

Physico-Chemistry of Surface Water Impacted by Crude Oil Spills in Bodo/Bonny Rivers, Nigeria

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Authors' contributions

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

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ABSTRACT

The surface water resources of Bodo/Bonny communities in Rivers State suffers regular pollution of its ecosystem due to increase in crude oil exploration, refining and activities of other industrial establishments operating within the coastal areas of the Ogoniland of the Niger Delta region of Nigeria. This have resulted in the wide scale contamination of most of its creeks, swamps and rivers with hydrocarbons and dispersant products resulting in the alteration of the ecological integrity of fragile aquatic systems, bioaccumulation of chemical contaminants by zoobenthos, sediment enrichment, and smothering or asphyxiation of the organisms in water by oil coating, thereby causing death. These conditions have resulted in serious threat to public health and the ecosystems. The study was aimed at determining the physico-chemical characteristics of Bodo/Bonny coastal waters impacted by crude oil spills and their effect on the marine ecosystems. Surface water was collected from 5 stations (BBW1, BBW2, BBW3, BBW4 and LFPW5) with LFPW5 serving as control. Physico-chemical parameters were investigated following standard methods. The results of the physicochemical characteristics of the various sampling points in the dry season showed that pH, TDS and Electrical conductivity values showed statistically significant

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differences at $P < 0.005$. pH was slightly acidic in all sampling locations except for the Link fish pond, the values ranged from 6.20–6.40 which was below DPR Limit of 6.5-8.5 for potable water, TDS recorded 43175–57075 mg/L above DPR permissible Limit of 5000mg/L. Electrical Conductivity (EC) values ranged from 54050 -57050 $\mu\text{S}/\text{cm}$. The Dissolved Oxygen, Biological Oxygen Demand, Turbidity, Chloride recorded in this study varied significantly at $P < 0.05$. Results of the physicochemical parameters of surface water in the wet season fell within the standard limits except for the conductivity that was above the permissible limits. Comparatively the mean pH value of surface river water with Linked fish pond water which served as the control revealed that the Link fish pond water had the highest pH value of 7.9 than the surface river water samples with a pH of 6.4, TDS (60,200 mg/L), Electrical Conductivity (EC) ($\mu\text{S}/\text{cm}^3$) followed a similar pattern with the mean EC value of 55,800 mg/L as against 750mg/L for the Link Fish pond water. Temperature recorded 31⁰C as against 30⁰C for the link fish pond while the Salinity (mg/L) of the surface river water was 31.63 mg/L. Dissolved Oxygen was 2.3 mg/L, Biochemical Oxygen Demand values for the surface river water was 0.49 mg/L while the Link fish pond water had 0.3mg/L. These values obtained in this study shows that the spilled oil in the water could impact on species abundance and biomass by depleting and depriving the fishes from available O₂ for survival thus resulting in asphyxiation.

Keywords: Surface water; oil spills; physico-chemical characteristics; pollution; bodo/bonny rivers; aquatic life.

1. INTRODUCTION

Rivers present a continuously renewable physical resource used for domestic, industrial, and agricultural purposes, as means for waste disposal, transportation, getting food resources, and recreational activities [1]. Rivers are the most important resource for man and socio-economic development because of its uses as sources of drinking water supply, irrigation of agricultural lands, industrial and municipal water supplies, navigation, fishing, boating and body-contact recreation as well as aesthetic value [2]. Despite the fact that the oil sector has contributed immensely to the development of the nation, it has also caused a lot of catastrophic damage to the environment and its resources. Oil pillage has a major impact on the ecosystem into which it is released. Immense tracts of the mangrove forests, which are especially susceptible to oil have been destroyed. An estimated 5 – 10% of Nigeria's mangrove ecosystem has been wiped out due to oil exploration [3]. The marine environment is affected by a number of human induced stressors and the degradation can be seen not only in coastal areas but has spread to very remote areas both in the deep seas and in polar areas. However, recent incidents show that marine oil spills are unpredictable events that may cause significant damage not only to the marine ecosystems and wildlife, but the coastal communities at large. The United Nations Development Programme estimates that 6,178 oil spills occurred in Ogoniland between 1976 and 2011 [4]. Once oil has contaminated

wetlands such as marshes and mangroves, it is often very difficult to remove without causing further damage to these environments [5-7], the resulted unmitigated pollution of land, air and water exposes the populace to miasma of health hazards [8]. This has resulted in a remarkable increase in the degradation of soil, fresh water, lakes, creeks, estuaries and the general ecology of the oil rich Niger Delta area [3]. The behavior of the petroleum hydrocarbons upon entering the fresh water system or marine ecosystems are intimately linked with the chemical type of contaminant, the mode of entry and physical characteristic of the receiving fresh water system [9,3]. The behavior of bulk oil spilled into rapidly flowing water will be different from one spilled into still water. Non-volatile components may restrict the evaporation of volatile ones by the formation of a physical barrier, this in turn may favour dissolution as the route of loss and hence encourage greater entry into the water than to the atmosphere.

Oil spillage is also a major threat to surface and ground water resources of the affected areas through infiltration and seepage, thereby reducing the quality of the affected resources. Oil spills on land are more readily containable but is also deadly due to infiltration which could percolate the underlying soil layers and thereby contaminate the groundwater [10]. According to UNEP [11], the impact of oil spillage in the Niger Delta can cause high mortality of aquatic animals, impairment of human health, loss of biodiversity in breeding grounds, vegetation

hazards, loss of potable and industrial water resources, reduction in fishing and farming activities, poverty and rural unemployment. However, it has been reported that oil pollution in coastal ecosystems by human mediated activities can adversely alter the ecological integrity of fragile aquatic systems, resulting in bioaccumulation of chemical contaminants by zoobenthos [12-15], sediment enrichment [16], and impact on species abundance and biomass [13]. Other causes of ecological change aside from oil pollution, may also include human disturbance, physical habitat alteration, other pollution, fishing, alteration of predation patterns, weather and climate.

However, the physicochemical parameters of an aquatic body not only reflect the type and diversity of aquatic biota but also the water quality and pollution. Pollution cause changes in the physicochemical parameters of water bodies such as pH, BOD, DO, COD, nitrate, phosphates etc and these constituents indicates about the health of a river body. These parameters has become of public interest in the world because not only in developed countries but also in developing nations who suffer the impact of pollution due to disordered economic growth associated with exploration of virgin natural resources [17]. In Nigeria, several studies have been documented on the physico-chemical, biological, and toxicological aspects of water bodies and sediments of rivers [18]. However, most physiochemical properties of sediment and water such as pH, conductivity, total organic carbon, total organic matter, etc. determines the level or the extent to which heavy metals can be retained in the media. These properties influence in the adsorption, absorption, desorption, solubility, movement and toxicological properties of the metals in such columns [19, 20]. Hence, the study of heavy metals in any media or space can better be done in association with the physicochemical qualities of that environment. Therefore, the study was aimed at determining the physico-chemical characteristics of Bodo/Bonny coastal waters impacted by crude oil spills from four (4) sampling stations and one control station and then making a comparison with previous studies.

2. MATERIALS AND METHODS

2.1 Sampling Location

Samples for this study were collected from four different location of surface water in Bodo/Bonny River in Gokana Local Government Area of

Rivers State. Control samples were taken from link a fish pond located away from the location where there was no record of crude oil pollution within the river environment. The sampling stations were chosen based on an experimental scheme design following ecological settings and human activities in the area. Bodo Creek is characterized by low tidal energy current, making its swamps and canals exceptional breeding grounds for a vast variety of fish and shellfish. It also provides an excellent habitat for periwinkles (*Tympanotonus fuscatus*; *Tympanotonus fuscatus varradula*; *Pachymelania aurita*; *Pachymelania fusca*) [21]. The original diversity of shellfish found in the Creek included bloody cockle (*Senilia senillis*), oyster (*Crassostrea gasar*), swimming crab (*Callinectis amnicola*), razor clam (*Tagelus adansonii*), land crab (*Cardisoma amatum*), and mangrove purple hairy crab (*Goniopsis pelli*) [21]. The Bodo/Bonny River meet several socio-economic needs including aquaculture, fishing, sand dredging and drainage of the various towns and villages bordering it. Fig. 1 is a map showing sampling points.

2.2 Sample Collection

Samples used for this study are surface water, and sediments from the river and Fish Link pond as control. Sampling was done between February 2019 and August 2020, covering both wet and dry seasons, at an interval of once a month. Sample were collected in duplicates from each location, monthly. Collection of the samples was done in the hours when tide in the river was at its peak in duplicates.

2.3 Surface Water

Surface water samples were collected using the method of Adesemoye *et al* [22]. Sterile 1.5 Litre bottles were used to aseptically collect the surface water. The samples were collected at four different points (about 50m apart) in the direction of water flow while the fifth sample served as control from link fish pond. To collect the surface water, base of the sterilized sample container was held with one hand, plunged about 30 cm below the water surface with the mouth of the sample container positioned in an opposite direction to water flow [23]. About 500 ml of the sample collected from each station were pooled together to get a composite sample. After collection, the samples were placed in a cooler containing ice blocks and transported immediately to the laboratory for analysis.

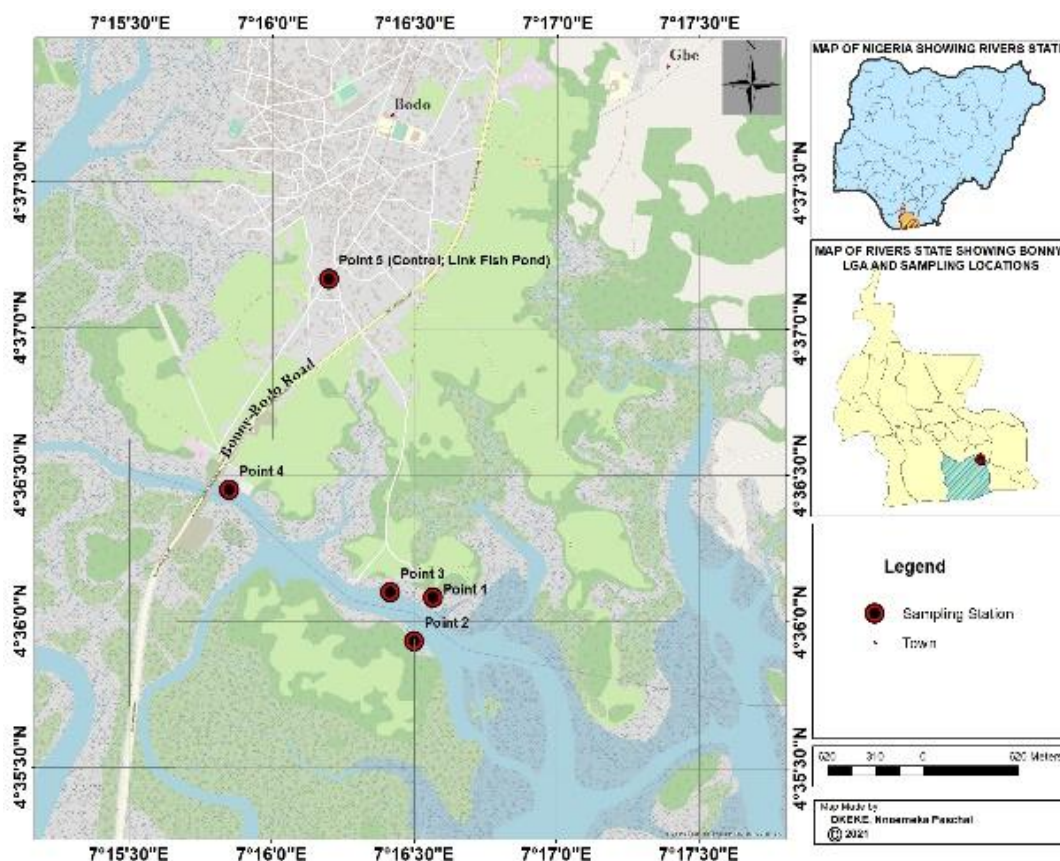


Fig. 1. Map indicating sampling stations in Bodo/Bonny River

2.3.1 Physiochemical characteristics of surface water samples

Physiochemical parameters such as Temperature, pH, Electrical conductivity, Turbidity, Salinity, Chloride, Total Dissolved Solids (TDS), Dissolved Oxygen (DO), and Biological Oxygen Demand (BOD), of the water samples were determined using standard methods [23].

2.3.2 Determination of pH

The pH of the surface water samples was determined using the (Hanna HI) pH meter (Model 8424, USA). Measurement of pH was carried out as described by (APHA, 2005). Using standard buffer solutions of pH 7, 4, 10, the pH meter was calibrated. This was done by pouring small amount of the buffer, pH 7 into a clean beaker and a magnetic stirrer bar dropped into it and the beaker placed on magnetic stirrer to get a homogenous mixture. The pH meter electrode was lowered into the beaker, so that the tip

became immersed in the buffer solution and the magnetic stirrer started. The meter was adjusted to take readings of the buffer. Electrode was removed, washed using distilled water and then dried. Same process was repeated using pH 4 and 10. After calibration of the meter, the pH of the sample was analyzed using the same procedure as stated above and the meter results recorded for the samples.

2.3.3 Determination of turbidity

The turbidity of the surface water was measured using Shimadzu UV-160A double beam UV recording Spectrophotometer at the wavelength of 400nm. The machine is a 20 parameter programmed and calibrated spectrophotometer. The program number four (4) for turbidity was entered and the meter was automatically ready for turbidity measurement at 400nm. Following standardization with distilled water, the measurement for the samples was made and the concentration read off from the in-built calibration curve which is displayed on the screen.

2.4 Determination of Total Dissolved Solids

The gravimetric method as described by APHA (1995) was used. The evaporating dish was heated first at 200°C in the oven for 1 hour. It was subsequently cooled to room temperature, weighed and stored in a desiccator. Fifty milliliters of the samples were filtered using a Whatman No 1 filter paper and transferred to the pre-weighed dish and then evaporated to dryness in the oven and dried for 1 hour at 105°C. The dish was subsequently cooled to room temperature in a desiccator and weighed. The level of Total Dissolved Solids (TDS) was calculated as shown below:

$$\text{TDS (mg/L)} = \frac{(A-B) \times 100}{\text{Sample volume}}$$

Where:

A= Weight of sample + dish in mg

B= Weight of dish in mg

2.5 Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD₅) was determined after incubation of the surface water for five days at 20°C. BOD tests are generally carried out by measuring the amount of dissolved oxygen present in the sample before and after incubation in the dark for 5 days at 20°C. The Azide Modification method as described by APHA [23] was used.

Phosphate buffer solution, Magnesium sulphate solution, Calcium chloride solution and Ferric chloride solution were prepared as the dilution water. The water sample was diluted by 2%. Into the 125ml BOD bottles, 100ml of the 2% diluted samples were placed using a 50ml long tipped pipette. Extra 25ml of the diluted sample was added to the bottle to bring it to brim. The stoppers were inserted leaving no air bubble in the bottle. An initial determination of the DO was taken before dilution from one of the duplicate bottles.

The samples and the blank were then incubated for 5 days at 20°C; then, on the 5th day, the DO of the incubated samples were measured including the blank.

$$\text{BOD (mg/L)} = \frac{\text{DO}_0 - \text{DO}_d}{\% \text{ dilution}}$$

Where:

DO₀ = DO of the sample immediately after saturation with air (initial DO)

DO_d = DO of the sample after 5 days incubation (final DO)

2.6 Determination of Chloride

The Silver-Nitrate Titration method of APHA [23], was used. Twenty five milliliter of the sample was measured into 100ml conical flask. Two drops of potassium dichromate were added and then titrated with silver nitrate until the appearance of a brick red colour which is the end point. The titre volume was recorded.

$$\text{Chloride (mg/L)} = \frac{\text{Titre (ml)} \times 100}{\text{Volume of sample (ml)}}$$

3. RESULTS

3.1 Physicochemical Characteristics of Surface River water

The results of the physicochemical characteristics of the various surface water at the Bodo/Bonny River both in the wet and dry seasons and the Link fish pond are presented in Tables 1 and 2. The pH of surface water samples, ranged from 6.20–6.40 which is below DPR Limit of 6.5-8.5, while Link fish pond pH is 7.8. The pH values show significant differences at P=0.005. The pH results obtained in this study shows that pH was slightly acidic (probably due to heavy effluent discharge from companies cited in the study area) in all sampling locations except for the Link fish pond. There were also changes in temperature which shows statistically significant differences at P < 0.005.

Results of Total dissolved solid (TDS) and Electrical Conductivity (EC) levels of the four sampling points showed significant differences. TDS recorded 43175–57075 mg/L and this is above DPR permissible limit of 5000mg/L in station BBW 2; other stations were within limit while the Link fish pond had 3075 mg/L which was also within the permissible limit. Electrical Conductivity (EC) values ranged from 54050 - 57050 µS/cm. The values for Dissolved Oxygen, Biological Oxygen Demand, Turbidity, Chloride recorded in this study varied at all sampling points and all also showed significant differences at P < 0.005 (Table 1).

Table 2 presents the results for the physicochemical parameters of surface river water samples during the wet season. The values obtained for surface water was compared with the WHO/DPR Limit for Brackish/ Saline water.

The table show that the surface water fell within the standard limits except for the conductivity that was above the permissible limits. Quantitative variation was observed in the two seasons in the different locations statistically.

Comparatively evaluation of the mean pH value of River water (BBW) with Linked fish pond water (which served as the control) revealed that the Link fish pond water had the highest pH value of 7.9 (Fig. 2a) (probably as a result of fish feed and their feces or intrinsic influences or due to initial fertilization of the ponds), than the surface water samples with a pH of 6.4 (Fig. 2b), next were BWW1, BWW5, BWW6 having equal value of pH 7.3; the least pH was observed in BBW4 and BBW8 (pH 7.1). (Fig 2a).

The Total Dissolved Solids (TDS) (mg/L) concentration of the River water (BBW) with Linked fish pond water evaluated showed wide variation ($y = -8376.x + 63037$ $R^2 = 0.8129$). The surface water at station BBW1 had the highest TDS (60,200 mg/L) (Fig 3a) while the least was observed in the Linked fish pond which served as control (395 mg/L) (Fig. 3b). Electrical Conductivity (EC) ($\mu\text{S}/\text{cm}^3$) value of the River water (BBW) with Linked fish pond water evaluated also followed similar pattern as the TDS with wide variation (750 – 55,800 mg/L). The mean EC value recorded 55,800 mg/L as against EC value of 750mg/L for the Link Fish pond water (Fig. 4b).

Temperature recorded at different sampling points along the River water (BBW) and the Link fish pond water revealed that BWW5, BWW6, BWW7 had the highest value of 31°C while the least Temperature was recorded in BBW4 with 29°C (Fig 5a). The comparative evaluation of mean Temperature of River water (BBW) with Link fish pond water showed BBW 30.25°C having higher Temperature than Link Fish pond water (30°C) (Fig. 5b). The Salinity (mg/L) at different sampling points along the River water (BBW) and the Link fish pond water showed that station BWW1 had the highest value of 39 mg/L > BBW2 (33 mg/L) > BBW6 (32 mg/L) while the least Salinity was recorded in BBW4 (28 mg/L) (Fig 6a). The comparative evaluation of mean Salinity (mg/L) of the River water (BBW) with Link fish pond water showed mean surface water (BBW) value of 31.63 mg/L while the Link Fish pond water had 30 mg/L (Fig. 6b). Turbidity (NTU) of River water (BBW) with Link Fish pond water evaluated showed slight variation with River Water (BBW 3) with a high Turbidity value

of 0.5 NTU while BBW5, BBW7 and the Link Fish pond water had turbidity value as low as < 0.01 or 0 NTU (Fig. 7b).

Dissolved Oxygen (DO)(mg/L) content of River water (BBW) with the Link fish pond water evaluated showed slight variation ($y = -0.16x + 1.92$; $R^2 = 1$) with BBW7 having the highest DO (2.3 mg/L) > BBW2 = BBW6 (1.9 mg/L) > BBW1 = BBW5 (1.8 mg/L) while the least value was observed in BBW8 (1.1 mg/L) (Fig 8a). Comparative evaluation of mean Dissolved Oxygen (DO)(mg/L) concentration of River water (BBW) with Link fish pond water showed that River water had a higher mean DO value of 1.76 mg/L while the Link Fish pond water had 1.6 mg/L (Fig 8b).

Biochemical Oxygen Demand values for the River water show that BB7 had the highest value with 0.9mg/L>BB6 0.7 mg/L while BB3>BB2>BB1 have 0.5mg/L respectively (Fig 4.8a). Comparative evaluation of mean Biochemical Oxygen Demand (BOD)(mg/L) had a higher mean BOD value of 0.49 mg/L while the Link fish pond water had 0.3mg/L (Fig 9b).

4. DISCUSSION

The pH of an environment where microbes and other aquatic organisms live affect their metabolic activities thereby affecting the functioning of the enzymes, hormones and proteins. pH is a major factor in all chemical reactions associated with the formation of, and alteration and dissolution of chemicals [24]. The pH of Bodo/Bonny River samples, ranged from 6.20–6.40 in the dry season which is below DPR Limit of 6.5-8.5, while link fish pond pH is 7.8 but was more of alkaline in the wet season (this could be attributed to increased rainfall which tends to increase the pH and the solubility of alkaline based substances). However the study area in Bonny Island hosts the Nigeria Liquefied Natural Gas Company (NLNG), an industry within the vicinity of sampling stations which could discharge waste products/effluents responsible for the differences in the Hydrogen ion concentration of the surface water. Many rivers receive flux of sewage, domestic waste, industrial effluents and agricultural waste as major sources which contain substances varying from simple nutrients to highly toxic chemicals. Such coastal ecosystems mediated by human activities can adversely alter the ecological integrity of fragile aquatic systems, as well as negative effects on ecology resulting in an

Table 1. Physicochemical characteristics of Bodo/Bonny River and link fish pond samples during dry season

Parameters	Stations					DPR Limit for Brackish/ Saline water
	BBW1	BBW2	BBW3	BBW4	LFPW5	
pH	6.40±0.18 ^a	6.26±0.21 ^b	6.40±0.52 ^a	6.60±0.100 ^b	7.8±0.2 ^{ab}	6.5-8.5
Temperature (°C)	29.36±0.29 ^b	29.33±0.21 ^b	29.50±0.06 ^b	26.60±2.10 ^a	30.40±0.44 ^b	Ambient ±2
Conductivity (µS/m ³)	56050±4.7 ^b	57050±3.10 ^c	54050±58.70 ^b	56050±5.30 ^a	750±51.7 ^{bc}	-
Salinity (mg/l)	0.26±0.10 ^a	0.35±0.04 ^{ab}	0.37±0.031 ^b	0.28±0.044 ^a	<0.00	2000
Turbidity (NTU)	1.13±0.10 ^a	1.90±0.70 ^c	1.39±0.32 ^d	1.35±0.040 ^a	0.50±0.58 ^{bc}	15
Total Dissolved Solid (TDS) (mg/l)	49075±61.51 ^{ab}	57075±17.44 ^b	42075±105.7 ^a	43175±43.09 ^a	395±37.9 ^a	5000
Dissolved Oxygen (DO) (mg/l)	1.80±0.153 ^a	1.60±0.12 ^a	1.70±0.100 ^a	2.20±0.551 ^b	4.50±0.513 ^b	-
Biological Oxygen Demand ((mg/l))	1.4 ±2.57 ^a	1.45±0.90 ^c	1.20 ±0.153 ^a	1.05 ±0.38 ^a	0.50±55.455 ^a	125
Chloride (mg/l)	11.33±2.60 ^c	21.06±0.71 ^d	10.00±0.557 ^c	16.50±0.306 ^b	14.30±0.200 ^a	-

Table 2. Physicochemical characteristics of Bodo/Bonny River and link fish pond samples during wet season

Parameters	Stations					DPR Limit for Brackish/ Saline water
	BBW1	BBW2	BBW3	BBW4	LFPW5	
pH	7.20±0.18 ^a	7.65±0.21 ^b	7.60±0.100 ^b	7.50±0.01 ^b	8.00±0.04 ^{ab}	6.5-8.5
Temperature (°C)	26.06±0.29 ^b	27.33±0.21 ^b	26.60±2.10 ^a	27.60±1.10 ^a	28.4±0.20 ^b	25 -36 ±2
Conductivity (µS/m ³)	36050±4.7 ^b	47050±3.10 ^c	38050±3.30 ^a	39050±3.30 ^a	250±51.7 ^{bc}	1000
Salinity (mg/l)	0.11±0.10 ^a	0.25±0.04 ^{ab}	0.28±0.046 ^a	0.22±0.046 ^a	<0.00	2000
Turbidity (NTU)	3.13±0.10 ^a	2.00±0.70 ^c	3.35±0.020 ^a	3.02±0.040 ^a	1.80±0.40 ^{bc}	15
Total Dissolved Solid (TDS) (mg/l)	29075±61.51 ^{ab}	27075±17.44 ^b	30175±43.09 ^a	31175±43.09 ^a	225±37.9 ^a	5000
Dissolved Oxygen (DO) (mg/l)	1.30±0.153 ^a	1.20±0.12 ^a	2.00±0.551 ^b	1.9±0.551 ^b	3.70±0.32 ^b	7.5 -10
Biological Oxygen Demand ((mg/l))	1.80 ±2.57 ^a	1.85±0.90 ^c	1.85 ±0.38 ^a	1.89 ±0.27 ^a	0.70±5.085 ^a	125
Chloride (mg/l)	17.30±2.60 ^c	22.06±0.71 ^d	19.50±0.306 ^b	20.50±0.27 ^b	17.30±0.200 ^a	250

Values are means of two replicates. Means of the same superscript are not significantly different at ($p \geq 0.05$) while means in the same column not followed by the same superscript are significantly different; BBW1=Point 1; BBW2= Point 2; BBW3= Point 3; BBW4= Point 4; LFPW=Bodo Link fish Pond

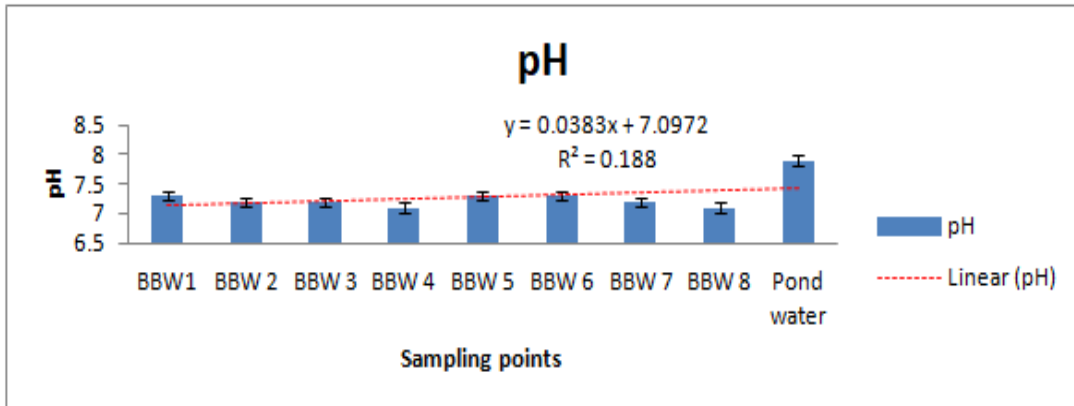


Fig. 2a. pH value of surface water at different sampling points and Link fish pond water
Note: BWW1-BWW4 represent Dry season while BWW5 – BWW8 represents Wet season

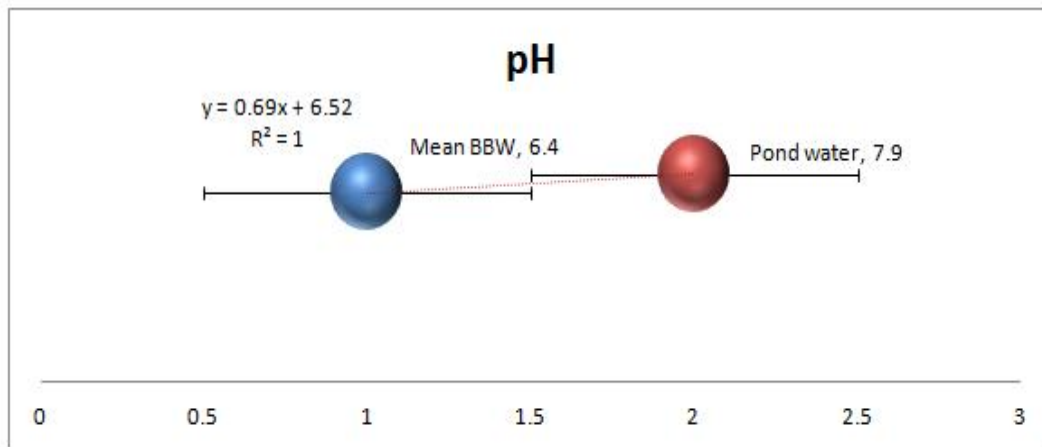


Fig. 2b. Mean pH value of surface water with the Link fish pond water

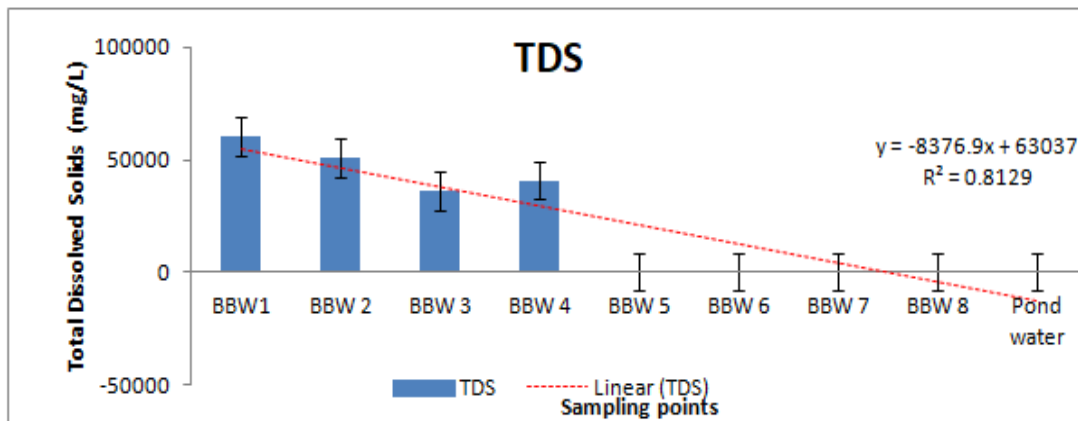


Fig. 3a. Total Dissolved Solids (TDS) (mg/L) concentration of surface water at different sampling points and Link fish pond water

Note: BWW1-BWW4 represent Dry season while BWW5 – BWW8 represents Wet season

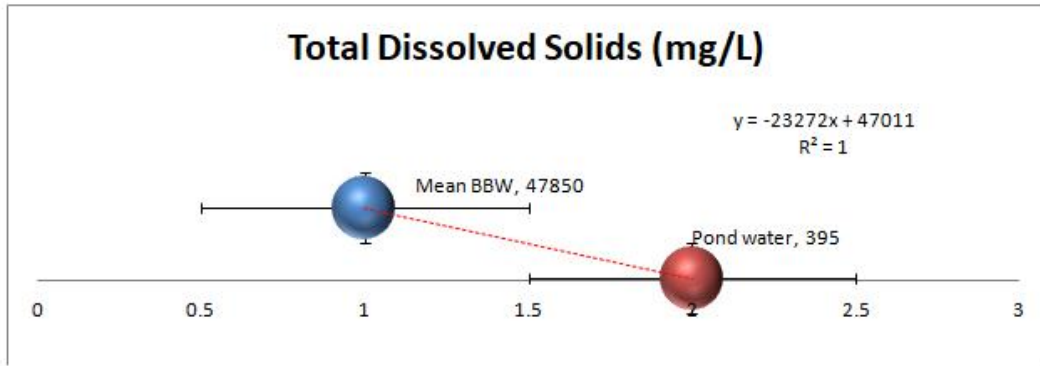


Fig. 3b. Comparative evaluation of Total Dissolved Solids (TDS) (mg/L) concentration of River water with Link fish pond water

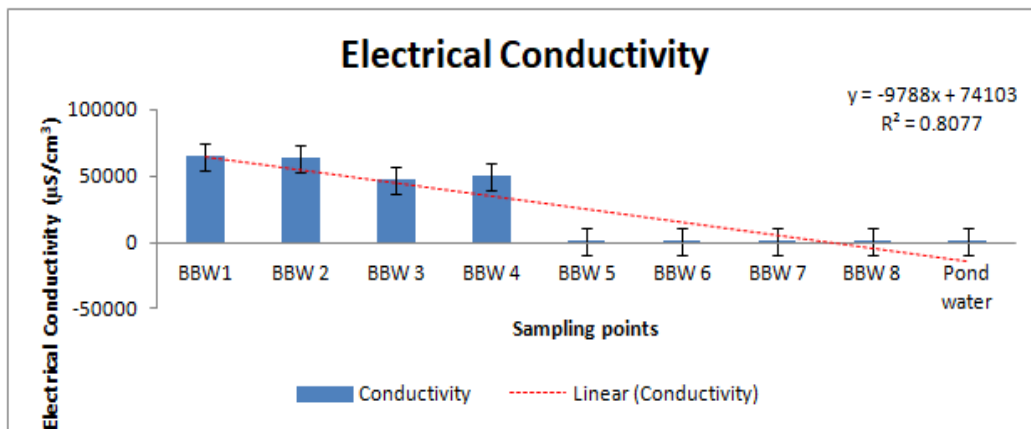


Fig. 4a. Total Dissolved Solids (TDS) (mg/L) concentration of surface water with Link fish pond water

Note: BWW1-BWW4 represent Dry season while BWW5 – BWW8 represents Wet season

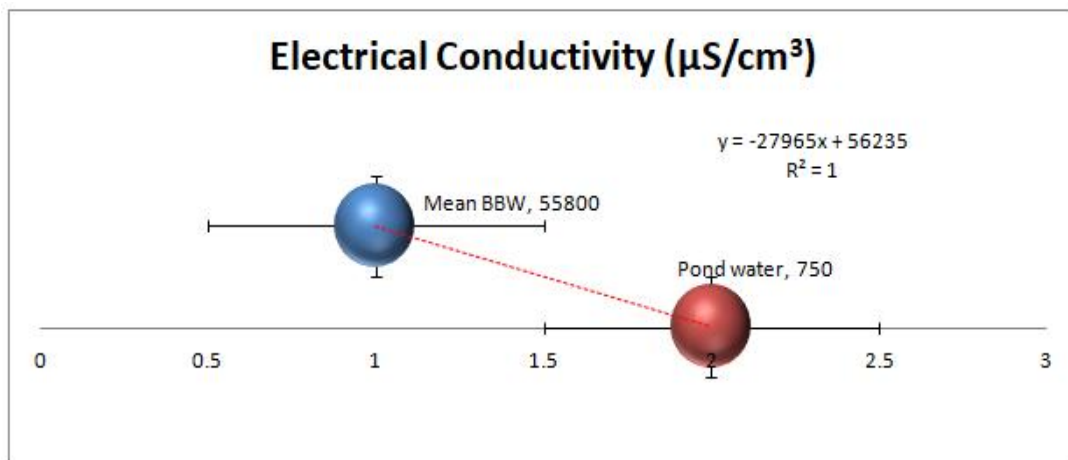


Fig. 4b. Comparative evaluation of mean Electrical Conductivity (EC) ($\mu\text{S}/\text{cm}^3$) Concentration of River with link fish pond water

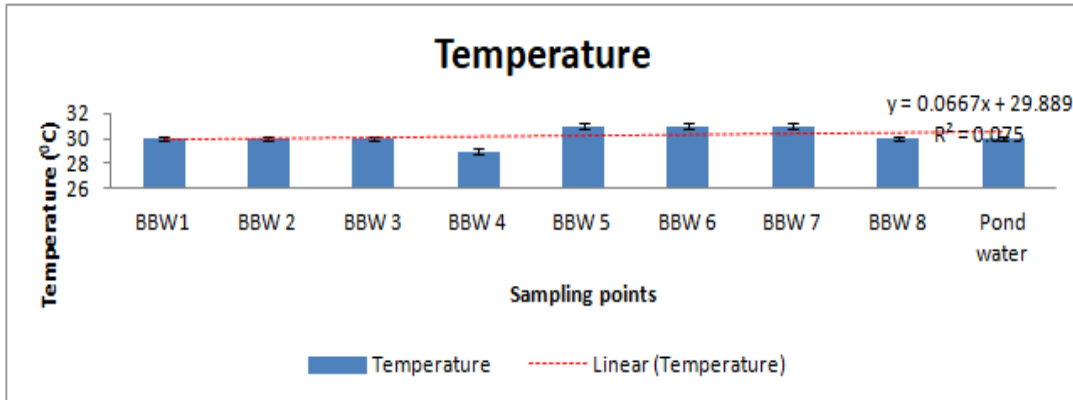


Fig. 5a. Temperature (°C) of surface water at different sampling points and Link Fish pond water (Control)

Note: BWW1-BWW4 represent Dry season while BWW5 – BWW8 represents Wet season

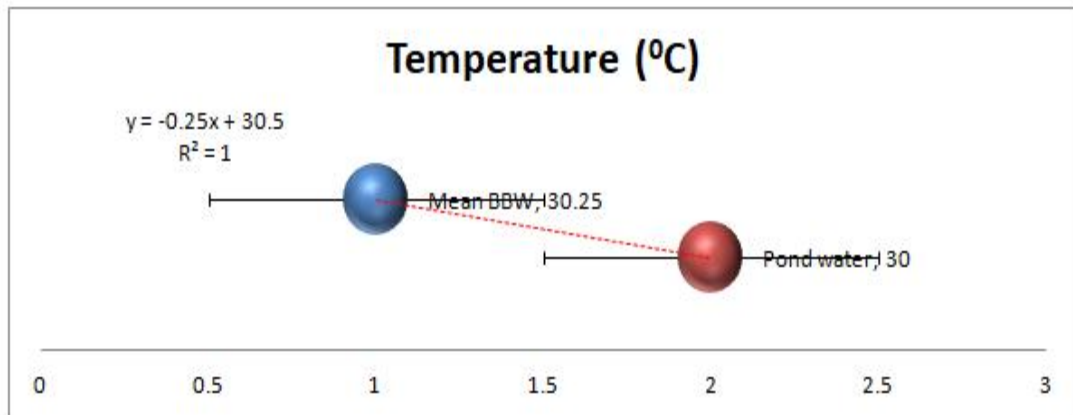


Fig. 5b. Comparative evaluation of Temperature (°C) of River Water with Link fish pond water (Control)

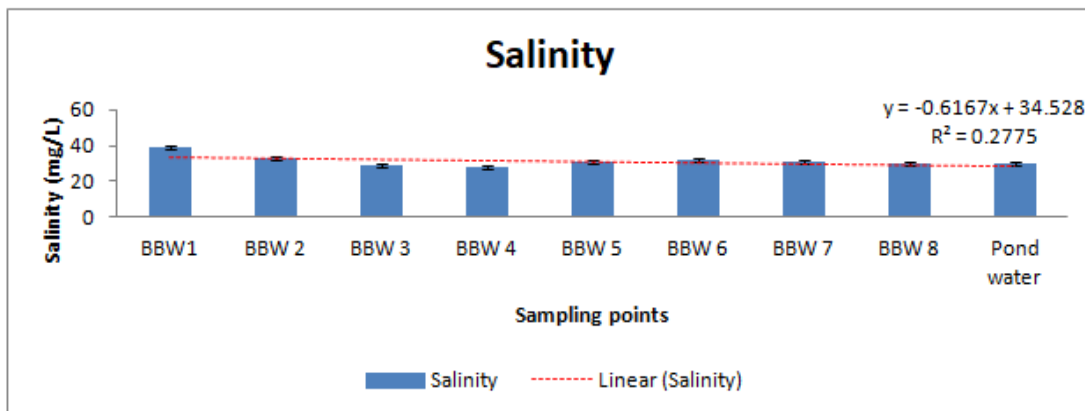


Fig. 6a. Salinity (mg/L) concentration of surface water at different sampling points and Link Fish pond water (Control)

Note: BWW1-BWW4 represent Dry season while BWW5 – BWW8 represents Wet season

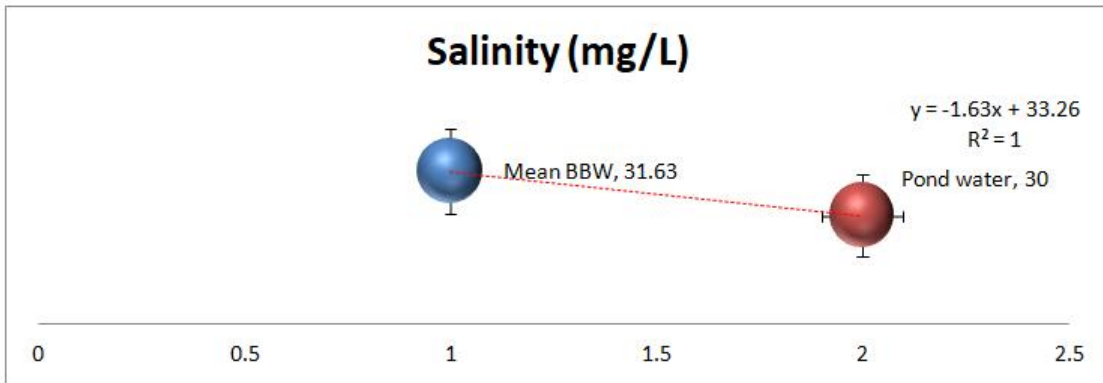


Fig. 6b. Comparative evaluation of Salinity (mg/L) concentration of Surface water with Link fish pond water

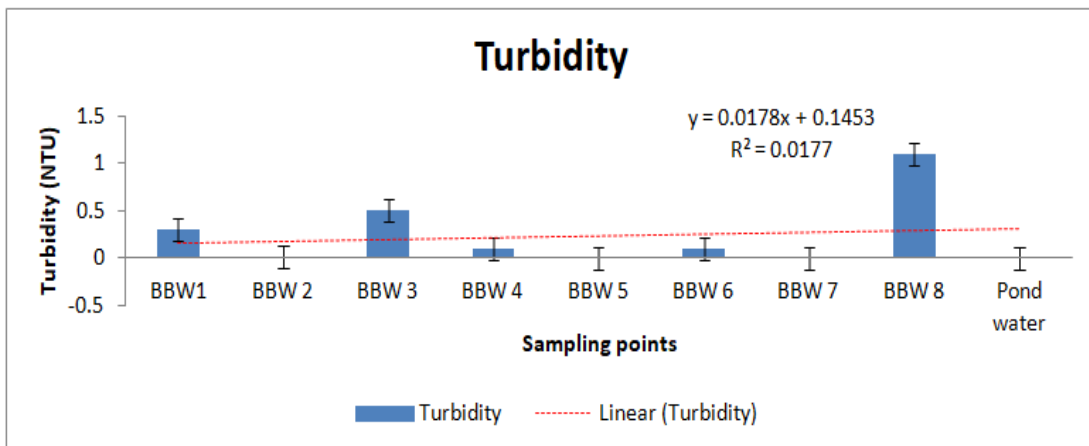


Fig. 7a. Turbidity (NTU) of surface water at different sampling points and Link fish pond water (Control)

Note: BWW1-BWW4 represent Dry season while BWW5 – BWW8 represents Wet season

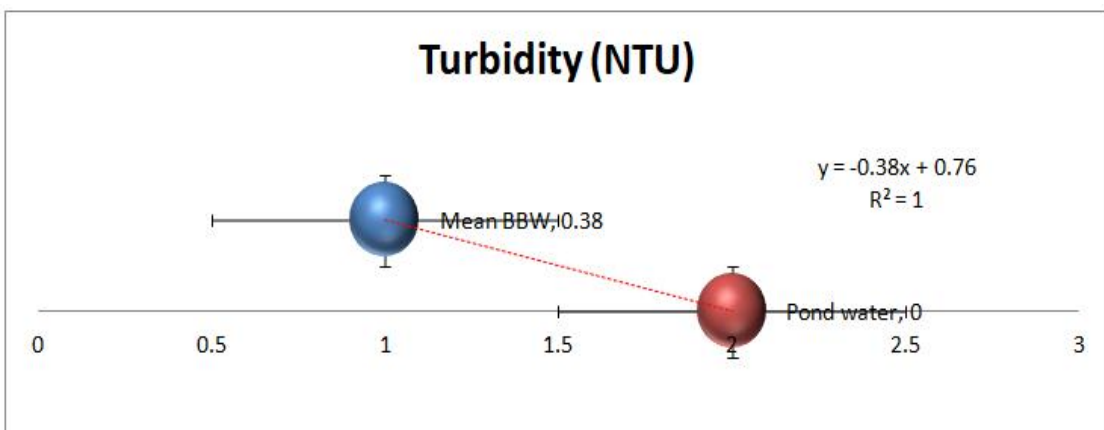


Fig. 7b. Comparative evaluation of Turbidity (NTU) of surface water with Link fish pond water (Control)

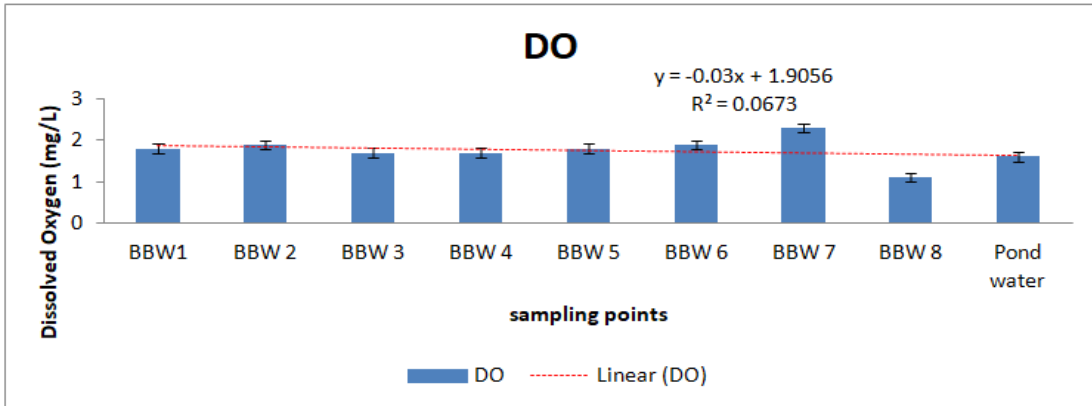


Fig. 8a. Dissolved Oxygen (DO)(mg/L) concentration of surface water at different sampling points and Link fish pond water
 Note: BWW1-BWW4 represent Dry season while BWW5 – BWW8 represents Wet season

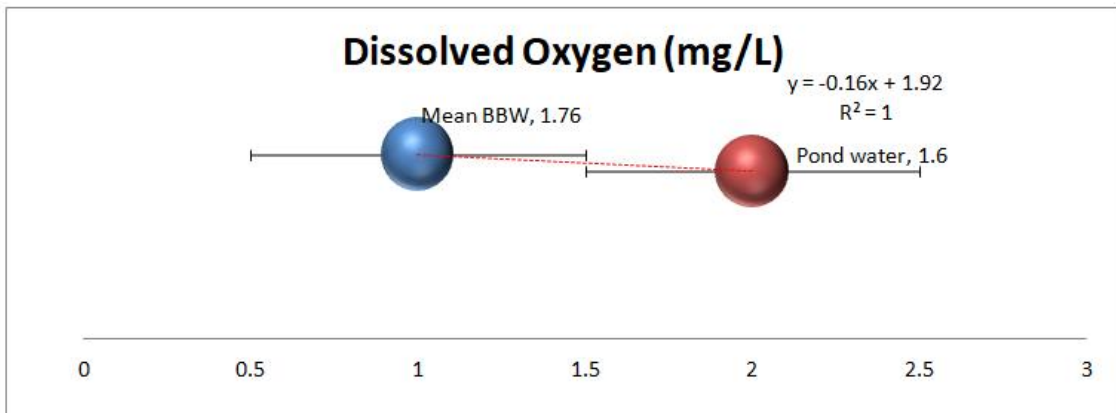


Fig. 8b. Comparative evaluation of Dissolved Oxygen (DO) (mg/L) concentration of surface water with Link fish pond water (Control)

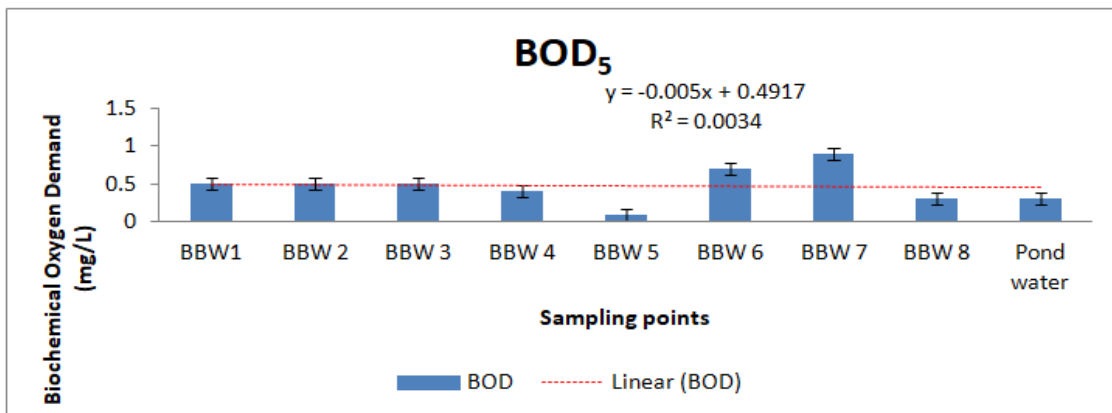


Fig. 9a. Biochemical Oxygen Demand (BOD) (mg/L) concentration of surface water at different sampling points and Linked fish pond water
 Note: BWW1-BWW4 represent Dry season while BWW5 – BWW8 represents Wet season

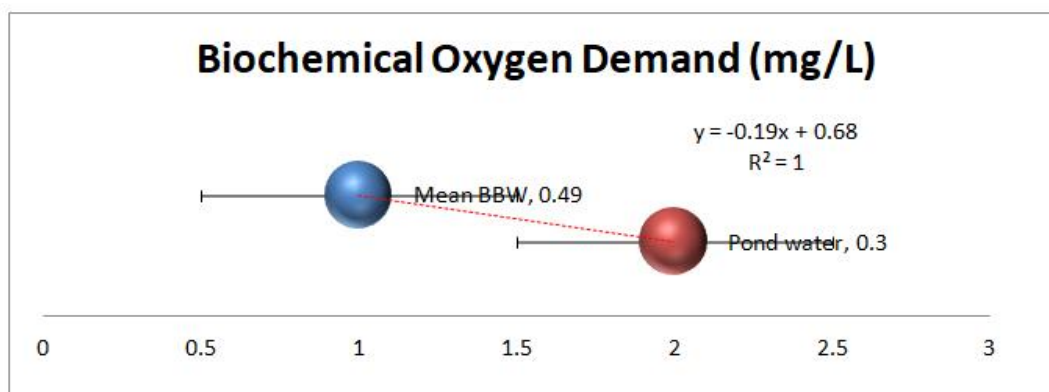


Fig. 9b. Comparative evaluation of Biochemical Oxygen Demand (BOD)(mg/L) concentration of surface with Link fish pond water

imbalance causing degradation, pollution of fishing grounds and destruction of aquatic life, alteration of predation patterns, weather and climate conditions in the river. The pH values showed significant differences at $P=0.005$. The pH results obtained in this study shows that pH was slightly acidic in all sampling locations. In water or sediments, acidic or alkaline values indicated the capacity of the media to hold heavy metals and dissolve more electrolytic ions in solution [25] and also affects the holding ability of nutrient components and levels in the sediment or water and thus determine their quality [26]. Leakage of acidic water into the river can directly harm the aquatic animals by lowering the sodium and oxygen activities within their systems. However, increased rate of decomposition of wastes from various anthropogenic sources have been linked with low pH [25], while accumulation of particles and dissolved materials contribute to increased pH [27]. The toxicity of ammonia is often increased at a high pH; whereas a low pH increases the toxicity of Hydrogen sulphide and cyanide levels. The toxicity of microbial poisons in water is also affected by pH change [28]. pH is important as it determines the functioning of almost all hormones, enzymes and proteins controlling growth, metabolism and development. It is also important in chemical reactions linked with the alteration, formation and dissolution of minerals [24,29].

Natural environments contains chlorine in varying degrees with the chlorine value increasing as the mineral content increases. Chlorides are inorganic compounds resulting from the combination of chlorine gas with metal. Some common chlorides include sodium chloride (NaCl) and magnesium chloride ($MgCl_2$). These

elements, some of which are toxic to aquatic microflora may find their way into the environment leading to an increase in the quantity of these chemicals and subsequently, may cause changes in the status of the water body [30]. The levels of chloride in the water samples were below the DPR Limit for Brackish/saline water in both seasons. The slight differences observed in the Chloride content during the wet and dry season may be associated with the continuous rainfall observed even during the dry which has made it difficult to differentiate between wet and dry seasons.

Total Dissolved Solids (TDS) is the dry weight of particles trapped by the filter in water columns. High concentrations of suspended solids can cause many problems for water health and aquatic life. The Total Dissolved Solids (TDS) (mg/L) concentration of the River water with link fish pond water evaluated showed wide variation ($y = -8376.x + 63037$ $R^2 = 0.8129$). Also, TDS during dry season was higher in all the stations than the wet season, probably this trend could be due to high rainfall which tend to decrease the concentration of dissolved salts and other substances in the river water, since the stations river consist of brackish – marine water (Figs. 2a, 2b). The River water TDS had 60,200 mg/L while the least was observed in the Link fish pond which served as control 395 mg/L. This value is very high when compared with the WHO recommended value of 2000 mg/L for domestic water use. The increased value may be a consequence of salt water incursion, human input through bunkering activities and the redox potential of the water system [19]. High concentration values were as a result of organic particles and other particulate matter scaled from

industrial activities being discharged into water. The level to which pollution has affected water or aquatic environment can be related to the quantity or level or concentration of TDS present. TDS is a good indicator of water quality due to the fact that it affects the taste, colour and smell of the water and also increases the ability of light penetration into the water body. Increased levels of TDS make water unfit for drinking and irrigation of farmlands, because they cause decreased photosynthetic capacity and rise in water temperature [31].

Electrical conductivity is the measure of a material's ability to allow the transport of an electric charge. It is measured by the presence of total concentration of ions and it is influenced by temperature of the system [32]. The conductance of any material or medium is a function of the number of ions present and is used to predict the concentration of ions or mineral present in the medium [33,34], but cannot be used to determine the specific ion present. The mean Electrical Conductivity value in the surface river water recorded 55,800 mg/L as against EC value of 750mg/L for the Link fish pond water. Similar trends was recorded for wet season across the sampling stations. The conductivity values were above the WHO 1000 μ S/cm³ limit for Brackish/Saline water. The high values may be as a result of decomposition and mineralization of organic matter or it may be related to influences of sea water on the river during high tide [35].

Temperature is one of the important parameters of physiochemical analysis of water. It helps to regulate the maximum dissolved oxygen concentration of the water, and influences the rate of chemical and biological reactions. Temperature is an important characteristic component that can vary widely; it can be influenced by a number of variables including: geographic location, shading, water body size and depth [36]. The comparative evaluation of mean Temperature of surface water was 30.25^oC while the Link fish pond water had 30^oC. These values are below the range of WHO standards for normal drinking water. This may be due to the effect of crude oil particles present in the contaminated water. The increase in temperature of water could lead to odour. Release of petroleum hydrocarbons into the water environment, whether accidentally or due to anthropogenic activities, could result to water pollution and may also contribute to regional atmospheric pollution. Contaminants in the water can affect the water quality and consequently the human health.

Salinity, expresses the amount of salt content of water. The salinity values recorded in this study ranged from 31.63mg/L in surface river water to 30 mg/L in the Link fish Pond water which served as control. According to Ogamba et al [37] and Meragini-Ikechukwu et al [38], it was revealed that low salinity values are attributed to the nature of the surface water body (brackish water) and also through the inflow of fresh water discharge and rainfall which could reduce the salt content especially in marine ecosystems. Salinity remains a vital parameter in the survival of aquatic organisms and renewal of other parameters. It is very essential to note that very low salinity might be attributed to the rainy season (rain-dependent) because of diluting influence of salt precipitations and greatly reduce the salinity [39].

Turbidity is the degree of clearness or opaqueness of water. The values of turbidity observed in the present study ranged from 0.38 NTU in the surface river water to 2.5 NTU in the link fish pond water. The level of suspended and dissolved particles in any water environment gives high turbidity to the environment. The high turbidity value may have originated from bunkering activities which discharge effluents without following due procedures and also from incessant dredging activities rampant in the area. Another possible reason might be from the amount of dissolved solids (organic or inorganic materials) present in the river as observed in the present study. Effects of high turbidity in water include prevention of light penetration, hindrance to photosynthetic activities and destruction of the normal aquatic life and also reduce the value and appearance of surface water [40,20]. The concentrations or the number of micro-organisms, phytoplanktons and zooplanktons in such environment increases water turbidity [41,42]. High turbidity in the fish pond may be due to introduction of fish feeds into the pond water to supply nutrients for the growth of the fishes and besides, the pond is stagnant but the river water flows thus dispersing excess organics that were introduced through road run-off, industrial seepage, storm water drains, shipping activities and spillage.

The life of any body of water depends to a large extent upon its ability to maintain a certain amount of dissolved oxygen, which is needed to maintain aquatic life. For example, without dissolved oxygen, fish suffocate and normal aquatic organisms are destroyed. This situation creates an imbalance in the ecosystem. Dissolved oxygen content of the surface river

water samples recorded 1.76mg/L while the link fish pond water recorded 1.6 mg/L. DO is a measure of the degree of pollution by organic matter, the destruction of organic substances as well as self-purification. Dissolved oxygen level with values below 2.0 mg/l is indicative of environmental stress. The values recorded in this study were above the USEPA permissible limits. DO is an important parameter in water analysis based on the fact that life in aquatic environment is a function of its availability. The cause of the low level of DO as observed might be the oily waste clearly visible on the surface of the water, a product of bunkery and sometimes oil spill. It is used to derive information on the level and extent of bacterial activity, photosynthetic characteristics, the abundance of nutrients and the ability of fishes to survive in that environment [43]. Temperature is a major factor that determines the amount of dissolved oxygen present in water.

Biochemical Oxygen Demand (BOD) is the amount of dissolved oxygen needed (ie. demanded by aerobic biological organisms to break down organic material present in a given water sample at certain temperature over a specific time duration. BOD₅ indicates the amount of organic matter degradable by microbial metabolism on the assumption that the water has no bactericidal or bacteriostatic effects [23]. Therefore, the more organic material present in the water the higher the BOD. Research has shown that the higher the quantity of decomposable organic matter, the higher the BOD₅. BOD₅ recorded in the surface river water samples were very low to 0.49mg/l while the pond water had 0.3 mg/L. This can be attributed to the activities of bunkering and other waste discharges coming into the water by the various industrial activities around the Ogoni area of the Niger Delta which generate huge organic and inorganic wastes. BOD is a measure of organic contaminants and the microbial action on such materials, in places where defecation is directly done on the river by the shore dwellers, it is expected to be high and it's used to express the level contamination of water by organic material. It assesses the level of organic pollution in an aqueous system [29]. High values depicts continuous breakup of biological and more or less mineral by microbes.

Chemical Oxygen Demand (COD) showed alternate result with various locations of the surface water around the Bodo/Bonny axis (6.67mg/L) which was slightly higher than the

location around the Andoni River water (6.42mg/L). This observation could be caused by more inorganic substances discharged from industries especially petroleum products from oil companies sited around the Bonny/Finima area whose effluent from the NLNG are discharged into the surface water without treatment. In most cases it could be as a result accidental discharges and bunkering activities or deposition of wastes from vessels transporting goods along the rivers, sometimes they are driven by tide of the river as it fluctuates which helps to generate huge organic and inorganic wastes. These contribute negative impacts on the sediments, water and the immediate environment which may constitute a major source of pollution. This observation has been recorded by other researchers who worked on the influence/impact of crude oil pollution and other industrial activities on the Niger Delta environment causing deterioration of its water quality due to different wastes that discharge into the water body [44]. Water quality indicates the relationship of all hydrological properties including physical, chemical and biological properties of the water body. Hence, water quality assessment involves analysis of physico- chemical, biological and microbiological parameters that reflects the biotic and abiotic status of ecosystems [45].

However, the results obtained for wet seasons show that the high rainfall and river discharge during the rainy season combined with the low, flat terrain, and poorly drained soils cause frequent and widespread flooding and erosion. This helped to reduce various properties of the surface river water due to the influence of the tides and at times floods in connection with rains, spilt oil is rapidly distributed over large areas and remobilized with rising tides. Oil slicks in such cases may enter such areas during high tide and as the tide recedes, oil is deposited on the vegetation causing asphyxiation of the plants due to seasonal floods [7]. Toxic effects may also occur if the oil is fresh and contain a high amount of light aromatic hydrocarbons. Obviously, if the mangrove vegetation dies, many plants and animals associated with this ecosystem will also suffer due to the keystone character of the mangrove vegetation.

5. CONCLUSION

The physicochemical characteristics of the various sampling points in the dry season show that pH, TDS and Electrical conductivity values showed statistically significant differences at P

< 0.005. pH was slightly acidic in all sampling locations except for the Link fish pond, the values ranged from 6.20–6.40 which is below DPR Limit of 6.5–8.5, TDS recorded 43175–57075 mg/L and this is above DPR permissible Limit of 5000mg/L TDS was higher in dry season more than wet season. Parameters of surface water in the wet season fell within the standard limits except for the conductivity that was above the permissible limits. These values obtained in this study shows that spilled oil in the water could result to asphyxiation of water thus depleting and depriving the fishes available O₂ for survival in the water.

The physicochemical parameters obtained in this study generally indicate that the various activities particularly oil spills mainly impacted the aquatic, vegetation and wildlife. The levels found in the more contaminated sites are high enough to cause severe impacts on the ecosystem and human health.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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