Akungah, 2003; Chindah *et al.*, 2004). Precipitation and flooding are other means by which impurities escape into surface water. Several studies carried out in the past on the quality of rivers in the Niger Delta region of Nigeria showed that industrial and anthropogenic activities contributed immensely to the pollution of these rivers (Ekpete, 2002; Marcus and Ekpete, 2014; Iyama and Edori, 2016; Ekpete e*t al.*, 2019; Ogboru and Ekpete, 2021). The World Health Organization characterizes water quality to communicate the extent of pollution that suits the various uses of water (WHO, 2017). Thus, water

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quality can be depicted as a scope of factors which might be physical, synthetic and organic which cut-off water use. Each person has a way and understanding about water quality. However, to guarantee safe water quality, water quality guidelines are set around the world. For instance, the World Health Organization had defined the risks associated to most water contaminants and had equally specified limits to which these water contaminants can be accepted especially for drinking purpose (WHO, 2017). Water contamination is a serious issue and it can lead to illness and even death. The bioaccumulation and drinking of contaminated water can be harmful to aquatic organisms, the ecosystems and human health. Fish eggs and sea-aquatic insects may suffocate and die due to lack of oxygen, while suspended solids can cause obstruction in fish gills and growth retardation (Ndeda and Manohar, 2014). Many parameters in water are termed as contaminants, while others are used as indicators for the determination of pollution level and extent water quality deterioration. The physicochemical and biological parameters often analysed in water include pH, temperature, electrical conductivity, turbidity, total dissolved and suspended solids, dissolved oxygen (DO), biological and chemical oxygen demand, alkalinity, salinity, chloride, phosphates, sulphates and nitrates among others. Every parameter in assessment of water quality is important in making decisive conclusion about the state of water. For instance, water with pH range of 10 – 12.5 is an indication that such water may cause swelling of hair fibres and gastrointestinal irritations (Taruna and Alankarita, 2013), while at pH less than 4, redness and irritation of the eyes may occur (WHO, 2017). Orashi and New Clabar Rivers are increasingly overwhelmed by activities that can release great amount of contaminants in the rivers. This situation can definitely reduce the river quality. Thus, the bioavailability and water quality of any river is a reflection of some vital parameters (Seiyaboh *et al*., 2016). Impairment on water quality is a threat to life. According to Akpe *et al*. (2018), water is one of the most common natural resources that profoundly influence life. Hence, water pollution by physical, chemical or biological condition not only harms water bodies, it also affects the quality of aquatic lives and every other organisms that consumed of the water including animal, plants and humans. However, the concentrations of the physicochemical parameters depend on seasons (dry and wet) and some factors such as water level, self-purification ability and intrusion from water runoff (Ezekiel *et al*., 2020; Rahman *et al*., 2021; Romin *et al*., 2021). The rivers, especially Orashi River, are a major source of water for domestic uses. Hence, it becomes imperative to assess the level of physicochemical parameters of these rivers due to the unwholesome approach and diverse of pollution loads these rivers received on daily basis.

MATERIALS AND METHODS

Description of Study Areas: Water samples were collected in triplicate from three (3) locations in New Calabar and Orashi Rivers. The samples were collected within the rivers close to communities located along the riverbank. The communities are located some few kilometres away from one another. In New Calabar River, the water samples were collected in locations within Choba, Ogbogoro and Rumuolumeni Towns in Obio/Akpor Local Government Area, while in Orashi River, the water samples were collected in locations within Mbiama, Odieke and Okarki Towns in Ahoada West Local Government Area. Both Local Governments are located in Rivers State of Nigeria. Table 1 shows the coordinates of the sample collection points, while Figures 1 and 2 showed the study areas.

Sampling Method: The water samples were collected few meters away from the river bank at specific intervals and about 15 – 20 cm below the water surface. Few drops of concentrated H_2SO_4 (pH≥2) was added to the water samples to avoid chemisorptions. All the samples were collected into an amber glass bottle and stored in a cooler packed with ice prior to the analysis, which was done almost immediately after the sample collection. Sampling was carried out for a period of one year at one month interval. Samples from December 2020 to April 2021 are considered as dry season, while samples from June to October 2021 are considered as wet season.

Analysis for physicochemical parameters: Some of the parameters were analysed right in the field, while others were analysed in the laboratory.

Temperature: Temperature was measured in the field using digital temperature recorder. The temperature sensor of the probe was immersed in water to a depth of 10cm, allowed to stabilize before taking reading.

Table 1: Coordinates of sample locations

S/No	River	Sample location	L.G.A.	Coordinates
1	New Calabar	Choba	Obio/Akpor	4.888617N, 6.897029E
2	New Calabar	Ogbogoro	Obio/Akpor	4.845140N, 6.922351E
3	New Calabar	Rumuolumeni	Obio/Akpor	4.811536N, 6.928650E
4	Orashi	Mbiama	Ahoada West	5.061525N, 6.451185E
5	Orashi	Odieke	Ahoada West	5.018959N, 6.432941E
6	Orashi	Okarki	Ahoada West	4.983985N, 6.431361E

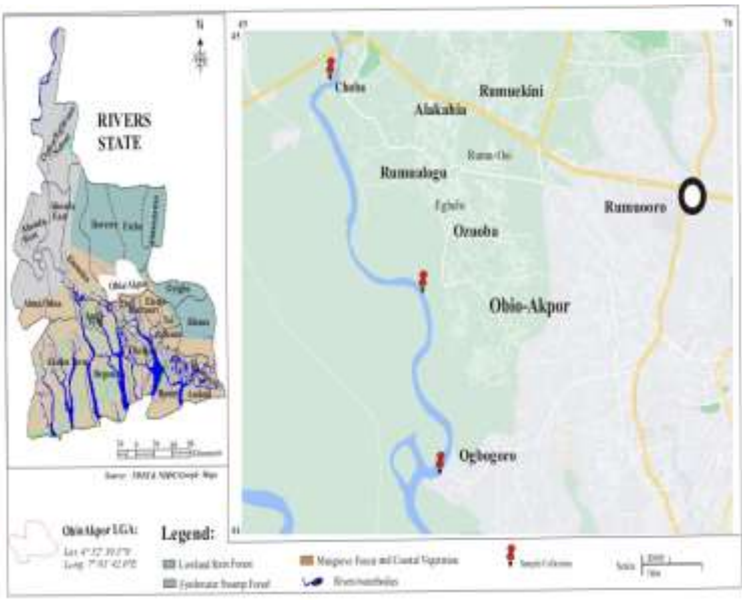

Fig 1: Map of the study area in Obio/Akpor local government area

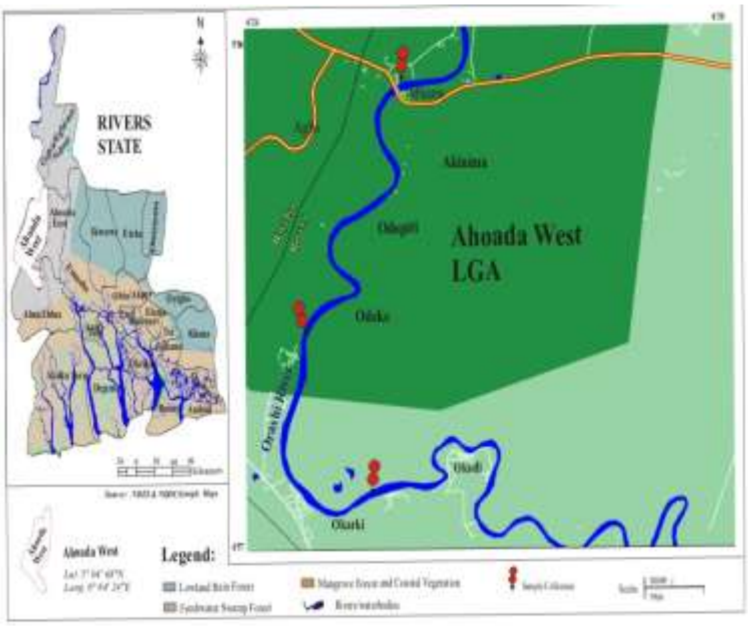

Fig 2: Map of the study area in Ahoada West local government area

Water pH: Water pH was measured in the field using electrometric method 4500-H B. The probe was lowered into the water to a depth of 10cm, and it was allowed to stabilize before recording the indicated pH value.

Electrical conductivity: The electrical conductivity was measured in the field using a Sens ION 5 conductivity meter (HACH-USA). The conductivity probe was immersed in water to a depth of 10cm, allowed to stabilize and the conductivity read in micro siemens per centimeter (μS/cm).

Turbidity: Turbidity was determined using standardized Hanna multiple H198703 turbidimeter. The samples were poured into the measuring bottle and the surface of the bottle wiped with silicon oil. The bottle was then inserted into the turbidimeter and the reading obtained.

Total dissolved solids: The gravimetric method was used to determine the total dissolved solids (TDS) according to World Health Organisation Standard (WHO, 2017). A portion of water was filtered out and 10ml of the filtrate was measured into a pre-weighed evaporating dish. It was then dried in an oven at temperature of 103 to 105ºC for two and half hours. The dish was transferred into desiccators and allowed to cool to room temperature. The cooled sample was then weighed to determine the final weight. The total dissolved solids content of the water was calculated as:

$$TDS = \frac{(W_1 - W_2)}{V} \times 1000 \text{ (mg/l)} \quad (1)$$

Where: W_1 = initial weight of evaporating dish (mg), W_2 = final weight of evaporating dish + residue (mg), V = volume of filtrate used (ml)

Total Suspended Solids: The total suspended solids (TSS) in the water samples were measured gravimetrically. A pre-gauged filter paper was utilized to channel 100ml of the water sample. The combined filter paper and filtered solids was dried at 105ºC and reweighed. This was done until a constant value was reached. The weight of suspended solids was computed using the formulae below:

$$TSS = \frac{(W_c - W_t)}{V} \times 106 \text{ (mg/l)} \quad (2)$$

Where: TSS = Total suspended solids, Wt = Weight of pre-combusted filter (mg), Wc= Constant weight of filter + residue (mg), V = Volume of water sample used (ml).

Total Solids: Total solids (TS) were simply calculated by summing the values of TDS and TSS obtained. Thus, TS was calculated as:

$$TSS = TS - TDS \quad (3)$$

Dissolved Oxygen: The dissolved oxygen (DO) was measured in the field using Winkler's Method. The DO probe was immersed in water to a depth of 10cm, while stirring the water. The readings were allowed to stabilize before taking reading.

Determination of Biochemical Oxygen Demand: Biochemical oxygen demand (BOD_5) was measured using Winkler's method. Water sample was filled into sample bottle to the brim and covered airtight. The sample in the bottle was incubated at the specified temperature for 5 days. Dissolved oxygen (DO) was measured initially and after incubation and the BOD_5 was computed as the difference between initial and final DO. Because the initial DO was determined shortly after the dilution was added, all oxygen uptake occurring after this measurement was included in the BOD_5 measurement. 1 ml of $MgSO_4$, $CaCl_2$, phosphate buffer and $FeCl_3$ were added to 1 L of water. The solution was then shaken thoroughly to saturate the dissolved oxygen. This solution was used to dilute the samples. 100 ml of the samples were measured into different flasks and were made up to 1 litre mark with the diluted water previously prepared. The diluted sample solution was then poured into BOD_5 bottles and subsequently incubated at 20ºC in the dark for 5 days.

Determination of Initial Dissolved Oxygen: 300 ml BOD_5 bottles were filled with the diluted samples previously prepared and the initial DO determined using the Winkler's method.

Determination of Final Dissolved Oxygen: After incubation for 5days, the final DO was determined using the same procedure above. The BOD_5 was calculated using the formula:

$$BOD_5 = \frac{DO_1 - DO_0}{B} \text{ (mg/l)} \quad (4)$$

Where: DO_0 = initial dissolved oxygen recorded immediately after preparation (mg/l), DO_1 = final dissolved oxygen after 5 days of incubation (mg/l) and B = fraction of sample used.

Determination of Chemical Oxygen Demand: In this analysis, 250ml of water sample was warmed to 27ºC and transferred to a cleaned flask. 10ml of $KMnO_4$ at 0.0125M was added and 10ml of 20% v/v H_2SO_4 was added. It was mixed gently and incubated at 27ºC for 4 hours. The mixture was examined at intervals, when the pink colour of permanganate tends to disappear. 10ml of $KMnO_4$ was added. After 4 hours, 1ml KI solution was added and titrated with 0.0125M $Na_2S_2O_3$ using starch as an indicator until the blue colour just disappeared. The COD in the water sample was calculated as:

$$COD = \frac{(V_o - V_2) \times 1000}{A \times V_1} \text{ (mg/l)} \quad (5)$$

Where: V_o = Volume of Blank (ml), V_1 = volume of sample used (ml), V_2 = final volume of sample (ml), A = total volume of $KMnO_4$ 0.0125M added to samples.

Chloride ion: Chloride content was determined using Argentometric-titrimetric method. Chloride was precipitated as silver chloride and potassium chromate indicator. A change of colour from yellow to pinkish yellow as the end-point titration indicates the chloride concentration. Thus, 100 ml water sample was titrated against silver nitrate solution in the presence of potassium chromate indicator. The end-point of the titration was indicated by appearance of pinkish yellow colour of silver chromate. A blank was also titrated simultaneously, and the obtained values were computed using the formula.

$$\text{Chloride} = \frac{(A-B)\times N \times 35{,}450}{V} \text{ (mg/l)} \quad (6)$$

Where: A = Titrant used for sample (ml), B = Titrant used for blank (ml), N = Normality of titrant, V = volume of sample (ml).

Alkalinity: Alkalinity was determined by titrating the sample with hydrochloric acid (HCl) using methyl orange as indicator and recorded as milligrams per litre of calcium carbonate. Thus, 50ml of the sample was pipette into a clean 250ml conical flask. Two drops of methyl orange indicator were added and the solution titrated against a standard 0.01M HCl solution until the colour change to pink at end-point. The alkalinity in the water samples was computed using the formula:

$$\text{Alkalinity} = \frac{V_a \times M \times 100{,}000}{V_s} \text{ (mg/l)} \quad (7)$$

Where: V_a = volume of acid used (ml), M = Molarity of acid used (M), V_s = volume of sample used (ml).

Salinity: Determination of salinity was by evaporation. Thus, salinity is the total mass of dissolved salts per one kilogram of water. Therefore, one kilogram of water was measured into a Petri dish. Carefully, the Petri dish was put into an oven and then heated gently to 80 - 100ºC until the water was evaporated. The dried sample was allowed to cool for a few minutes, then weighed with the Petri dish (dish + salt). The weight of dried salt was obtained by subtracting the weight of empty dish from the weight of dish + salt. Thus, the salinity of the sample was determined using the formula:

$$\text{Salinity} = \frac{W_s}{W_w} \times 1000 \text{ (mg/l)} \quad (8)$$

Where: W_s = weight of salt (mg), W_w = weight of water (mg)

Phosphate: Phosphate concentration was measured as follows. The raw river water was oxidized to PO_4-P by autoclaving the samples at 120ºC for 40 minutes utilizing ammonium per sulphate as oxidizing agent. Phosphate particles join with ammonium molybdate to shape a molybdophosphate complex. The water sample was then filtered and ascorbic acid added into the filtrate to reduce the complex ions. The molybdophosphate complex was promptly reduced by ascorbic acid to a seriously blue molybdophosphate complex. The colour intensity was estimated calorimetrically at a frequency of 690nm utilizing a digital spectrophotometer (HACH Model).

Sulphate: Sulphate was determined using turbidimetric method. Sulphate ions were precipitated in HCl acid medium with barium chloride to form barium sulphate crystals of uniform size. 5ml of the water sample was diluted to 100ml distilled water in an Erlenmeyer flask. 5ml conditioning reagent was then added and mixed in stirring apparatus. A spoon full of $BaCl_2$ crystals (0.5g) was added and stirred for 1 minute at constant speed. Immediately after stirring, the solution was poured in spectrophotometer. The quantity of sulphate was calculated using calibration curve, which is then used to calculate the sulphate in water.

$$\text{Sulphate} = \frac{m_s}{V} \times 1000 \text{ (mg/l)} \quad (9)$$

Where: m_s = mass of SO_4^{2-} (mg), V = volume of sample (ml).

Nitrate: The Nitrate concentration was determined using filtered water samples following modified sodium salicylate procedure. Nitrate was reacted with sodium salicylate and sulphuric acid to produce a yellow compound (nitro salicylic acid). Colour intensity was then estimated calorimetrically utilizing a digital spectrophotometer (HACH Model) at a frequency of 420nm.

RESULTS AND DISCUSSION

The results of the physiochemical parameters obtained from the water samples from New Calabar and Orashi Rivers are presented and discussed in this section. The mean values of the physicochemical parameters obtained during the dry season (from the months of December 2020, February 2021 and April 2021) and wet season (June, August and October 2021) across the sampling locations in New Calabar and Orashi Rivers are presented in Tables 2 and 3. The results showed there was seasonal variation across the measured parameters in New Calabar and Orashi Rivers. Thus, the comparison of the values of parameters presented in Table 2 and Table 3 showed that pH, temperature, EC, TDS, TSS, TS, DO, BOD_5, COD, chloride, alkalinity, salinity and sulphate levels recorded across the locations in dry season were higher than the levels recorded in the wet season for both New Calabar and Orashi Rivers. In contrast, the average turbidity, phosphate and nitrate recorded across the locations in wet season were higher than values recorded during the dry season. The pH value obtained in dry and wet seasons ranged from 6.43 – 6.88 and 6.14 – 6.26 for New Calabar River and 6.29 – 6.77 and 6.15 – 6.53 for Orashi River. The pH range in some locations in the dry season and all the samples in wet season is below the recommended values by WHO (2017). It is also below the value reported by Marcus and Ekpete (2014) for refinery effluent receiving streams, but within the mean value reported for dry season (6.51±0.07) in another study in New Calabar River (Ogboru and Ekpete, 2021). The seasonal variation in pH was attributed to rain water runoff as well as escalating rate of photosynthesis by aquatic plants (Ezekiel *et al*., 2020). Temperature in dry and wet seasons ranged from 28.68 – 30.23ºC and 26.61 – 27.09ºC for New Calabar River and 28.37 – 29.25ºC and 26.65 – 27.48ºC for Orashi River. The temperature range is within the recommended values by WHO (2017). It is also within 27.20±0.40 reported for refinery effluent receiving streams (Marcus and Ekpete, 2014). A previous study in Orashi River reported 26.77 – 28.07ºC and 26.37 – 27.13ºC for dry and wet seasons (Seiyaboh *et al*., 2016), while a mean of 30.70±0.27ºC was recorded in New Calabar River (Ogboru and Ekpete, 2021). The temperature variation was caused by daily, monthly and annually temperature changes. Other factors like sunlight, nutrient loads (Ngah *et al*., 2017) and high rainfall (Onojake *et* al., 2017) can also cause seasonal variation in river temperature, which may result to discomfort of aquatic species. EC in dry and wet seasons ranged from 778.17-828.40µS/cm and 626.63 – 686.69µS/cm for New Calabar River and 105.02 – 114.02µS/cm and 92.98 – 97.21µS/cm for Orashi River. The EC range across the seasons is below the value recommended by WHO (2017). However, the EC values recorded in Orash Rivers across the seasons is above reported in a previous study (25.07 82.33µS/cm) (Seiyaboh *et al*., 2016), the values recorded in New Calabar River was far below 29156± 1350µS/cm reported in another study (Ogboru and Ekpete, 2021). Decline in EC during the wet season can be attributed to dilution from rain water, while higher EC during the dry season maybe due to dissolved solids and tidal effect (Ezekiel *et al*., 2020; Rahman *et al*., 2021) or high concentrations of heavy metals and temperature (Ngah *et al*., 2017). Turbidity in dry and wet seasons ranged from 4.14 – 4.63NTU and 13.80 – 16.12NTU for New Calabar River and 7.89 – 8.87NTU and 26.94 – 29.56NTU for Orashi River. Turbidity in both rivers is above the recommended limit of 5NTU (WHO, 2017). A previous study had reported a range of 14.50 – 18.00NTU (Onojake *et al*., 2017) in New Calabar River, while in Trans-Woji stream, 26.30 – 36.40NTU and 25.60 – 33.40 NTU was recorded in dry and wet seasons respectively (Ezekiel *et al*., 2020). Higher turbidity in the rivers during the wet season is an indication that organic and particulate matters were more discharged into the rivers during the wet season. Erosion, excessive water runoff and wastes deposited in the river are other reasons for increased level of turbidity in rivers during the wet season compared to the dry season Onojake *et al*., 2017). TDS in dry and wet seasons ranged from 92.01 – 125.22mg/l and 63.93 – 74.94mg/l for New Calabar River and 109.51 – 132.10mg/l and 69.34 – 72.05mg/l for Orashi River. Also, TSS in dry and wet seasons ranged from 17.49 – 23.81mg/l and 12.15 – 14.25mg/l for New Calabar River and 20.82 – 25.11mg/l and 13.18 – 13.70mg/l for Orashi River, while TS in dry and wet seasons ranged from 109.51 – 149.03mg/l and 76.08 – 89.18mg/l for New Calabar River and 130.33 – 157.21mg/l and 82.53 – 85.74mg/l for Orashi River.

Table 2: Mean values of physicochemical parameters in dry season

	New Calabar River			Orashi River			
Parameter	**Choba**	**Ogbogoro**	**Rumuolumeni**	**Odieke**	**Mbiama**	**Okarki**	**WHO**
pH	6.88±0.33	6.43±0.32	6.87±0.47	6.77±0.12	6.29±0.17	6.74±0.11	6.5-8.5
Temp. (ºC)	28.68±0.62	30.23±1.25	29.31±0.99	28.37±0.94	28.56±1.40	29.25±0.79	25-30
EC (µS/cm)	812.69±22.35	778.17±38.80	828.40±23.33	110.01±3.94	114.02±4.24	105.02±4.26	1000
Turb.(NTU)	4.14±0.54	4.46±0.17	4.63±0.56	8.39±0.48	8.87±0.44	7.98±0.56	5
TDS (mg/l)	95.19±8.13	125.22±7.72	92.01±6.08	129.24±7.42	132.10±18.44	109.51±20.00	1000
TSS (mg/l)	18.10±1.55	23.81±1.47	17.49±1.16	24.57±1.41	25.11±3.51	20.82±3.80	30
TS (mg/l)	113.29±9.67	149.03±9.19	109.51±7.23	153.81±8.84	157.21±21.95	130.33±23.81	Nil
DO (mg/l)	7.34±0.09	6.59±0.28	7.95±0.53	5.45±0.38	5.73±0.29	5.43±0.27	5.0-7.0
BOD_5 (mg/l)	8.78±0.19	10.02±1.25	10.37±0.85	12.20±0.49	14.04±0.75	11.61±0.87	4
COD (mg/l)	101.57±13.56	110.23±8.69	112.37±5.42	123.19±6.26	129.80±5.05	133.29±4.32	Nil
Chlorides (mg/l)	1253.61±39.07	1228.85±47.43	1299.10±18.16	372.17±67.88	457.93±57.16	354.53±83.15	250
Alkalinity (mg/l)	14.84±1.75	16.32±0.99	17.49±1.73	7.47±0.88	10.08±1.32	7.69±0.60	Nil
Salinity (mg/l)	17.47±1.15	16.66±1.20	18.29±1.21	10.39±0.88	11.42±1.02	9.81±0.81	Nil
Phosphates (mg/l)	0.52±0.07	0.59±0.07	0.65±0.08	0.45±0.04	0.52±0.08	0.41±0.04	6.5
Sulphates (mg/l)	265.79±49.25	258.14±41.53	277.50±42.65	4.54±0.38	5.76±0.34	4.97±0.42	250
Nitrates (mg/l)	4.69±0.57	4.36±0.44	5.56±0.26	3.17±0.34	3.89±0.32	3.29±0.15	50

Table 3: Mean values of physicochemical parameters in wet season

	New Calabar River			Orashi River			
Parameter	**Choba**	**Ogbogoro**	**Rumuolumeni**	**Odieke**	**Mbiama**	**Okarki**	**WHO**
pH	6.14±0.09	6.26±0.14	6.23±0.20	6.27±0.04	6.53±0.11	6.15±0.06	6.5-8.5
Temp. (ºC)	26.61±0.92	26.95±1.27	27.09±0.72	26.65±0.83	27.48±1.58	27.10±0.98	25-30
EC (µS/cm)	661.61±28.47	626.63±21.63	686.69±21.56	95.30±2.99	97.21±2.62	92.98±3.53	1000
Turb.(NTU)	13.80±1.81	14.33±1.24	16.12±0.82	27.96±1.58	29.56±1.47	26.94±1.30	5

TDS (mg/l)	63.93±9.66	74.94±5.05	68.99±2.07	69.34±8.86	72.05±7.20	71.71±9.99	1000
TSS (mg/l)	12.15±1.84	14.25±0.96	13.12±0.39	13.18±1.68	13.70±1.37	13.63±1.90	30
TS (mg/l)	76.08±11.50	89.18±6.01	82.11±2.47	82.53±10.54	85.74±8.56	85.34±11.89	Nil
DO (mg/l)	3.78±0.37	4.37±0.30	4.54±0.29	3.88±0.34	4.01±0.33	3.85±0.19	5.0-7.0
BOD_5 (mg/l)	6.30±0.20	6.52±0.46	7.27±0.21	9.23±0.43	10.50±0.50	8.68±0.49	4
COD (mg/l)	55.93±6.52	54.64±4.79	56.69±1.22	67.67±4.06	70.82±4.45	71.77±9.82	Nil
Chlorides (mg/l)	885.44±72.57	778.89±63.95	1004.95±70.67	373.21±68.18	402.95±19.37	355.94±21.79	250
Alkalinity (mg/l)	11.69±2.32	13.39±2.31	14.11±1.97	5.58±0.88	7.47±2.12	5.98±1.37	Nil
Salinity (mg/l)	13.86±1.60	12.41±1.25	14.46±1.56	7.35±1.29	8.27±0.98	6.73±1.28	Nil
Phosphates (mg/l)	0.78±0.12	0.87±0.04	0.91±0.37	0.65±0.03	0.69±0.05	0.57±0.08	6.5
Sulphates (mg/l)	166.77±34.70	158.88±38.11	181.73±32.93	3.20±1.95	3.25±1.20	3.08±1.49	250
Nitrates (mg/l)	5.91±0.30	5.49±0.21	6.10±0.19	4.56±0.08	5.01±0.15	4.10±0.11	50

The values of TDS and TSS in both rivers meet the recommended value by WHO (2017). The TDS range recorded in Orashi River is lower than 12.58 – 41.17mg/l and 6.77 – 8.10mg/l reported for dry and wet seasons in the same river by Seiyaboh *et al*. (2016), but the range recorded in New Calabar River is far lower than 13784 – 15050mg/l reported by Ogboru and Ekpete (2021) in same river and 26630mg/l in Okirika/Bonny River (Marcus and Ekpete, 2014). Similarly, the range of TSS recorded in this work is less than 27.50 – 36.00mg/l reported by Ogboru and Ekpete (2021). The seasonal variation in TDS, TSS and TS can be attributed to differences in rate of evaporation between the dry and wet seasons, which changed the concentration of dissolved solid. Low temperature and precipitation in wet season also promote poor dissolution of solids due to reduced evaporation rate (Akpe *et al*., 2018; Ezekiel *et al*., 2020; Akankali and Davies, 2021). DO in dry and wet seasons ranged from 6.59 – 7.95mg/l and 3.78 – 4.54mg/l for New Calabar River and 5.43 – 5.73mg/l and 3.85 – 4.01mg/l for Orashi River, while BOD_5 in dry and wet seasons ranged from 8.78 – 10.37mg/l and 6.30 – 7.27mg/l for New Calabar River and 11.61 – 14.04mg/l and 8.68 – 10.50mg/l for Orashi River. Also, COD in dry and wet seasons ranged from 101.57 – 112.37mg/l and 54.64 – 56.69mg/l for New Calabar River and 123.19 – 133.29mg/l and 67.67 – 70.82mg/l for Orashi River. The level of DO recorded in the dry season meets the required recommendation, while DO in wet season and BOD_5 levels in dry and wet seasons for both rivers fall short of the required standard (WHO, 2017). Other studies reported a similar level of DO in some rivers/streams within the study areas 3.73±0.29mg/l (Marcus and Ekpete, 2014), (4.6 – 6.3mg/l and 4.6 – 5.8mg/l in dry and wet seasons) (Ezekiel *et al*., 2020), (3.23 – 4.65mg/l and 6.25 – 6.53mg/l in dry and wet seasons) (Ngah *et al*., 2017) (3.6 – 4.35mg/l and 2.45 – 2.60mg/l in dry and wet seasons) (Akankali and Davies, 2021) and (5.50 – 6.45mg/l in dry season) (Ogboru and Ekpete, 2021). Other works have equally recorded lower values of BOD_5 in similar water bodies (1.2 – 5.2mg/l) (Ezekiel *et al*., 2020) and (1.02 – 1.78mg/l and 1.40 – 5.38mg/l in dry and wet seasons) (Ngah *et* al., 2017). A higher value of 10.75 – 14.57mg/l was recorded in New Calabar River (Ogboru and Ekpete, 2021). High BOD_5 in river is attributed to decayed organic matter, nutrient load and dead macrophytes released via surface water runoff that utilize oxygen for their biodegradation (Ngah *et* al., 2017), while high COD is attributed to decomposed organic matters and oxidation of inorganic chemicals like ammonia and nitrite (Ezekiel *et al*., 2020). Very low DO and high BOD_5 can lead to death of fish. Chloride in dry and wet seasons ranged from 1228.85 – 1299.10mg/l and 778.89 – 1004.95mg/l for New Calabar River and 372.17 – 457.93mg/l and 355.94 – 402.95mg/l for Orashi River. The values of chloride in both rivers are above the recommended value by WHO (2017). The chloride concentration (0.04 – 0.38mg/l) reported by (Seiyaboh *et al*., 2016) in Orashi River is far below the values obtained in this work. The higher concentration may have occurred because of high intrusion of salt and heavy metals into river at the time of this analysis. Alkalinity in dry and wet seasons ranged from 14.84 – 17.49mg/l and 11.69 – 14.11mg/l for New Calabar River and 7.47 – 10.08mg/l and 5.58 – 7.47mg/l for Orashi River. Seiyaboh *et al*. (2016) recorded just 2.53 – 6.33mg/l in Orashi River, while Marcus and Ekpete (2014) reported an average of 94.30±25.40mg/l in Okirika/Bonny River. Higher alkalinity in water indicates the presence of dissolved anions from carbonates and hydrogen carbonates (Seiyaboh *et al*., 2016; Rahman *et al*., 2021). Salinity in dry and wet seasons ranged from 16.66mg/l – 18.29mg/l and 12.41mg/l – 14.46mg/l for New Calabar River and 9.81 – 11.42mg/l and 6.73 – 8.27mg/l for Orashi River. Marcus and Ekpete (2014) reported a very high average salinity of 13245.40±123.80mg/l in Okirika/Bonny River, while a low concentration was reported in Trans-Woji Stream (0.90 – 2.10mg/l and 0.70 – 1.70mg/l in dry and wet seasons). Also in Bonny River, (Akankali and Davies (2021) reported 62.40 – 134.20mg/l and 62.3 – 138.60mg/l in dry and wet seasons, respectively. High salinity level in rivers is attributed to elevated level of salinity and proximity of river to sea (Onojeke *et al*., 2017; Ezekiel *et al*., 2020; Akankali and Davies, 2021). Low salinity can cause rise in volume of fresh water, particularly in wet season (Ngah *et al*., 2017; Ezekiel *et al*., 2020). Sulphate in dry and wet seasons ranged from 258.14 – 277.50mg/l and 158.88 – 181.73mg/l for New Calabar River and 4.54 – 5.76mg/l and 3.08 – 3.25mg/l for Orashi River. The sulphate levels in New Calabar River are above the recommended value, but in Orashi River, it meets the required limit. Marcus and Ekpete (2014) reported an average of 22.40±3.40mg/l in Okirika/Bonny River. A similar range of sulphate concentrations in dry season (2.46 – 4.53mg/l) and wet season (2.10 – 3.57mg/l) were reported in Orashi River (Seiyaboh *et al*., 2016). However, a lower value of 2.50 – 16.50mg/l was recorded in New Calabar River (Ogboru nad Ekpete, 2021). Excessive sulphate concentration in rivers indicates high release of organic matters and domestic effluents (Seiyaboh *et al*., 2016; Ngah *et al*., 2017). Phosphates in dry and wet seasons ranged from 0.52 – 0.65mg/l and 0.78 – 0.91mg/l for New Calabar River and 0.41 – 0.52mg/l and 0.57 – 0.69mg/l for Orashi River, while nitrates in dry and wet seasons ranged from 4.36 – 5.56mg/l and 5.49 – 6.10mg/l for New Calabar River and 3.17 – 3.89mg/l and 4.10 – 5.01mg/l for Orashi River. Phosphate and nitrate levels in both rivers are within the recommended values (WHO, 2017). Marcus and Ekpete (2014) reported 0.39±0.15mg/l phosphate and 0.86±0.50mg/l nitrate in Okirika/Bonny River, while 0.05 – 2.50mg/l was reported in Elechi Creek (Ngah *et al*., 2017). Ogboru and Ekpete (2021) reported a nitrate concentration range of 0.26 – 4.15mg/l in New Calabar River. A similar study in Orashi River reported very low concentration of nitrate in dry season (0.04 – 0.38mg/l) and wet season (0.03 – 0.30mg/l) (Seiyaboh *et al*., 2016). The levels of phosphate and nitrate concentrations indicate that the rivers are not loaded with wastes rich in nutrients. The level variations in the physicochemical parameters across the sampling points and between the seasons showed that both New Calabar and Orashi Rivers received wastes at different degree, which may vary depending on the amount, nature and self-purifying ability of the rivers. However, proper monitoring and control of the rivers are needed to curtail excessive release of pollution loads in New Calabar and Orashi Rivers.

Conclusion: This study assessed the quality of New Calabar and Orashi Rivers. The levels of pH, DO, BOD_5 and turbidity were above the acceptable limit. Chloride and sulphate in New Calabar River were above the threshold limit, but in Orashi Rivers, they were within the limits. Generally, both rivers are contaminated and not suitable for domestic use. Hence, disposal of wastes into the rivers should be discouraged. Finally, government and organizations are advised to provide portable water, particularly for the people located along Orashi River.

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