

Seasonal Variation of The Physico-Chemistry Quality of ATributary of The Bonny Estuary, Rivers State, Nigeria

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Abstract

Okpoka Creek is a tributary of the Upper Bonny Estuary in the Niger Delta, Nigeria. The study evaluated the effects of season (wet and dry) on the physico-chemical characteristics of this creek. Surface water samples were collected monthly from May 2004 – April 2006 to cover two seasons according to standard methods. Turbidity, 2.31±0.14 NTU (dry) and 4.68±0.55 NTU (wet) and temperature, 28.38± 0.09°C (wet) and 28.94±0.08°C (dry) showed significant seasonal variations (P<0.001). Dry season dissolved oxygen (5.14 ±0.16 mg/L) and biological oxygen demand (3.43±0.15 mg/L) were significantly higher than wet season values (4.80 ± 0.14 mg/L and 3.11±0.12 mg/L respectively)(P<0.05). Wet season total organic carbon (TOC) (114.16±4.39 mg/L) and total organic matter (TOM) (207.46±7.32 mg/L) significantly exceeded that of dry season (89.26±4.26 mg/L and 153.27±7.35 mg/L respectively) (P<0.05). TOC values at both seasons were above 1 to 30 mg/L for natural aquatic environment. Phosphate and ammonia exceeded FEPA and USEPA acceptable levels of 0.10 mg/L each for natural water bodies. Nitrate, phosphate and sulphate had significant seasonal variations (P<0.05). The presence of high levels of TOC and phosphate especially at wet season indicates organic pollution and stress. Run-offs from the creek environs, increasing inflow of water from Bonny Estuary and anthropogenic wastes especially dredged materials, slaughter effluents and raw human faeces lead to high organic loads at wet season. The study therefore suggests concerted environmental surveillance on Upper Bonny Estuary to reduce the inflow of pollutants from Bonny Estuary and anthropogenic sources into this creek especially at wet season.

Keywords: Water quality, season, influence, organic pollution, Okpoka Creek.



Council for Innovative Research

Peer Review Research Publishing System

Journal: Journal of Advances in Biology

Vol. 2, No. 1 editor@cirworld.com <u>www.cirworld.com</u>, member.cirworld.com



Introduction

The physico-chemical parameters of water are very vital for the life of aquatic organisms including fish. Environmental variables (pH, temperature salinity, dissolved oxygen, biological oxygen demand, turbidity, transparency, etc) have effects on indicator species as well as other organisms. These abiotic features as well as these biotic parameters are used to detect any perturbation in the aquatic environment. Pollution monitoring is a continual systematic, time-series observation of pre-determined pollutants or persistent components of the ecosystem over a period of time sufficient to determine the existing level, trend and natural variation of measured components in water column, sediments or biota [1]. Dissolved oxygen is the dissolved gaseous form of oxygen. Oxygen enters water by diffusion from the atmosphere and as by-product of photosynthesis by algae and other plants. It is essential for respiration of fish and other aquatic organisms [2, 3]. It is required for bacterial decomposition of plant and animal matter. The properties of solubility and especially the dynamics of oxygen distribution in lakes, reservoirs and other aquatic environments are basic to the understanding of aquatic organisms. The minimum concentration of dissolved oxygen to support fish and other aquatic life is about 4 mg/L [2]. Typically the concentration of dissolved oxygen in natural surface water is less than 10 mg/L. The solubility of atmospheric oxygen (i.e. saturation) in freshwater ranged from approximately 15 mg/L at 0°C to 8 mg/L at 25°C at sea level. Seawater saturation ranges from 11 mg/L at 0°C to 7 mg/L at 25°C [4].

The dissolved oxygen depends on temperature. The amount of oxygen that can be dissolved in water decreases with higher temperatures and with increase in altitudes and salinities [5]. It varies greatly from organism to organism hence a single arbitrary oxygen concentration for all organisms in all types of waters are not very useful. Water saturated with dissolved oxygen is acceptable for all uses except for industrial application, since the presence of dissolved oxygen increases the corrosiveness of water [4]. Dissolved oxygen of above 5.0 mg/L is recommended as the desirable range for fish production. Fish can survive in dissolved oxygen range of 1.0-5.0 mg/L but growth will be slow for prolonged exposure (Boyd, 1981; Swann, 2006). Death of fish will occur below 1mg/l.

Salinity is one of the major factors influencing algal zonation and distribution within the estuaries both in terms of range of values and rate of change [6]. Chindah [6] observed that periphyton community responded to salinity gradient in a tropical estuary, Niger Delta. The salinity of the coastal water is usually in the range of 34.40 - 34.50 % although lower values do occur (McNeely, *et al.*, 1979). Chindah and Nduaguibe [7] reported a salinity range of $11.5 \pm 1.8 - 20.3 \pm 3.0$ % for lower Bonny river in Niger Delta. Nweke [8] reported salinity range of $12.25 \pm 1.47 - 18.07 \pm 1.17$ % for Upper Bonny River and, Hart and Zabbey [9] gave 0.0 - 12.7 % salinity range for Woji creek in the Upper Bonny Estuary, lower Niger Delta. However, Chindah [6] reported 0.00-10.5 % as the salinity range for the New Calabar River, Upper Bonny Estuary.

Turbidity is a description of how clear water is, or in other word, the clarity of the water [10]. It is a natural phenomenon that occurs in most water bodies. Phytoplankton is a major source of turbidity in an aquatic ecosystem. Other sources are clay, silts from shorelines erosion, resuspension bed sediments and organic detritus from streams. Turbidity can also have anthropogenic origins. Sediment loading leads to increase in turbidity and its concomitant effects on the available light for growths of phytoplankton, periphyton as well as other aquatic lives. Turbidity is generally high during the rainy season and low during the dry season due to less natural erosion and runoff. High turbidity reduces photosynthesis of submerged, rooted aquatic vegetation and algae which result in reduction of plant growth and in turn suppress fish productivity [4]. Turbidity is therefore said to affect aquatic biological communities. It also affects recreational uses of water. The recommended range of turbidity for direct recreational contact is from 5 to 50 JTU [11]. High turbidity adversely affects domestic and industrial uses of water. Turbidity in natural water systems seldom exceeds 20,000 mg/L and even muddy waters usually have less than 2,000 mg/L [12]. Suspended soil particles cause turbidity and this seldom have direct effects on fish. It may adversely affect fish population, smother fish eggs and destroy communities of bottom organisms. Turbidity by plankton is not harmful to fish when in moderate level it makes it easier to catch fish as they are less wary (Swann, 2006). Turbidity limits the production of undesirable macrophytes in ponds.

Biological oxygen demand (BOD) is of vital importance in pollution monitoring. It is an index of aquatic pollution. A high BOD load can pose a threat to the aquatic environment by depressing the dissolved oxygen concentrations to levels that affect aquatic organisms. Waters with BOD levels less than 4 mg/L are considered clean but those with levels greater than 10 mg/L are regarded as polluted as they contain large amounts of degradable organic material [4]. Edoghotu [13] and Hart and Zabbey [9] reported BOD values of 1.2–36.7 mg/L and 0.2 – 98.9 mg/L for Okpoka Creek and Woji Creek respectively.

pH is an index of the hydrogen ion concentration and a very important environmental variable. Surface water generally tends to be alkaline while ground waters are more acidic. The range of pH is broader in freshwater than in seawater; seawater ranges from 8.0 to 8.3. The pH of the water may influence the species composition of an aquatic environment and the availability of nutrients as well as the relative toxicity of many trace elements. International Joint Commission [14] suggested a pH range of 6.5 to 9 and discharges should not alter the ambient pH by more than 0.5 pH units in the mixing zones for the protection of the aquatic environment. California State Water Resources Control Board (SWRCB) [15] stated that changes in normal pH shall not exceed 0.2 units for waters with marine or saline beneficial uses, 0.5 units for freshwaters supporting coldwater or warm water fisheries. Boyd (1981) recommended pH 6.5-9.0 for optimum fish production below or above is not desirable for this purpose. Studies on the chemical parameters of Bonny Estuary have reported pH range of 5.5 to 8.8 [6, 16, 17].



Nitrate is an important nitrogen source for phytoplankton in aquatic ecosystem. Other combined forms of this element do occur (ammonia, nitrite and organic compounds) and may well be utilized by some organisms in periods of nitrate starvation. It is present in much larger quantities in natural water bodies with available oxygen [2]. Sources of nitrogen include fertilizers, human and animal wastes, atmospheric deposition in rainwater and yard waste or other plant material that reaches the streams. Nitrogen can also diffuse from the air into aquatic bodies. Nitrogen in solutions may be used by those blue-green algae capable of nitrogen fixation. Utilization of nitrate by phytoplankton involves its conversion ultimately to ammonia before assimilation into cell materials, so it would seem likely that direct uptake of ammonium compounds would be advantageous. Most surface waters contain some nitrate (<5 mg/L) but when the concentration is up to 5 mg/L is a reflection of organic pollution as one major source of nitrates is human and animal wastes. Although surface waters may contain <1 mg/L or >100 mg/L nitrate. Nitrate concentrations in surface waters may fluctuate with season; higher in cold months and rainy season. Nweke [8] observed nitrate concentrations range of 0.23 \pm 0.09 mg/L (dry) – 0.85 \pm 0.35 mg/L (wet) for surface water of Upper Bonny Estuary. However, Obunwo *et al.* [17] reported a range of 0.35 \pm 0.25 mg/L (dry) – 0.57 \pm 0.12 mg/L (wet) for Minichida Stream in the Eastern Niger Delta.

Other aspects of the physico-chemistry of Bonny Estuary have been studied. Its physico-chemical parameters as well as the biological features vary with season (temporal variation), location (spatial variation) and time (diurnal variation) [13, 8, 9, 16, 17,18]. Studies on the physico-chemistry of Lagos Lagoon have shown that total solids, temperature, transparency, salinity, pH, conductivity, total number of plankton were higher in the dry season than wet season [19]. However, higher values of nitrate-nitrogen and total solids in rainy season and low pH in dry season have recorded in the Lagos Lagoon [20].

Okpoka Creek is one the river systems of the Upper Bonny Estuary, Niger Delta, Nigeria. It contributes to the Rivers State fish resource. There is urgent need to study the seasonal influence of the physico-chemical parameters of this creek due to its location, and the various human's activities going on around and on it. There have been increasing concerns on the need to conserve the aquatic environment in order to ensure sustainable resources and development at the local and international levels. This can only be achieved if the physico-chemical and biological integrity of the aquatic environment are maintained. There are various industrial set-ups and jetties located along its shores. These industries and jetties discharge effluents including crude oil and its products directly into the system. Apart from these effluents, wastes are released into the system from domestic sources. Other human activities (dredging, transportation [boating, navigation], fishing, etc) also impact on this estuary. This study thus studied the seasonal variation of the physic-chemistry quality of Okpoka Creek.

Materials and methods

Study Area

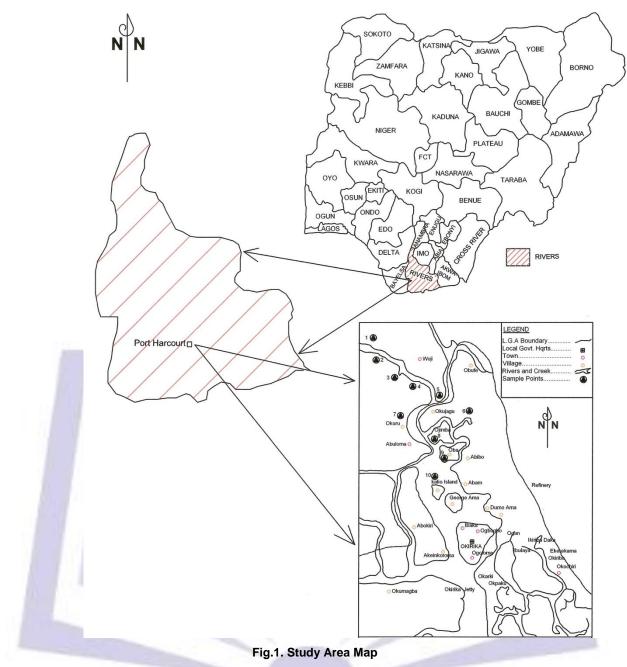
The Okpoka Creek is located between longitudes 7°00"E and 7°15"N and latitudes 4°28"E and 4°40"N. It is a tributary of the Upper Bonny Estuary in the Niger Delta, South South of Nigeria (Fig.1). The vegetation is dominated by nypa palm (*Nypa fructican*) and mangroves, red mangrove (*Rhizophora racemosa*) and white mangrove (*Avecennia nitida*). It passes through many communities namely: Oginigba, Woji, Azubiae, Okujagu, Okuru-ama, Abuloma, Ojimba, Oba, Kalio and Okrika. Many man's activities going on within and around this creek include dredging, fishing, boating, navigation, washing, disposal of excreta, bathing and swimming, to mention but a few. This aquatic body receives effluent discharges from the many industries (Snig, Far East paints, RIVOC, General-agro, Michelin tyres, Cocacola, Hallibuton, Schlumberger, Acorn, etc) and main abattoir house sited close to it.

Duration of samplings

Samples were collected following standard methods twice a month from ten stations for twenty-four months (May 2004 – April 2006) mostly during the low tides or ebb tides. The samplings covered the two conventional seasons (wet-April to September; dry-March to October) in Nigeria.

Sampling stations

A total of ten stations were chosen at least 500 metres apart along the main creek course. These stations were Station 1 (Oginigba), Station 2 (Trans-Amadi by Schlumberger), Station 3 (by main abbatoir house), Station 4 (Azubiae), Station 5 (Woji), Station 6 (Okujagu), Station 7 (Okuru-ama), Station 8 (Ojimba), Station 9 (Oba-ama) and Station 10 (Kalio-ama). There are many industries sited close to the river shore discharging effluents into the creek. Manual dredging of sand is constantly going on.



Field and laboratory measurements of relevant water physico-chemical parameters

Temperature

A mercury-in-glass thermometer (in Celsius) was used to measure temperature to the nearest whole number insitu.

рΗ

The pH values of the water were determined in-situ using pH-EC-TDS meter model Hanna HI 9812 (range 0.0-14.00pH). The pH was measured by dipping the electrode into the surface water (20cm below) for two minutes.

Transparency

The transparency of the water was measured by a Secchi disc (20cm diameter) as described by Boyd [12]. The average of the depth of disappearance and appearance was measured as the Secchi disc transparency of the water. It was measured in meter.

Dissolved oxygen (DO₂)

Samples for dissolved oxygen were taken using the BOD glass bottles (70 ml) [12, 21]. In the field, the dissolved oxygen was fixed using 5 drops each of Winklers' solutions A (Manganese sulfate solution) and B (alkaline iodine-azide



solution). In the laboratory, DO_2 and BOD_5 samples were analysed by titrimeteric method [12, 21]. The DO_2 was calculated by using the following formula

 $DO (mg/l) = 8 \times 1000 \times N \times v$

V

Where V = Volume of water sample used for titration

v = volume of sodium thiosulfate (titrant)

N = Normality of titrant

8 - It is a constant since 1ml of 0.025N sodium thiosulfate solution is equivalent to 0.2 mg oxygen.

Biological Oxygen Demand (BOD)

There were two methods employed, the direct and indirect methods. In the direct method samples were collected just like DO_2 samples but not fixed with Winklers' solutions A and B until after five days incubation in the dark laboratory condition (20°C). They were not diluted. The dilution method involved dilution of sample water with aerated distilled water [22]. Volume of aerated water decreased with increase in salinity (that is, decreased downstream). The dilution ratio is selected on the basis of expected range of BOD so that adequate nutrients and oxygen will be available during the incubation period [23].

BOD₅ was calculated thus for the direct method.

 $BOD_5 (mg/L) = D_1 - D_2$

Where, D1 Initial dissolved oxygen (mg/L) In the first sample (mg/L)

 D_2 = Dissolved oxygen (mg/l) in the second sample after 5 days of incubation

For the dilution method the following formula was used

 $BOD_5 = (Oxygen consumed) x dilution ratio$

Where dilution ratio = <u>Vol. of diluted sample</u>

Vol. of undiluted sample

Electrical conductivity (EC)

The electrical conductivity was determined in the laboratory using conductivity meter Horiba-U:10 μ multimeter. It was expressed as μ s/cm.

Turbidity

Turbidity of the water was measured using the same meter for conductivity. It was expressed as NTU (Nephelometric Turbidity Unit) [22].

Salinity

The salinity of the water was measured using the same meter for conductivity. It was expressed as part per thousand (ppt, ‰).

Total alkalinity

The titrimetric method using standard sulfuric acid and methyl orange indicator as described by Boyd [12] was used to determine the alkalinity of the water. The level of the alkalinity of the sample water was calculated by the formula:

Total alkalinity = (ml of titrant) (N) (50) (1000) (mg/L)

Sample volume in ml

ml of titrant = volume of acid (H₂So₄) used in titrating to methyl orange end point

N = Normality of acid used

Source: Boyd [12]

Chloride

The chloride of the sample water was measured using the argentometric method described by APHA [22]. 100ml of sample water was titrated with standard Silver Nitrate (AgNO₃) to a pinkish yellow end point with Potassium Chromate ($K_2Cr_2O_4$) as indicator. The following formula was used to calculate the chloride of the water.

[23]

[12]



Chloride (mg/L) =
$$(A - B) \times N \times 35, 450$$

ml sample

A = ml titration for sample

B = ml titration for blank

 $N = Normality of AgNO_3$ (Silver nitrate) [22]

Calcium hardness

Ethylenediamine tetraacetic acid disodium salt (EDTA) titrimetric method was used to determine the calcium content of the sample water [12, 22]. Sample water was titrated with EDTA solution to purple end point using murexide indicator. The below formula was used to calculate the calcium level.

Calcium hardness (mg/L) = (ml of EDTA) (M) (100.1)(1000)

as CaC0₃ Sample volume in ml

Total hardness

EDTA titrimetric method as described by Boyd (1981) was used to measure the total hardness of the sample water. Sample water was titrated with EDTA solution to black-blue end point using Eriochrome black indicator. The same formula for calcium was used.

Total hardness in mg/L as $CaCo_3 = (ml of EDTA) (M) (100.1)(1000)$

Sample volume in ml

[12]

Nitrate

Nitrate was determined by the Brucine method by APHA [22]. Spectrophotometer (spectronic 21D) was used to measure the nitrate at 410nm wavelength.

Sulphate (SO₄)

Sulphate determination was carried out by turbidimetric procedure [22]. This involved the use of spectrophotometer (Spectronic 21D). The concentration of sulphate (mg/l) was measured thus:

Sulphate = $mgSO_4 \times 1000$

Volume of sample used (ml)

Phosphate

Phosphate-in-water levels were determined by standard test [22]. It involved the use of spectrophotometer (Spectronic 21D). The concentration of phosphate (mg/l) was measured thus:

Phosphate = mgPO₄ x 1000

Volume of sample used (ml)

Ammonia

Ammonia concentrations in water samples were determined by the indophenol or phenate (Phenol-hypochlorite) method. It was spectrophotometrically measured at 630nm wavelength with spectronic 21D [22]. The concentration of total ammonia in the samples was computed from the equation:

C1/C2 = A1/A2

Where A_1 = the absorbance of the total ammonia-nitrogen standard

 A_2 = the absorbance of the sample

 C_1 = the concentration of the total ammonia-nitrogen standard.

 C_2 = the concentration of total ammonia-nitrogen in the sample [12]

Dissolved oxygen and biological oxygen demand

In the laboratory, DO_2 and BOD_5 samples were analysed by titrimeteric method [12, 21]. The DO_2 was calculated by using the following

 $DO (mg/l) = 8x 1000 \times N \times v$

V



Where V = Volume of water sample used for titration v = volume of sodium thiosulfate (titrant) N = Normality of titrant 8 - It is a constant since 1ml of 0.025N sodium thiosulfate solution is equivalent to 0.2mg oxygen. [21] BOD₅ was calculated thus for the direct method. $BOD_5 (mg/L) = D_1 - D_2$ Where D1 Initial dissolved oxygen (mg/l) In the first sample (mg/L) D_2 = Dissolved oxygen (mg/L) in the second sample after 5 days of incubation [12] For the dilution method the following formula was used $BOD_5 = (Oxygen consumed) x dilution ratio$ Where dilution ratio = Vol. of diluted sample Vol. of undiluted sample [23] Data analyses Data was analysed for analysis of variance (ANOVA), Duncan multiple range (DMR) and descriptive statistics using [24].

Results

Surface water physical parameters

The three measured surface water physical parameters were turbidity, transparency and temperature. Turbidity was higher during the wet season (4.68 ± 0.55 NTU) than during the dry season (2.31 ± 0.14 NTU) and seasonal variation was significant (P<0.01, DMR) (Fig.2). There was no significant seasonal variation of transparency (P>0.05). Mean wet season transparency was the same as mean dry season. However, dry season temperature was higher ($28.94\pm0.08^{\circ}C$) than wet season ($28.38\pm0.09^{\circ}C$) and seasonal variation was significant (P<0.001, DMR).

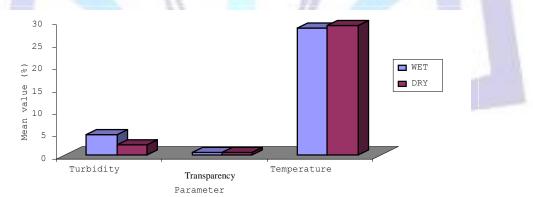


Fig.2. Variation of turbidity, transparency and temperature in relation to season in Okpoka Creek

Surface water chemical parameters

The measured chemical parameters include salinity, dissolved oxygen, biological oxygen demand, total organic carbon, total organic matter, pH, alkalinity, conductivity, total dissolved solids, chloride, calcium, magnesium and hardness. There were significant seasonal effects on salinity, conductivity, total dissolved solids, chloride and calcium (P<0.05, DMR).



Surface water salinity

Dry season salinity ($20.00 \pm 10.17\%$) was higher than wet season ($9.67 \pm 0.37\%$) and seasonal variation was significant (DMR) (Fig. 3).

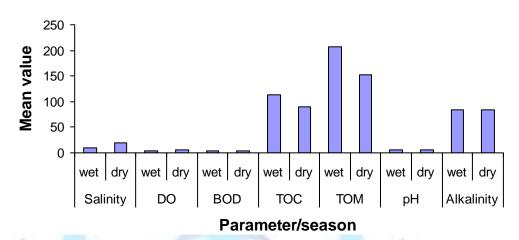


Fig. 3. Variation of surface water chemical parameters in relation to season in Okpoka Creek

Surface water dissolved oxygen (DO)

Dry season dissolved oxygen (5.14 \pm 0.16 mg/L) was higher than wet season dissolved oxygen (4.80 \pm 0.14 mg/L). Seasonal variation on dissolved oxygen was significant (DMR).

Surface water biological oxygen demand (BOD)

Wet season biological oxygen demand 3.11±0.12 mg/L) varied significantly with dry season biological oxygen demand (3.43±0.15 mg/L) at P>0.05.

Total organic carbon (TOC)

Wet season total organic carbon (114.16±4.39 mg/L) exceeded that of dry season (89.26±4.26 mg/L). Seasonal influence was highly significant (P>0.001, DMR).

Total organic matter (TOM)

Wet season had total organic matter value of 207.46±7.32 mg/L and dry season value of 153.27±7.35 mg/L. Seasonal variation of total organic matter was highly significant (P<0.001).

Surface water pH

Higher pH (6.78 \pm 0.04) was recorded for dry season and lower pH (6.63 \pm 0.03) for wet season. Seasonal variation was significant (P<0.001, DMR).

Alkalinity

Wet season alkalinity was 84.60±2.00 mg/L (higher) and dry season was 83.41±1.98 mg/L (lower). There was significant seasonal variation (P<0.05).

Surface water conductivity

Seasonal impact was not significant (P> 0.05). Wet season had mean conductivity of 15450±730µs/cm and dry season was 14610±760µs/cm (Fig. 4).

Total dissolved solids (TDS)

Total dissolved solids value (10500±440 mg/L) at wet season was higher than total dissolved

solids (10190±530 mg/L) at dry season. Seasonal impact was not significant P>0.05).

Chloride

Dry season chloride concentration (17723.14±652.99 mg/L) was higher than that of wet season

chloride concentration (17698.17±867.49 mg/L) There was no seasonal influence on chloride

(P>0.05).



Calcium

Dry season calcium level (898.81±38.25 mg/L) was higher than that of wet season level (856.77±32.81 mg/L). Seasonal change of calcium were not significant (P>0.05).

Magnesium

Dry season effect on magnesium concentration (3924.80±360.40 mg/L) was higher than wet season concentration of 2587.44±148.29 mg/L. Season had a high significant influence on magnesium.

Hardness

Wet season hardness value was 3457.09±161.78 mg/L and dry season was 4539.84±243.81 mg/L.

Seasonal fluctuation was highly significant (P<0.001, DMR).

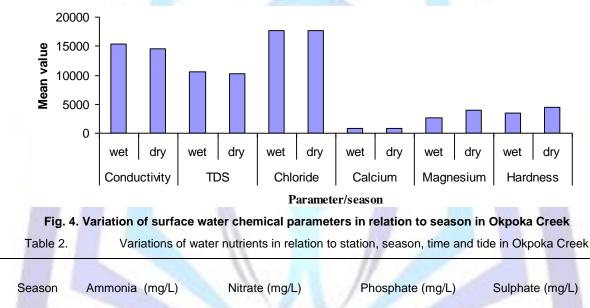
Nutrients of surface water from Okpoka Creek

Ammonia

Dry season had higher ammonia level (0.18±0.01 mg/L) than the wet season (0.16±0.01 mg/L) (Table 2).

Nitrate

Wet season nitrate was 0.71 ± 0.03 mg/L and dry season was 0.56 ± 0.03 mg/L. Seasonal fluctuation was highly significant (P<0.001, DMR).



			110	
Wet	0.16 ± 0.01 ^a	0.71 ± 0.03^{a}	0.67 ± 0.07^{a}	661.68 ± 51.57 ^a
Dry	0.18 ±0.01 ^a	0.56 ± 0.03^{b}	0.73 ± 0.06^{a}	441.49 ± 20.81^{b}

Means with the same letter in the same column are not significantly different (P>0.05)

Phosphate

Dry season phosphate (0.73±0.06 mg/L) was higher than wet season (0.67±0.07 mg/L).

Sulphate

Seasonal variations of sulphate were highly significant (P<0.001). Wet season sulphate level (661.68 ± 51.57 mg/L) was higher than that of dry season (441.49 ± 20.81 mg/L).

Relationships between surface water physical parameters and chemistry

Transparency had low negative correlation with turbidity (-0.058). Relationship was not significant (Table 3). Temperature exhibited low negative correlation with turbidity (-0.08511) and low positive correlation with transparency (0.164). Relationship between temperature and turbidity was not significant but significant for temperature and transparency



	Tur b.	Tra ns.	Te mp.	то С	TO M	Mag nesi um	DO	Chl orid e	Alk alini ty	BO D	Sali nity	Har dne ss	Cal ciu m	Con ducti vity	TDS	рН
Turbi dity	1.00 000															
Trans paren cy	- 0.05 800 ns	1.00 000														
Temp eratu re	- 0.08 511 ^{ns}	0.16 400 ***	1.00 000													
тос	0.00 176 ns	0.01 990 ns	0.02 772 ns	1.00 000												
ТОМ	0.00 808 ns	0.01 170 ns	0.02 278 ns	0.99 443 ***	1.0 000 0	1										
Magn esiu m	- 0.10 467 *	0.02 285 ns	0.06 425 ns	- 0.15 380 **	- 0.1 494 5**	1.00 000										
DO	0.06 163 ns	- 0.03 098 ns	- 0.05 998 ns	- 0.11 973 *	- 0.1 206 3**	0.04 090 ns	1.00 000									
Chlor ide	0.01 699 ns	- 0.00 419 ns	0.21 695 ***	- 0.14 128 **	- 0.1 398 8**	0.00 411 ns	0.19 931 ***	1.00 000								
Alkali nity	0.01 932 ns	0.07 895 ns	0.16 508 ***	0.09 133 ns	0.0 925 0 ^{ns}	- 0.06 526 ns	- 0.10 667 *	0.12 865 **	1.00 000							
BOD	0.02 940 ns	- 0.10 540 *	0.02 868 ns	- 0.09 289 ns	- 0.0 997 9*	0.07 544 ns	0.41 494 ***	0.14 913 **	0.02 185 ns	1.00 000						
Salini ty	- 0.02 390 ns	0.20 664 ***	- 0.50 604 ***	- 0.03 142 ns	- 0.0 278 0 ^{ns}	0.00 677 ns	0.10 746 *	0.26 842 ***	0.30 697 ***	- 0.00 537 ns	1.00 000					
Hard ness	- 0.17 563 ***	0.06 615 ns	0.12 332 ***	- 0.14 468 **	- 0.1 401 6**	0.88 554* **	0.02 735 ns	0.02 687 ns	0.07 167 ns	0.07 967 ns	0.11 535 *	1.00 000				
Calci um	- 0.14 894 **	0.10 755 *	0.32 081 ***	- 0.04 806 ns	0.0 461 3 ^{ns}	- 0.25 704* **	- 0.00 561 _{ns}	0.08 249 ns	0.27 044 ***	0.00 550 ns	0.23 837 ***	0.19 454 ***	1.00 000			
Cond uctivit y	0.02 591 ns	0.16 718 ***	0.37 201 ***	0.01 182 ns	0.0 143 9 ^{ns}	- 0.04 933 ns	0.08 123 ns	0.12 698 **	0.14 316 ***	- 0.14 968 **	0.71 198 ***	0.02 958 ns	0.17 296 ***	1.000 00		

Table 3. Correlation matrix between surface water physical and chemical parameters



TDS	0.02 630 ns	0.19 712 ***	0.39 736 ***	0.02 488 ns	0.0 253 5 ^{ns}	- 0.07 443 _{ns}	0.10 494 *	0.13 505 **	0.16 335 ***	- 0.16 145 ***	0.78 112 ***	0.01 563 ns	0.19 858 ***	0.917 28***	1.00 000	
рН	- 0.11 169 *	0.06 286 ns	0.30 235 ***	- 0.01 243 ns	- 0.0 086 7 ^{ns}	0.02 924 ns	0.11 544 *	0.22 527 ***	0.28 587 ***	- 0.05 208 ns	0.37 919 ***	0.13 977 **	0.22 451 ***	0.225 34***	0.25 476 ***	1.0 00 00

- * Significant at P<0.05
- ** Significant at P<0.01
- *** Significant at P<0.001
- ns Not Significant

(P<0.001). Temperature exhibited negative correlation with dissolved oxygen (-0.060), biological organic demand (-0.0291), salinity (-0.506), total organic carbon (-0.0277) and total organic matter (-0.0278) but relationships were insignificant except salinity at P<0.001. Temperature had positive correlation with pH (0.302), total dissolved solid (0.397), calcium (0.321), hardness (0.213), alkalinity (0.165), chloride (0.217), magnesium (0.064) and conductivity (0.372). The relationships were significant with all these parameters (P<0.001) except magnesium (P>0.05).

Turbidity showed positive correlation with total organic carbon (0.002), total organic matter (0.008), dissolved oxygen (0.062), chloride (0.017), alkalinity (0.019), biological oxygen demand (0.003), conductivity (0.026) and total dissolved solid (0.026). Its relationships with these parameters were not significant (P>0.05). However, turbidity had negative correlations with magnesium (-0.105), salinity (-0.024), hardness (-0.176), calcium (-0.149) and pH (-0.112). Significant relationships were found with all parameters (P<0.05, 0.01, 0.001) except salinity (>0.05). Transparency correlated negatively with the following parameters; dissolved oxygen (-0.031), chloride (-0.004), biological oxygen demand (-0.105) but relationships were insignificant except biological oxygen demand (P<0.05). It showed positive relationship with other parameters and it is significant for salinity, calcium, conductivity and total dissolved solid (P<0.05, 0.001).

Dissolved oxygen had negative correlations with total organic carbon (-0.120), total organic matter (-0.120), alkalinity (-0.107) and calcium (-0.006). Correlations were significant (P<0.05) except with calcium (P>0.05). Dissolved oxygen exhibited positive relationships with magnesium (0.041), Chloride (0.199), biological oxygen demand (0.415), salinity (0.107), hardness (0.027), conductivity (0.081), total dissolved solid (0.105) and pH (0.115) and correlations were significant (P<0.05) except magnesium, hardness, calcium and conductivity (P>0.05). Total organic carbon correlated positively with total organic matter (0.994), alkalinity (0.091), conductivity (0.012) and total dissolved solid (0.025). However, total organic carbon was negatively correlated with magnesium (-0.154), dissolved oxygen (-0.120), chloride (-0.141), biological oxygen demand (-0.093), salinity (0.031), hardness (-0.145), calcium (-0.048) and pH (-0.012). Total dissolved solid showed positive correlations with total organic carbon (0.025), total organic matter (0.025), dissolved oxygen (0.105), chloride (0.135), alkalinity (0.163), salinity (0.781), hardness (0.016), calcium (0.199), conductivity (0.917) and pH (0.255) but negative correlations with magnesium (-0.074), biological oxygen demand (-0.162). pH had positive correlations with magnesium (-0.074), biological oxygen demand (-0.162). pH had positive correlations with magnesium (-0.074), biological oxygen demand (-0.162). pH had positive correlations with magnesium (-0.074), biological oxygen demand (-0.162). pH had positive correlations with magnesium (0.225), alkalinity (0.286), salinity (0.379), hardness (0.140), calcium (0.225), conductivity (0.2253) and total dissolved solid (0.255) but correlated negatively with total organic carbon (-0.012), total organic matter (-0.009) and biological oxygen demand (-0.052).

Discussion

Surface water physico-chemical parameters

Turbidity is a vital water quality parameter due to sediment loading and the concomitant effect it will have on the light available for phytoplankton and epiphyton growths as well as other aquatic life [10]. There has been no standard range of values assigned to turbidity of natural waters [4]. Turbidity controls the dynamic of phytoplankton [25]. The record of this present study did not exceed the level found in natural water bodies. Boyd [12] reported that turbidity in natural waters seldom exceeds 20,000 mg/L and even muddy waters usually have less than 2000 mg/L. Also, the observed turbidity level in this study agrees with the range of 2 NTU to 47 NTU recorded by Asonye *et al.* [26] for the turbidity of Nigerian rivers, streams and waterways. The observed turbidity might be attributed to plankton. Swann [5] reported that plankton is one of the causes of turbidity. The recorded high rainy season turbidity was probably due to the high natural erosion and run offs from the surroundings. This might be responsible for the low algae abundance in the wet season. It has been reported that high turbidity reduces photosynthesis of phytoplankton, submerged and rooted aquatic vegetation which results to reduce plant growths and in turn suppress fish productivity.

Naturally, transparency is inversely proportional to turbidity. This was evident by the negative correlation between transparency and turbidity in this study. Chrzanowski and Grover [27, 28] and Roelke *et al.* [29] revealed that balance of light energy is assumed to regulate algae ecosystem structure. The present study agrees with transparency values in Ajao [30] of 0.3 m to 1.9 m in Lagos Lagoon and, Sikoki and Zabbey [31] of 0.6 m-1.5 m in Imo River, Nigeria. The insignificant seasonal variation could be attributed to shallow water depth and brackish characteristic of the creek water. The same value of transparency recorded for both dry and wet season contradicts the observations of Clarke [32] in Ologe lagoon in



Lagos State of high transparency in dry season and low in wet season. Transparency reduces with depth as temperature decreases with depth. This is shown in the positive correlation transparency had with temperature in this study.

In estuaries, temperatures are less significant than variations in salinity and types of substratum in determining distribution patterns and relative abundance of species [33. 34]. The observed temperature demonstrated narrow amplitude of variation. It showed the characteristic of the tropical environment and falls within the acceptable ranges [9, 31, 35]. The seasonal variations in this study were in consistent with tropical environments; in dry season, temperature is usually higher than in wet season. This might be attributed to the longer photoperiod and high intensity of the sun. Temperature controls the seasonal variations of phytoplankton and epiphyton [25, 36, 37, 38].

Salinity affects the distribution patterns and relative abundance of organisms [6, 37, 39]. Salinity variations that could be expected are due to the distribution of rainfall. The salinity of the coastal water is usually in the range of 34.40 % to 34.50 % although lower values do occur [4]. The present study record of salinity is within this acceptable range for coastal waters. It is also within the range reported by Chindah and Nduaguibe [7] of $11.5\pm1.8 \%$ to $20.3\pm3.0 \%$ for Lower Bonny River, Nweke [8] of $12.25\pm1.47 \%$ to $18.07\pm1.17 \%$ for Upper Bonny Estuary, Chindah [6] of 0.0 % to 10.50 % for New Calabar River and Hart and Zabbey [9] of 0.0 % to 12.70 % for Woji Creek. The recorded higher salinity in the dry season could be as a result of high sunlight intensity that increased the water evaporation rate. Clarke ([32] reported higher salinities in the dry season than in the wet season.

Conductivity is the ions capacity of the water and how these ions are be conducted or distributed. This ability depends on the presence of ions and on their total concentration, mobility and valence [22].Carbonates and other charged particles increased the conductivity of a water body. It naturally increases towards the sea like salinity. The observed conductivity of this creek might be due to its brackish nature. The insignificant higher conductivity in wet season could be due to the large volume of water from the sea.

The seasonal variation was significant with higher pH in the dry season. This could be attributed to the increase rate of photosynthesis by the phytoplankton, epiphyton and other aquatic plants. Eyesink and Solomon [40] reported that the uptake of carbon dioxide by algae for photosynthesis and carbon dioxide exchanged between the surface water and atmosphere are responsible for pH increase during sunshine. Val Saraji *et al.* [41] also recorded high pH on days of intense photosynthetic activity. However, studies by Nweke [8], Ebere [42] and Clarke [32] confirmed higher pH in dry season than in wet season. The more acidic water in wet season could be due to the combined effects of reduced sunshine and the inflow of humic substances and organic matter brought in by the rain during runoff. Also, low temperature in wet season might be the reason for the low pH. Temperature correlated positively with pH and the relationship was highly significant.

Dissolved oxygen is probably the most universal applied water quality criterion. The observed dissolved oxygen concentrations were within the acceptable range. IJC [14] recommended that dissolved oxygen concentration above 4 mg/L is good while below 4mg/l is detrimental to the aquatic life. Also, it is within the concentration expected to be found in natural surface water. The recorded desirable of dissolved oxygen might be traced to tide. Tide helps to circulate the atmospheric air containing oxygen within the water column. McNeely *et al.* [4] reported that natural surface water has dissolved oxygen less than 10mg/l. The observed higher dissolved oxygen in dry season might be attributed to the increased photosynthetic activities of algae and the recorded temperature was moderate for photosynthesis of aquatic plants. The lowered dissolved oxygen in wet season might be explained by the reduced photoperiod and photosynthetic activities of algae. The seasonal ranges of dissolved oxygen were still within the acceptable limit for aquatic life.

Biological oxygen demand is of vital importance in pollution monitoring. The recorded biological oxygen demand is within the acceptable range for aquatic environments. Waters with biological oxygen demand levels less than 4mg/l are regarded clean and those with levels greater than 10 mg/L are considered as polluted as they contain large amounts of degradable organic material [4]. However, the present biological oxygen demand range was less than that reported by Edoghotu [13] of 1.2 mg/L to 36.7 mg/L for Okpoka creek and Hart and Zabbey [9] of 0.2 mg/L to 98.9 mg/L for Woji creek. This indicates that the biological oxygen demand load in this present study did not pose a threat to the aquatic environment. The higher biological oxygen demand level in dry season could be the effect of higher temperature, salinity and putrefaction of substances deposited in the river from the surroundings.

The total dissolved solid is an index of the amount of dissolved substances from anthropogenic sources in a water body. The presence of such solutes alters the physical and chemical properties of water. The observed total dissolved solid load is higher than the recommended 1,001-10,000 mg/L for brackish water [4]. This is an indication of organic pollution from anthropogenic sources. The present total dissolved solid range is in accordance with that reported by Edoghotu [13] of 14 to 15000 ppm in Okpoka Creek. The higher total dissolved organic solid concentration at wet season might be attributed to high surface runoff, overland flow as well as higher discharge of organic wastes into the river.

The total organic carbon contains the dissolved and particulate organic carbon. The recorded range of total organic carbon concentrations is above the 1 to 30 mg/L for natural water. Higher levels in water indicate pollution and results from anthropogenic inputs [43] Water with less than 3.0 mg/L total organic carbon is said to be relatively clean [4]. The high runoffs from the surrounding and increased discharge of domestic and industrial wastes might be attributed to the higher total organic carbon level in the wet season than in dry season.

Alkalinity is the buffering (alkaline) capacity of the water. The range of alkalinity observed is characteristic of estuarine environment. Waters with high alkalinity are undesirable because of the associated excessive hardness or high concentrations of sodium salts. The reported alkalinity in this present study is within the acceptable range for natural



surface water. Department of National Health and Welfare [44] recommended a acceptable range of 30 mg/L to 500mg/l for natural waters. For the aquatic environment to be protected, guidelines stipulate that alkalinity must be maintained at natural background levels with no sudden variation [45]. The water of this creek is desirable for aquatic life and industrial uses as it has alkalinity above 30mg/l. The results of alkalinity in this study are higher than the alkalinity levels reported by Obunwo *et al.* [17] for five streams in the Niger Delta. Generally, brackish water alkalinity is greater than freshwater alkalinity. The present observation of alkalinity agrees with those studies on estuarine environment [8, 42, 46, 47]. The higher level of alkalinity in wet season might probably be due to the increased runoffs from the surroundings. This observation contradicts that of Chindah and Braide [47] of higher values in the Niger Delta. However, the observed alkalinity in this creek could be linked to the natural carbonates, bicarbonates, hydroxide, borates, silicates, phosphates and organic substance concentrations.

The mean chloride concentration in Okpoka creek agrees with the acceptable concentration of less than 19,000 mg/L in seawater though higher levels may occur [4]. The present study range of chloride is in accordance with those recorded by Edet [49] of 9.500 mg/L to 20,000 mg/L in Okrika Creek, Ebere [42] of 6,062 mg/L to 20, 979.16 mg/L also in Okrika Creek. Also, Pillard *et al.* [48] reported mean values of 20,000 mg/L and 19,000 mg/L respectively for Amococadiz oil spill in United States of America. The chloride concentrations increased downstream suggest the influence of the seawater on chloride level. This is evident from the highly significant positive correlation chloride had with salinity and conductivity in this study. The lower mean chloride values recorded in the wet season explain the dilution effect of increased municipal runoffs during the rains. This observation agrees with Chindah and Braide [47] and Ebere [42] reports of low chloride in the rainy season.

High concentrations of calcium in water are relatively harmless to all organisms and may reduce toxicity of certain chemical compounds to fish. The observed calcium concentration in this study is higher than the expected concentrations in seawater, usually 400mg/l [4]. The varied calcium concentrations along the stations might be attributed to different degree of leaching from the surrounding soils. The high amounts of human faeces and animals wastes from the waterfront dwellers and abattoir respectively could account for the higher calcium concentrations in this creek. Also, the industrial wastes from the numerous companies located around and far from the creek might equally be responsible for these calcium levels. The calcium concentrations in this creek might further be attributed to the high salinity and conductivity concentrations. Calcium had significant positive relationships with salinity and conductivity. The higher values in the dry season are expected due to the higher salinity concentrations in the dry season.

The mean magnesium concentration in this study exceeded that have been recorded in seawater (1000 mg/L). The seasonal variation with higher values in dry season could be linked with higher salinity concentrations at these periods. Salinity had positive relationship with magnesium in this study. Hardness of water from this creek is high based on the calcium and magnesium concentrations. The range of total hardness observed in this study is characteristic of brackish environment. Edet [49] recorded a hardness range of 95 mg/L to 4,000 mg/L and 95 mg/L to 3,500 mg/L for Okrika Creek mixed with refinery effluents and unmixed with effluents respectively. Dambo [46] observed a range of total hardness from 3.395.15 mg/L to 4710.23 mg/L for Lower Bonny Estuary. However, Ebere [42] reported a range of 653.15 mg/L to 3281.78 mg/L for Okrika Creek of the Central Bonny Estuary. The present observation of water hardness is in agreement with these workers reports. Water with hardness less than 120 mg/L calcium carbonate can be deemed desirable for most uses, but only if hardness exceeds 500 mg/L can be labelled undesirable for both industrial and domestic uses [44]. The possible reasons for seasonal variations of calcium and magnesium might be applicable for hardness concentrations in this creek.

Nutrients of surface water from Okpoka Creek

The creek is rich in organic and biogenic nutrients. This observation is in accordance with Adeniyi [50] on rivers and creek of the Bonny Estuary. Nutrients availability especially phosphorus structures the algae assemblage [25, 27, 37, 29, 51, 52]. Ammonia contributes to the fertility of water since nitrogen is an essential plant nutrient. It is also one of the most important pollutants in aquatic environment because of its relative high toxic nature and its ubiquity in surface water systems [53]. Ammonia enters natural water systems from several sources including industrial wastes, sewage effluents, coal gasification and liquefaction conversion process plants and agricultural discharge including feedlot runoff.

The study ammonia exceeded the concentration of less than 0.1 mg/l found in natural waters [4]. This possibly indicates anthropogenic and domestic inputs. The mean ammonia concentration is also higher than the level of 0.02 mg/L unionized ammonia (NH₃) required for the protection of aquatic life [45]. Fish cannot tolerate large quantities of ammonia since it reduces the oxygen-carrying capacity of the blood and thus the fish may suffocate (Weis *et al.*, 1989). The recorded range of ammonia in this creek is within the range of 0.093 mg/L to 2.65 mg/L reported by Nweke [8], Ebere [42], Chindah and Nduaguide [7] and Obunwo *et al.* [17] in the Niger Delta. The seasonal variations of ammonia concentration were insignificant suggesting similar anthropogenic and natural inputs.

The observed mean nitrate is below the more than 100 mg/L expected to be found in natural surface water. Nitrogen is most often limiting in marine systems (Creswell *et al.*, 2001). The reasons being that molybdenum, phosphorus or energy constraint can be limiting to nitrogen fixers, which makes for lower nitrogen fixation [54]. There is also significantly higher denitrification in marine sediments.

The higher nitrate concentrations in wet season might be attributed to high anthropogenic inputs. Ebere [42] also reported high nitrates levels in rainy seasons with lower levels in dry season. The decreased value in the dry seasons might be explained by the high uptake of nitrate by phytoplankton and epiphyton during photosynthesis. Photosynthetic



activities are usually higher in dry season. The low pH generally makes nitrate available to primary producers. This might be ascribed to the recorded nitrate level in the creek. The range of nitrate recorded in this study was below the statutory limit of 25 –50 mg/L given by the EEC [55] and 20 mg/L USEPA [56]. Nitrate does not pose a health threat but it is readily reduced to nitrite by the enzyme Nitrate reductase which is widely distributed and abundant in both plants and micro-organisms [57]. Nitrite causes cancer and methaemoglobinaemia (blue-baby syndrome) in human beings [4].

The recorded phosphate concentrations in this study were higher than the acceptable limit of 0.10 g/L in flowing waters recommended by USGS [3]. This observation agrees with that of 0.43 to 3.52 mg/L of Chindah and Nduaguibe [7]. Falomo [58] reported a mean phosphate of 1.4 mg/L Okrika Creek central Bonny Estuary while Ebere [42] recorded 0.176 mg/L to 0.402 mg/L for Okrika Creek. However, natural inputs from decomposition of organic matter might be a contributor to the phosphate concentrations in this creek. The higher phosphate concentration in dry season is in accordance with the observations of Chindah and Braide [47]. This might be attributed to the higher biomass of phytoplankton and eiphyton in the dry season. Phosphorus stimulates algae growth.

The high sulphate level observed in this study is characteristic of brackish water. Ebere [42] reported that marine waters are known to contain relatively high concentrations of sulphate. McNeely *et al.* [4] observed 2650 mg/L sulphate in seawater. The recorded sulphate is below the sulphate values in seawater, that is, within the acceptable levels. The observed levels were probably from oxidation of organic materials and burning of fossil fuel, and from industrial effluents due to high organic matter in the creek. Also, it could be a result of wet and dry precipitation from burning of fossil fuels. When organic materials are oxidized, sulphates are released into the water. This might be responsible for the higher sulphate level in wet season than in dry season. The low dissolved oxygen concentration and sulphate level in the wet season explains this observation. Oxidation process used up oxygen thus the low dissolved oxygen concentration and sulphate level in the wet season.

Conclusion

Season (wet and dry) has varied effects on the physico-chemical characteristics of Okpoka Creek. Turbidity and temperature showed significant seasonal variations while transparency demonstrated insignificant seasonal differences. Dry season dissolved oxygen and biological oxygen demand were significantly higher than wet season values. TOC, phosphate and ammonia values at both seasons were above FEPA and USEPA permissible levels for natural aquatic environment. Nitrate, phosphate and sulphate had significant seasonal variations. The presence of high levels of TOC and phosphate especially at wet season indicates organic pollution and stress in this creek.

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