# Assessment of Total Hydrocarbon Content in Water, Sediment and Fish from Koniju-Toru Upper Bonny Estuary, Nigeria.

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***Abstract*: A river's physical, chemical and biological states indicate the quality of the aquatic system. This study assessed the level of total hydrocarbon content (THC) and other water and sediment characteristics in the Koniju-toru River of Okrika - an estuary of the Bonny River - for three months. Surface water, sediment and fish samples were collected from three stations (upstream, midstream and downstream) for three months. Composite samples of each station were tested for pH, total dissolved solids (TDS) and dissolved oxygen (DO) in-situ using HANNA multi-parameter meter while conductivity, nitrate, sulphate, phosphate, chloride and biochemical oxygen demand (BOD) were determined in the laboratory. Spectrophotometry was used for the determination of hydrocarbon content in the samples. The hydrocarbon content in surface water, sediment and fish ranged from 0.05 -0.12 mg/L, 2.13 - 3.83 mg/kg and 0.24 - 0.35 mg/kg, respectively. Other results characterizing the surface water included; pH (6.62 - 6.73), temperature (26.10 - 26.53 ℃), TDS (8888.3 - 10972.3 mg/L), chloride (6697.6 - 7598.3 mg/L), sulphate (259.1 - 346.5 mg/L), nitrate (0.17 - 0.29 mg/L), phosphate (0.002 - 0.066mg/L), DO (4.10 - 4.86 mg/L) and BOD (2.02 - 2.22 mg/L). Parameters in sediment ranged as follows; pH (5.12 - 5.60), alkalinity (50.3 - 100.3 mg/kg), chloride (504.7 - 604.8 mg/kg), sulphate (125.2 - 183.6 mg/kg), nitrate (0.11 - 0.30 mg/kg) and Total Organic Matter (0.60 - 0.73 mg/kg). Statistical tests showed significant difference ($p < 0.05$) between stations for all parameters. The study concluded that the physicochemical characteristics of water and sediment were within regulatory limits of WHO and other national standards excluding TDS, chloride and sulphate. levels of THC in surface water, sediment and fish were low suggesting little or no impact of industrial waste which may not be unassociated with the fact that the refinery with the most impact on the community was under rehabilitation.**

***Keywords*: Fish; hydrocarbon; water; sediment; upper bonny estuary**

## I. INTRODUCTION

Oil exploration/exploitation has been identified as a major pollution source of aquatic systems in the Niger Delta [1]. [2] lists some sources of oil spills including refinery effluents, sabotage and leakages from marine vessels. Oil contains a mixture of hydrocarbons including aromatic and aliphatic ([3], [4], [5]); therefore, estimating the total hydrocarbon content of water is an indicator of an oil-contaminated water body.

The presence of oil films in rivers affects productivity by impeding light penetration necessary for phytoplankton productivity, affecting the entire food chain; fish can take up hydrocarbon dissolved in water through their gills and store it in their liver, stomach and gall bladder, thereby making them unfit for human consumption ([6], [7]). Whereas, sediment serves as a sink in oil-contaminated water systems which is detrimental to benthic organisms [8]. Fish are good bioindicators of pollutants as they mostly respond to toxic chemicals the same way as higher vertebrates, specifically man ([7], [9]).

The Koniju-toru river is in proximity to water bodies that have undergone assessment due to direct effluent discharge from industries ([10], [11]). Ideally, it serves as a fishing ground, for recreational activities, and as a minor transportation route by canoe. However, urbanization has led to increasing water pollution sources; thus, making this river susceptible to contaminants from industrial discharge, oil exploration and other anthropogenic activities which can lead to hydrocarbon contamination in turn, posing a risk of increased mortality of the aquatic organisms and health risks to humans by direct contact with this water body or by consumption of edible organisms from the water.

Management and observation of the aquatic ecosystem depend on the knowledge of the physicochemical and biological properties of the water body which makes it necessary for periodic analysis of the systems [12]. Therefore, the study aims to assess the total hydrocarbon content (THC) level and physicochemical parameters in surface water, sediment and biota of Koniju-toru River, Okrika, Rivers state, Nigeria, with comparison to regulatory limits.

## II. MATERIALS AND METHODS

### *A. Study site*

The study was carried out in Koniju-toru River in Okrika of Rivers State, Nigeria. Okrika is situated on a small island south of Port Harcourt and lies on the north of Bonny River and Okrika Island, 56km upstream from the Bight of Bonny with geographical coordinates of Upstream- 4°44′18"N 7°5′23"E, 4°44′20"N 7°5′23"E and 4°44′23"N 7°5′23"E; Midstream- 4°44′24"N 7°5′20"E, 4°44′27"N 7°5′20"E and

4°44′30"N 7°5′20"E; Downstream- 4°44′31"N 7°4′36"E, 4°44′34"N 7°4′36"E and 4°44′36"N 7°4′36"E.

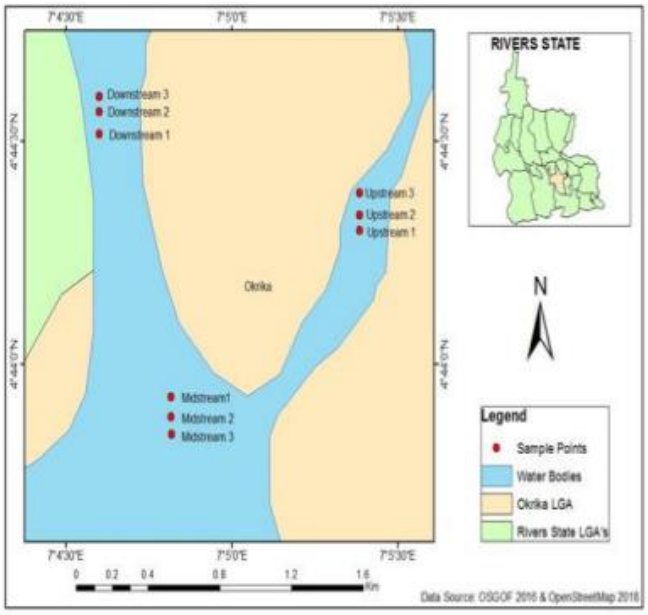


Fig. 1 Map showing the sampling points in the study area, Source: OSGOF 2016 & OpenStreetMap 2018

*B. Sample collection*

Three sampling points (Upstream, Midstream and Downstream) were chosen randomly from the three distinct stations across the study area as shown in Figure 1. Stations were identified with striking features; Station 1 (upstream) serves primarily as a fishing ground and measures about 97.3m from Station 2 (midstream) which serves primarily as a transportation route for canoes. Station 3 (downstream) is associated with high domestic waste input, measuring a further distance of about 1.3m from Station 2. Samples were collected from the three points and a composite sample of each station was analyzed for three months. Surface water samples were collected directly into clean sterilized 250mL sample bottles while sediment samples were collected into foil paper. Biota (fish; *Oreochromis niloticus*) were collected on purchase from fishermen. All samples were stored in an ice chest and transported to the laboratory for extraction and analysis.

*C. In-situ analysis*

pH, Total dissolved solids (TDS) and Dissolved Oxygen (DO) were determined in-situ using HANNA multi-parameter meter (HI9829) for potable water. The meter was calibrated using HANNA quick Cal solution (HI9828-0). The tip of the probe was rinsed with deionized water and then immersed in the sample and corresponding steady reading was taken in each case.

*D. Ex-situ analysis*

Methods described in APHA were used in analyzing ex-situ parameters [13]. First, for BOD, 250ml volume of the sample was treated with dilution water containing nutrients to the one litre mark and the initial DO was recorded. 200ml of the diluted samples was incubated for 5 days at $20^0$C. The final DO measurement was taken after the incubation. The BOD value was then obtained by subtracting the final DO from the initial DO and further dividing by the dilution decimal fraction.

Second, ascorbic acid reduction method was adopted in determining the phosphate concentration in the sample [14]. Ammonium-molybdate and potassium antimony tartrate usually react with orthophosphate to form antimony phosphate-molybdate complex. The complex was then reduced with ascorbic acid to form a deep-coloured, blue Molybdenum complex. The intensity of the colour is proportional to the phosphate concentration and this was measured at a wavelength of 880nm using 25mm cell. Analysis was done using UV VIS 3000.

Third, brucine method was used for nitrate concentration determination in the sample using UV VIS 3000 [14]. The reaction between nitrate and brucine usually produces a yellow colour that is used for colorimetric estimation of nitrate. The intensity of the colour is proportional to the nitrate concentration and this was measured at a wavelength of 410nm using 25mm cell.

Fourth, the Mohr method was used in determining the chloride content of the samples. Suitable volume of the sample was taken and then made up to 100ml; 1ml $K_2CrO_4$ was then added and titrated with 0.0141N $AgNO_3$.

Last, THC values were achieved by grounding the tissue sample (fish) with a blender, 5g of the grounded tissue was extracted using 25ml of n-hexane. This was accomplished by shaking vigorously in a mechanical shaker for 2 hours. The extract was filtered through Whatman filter paper into a 25ml standard flask. A simple cuvette was first filled with n-hexane as the blank solutions and it was placed in the sample holder of the Genesis 10 UV spectrophotometer. The wavelength was set at 425nm and the transmittance adjusted to 100 percent that is, zero absorbance. The absorbance of the extracted oil was taken. From the gradient of the calibration curve, the total hydrocarbon content was calculated.

*E. Data analysis*

The SPSS version 22 and IBM 2013 statistical analysis software program was used for the statistical analysis of data. Tukey HSD was used for multiple comparison of means for significant difference. Results were regarded as significantly different at a significant level below $p \leq 0.05$.

## III. RESULTS

Table 1 represents the mean values of physico-chemical parameters of surface water across the three stations. pH had a mean range of 6.68±0.00 - 6.6 2±0.00 and were significantly different across the stations while Tukey test was in the order of; Station 1 > Station 2 > Station 3. Water temperature across the stations were in the mean range of 26.53±0.00 -

26.10±0.00 ℃; while Tukey test for pair-wise comparison indicated significant difference between the stations; Station 3 > Station 1 > Station 2. Pair-wise comparison of TDS values from this study indicated significant difference between stations (Station 3 > Station 2 > Station 1). Mean values of chloride ranged from 7598.3±0.33 - 6697.6±0.33 mg/L and showed significant difference between stations as indicated by pair-wise comparison; Station 3 > Station 2 > Station 1. Sulphate mean values obtained in this study ranged from 346.5±0.03 - 259.1±0.03 mg/L with Tukey test indicating significant difference between stations (Station 1 > Station 2 > Station 3). Phosphate ranged from 0.066±0.00 - 0.002±0.00 mg/L while Tukey test indicated significant difference across stations (Station 1 > Station 2 > Station 3). Nitrate had its range from 0.29±0.00 - 0.17±0.00 mg/L while tukey test showed significant difference between stations (Station 1 > Station 3 > Station 2). Whereas, phosphate recorded mean values in the range of 0.066±0.00 - 0.002±0.00 mg/L with significant difference between stations (Station 1> Station 2> Station 1). DO was not similar between stations 2 and 3, but differed significantly in station 1 (Station 1 > Station 2 = Station 1) as revealed by Tukey test. Finally, BOD was in the mean range of 2.22±0.00 - 2.02±0.00 mg/L while pair-wise comparison showed significant difference between stations in the order; Station 2 > Station 1 > Station 3.

Table 1: Mean values of physico-chemical parameters of surface water of koniju-toru river

| | pH | Temp. ºC | TDS mg/L | Chloride mg/L | Sulphate mg/L | Nitrate mg/L | Phosphate mg/L | DO mg/L | BOD mg/L |
|---|---|---|---|---|---|---|---|---|---|
| Station 1 | 6.73 ± 0.00 $^{c}$ | 26.17± 0.00 $^{b}$ | 8888.3± 0.66 $^{a}$ | 6697.6± 0.33 $^{a}$ | 346.5± 0.03 $^{c}$ | 0.29± 0.00 $^{c}$ | 0.066± 0.00 $^{c}$ | 4.86± 0.03 $^{b}$ | 2.12± 0.00 $^{b}$ |
| Station 2 | 6.68 ± 0.00 $^{b}$ | 26.10± 0.00 $^{a}$ | 9297.3± 0.33 $^{b}$ | 6798.3± 0.33 $^{b}$ | 328.4± 0.03 $^{b}$ | 0.17± 0.00 $^{a}$ | 0.005± 0.00 $^{b}$ | 4.18± 0.00 $^{a}$ | 2.22± 0.00 $^{c}$ |
| Station 3 | 6.62 ± 0.00 $^{a}$ | 26.53± 0.00 $^{c}$ | 10972.3± 0.33 $^{c}$ | 7598.3± 0.33 $^{c}$ | 259.1± 0.03 $^{a}$ | 0.25± 0.00 $^{b}$ | 0.002± 0.00 $^{a}$ | 4.10± 0.00 $^{a}$ | 2.02± 0.00 $^{a}$ |

At p<0.05 With same superscript, there is no significant difference

Table 2 presents the mean of physico-chemical parameters of the sediment across the three stations. pH and alkaline had mean value range of 5.60±0.00 - 5.12±0.00 and 100.3±0.33 - 50.3±0.33 mg/kg, respectively. Pair-wise comparison of pH mean values indicated significant differences across stations (Station 2 > Station 1 > Station 3) while alkaline mean values were in the pattern; Station 1 = Station 3 > Station 2. Chloride mean values ranged from 604.8±0.03 - 504.7±0.03 mg/kg and Tukey test showed similarity between stations 2 and 3 with significant difference in station 1 (Station 3 = Station 2 > Station 1). Sulphate mean concentration ranged from 183.6±0.03 - 126.2±0.03 mg/kg and showed no significant difference between stations 2 and 3 but significant difference in Station 1 as observed from Tukey test in the pattern; Station 2 = Station 3 > Station 1. Nitrate mean values ranged from 0.30±0.00 - 0.11±0.00 mg/kg and differed significantly between stations in the pattern (Station 3 > Station 1 > Station 2) as shown by pair-wise comparison using Tukey test. Phosphate mean concentrations ranged from 0.03±0.00 - 0.00±0.00 mg/kg and differed significantly across stations (Station 2 > Station 3 > Station1). TOM varied from 0.73±0.00 - 0.60±0.00 mg/kg. Pair-wise comparison showed a significant difference between stations in the pattern Station 3 > Station 2 > Station 1.

Table 2: Mean of physico-chemical properties of sediment samples of the river

| | pH | Alkalinity mg/kg | Chloride mg/kg | Sulphate mg/kg | Nitrate mg/kg | Phoshate mg/kg | TOM mg/kg |
|---|---|---|---|---|---|---|---|
| Station 1 | 5.47± 0.00 $^{b}$ | 100.3± 0.33$^{b}$ | 504.7± 0.03 $^{a}$ | 126.2± 0.03 $^{a}$ | 0.14± 0.00$^{b}$ | 0.00± 0.00$^{a}$ | 0.60± 0.00$^{a}$ |
| Station 2 | 5.60± 0.00 $^{c}$ | 50.3± 0.33$^{a}$ | 604.8± 0.03 $^{b}$ | 183.6± 0.03 $^{b}$ | 0.11± 0.00$^{a}$ | 0.03± 0.00 $^{c}$ | 0.67± 0.00$^{b}$ |
| Station 3 | 5.12± 0.00 $^{a}$ | 100.3± 0.33$^{b}$ | 604.7± 0.00 $^{b}$ | 183.6± 0.03 $^{b}$ | 0.30± 0.00$^{c}$ | 0.01± 0.00$^{b}$ | 0.73± 0.00$^{c}$ |

At p<0.05 With same superscript, there is no significant difference

From Fig. 2, the levels of THC in surface water, sediment and fish ranged from 0.12 - 0.05 mg/L, 3.83 - 2.13 mg/kg and 0.36 -0.24 mg/kg, respectively for all stations. Tukey test revealed significant differences across stations for each matrix; mean concentrations were in increasing magnitude of water < fish < sediment.

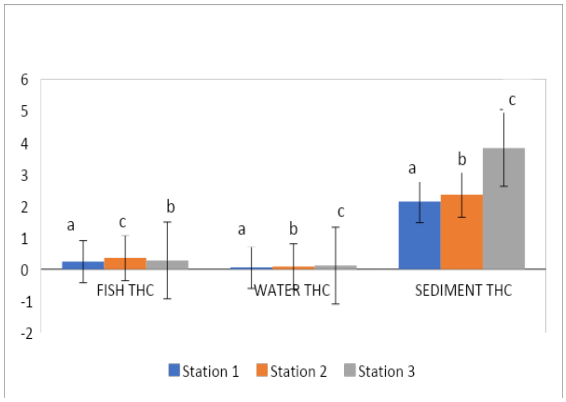


Fig. 2 Variation in means of total hydrocarbon content (THC) in water, sediment and fish samples across the different locations

At $p<0.05$ With same alphabet, there is no significant difference.

## IV. DISCUSSION

### *A. Physicochemical properties of surface water from koniju-toru river*

Physico-chemical properties of the study area were analyzed to characterize the overall pollution level of the study area. The mean temperature across the three stations (26.53 – 26.10 ℃) recorded higher values compared to another study carried out in the western part of Nigeria [15]. The temperatures obtained were within regulatory limit of <35℃ of the Federal Ministry Environment (FMEnv).

The pH values were in a range of 6.68 - 6.62 with all three stations indicating acidity and well within the permissible limits of WHO (7.0 - 8.5) and FMEnv (6.5 – 8.5. Values from this study were lower than the values of 6.90 - 6.26 reported from a similar water body in the Niger Delta [16].

Generally, the mean values for DO (4.86 - 4.10 mg/L) opposed the low values recorded across different estuaries in Nigeria which could be attributed to a lower pollution level in the studied area [1]. DO was higher in Station 1 which accounted for its suitability for aquatic life and as a fishing ground. The mean values of BOD in this study were lower than the mean values of DO which is supported by a similar work [17]. Both BOD and DO fell within regulatory limits of 25 mg/L and 4.0 mg/L set by NESREA.

High value of TDS is an indicator of the high level of waste discharge which is harmful to human and aquatic life, posing health hazards [18]. TDS value for station 3 was recorded to be the highest which resulted from human waste input; meanwhile, obtained values across all stations (8888.3 - 10972.3 mg/L) were similar to high values of 7920 - 80 mg/L reported in a comparative study of river bodies in the Niger Delta [19]. The values from all stations fell above the regulatory limit of WHO and NESREA (500 mg/L).

Chloride concentration serves as an indication of pollution by sewage [20]. All three stations recorded high chloride values with Station 3 being the highest as traditional toilet sheds are constructed on the river.

Sulphate increase is an indication of an increase in industrial wastes and domestic sewage, and is also an important constituent of hardness alongside calcium and magnesium [21]. Sulphate concentrations across the stations (346.5 - 259.1mg/L) were significantly higher than concentration level of 6.34 – 40.7 mg/L obtained in a recent study of the New Calabar River [22]. The values were above the NESREA and FMEnv permissible level of 500 mg/L.

High concentration of nitrates in aquatic systems increases nuisance algae and macrophytes, and triggers eutrophication and pollution [23]. While Station 1 recorded the highest values, the values obtained throughout the stations were lower than the limits set by WHO and FMEnv of 20 mg/L. Generally, nitrate concentration across the stations (0.293 - 0.173 mg/L) was lower than 5.7 - 4.2 mg/L from a study reported by [24].

Phosphorus is an essential nutrient and is also largely responsible for eutrophication. The highest value from this study was recorded in Station 1, but like nitrate, the value was below regulatory limit of WHO and FMEnv (3.5 mg/L and 5.0 mg/L, respectively). Values from the study differed from the 2.144 - 9.741 mg/L obtained by [25] while mean values were below regulatory limit of WHO and FMEnv (3.5 mg/L and 5.0 mg/L, respectively).

### *B. Physicochemical properties in sediment from koniju-toru river*

pH and alkaline levels of sediment affect other sediment properties, pH below 5 increases soluble magnesium and aluminum concentrations, affects important microbial population and ultimately, affect the entire food chain ([26], [27], [28], [29], [30]). In this study, pH and alkaline mean values (5.60 - 5.12 and 100.3 – 50.3, respectively) were highest and lowest in station 1, respectively; however, values from all stations fell below permissible limits of NESREA and FMEnv (6.5 - 8.5) and this is detrimental to aquatic organisms in the river as most metabolic activities are pH dependent [31]. pH values in this study differed from the values recorded in the Sombreiro river of the Bonny estuary 5.06 - 5.85 [32].

High values of chloride were observed across the three stations (504.7 - 604.8 mg/kg) with Stations 2 and 3 recording the highest values. High concentrations may be associated with sewage discharge which is most likely due to poor toilet facilities in the community [33]. Chloride concentrations were above the regulatory limit of NESREA (350 mg/kg).

Sulphate concentration was higher in Stations 2 and 3 from this study, though values gotten were lower than regulatory limits of NESREA and FMEnv (350 mg/kg). Sulphate values from this study (183.6 - 126.2 mg/kg) exceeded 1.06 - 3.81 mg/kg reported by [34].

Nitrate concentration was highest in Station 3 and lowest in Station 2. However, sediment concentrations across the

three stations were below the NESREA limit of 40mg/kg indicating the absence of excess nitrate. Generally, the mean concentration (0.30 - 0.11 mg/kg) was lower than 57.4 - 68.28 mg/kg recorded by [1].

Phosphate concentration in sediment was lower in Station 1 attributing to its suitability for aquatic life. Generally, values from this study (0.03 - 0.00 mg/kg) were lower than the values of 5.6 - 16.89 mg/kg reported by [35] and were within NESREA permissible limit (3.5 mg/kg).

The concentration of TOM indicates the ability of the sediment to retain minerals to itself; therefore, a high concentration equals increased heavy metal content [36]. Station 3 recorded the highest TOM and this can be linked to higher anthropogenic activities including indiscriminate waste disposal in this station. The values gotten from the studied sediment (0.73 - 0.60) were very low compared to the 52400 - 93100 mg/kg obtained in a river outside of Nigeria [37].

*C. THC in surface water, sediment and fish of the studied river*

THC levels were highest in sediment across the three stations which could be linked to it being a sink [8]. Observed levels of THC in surface water from this study were lower than 8.81 - 2.83 mg/L by [15]. Sediment THC levels were lower than 16.01-136.04 mg/kg reported by [38] while fish THC levels were also lower than the range of 121.51 - 415.06 µg/g observed by [39].

Generally, the THC across all stations was low. In particular, the THC of surface water was within the limit set by WHO, NESREA and FMEnv (10 mg/L in water). Likewise, sediment THC was within permissible levels of WHO of 30 mg/kg, though Station 3 recorded the highest THC value, accounting for the highest anthropogenic disturbance. Overall, THC was higher in the sediment samples than in the surface water and biota samples. This can be attributed to the fact that hydrocarbons being volatile will evaporate the ones at the surface of the river and the remaining will sediment at the bottom of the river thus increasing the concentration in the sediment over time [40]. Lower THC concentrations in fish compared to surface water could be likened to the influence of various factors including; species' retention rate, duration of exposure and environmental factors, among others [41], [42]. The acceptable levels of THC in the various aspects of the studied River could be associated with the rehabilitation of the refinery closest to the community which is supported by the World Bank report that states the petroleum industry is the major producer of hazardous waste including hydrocarbon in Rivers state [43]. Furthermore, the dilution and tidal effect of the river, and carbon sequestration by mangroves might have contributed to the observed levels of THC in the studied area ([44], [45]).

## V. CONCLUSION

Physico-chemical properties and THC of Koniju-toru river have been investigated by this study. The investigation has shown the suitability of this system for aquatic life, human consumption and human activities to a great extent as observed values were within regulatory limits of WHO and other environmental agencies, excluding TDS and sulphate in surface water. Needless to say, it is most important for routine analysis to be carried out on this water body to ensure its continued good health.

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